



Recent Progress on Nitrogen-Rich Energetic Materials Based on Tetrazole Skeleton

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Abstract

Development of nitrogen-rich energetic materials has gained much attention because of their remarkable properties including large nitrogen content and energy density, good thermal stability, low sensitivity, good energetic performance, environmental friendliness and so on. Tetrazole has the highest nitrogen and highest energy contents among the stable azoles. The incorporation of diverse explosophoric groups or substituents into the tetrazole skeleton is beneficial to obtain high-nitrogen energetic materials having excellent energetic performance and suitable sensitivity. In this review, the development of high-nitrogen energetic materials based on tetrazole skeleton is highlighted. Initially, the property and utilization of nitrogen-rich energetic materials are presented. After showing the advantage of the tetrazole skeleton, the high-nitrogen energetic materials based on tetrazole are classified and introduced in detail. Based on different types of energetic materials (EMs), the synthesis and properties of nitrogen-rich energetic materials based on mono-, di-, tri- and tetra-tetrazole are summarized in detail.

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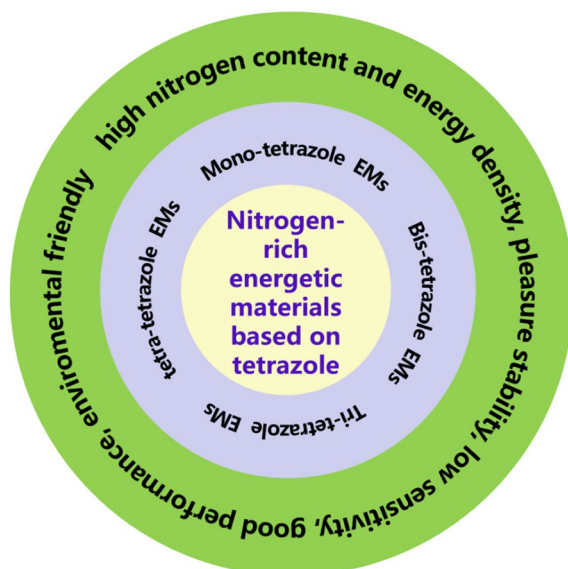
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Graphical Abstract



Keywords Energetic materials · Tetrazole · Nitrogen rich · Energy

1 Introduction

Energetic materials (EMs) refer to substances whose chemical reactions are accompanied by energy liberation. According to the energy amount contained in EMs and the rate of release, EMs are classified as pyrotechnics, propellants, “tertiary” explosives, secondary explosives and primers. Preferable EMs should satisfy the following requirements: tailored and high performance, stability, insensitivity, high thermal stability, environmental safety, vulnerability, hydrolytic stability and small solubility in water, compatibility and longevity [1–3]. Traditional energetic materials such as 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) [4], trinitrotoluene (TNT) [5], hexanitrohexaazaisowurtzitane (CL-20) [6] and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) [7] suffer from several deficiencies such as being environmentally unfriendly, expensive, showing polymorphism, involving harsh synthetic methods and so on. The key challenge to developing new suitable EMs is the compatibility of large energy content with mechanical and chemical stability, even though the two properties are generally contradictory [8–11].

Nitrogen plays an important role among the elements. The strong and short nitrogen–nitrogen triple bond involved is a powerful energetic driving force for the generation of nitrogen molecules. The more contiguous nitrogen atoms in the doubly and singly bonded system result in larger formation heats and thus better performances [12, 13]. In recent years, development of novel nitrogen-rich

energetic materials has become an interesting research field because of their outstanding features like high energy density and content, good thermal stability, suitable solubility in ordinary solvents and lower sensitivity towards mechanical stimuli [14–17]. Besides, the decomposition of these high-nitrogen energetic materials release a large amount of environmental-friendly gas N_2 ; thus, they are improved and “green” candidates for applications which require environmental protection [18].

In the past decade, high-nitrogen heterocycles have attracted increasing attention in the field of high energy density materials (HEDMs) meanwhile obtaining a balance of environmental concerns, sensitivity and high detonation performance [19, 20]. Heterocyclic five-membered cycles like pyrazole, oxazole, tetrazole, triazole and six-membered cycles like tetrazine and triazine are usually utilized in nitrogen-rich energetic materials to improve nitrogen and energy contents, densities, oxygen balance, planarity and detonation performance [21–24]. The formation enthalpies of these heterocycles increase with the catenated N atoms number, while pentazole is not isolated in macroscopic amounts and alkyl substituted pentazoles are often thermally instable and extremely sensitive to mechanical stimuli [25]. Among the stable azoles, tetrazole has the largest nitrogen content and imparts the highest energy content [26]. Introducing diverse explosophoric groups to the tetrazole scaffolds and their aromatic nature would be beneficial toward realizing the contradictory balance between detonation performance and safety, making the tetrazole motifs the most prospective backbones. Introduction of electron-donating groups to tetrazole rings (methyl, amine, etc.) enhanced the stability of tetrazole-based Ems [27, 28]. Additionally, linkages like methylene not only lowered the mechanical sensitivity but also increased the density and thermal stability [29]. Tetrazole-based EMs with $-NH-$ bridges have superior inter- and intramolecular H-bonding, effectively reducing the sensitivity [30, 31]. Combination of tetrazoles with other heterocyclic rings could improve the performance [32, 33]. Compared to monotetrazole-based EMs, bistetrazole- or polytetrazole-based EMs have additional superiorities resulting from the larger number of N–N bonds and higher formation heats [34, 35].

Although some reviews on high-nitrogen energetic materials have been published recently, just two or three examples of tetrazole scaffolds have been reported [36–38]. Because of the well-established synthetic method, distinctive performance and potential application, a systematic review on tetrazole-based nitrogen-rich EMs is needed. In this review, we present the recently developed synthetic approaches, interesting performance and potential use of nitrogen-rich tetrazole EMs. High-nitrogen EMs of both tetrazole and trazole are covered in detail. According to the number of tetrazole rings involved, the EMs based on tetrazole and trazole in this review were mainly divided into the following categories: (1) nitrogen-rich EMs based on mono-tetrazole skeletons, (2) nitrogen-rich EMs based on bis-tetrazole skeletons, (3) nitrogen-rich EMs based on tri- and tetra-tetrazole skeletons and (4) other nitrogen-rich EMs based on tetrazole skeletons. References in this review on nitrogen-rich energetic materials of tetrazole were collected up to May 2023. We apologize to the authors whose contributions were not presented here because of the limitations of the search profiles and tools employed.

2 Nitrogen-Rich EMs Based on Mono-Tetrazole Skeleton

Numerous nitrogen-rich EMs based on tetrazole have been developed in recent years. Among them, amino-, nitro-, aryl-, and bridged tetrazole derivatives are important categories of high-nitrogen EMs with some advantages like high nitrogen and energy content, excellent performance, suitable stability and being environmentally friendly.

2.1 Nitrogen-Rich Molecules Based on Mono-Tetrazole

Early in 2011, Zhang investigated the tautomers/rotamers of diazido-tetrazole (**I–IV**, CN_{10}) bearing two azide groups by theoretical computations (Fig. 1). The geometries were wholly measured at the level of B3LYP/6–311 + +G(d). The harmonic vibrational frequencies, thermodynamic properties and electronic structures were studied at the same level for the optimal structure. The predicted stability order at MP2/6–311 + +G(d) was **II** < **I** < **V** < **IV** < **III**. Additionally, the detonation property was investigated. The results showed that CN_{10} has high detonation energy and heat formation and should be a novel potential HEDM candidate if synthesized successfully [39]. This investigation could give significant information toward developing novel HEDMs with high performance and good stability.

1,5-Diamino-1*H*-1,2,3,4-tetrazole (DAT), a common building framework for a broad range of HEDMs, has attracted increasing attention because of its large nitrogen content and high thermal stability. Wang studied the pressure structural (Fig. 2) and vibrational nature of DAT in 2021 [40]. First, the author investigated the static compression property of DAT at 0–20 GPa pressure range through theoretical calculations. The calculated geometry, vibrational modes and crystal parameters were matched with those obtained by experimental results at ambient pressure. Additionally, the compressibility of the lattice parameters demonstrated an isotropic pattern. Subtle abrupt changes were obtained in the lattice angle, vibrational modes, dihedral angles and bond lengths at 17 and 7 GPa, indicating the transitions of isostructural phase took place. The results of vibrational modes and Hirschfeld surface analysis showed that the molecular interaction strengthening enhanced crystal packing. This report not only revealed the influence of hydrostatic pressure on the structure and crystal of DAT but also showed the intermolecular interactions and molecular packing mode in response to pressure, which were very important for exploring the high-pressure structural stability of DAT.

To enhance the density of 5-aminotetrazole, 4-amino-3,5-dinitropyrazole was introduced to 5-aminotetrazole as a skeleton. The target compounds *N,N*-methylene linked pyrazole and 5-aminotetrazole **DMPT-1** and **DMPT-2** were synthesized successfully through treatment of chloriodomethane with ammonium 4-amino-3,5-dinitropyrazolate followed by treatment with 5-aminotetrazole. These two compounds were systematically determined via NMR and IR, differential scanning calorimetry, elemental and x-ray diffraction analysis. The experimental results and theoretical calculation showed that nitropyrazole

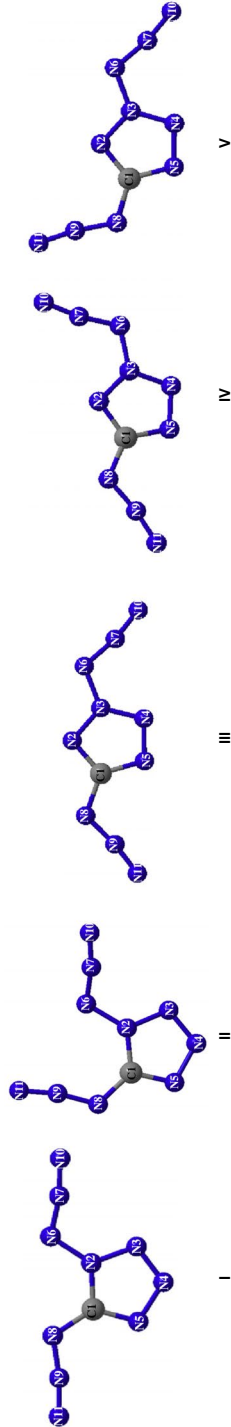
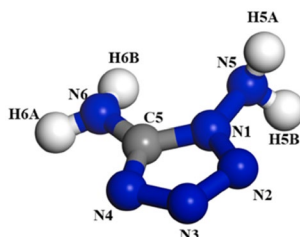


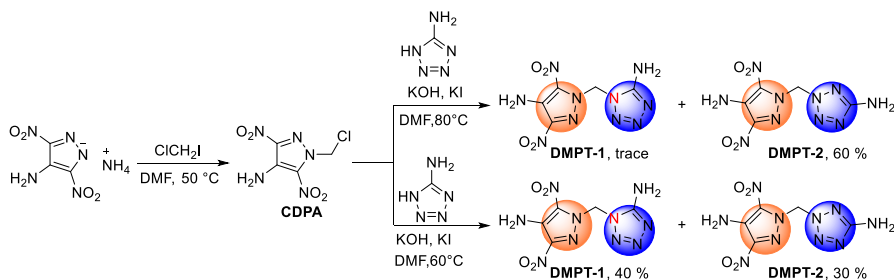
Fig. 1 Optimized geometries and numbering of CN₁₀ isomers. (Images reproduced from Ref. 39 with permission of Elsevier [39])

Fig. 2 Crystal structure of DAT. (Images reproduced from Ref. 40 with permission of Elsevier) [40]



functionalization improved mechanical sensitivity and energetic performance. In comparison with *N,N'*-ethylene-linked molecules, the two methylene-linked molecules **DMPT-1** and **DMPT-2** exhibited higher detonation performance and density. **DMPT-2** showed a large crystal density ($1.806 \text{ g}\cdot\text{cm}^{-3}$), high detonation pressure ($P = 30.2 \text{ GPa}$), good pressure velocity ($v_D = 8610 \text{ m}\cdot\text{s}^{-1}$) and low impact sensitivity (30 J) (Table 1) [41]. This research showed that involvement

Table 1 Synthesis and physicochemical properties of **DMPT** [41]



Compd	$T_d^a/^\circ\text{C}$	$D^b/\text{g}\cdot\text{cm}^{-3}$	$\Delta H_f^c/\text{kJ}\cdot\text{mol}^{-1}$	$D^d/\text{m}\cdot\text{s}^{-1}$	p^e/GPa	IS^f/J	FS^g/N
DMPT-1	191	1.806	486.93	8610	30.2	30	108
DMPT-2	209	1.77	484.26	8450	28.6	30	192
A8^h	105	1.695	255.7	8609	29.8	10	108
B5ⁱ	257	1.67	373.7	7889	23.2	> 40	360
Cl^j	209	1.62	1289.1	8331	24.98	1.5	–
ADNP^k	178	1.90	96.3	8573	34.2	> 40	> 360
TNTⁱ	295	1.65	– 59.4	7303	21.3	15	> 353
RDXⁱ	205	1.80	92.6	8795	34.9	7.5	120

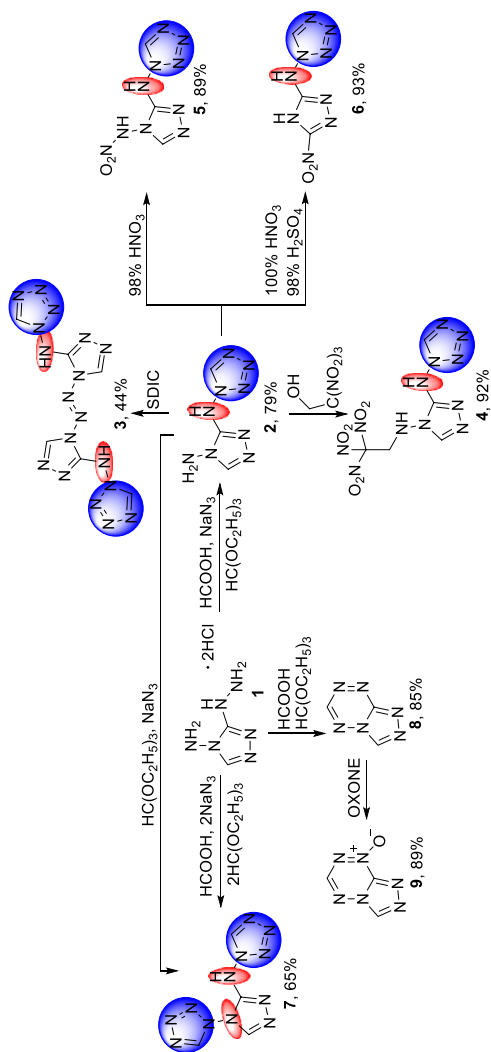
^aDecomposition temperature. ^bCrystal density. ^cHeat of formation. ^dCalculated detonation velocity. ^eCalculated detonation pressure. ^fImpact sensitivity. ^gFriction sensitivity. ^h**A8**: 1-Hydroxy-5-aminotetrazole. ⁱ**B5**: 1-(2-(4-amino-3,5-dinitro-1H-pyrazol-1-yl)ethyl)-1H-tetrazol-5-amine. ^j**Cl**: *N,N'*-(1,2,4,5-tetrazine-3,6-diyl)bis-(1,5-diamino-1H-tetrazole). ^k**ADNP**: 4-amino-3,5-dinitropyrazole

of 4-amino-3,5-dinitropyrazole in the 5-aminotetrazole skeleton could improve the energetic performance, which was very useful for designing efficient nitrogen-rich EMs based on 5-aminotetrazole.

One-step synthesis of tetrazole compounds bearing N_5 group as well as fused compounds **2–9** was developed by Cheng in 2020 (Table 2) [42]. The structure of **2–9** was well characterized through NMR, elemental analysis, thermal analysis and IR spectroscopy. Compounds **2**, **4**, **6**, **8** and **9** were characterized by x-ray diffraction analysis as well. These compounds exhibited high formation heats ($3308–6180 \text{ kJ}\cdot\text{kg}^{-1}$) and nitrogen content ($50.9\%–76.4\%$). Compounds **2–9** showed high energy performances and low sensitivities because of their distinctive structure particularly for compound **4** ($D = 9004 \text{ m}\cdot\text{s}^{-1}$, $IS = 22 \text{ J}$, $IsP = 289 \text{ s}$). Additionally, all of these compounds displayed low sensitivities of friction (204 to $> 360 \text{ N}$) and impact sensitivities (18 to $> 40 \text{ J}$). The hydrogen bonding and π - π interaction in **2–9** were proved through fingerprint plots and NCI plots according to Hirschfeld surfaces. Moreover, the structure-property relationship was well established through theoretical calculations, crystal structure analysis and detonation performance. These above results demonstrated the potential applications of these tetrazole derivatives as novel nitrogen-rich HEDMs. This study not only offered guidelines for development of energetic materials but also opened a prospect in this field.

Incorporation of oxygen-rich scaffolds, $C(\text{NO}_2)_3$, $C(\text{NO}_2)_2\text{NF}_2$ or $C(\text{NO}_2)_2\text{F}$, onto an endothermic skeleton, which integrated nitropyrazole and tetrazole, was used to develop new oxygen- and nitrogen-rich energetic compounds [45]. The desired compounds **18–20**, **24** were obtained by the synthetic routes demonstrated in Table 3. The structures of **18–20**, **24** were characterized by x-ray analysis. According to a combination of the Δ_{OED} criterion and molecular density (d_{mol}), the authors presented a useful and convenient method for crystal packing analysis, which was the determination of molecular packing tightness upon formation of crystal. Target compounds **18–20** and **24** decomposed at the range of 110 to $170 \text{ }^\circ\text{C}$, indicating **18–20**, **24** were more stable thermally than the analogous one with no pyrazole bridge. Difluoroamine **20** exhibited the largest onset decomposition point at $138 \text{ }^\circ\text{C}$. Notably, compound **19** bearing $C(\text{NO}_2)_2\text{F}$ module melted along with decomposition while other compounds decomposed without melting. For safety testing, friction (FS) and impact (IS) sensitivities of **18–20**, **24** was measured through a standard BAM techniques. Interestingly, the group (F, NO_2 , NF_2) at the dinitromethyl framework showed a few effects on the sensitivity, and a narrow range (1.5 J to 1.6 J) of impact sensitivity was observed (Table 3). Difluoroamino compound **20**, showing good nitrogen and oxygen contents, high density, acceptable sensitivities and high enthalpy of formation, could serve as a promising candidates for nitrogen-rich EMs. This investigation, introducing oxygen- and fluorine-rich groups to tetrazole derivatives, is of considerable interest for the development of fluorine-containing EMs.

5-Nitro-2-nitratomethyl-1,2,3,4-tetrazole **23** was prepared successfully in 38% yield by nitration of the alcohol **22** with acetic anhydride and dilute nitric acid. Intermediate **22** could be generated from 5-nitrotetrazole sodium salt (**21**), which was obtained from 5-aminotetrazole by a one-pot reaction [47]. The structure of **23** was characterized via NMR, FT-IR, MS techniques and x-ray diffraction. Target **23** was the orthorhombic system with space group $Pna2(1)$. The results of theoretical

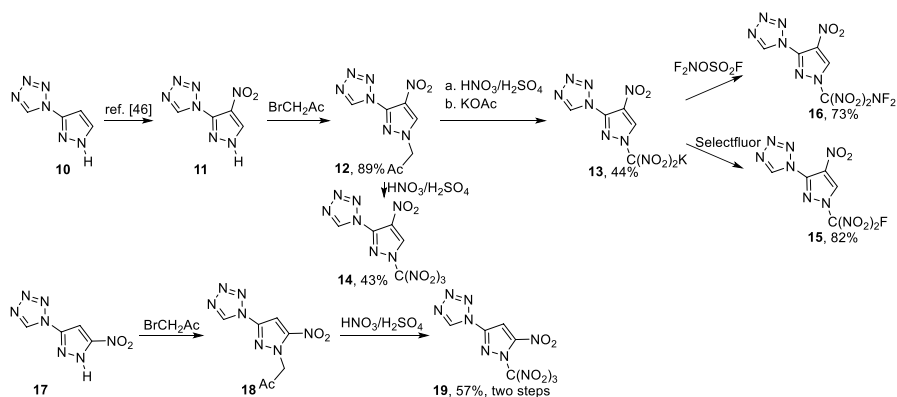
Table 2 Synthesis and energetic performance of tetrazole compounds **2–9** [42]

Compd	T _{dec} ^a [°C]	Δ _f H ^b [kJ·kg ⁻¹]	D ^c [m·s ⁻¹]	P ^d [GPa]	ρ ^e [g·cm ⁻³]	IS ^f [J]	FS ^g [N]	N [%] ^h	V ₀ [L·kg ⁻¹] ⁱ	I _{sp} [s] ^j	I _{sp} [s] ^j (AI15%)	I _{sp} [s] ^j (AI 15%, binder 14%)
2	215	5167	8789	27.7	1.65	>40	>360	75.4	804	327	320	293
3	170	5450	8599	27.6	1.68	27	310	76.4	750	249	242	229
4	182	3308	9004	34.9	1.77	22	240	50.9	775	289	272	249
5	177	4355	9141	33.6	1.78	18	180	66.0	805	270	263	245
6	186	4822	8885	32.1	1.74	22	204	64.0	788	279	265	249

Table 2 (continued)

Compd	T_{dec}^a [°C]	ΔH^b [kJ·kg ⁻¹]	D^c [m·s ⁻¹]	P^d [GPa]	ρ^e [g·cm ⁻³]	IS^f [J]	FS^g [N]	N [%] ^h	V_o [L·kg ⁻¹] ⁱ	I_{sp} [s] ^j	$I_{sp}[s]^j$ (Al15%)	$I_{sp}[s]^j$ (Al15%, binder 14%)
7	183	5711	8695	28.4	1.71	24	240	76.4	760	249	242	229
8	243	6180	8176	27.2	1.68	>40	>360	68.9	689	249	237	227
9	220	4948	8292	27.0	1.72	>40	>360	60.9	721	253	245	232
TNT^k	295	– 1700	6881	19.5	1.65	15	353	18.5	–	–	–	–
RDX^k	204	320	8795	34.9	1.80	7.5	120	37.8	–	258	–	–
AP^l	240	– 2517	6368	15.8	1.95	20	360	–	–	157	235	261

^aThermal decomposition temperature. ^bHeat of formation. ^cDetonation velocity. ^dDetonation pressure. ^eDensity determined by gas pycnometer. ^fImpact sensitivity. ^gFric-tion sensitivity. ^hNitrogen content. ⁱGas volume after detonation. ^jSpecific impulse Isp of the neat compound and compositions with aluminium or aluminium and binder (polybutadiene acrylic 6%, polybutadiene acrylonitrile 6% and bispheno A ether 2%) by using the EXPLO5 (version 6.05) program package (70 kbar, isobaric combustion, equilibrium expansion). ^kRef. [43]. ^lRef. [44]

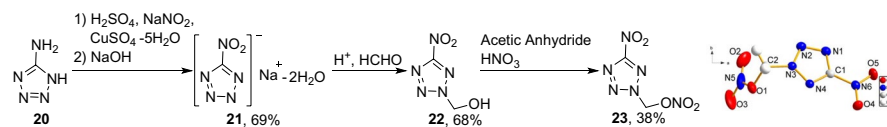
Table 3 Synthesis and energetic performance of compounds **10**–**16**, **19** [45]

Compd	T_{dec}^a [°C]	α^b	$N,^c$ [%]	d^d [g·cm ⁻³]	ΔH_f^{0e} [kJ·mol ⁻¹]	D_f^f [m·s ⁻¹]	P_{CJ}^g [GPa]	Lsp^h [s]	Tad^i [K]
14	127	0.73	42.43	1.794	602	8860	34	273	3772
15	111	0.59	41.59	1.810	386	8470	31	262	3681
16	138	0.64	41.67	1.905	589	8990	36	282	4050
19	132	0.73	42.43	1.757	629	8780	32	275	3796
NG	125	1.06	18.50	1.595	- 351.5	7630	22	259	3294
PETN	181	0.86	17.72	1.77	- 538	8330	30	263	3328
TNT	295	0.36	18.50	1.654	- 67	6663	21	210	2007
RDX	204	0.67	37.84	1.82	67	8850	35	266	3290

^aExtrapolated onset temperature. ^bOxygen coefficient. ^cNitrogen content. ^dDensity. ^eCalculated enthalpy. ^fDetonation velocity at maximal density. ^gCalculated detonation pressure. ^hCalculated specific impulse and adiabatic temperature for isobaric combustion. ⁱAdiabatic flame temperature for combustion

and experimental study showed that **23** had high energetic performances with large formation heat (228.07 kJ·mol⁻¹), high pressure of detonation (37.92 GPa), high velocity of detonation (9260 m·s⁻¹) and good oxygen balance (Scheme 1) [48]. This report introduced oxygen atoms into the tetrazole motif, achieving good balance of oxygen and high performances.

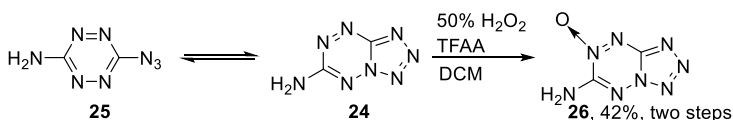
The preparation and energetic nature of a new *N*-oxide high-nitrogen energetic molecule, 5-nitro-2-nitratomethyl-1,2,3,4-tetrazole (4), were reported

**Scheme 1** Preparation of 5-nitro-2-nitratomethyl-1,2,3,4-tetrazole [48]

[49]. Compared with known nitrogen-rich molecules, like 2,4,6-tri(azido)-1,3,5-triazine (TAT) [50], 4,4',6,6'-tetra(azido)azo-1,3,5-triazine (TAAT) [51] and 3,6-diazido-1,2,4,5-tetrazine (DiAT) [52], target **26** displayed excellent properties of detonation, acceptable sensitivities of friction and impact, and high density. The high performance of **26** might result from the fused ring system and *N*-oxide (Table 4). This study suggested that fused tetrazole compound **26** had potential application as a nitrogen-rich EM.

1,1-Diamino-2,2-dinitroethene (**FOX-7**) is a skeleton having good energetic property, high stability and low sensitivity [53]. In 2021, Shreeve and Tang modified the structure of **FOX-7** by introducing a tetrazole block and hydrazino group, developing (*Z*)-1-amino-1-hydrazinyl-2-nitro-2-(1H-tetrazol-5-yl)ethene (**HTz-FOX**) as a promising nitrogen-rich compound [54]. The structure of **HTz-FOX** was measured via elemental analysis, NMR and x-ray diffraction. The authors discovered that the target **HTz-FOX**, which displayed parallel molecular layers, was a planar molecule. For this coplanar structure, **HTz-FOX** showed a high temperature of decomposition ($TD = 237\text{ }^{\circ}\text{C}$) and good performance of detonation ($P = 28.3\text{ GPa}$, $D_v = 8883\text{ m}\cdot\text{s}^{-1}$), which was superior to **FOX-7** ($P = 31.6\text{ GPa}$, $D_v = 8613\text{ m}\cdot\text{s}^{-1}$, $TD = 220\text{ }^{\circ}\text{C}$) and 1-amino-1-hydrazino-2,2-dinitroethene (**H-FOX**) [55] ($P = 33.8\text{ GPa}$, $D_v = 8803\text{ m}\cdot\text{s}^{-1}$, $TD = 125\text{ }^{\circ}\text{C}$). **HTz-FOX** displayed an outstanding combustion nature with shorter delay combustion time ($0.09\text{ m}\cdot\text{s}^{-1}$) and larger P_{max} (20.13 GPa) (Table 5). This work offered potential guidance to develop advanced nitrogen-rich EMs through structural modification, constructing planar configuration for allowing parallel molecular layers to balance the thermostabilities, sensitivities and detonation performances.

Table 4 Synthesis and physical properties of **25** and **26** [49]



Compd	$T_d^{[a]}$ [$^{\circ}\text{C}$]	d [$\text{g}\cdot\text{cm}^{-3}$]	$\Delta_f H^{[b]}$ [$\text{kJ}\cdot\text{mol}^{-1}/(\text{kJ}\cdot\text{g}^{-1})$]	$VD^{[c]}$ [$\text{m}\cdot\text{s}^{-1}$]	$P^{[d]}$ [GPa]	$IS^{[e]}$ [J]	$FS^{[f]}$ [N]
DiAT	130	1.62	1130/(6.71) ^[g]	8306	26.5	< 1	–
TAT	187	1.74	1053/(5.16) ^[i]	8308	26.9	< 1 ^[i]	–
TAAT	200	1.67	2171/(6.16) ^[i]	8252	26.4	< 1 ^[i]	–
25	200	1.68	686.2/(4.97)	8449	27.0	1.5 ^[k]	15
26	185	1.87	631.4/(4.09)	9326	36.4	10	160
RDX	210	1.82	80.0/(0.36)	8748	34.9	7.4	120
HMX	280	1.91	104.8/(0.36)	9320	39.5	7.4	120

^aDensity measured by gas pycnometer at $25\text{ }^{\circ}\text{C}$. ^bCalculated molar enthalpy of formation in solid state.

^cCalculated detonation velocity-Explo5 v6.05.02. ^dCalculated detonation pressure-Explo5 v6.05.02.

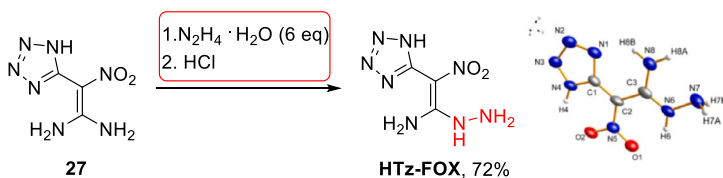
^eTemperature of decomposition (onset). ^fImpact sensitivity

2.2 Nitrogen-Rich Salts Based on Mono-Trazolate

Several high-nitrogen energetic salts **28–39** of tetrazole azasydnone were prepared and characterized, leading to the development of novel secondary and primary explosives. The structures of **28–39** were measured by IR, NMR and x-ray analysis. The authors also studied their energetic performances and sensitivity. All salts had larger densities than azidotetrazole analogs [59, 63]. Density of **30** exceeded RDX (1.820 g·cm⁻³) and the densities of **31**, **32** and **37–39** exceeded their analogous nitrotetrazole [59, 64]. The silver **34** salt and free acid **30** showed higher sensitivity than RDX. Compared to RDX, **30** possessed the best performance of detonation (327 kbar, 8906 m·s⁻¹), and **30** also exhibited the highest heat of formation although its nitrogen content was lower. The silver salt **34** displayed a suitable sensitivity regarding primary explosive power. Among these compounds, **30** and **34** were the best replacements for the primary explosives (Scheme 2) [64]. Compared to the lead-based Ems [65], this silver salt is obviously less toxic.

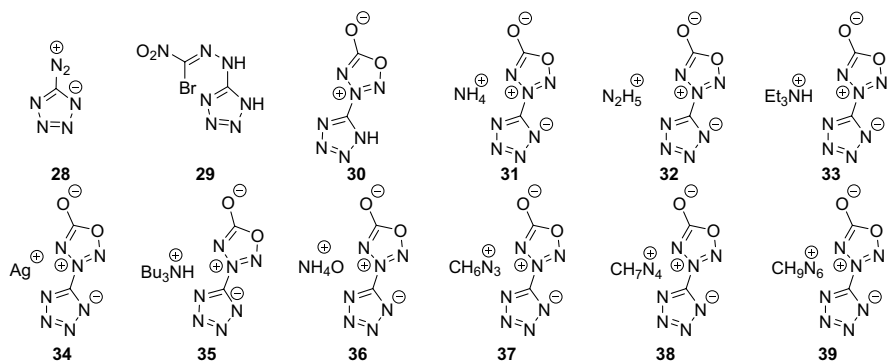
A novel high-nitrogen methylene and azo linked mixed azole **41** was prepared by simple reactions as well as the methylene bridged azole molecule **40**, which was not just easily converted to its salts **42–44** but also could be applied as a starting material to synthesize a nitroimino involved azole **45** and its energetic salts **46–48** (Scheme 3). Most of the molecules exhibited high thermostabilities and low sensitivities. These energetic molecules also showed high heats of formation for compound **45** with P, 32.87 GPa; Dv, 8759 m·s⁻¹. The salts **48** (P, 31.92 GPa; Dv, 8870 m·s⁻¹), **47** (P, 30.53 GPa; Dv, 8933 m·s⁻¹) and **44** (P, 28.04 GPa; Dv, 8590 m·s⁻¹) displayed higher detonation performances than ANTA and TNT [66]. This research provided possible candidates which could be applied to the field of insensitive EMs.

Table 5 Synthesis, energetic and detonation property of HTz-FOX [54]



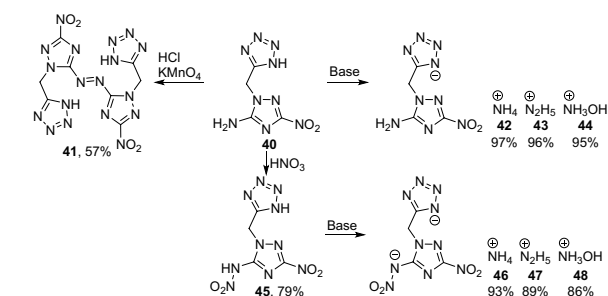
Compd	ρ^a (g·cm ⁻³)	ΔH_f^b (kJ·mol ⁻¹ /kJ·g ⁻¹)	D_v^c (m·s ⁻³)	P^d (GPa)	T_d^e (°C)	IS^f (J)	FS^g (N)
HTz-FOX	1.76	264.5/1.42	8883	28.3	237	10	240
H-FOX^h	1.78	71.6/0.43	8803	33.8	125	6	–
FOX-7ⁱ	1.85	– 134.1/– 0.91	8613	8613	220	24.7	> 360
RDX^j	1.80	70.3/0.32	8801	8810	204	6.0 ^j	120

^aDensity. ^bCalculated molar enthalpy of formation. ^cCalculated detonation velocity. ^dCalculated detonation pressure. ^eTemperature of decomposition. ^fImpact sensitivity. ^gFriction sensitivity. ^hRef. [55]. ⁱRef. [56]. ^jRef. [57, 58]



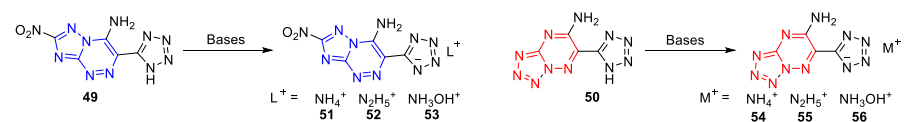
Scheme 2 Structure of nitrogen-rich energetic salts 28–39 [64]

Scheme 3 Synthesis of nitro-rich energetic compounds and salts 42–48 [66]



Two kinds of fused high-nitrogen EMs **49**–**50** and their salts **51**–**56** were prepared. The structures were characterized by NMR and IR, elemental and thermal analysis. Because of the ring-strain energy and large nitrogen contents (59.6%–76.8%), these high-nitrogen compounds showed a large range of formation heats (2.35 to 4.23 kJ·g⁻¹), which were much larger than those of HMX (0.25 kJ·g⁻¹) and RDX (0.32 kJ·g⁻¹). The larger noncovalent interactions and enthalpies (hydrogen bonds) provided them with significant detonation performance. Their energetic properties were tested with *EXPLO5*. **49**, **52** and **53** displayed large densities, good mechanical stabilities and high detonation performances, thus accentuating their potential uses as new nitrogen-rich HEDMs (Table 6) [67]. This work developed a series of high-nitrogen compounds with triazolo-triazine and tetrazolotriazine as the skeletons, bearing amino and tetrazole substituents. They not only realized good balance between detonation performance and molecular stability but also offered a new strategy to create novel nitrogen-rich HEDMs with excellent performance and suitable stability.

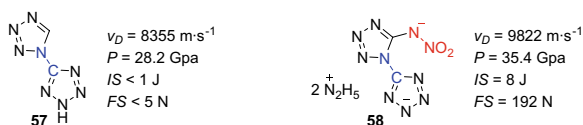
Several salts of C–N bridged 1-(2*H*-tetrazol-5-yl)-5-nitraminotetrazole were successfully prepared from easily available 5-aminotetrazole (Scheme 4). These novel high-nitrogen energetic molecules were totally measured by NMR, IR, elemental analysis, and x-ray diffraction. Among them, **58** (3.25 kJ·g⁻¹) was found to show interesting energetic properties with excellent calculated data ($v_D = 9822$ m·s⁻¹, IS = 8 J and FS = 192 N) [69]. This good performance of

Table 6 Physiochemical properties of compounds **49**–**56** [67]


Compd	N ^a [%]	ΔH_f^b [kJ·mol ⁻¹]/ [kJ·g ⁻¹]	T _d ^c [°C]	ρ^d [g·cm ⁻³]	D ^e [m·s ⁻¹]	P ^f [GPa]	IS ^g [J]	FS ^h [N]
49	61.8	721.6/2.90	181	1.873	9010	32.8	35	300
50	75.1	866.5/4.23	220	1.795	8367	25.6	31	300
51	63.2	625.3/2.35	185	1.811	8793	28.6	40	360
52	64.8	781.2/2.78	196	1.855	8950	32.9	40	360
53	59.6	677.4/2.40	200	1.859	9220	33.1	40	360
54	75.7	739.5/3.33	216	1.725	8313	24.9	33	320
55	76.8	882.1/3.72	230	1.742	8679	27.6	33	310
56	70.6	785.7/3.30	192	1.751	8618	28.0	35	330
RDX	37.8 ⁱ	70.3/0.32 ⁱ	204 ⁱ	1.800 ⁱ	8795 ⁱ	34.9 ⁱ	8	140
HMX	37.8 ⁱ	70.4/0.25 ⁱ	280 ⁱ	1.905 ⁱ	9144 ⁱ	39.2 ⁱ	5	102

^aNitrogen content. ^bCalculated molar enthalpy of formation. ^cThermal decomposition temperature. ^dMeasured density. ^eDetonation velocity. ^fDetonation pressure. ^gImpact sensitivity. ^hFriction sensitivity. ⁱRef. [68]

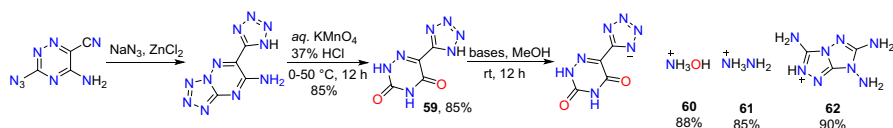
Scheme 4 Structure of C-N bridged 1-(2H-tetrazol-5-yl)-5-nitraminotetrazole and its salts [69]



detonation and suitable sensitivities made compound **7** an improved candidate to use as high-performance EMs.

Dharavath and the co-authors synthesized high-nitrogen energetic salts **60**–**62** with good performance and thermal stability from readily obtainable starting material (Scheme 5). These molecules were fully measured by NMR, IR, TGA–DSC measurements, ESI–MS and EA techniques. All the salts showed high density, low sensitivity towards friction and impact, large heat of formation and good detonation velocity. Because of the large nitrogen content, they could be potentially employed as pyrotechnic applications and gas generators [70]. The large thermal decomposition temperature (>220 °C) enabled them to be good replacements of heat-resistant explosives and thermally stable secondary EMs.

Aminotetrazole (**AT**) showed an acidic property and could be applied to synthesize high-nitrogen energetic ionic liquids and salts **63**–**70** (Table 7). These prepared



Scheme 5 Synthesis of high-nitrogen energetic tetrazole salts **60**–**62** [70]

AT salts were fully determined by NMR, IR, phase behavior, density, thermal stability and elemental analysis. The nitrogen content of salt **63** was 82%, while **68** possessed the largest nitrogen content (68%) among the reported room temperature ionic liquid. These salts also displayed other promising properties of energy, including high content and densities of nitrogen, and excellent thermal and hydrolytic stabilities. The results of theoretical calculations and experiments demonstrated that these salts showed large densities of energy ($> 3.0 \text{ kJ}\cdot\text{g}^{-1}$) and good heats of formation. Additionally, all of them were impact insensitive EMs with excellent calculated detonation performances [71]. These reported AT ionic liquids and salts would be applied as potential safe EMs. Importantly, this work provided some advice for development of insensitive EMs.

(Trinitromethyl)-2*H*-tetrazole (**HTNTz**) **77** could be synthesized conveniently through nitration of acid **76** and basic hydrolysis. **HTNTz** could be transformed to the salts **78**–**83**. Moreover, the ammonia adducts, **82a** and **83a**, could be obtained by addition of NH_3 . Tetrazolate **84** and **85** were also produced via treatment of **77** with hydroxylamine and hydrazine. Acid treatment of **84** and **85** led to 5-(dinitromethylene)-4,5-dihydro-1*H*-tetrazole **86**, which was transformed into **87** by reaction with K_2CO_3 (Scheme 6). The authors also implemented thermal stability testing (DTA) and initial safety measurements (friction, electrostatic and impact sensitivity) and found that introduction of ammonia or water to the crystal lattice of the salts led to lowered impact sensitivity. The authors also demonstrated that the target salts **80**–**82** and **84** possessed a positive oxygen balance and were overoxidized, while **79**, **83a** and **85**–**87** had a negative oxygen balance and ammonium salt **78** was oxygen-balanced. The salts **84**, **85** and **87** showed higher decomposition temperatures than the related free acid **86** [74]. Notably, this report provided meaningful guidance to design EMs with good oxygen balance and energetic performance.

3 Nitrogen-Rich EMs Based on Di-Tetrazole Skeleton

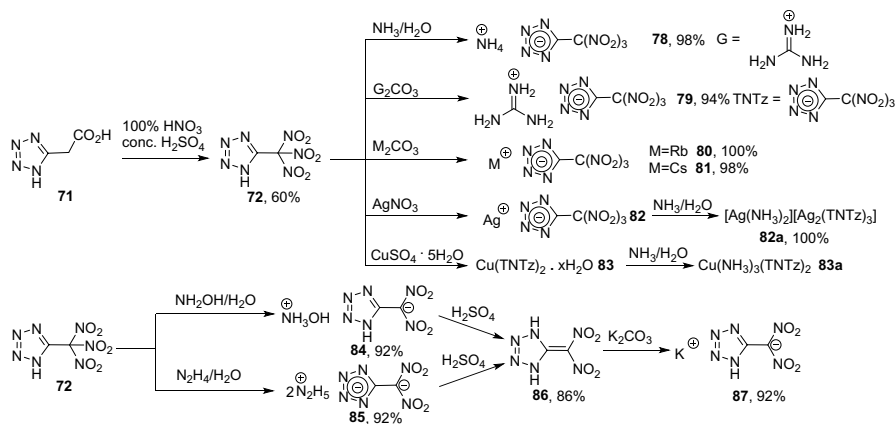
3.1 Nitrogen-Rich Molecules Based on Di-Tetrazole

In 2012, Sinditskii and the co-author synthesized 3,6-bis(1*H*-1,2,3,4-tetrazol-5-ylimino)-1,2,4,5-tetrazine (**BTATz**) as well as 3,6-dihydrazino-1,2,4,5-tetrazine (**DHT**) and examined their thermal stability through nonisothermal and isothermal means (Scheme 7). The authors considered that the first period for the decomposition of **DHT** was a unique redox process, during which tetrazine was reduced by hydrazine functional group to generate nitrogen molecule as well as

Table 7 Physiochemical properties of compounds **63**–**70** [71]

Compd	T_m^a (T_g)/°C	T_d^b /°C	d^c (calcd)/g·cm ⁻³	$\Delta H_f^{d,e}$ (cation)/ kJ·mol ⁻¹	ΔH_L^f /kJ·mol ⁻¹	ΔH_f^g /kJ·mol ⁻¹	ΔH_f^h /kJ·g ⁻¹	p^h /GPa	D^j /m·s ⁻¹
63	125	164	1.48(1.55)	770.0	570.2	383.6	3.28	24.8	8786
64	141	207	1.41(1.44)	620.9	497.8	306.9	1.65	16.3	7529
65	114	217	1.62(1.55)	910.7	529.5	565.0	3.34	23.3	8360
66	126	220	1.54(1.46)	566.7	545.1	205.4	1.43	19.4	8055
67	96	211	1.51(1.49)	646.7	528.2	302.3	1.90	20.1	8149
68	(-24)	174	1.46(1.49)	866.7	504.5	546.0	2.98	18.9	7334
69	(-38)	171	1.39(1.44)	828.2	488.6	523.4	2.65	16.4	7397
70	171	190	1.57(1.56)	974.3	503.0	655.1	3.29	23.2	8385
A ^j	159	163	1.75	–	516.9	571.4	2.86	31.4	8843
B ^j	165	165	1.63	–	497.9	487.5	2.27	25.5	8276
C ^k	147	214	1.85	–	466.5	400.6	1.28	29.5	8182

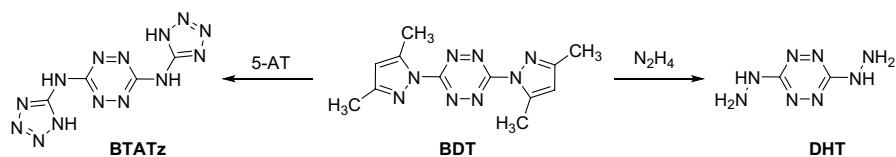
^aMelting point/phase transition temperature. ^bThermal degradation. ^cDensity, gas pycnometer, 25 °C. ^dMolar enthalpy of the formation of cation. ^eMolar enthalpy of the formation of AT anion, 183.8 kJ mol⁻¹. ^fLattice energy. ^gMolar enthalpy of the formation of salt. ^hDetonation pressure. ⁱDetonation velocity. ^jA: 5-Aminotetrazolium 5-nitrotetrazolate; B: 5-aminotetrazolium 5-nitrotetrazolate; Ref. [72]. ^kC: 5-aminotetrazolium picrate; Ref. [73]



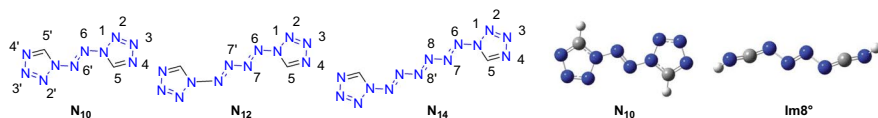
Scheme 6 Synthesis of high-nitrogen energetic tetrazole salts **78–87** [74]

diaminodihydropyridazine. For **BTATz**, decomposition started with tetrazole units. The existence of preliminary isomerization in tetrazole decomposition caused the high observable activating energy for decomposition (57.5 kJ/mol or 240.6 kcal/mol) in the 250–334 °C interval. At higher temperatures in the wave of combustion, the activating energy for the decomposition of **BTATz** was relatively lower (128.4 kJ·mol⁻¹ or 30.7 kcal·mol⁻¹), close to theoretical data [75]. This report provided value to obtain thermostable EMs.

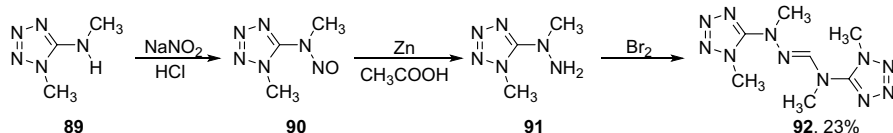
Among the azo-stabilized high-nitrogen molecules, 1,19-azobis(tetrazole) (**N**₁₀), a possible candidate eco-friendly compound, possessed the largest content of nitrogen. Zhang and the co-authors investigated the potential energy surface of **N**₁₀ in details by theoretical calculations and also calculated the major decomposition manners through theory modeling of canonical transition state [76]. The authors predicted that the cycle break of the **N**₁₀ and the release of N₂ to produce the linear **Im8**^o were a main decomposition pathway. The generated **Im8**^o was determined through a fournitrogen atom linkage, which was stabilized via two HNC substituents. Its complete decomposition was dramatically exothermic having an energy barrier of 67.5 kcal·mol⁻¹. The overall liberated heat of **N**₁₀ complete decomposition was 167.12 kcal·mol⁻¹, with the formation of final products including 2HNC and 4N₂. According to the mechanism of **N**₁₀ thermal decomposition, the new species **N**₁₄ and **N**₁₂ were demonstrated (Scheme 8). The energy barriers for beginning N₂ elimination from the tetrazoles of **N**₁₄ and **N**₁₂



Scheme 7 Synthesis of **BTATz** and **DHT** [75]



Scheme 8 Structure of N_{10} , N_{12} and N_{14} [76]

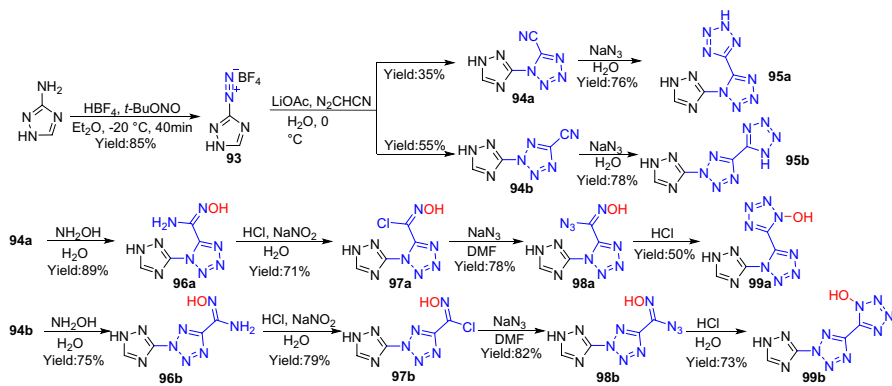


Scheme 9 Synthesis of **92** [77]

were $5.1 \text{ kcal mol}^{-1}$ less than that of N_{10} , which implied that the new compounds N_{14} and N_{12} have longer nitrogen linkages stabilized through two tetrazole cycles, which should be obtained predictably in the near future.

1,4-Bis-[1-methyltetrazol-5-yl]-1,4-dimethyl-2-tetrazene **92** is facilely obtained by a one-pot process by applying **89** as a reactant (Scheme 9) [77]. First, **89** was transformed to the *N*-nitrosamino-1*H*-tetrazole **90** and then reduced by CH_3COOH and Zn system to form the desired 1,1-substituted hydrazine derivative **91**. In the presence of Br_2 , the in situ oxidation of **91** occurred to produce the target **92**. The structure of **92** was determined by x-ray, NBO and MO analysis. The physical natures of **92** were demonstrated by MS and IR pyrolysis experiments and drop hammer. The results showed that **92** could be described as a novel stable HEDM with the high performances required for a potential gas generator [78]. Notably, the author successfully stabilized an acyclic nitrogen with four N atoms (2-tetrazene) by two tetrazolyl groups in this report.

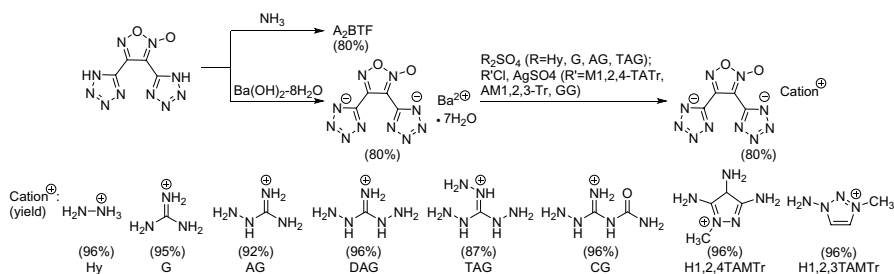
In 2022, Liu and Tang developed a lithium-promoted cycloaddition of salt **93** and diazoacetonitrile, which resulted in the generation of two cyanotetrazoles (**94a**, **94b**). Additionally, the cyano in cyanotetrazoles (**94b** and **94a**) was transformed to tetrazole *N*-oxide or tetrazole for producing heterocyclic compounds (**95a**, **95b**, **99a** and **99b**) (Scheme 10). The energetic performances of these compounds were investigated. 1,5-Disubstituted tetrazoles (**94a**, **95a** and **99a**) displayed lower sensitivities and higher decomposition temperatures than 2,5-disubstituted tetrazoles (**94b**, **95b** and **99b**). Compared to RDX, compound **95a** ($D = 9052 \text{ m}\cdot\text{s}^{-1}$, $TD = 220 \text{ }^\circ\text{C}$, $FS = 200 \text{ N}$, $IS = 13 \text{ J}$) exhibited higher stability, lower sensitivities and better detonation performances, which was expected for use as a potential Ems [79]. This work provided important references to design heterocyclic nitrogen-rich energetic EMs with good stability and high performance.



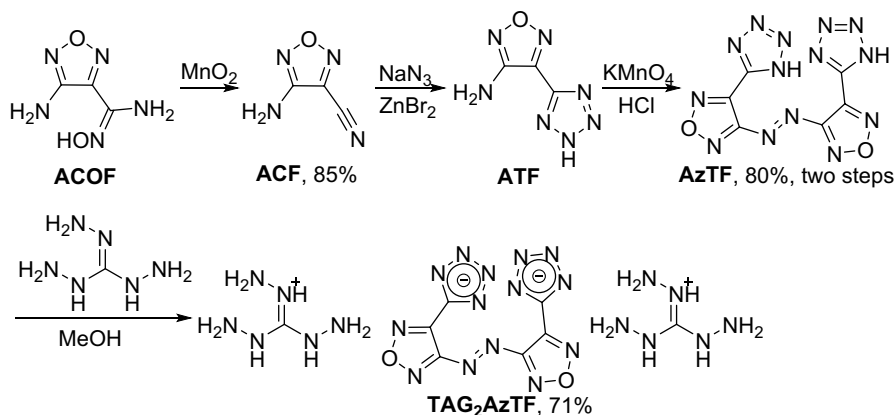
Scheme 10 Synthesis of cyanotetrazoles and tricyclic heterocyclic compounds [79]

3.2 Nitrogen-Rich Salts Based on Di-Triazole

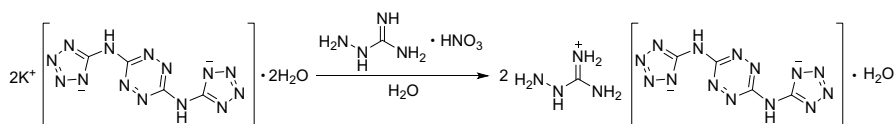
In 2015, Klapötke and co-authors prepared a series of salts based on H_2BTF through metathesis of the barium salt with the sulfate salts obtained in advance by treatment of Ag_2SO_4 with chloride or iodide salts. The authors used the following nitrogen-containing counter anions to produce these energetic salts: hydrazinium (Hy), ammonium (A), aminoguanidinium (AG), guanidinium (G), triaminoguanidinium (TAG), diaminoguanidinium (DAG), 1-methyl-3,4,5-triamino-1,2,4-triazolium (H1,2,4TAMTr), N-carbamoylguanidinium (CG) and 1-amino-3-methyl-1,2,3-triazolium (H1,2,3AMTr) (Scheme 11). Compared to the corresponding neutral molecule, most of these salts exhibited higher decomposition temperatures. TAG₂BTF displayed the lowest temperature of decomposition ($TD = 2208\text{ }^\circ\text{C}$), while the diaminoguanidinium ($TD = 2908\text{ }^\circ\text{C}$) and barium ($TD = 2978\text{ }^\circ\text{C}$) salts possessed the best thermal stability. The densities were located at the range of 1.56 to $1.85\text{ g}\cdot\text{cm}^{-3}$. Additionally, these salts were endothermic molecules (formation enthalpies were 471.6 to $1762.0\text{ kJ}\cdot\text{mol}^{-1}$). Moreover, Hy₂BTF salt displayed the best detonation performance ($p_{C-J} = 32.0\text{ GPa}$, $V_{Det} = 8915\text{ m}\cdot\text{s}^{-1}$) [80]. Notably, the authors realized high energetic performance,



Scheme 11 Synthesis of dianionic salts of H_2BTF [80]



Scheme 12 Synthesis of triaminoguanidinium salt (**TAG₂AzTF**) [81]



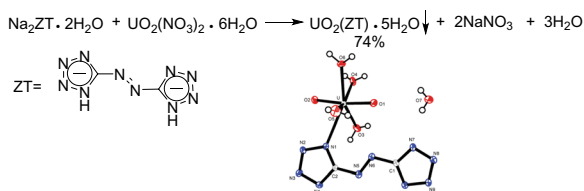
Scheme 13 Synthesis of triaminoguanidinium salt (**TAG₂AzTF**) [82]

suitable thermal stability and good oxygen balance of EMs through cooperation of tetrazolate with oxygen involved furoxan.

Triaminoguanidinium salt (**TAG₂AzTF**) was prepared successfully by treatment of ammonia with (*E*)-1,2-bis(4-(1*H*-tetrazol-5-yl)-1,2,5-oxadiazol-3-yl)diazene (**AzTF**) (Scheme 12). Benefiting from the high-nitrogen content, this **TAG** salt possessed a $\Delta_f H$ of 1481 kJ·mol⁻¹. Compared to compound **AzTF**, the salt **TAG₂AzTF** exhibited relatively large impact sensitivity and low thermal stability [81]. **AzTF** showed the most promise for application as an explosive because of the high thermal stability as well as good performance, while the corresponding salt (**TAG₂AzTF**) was favored as a high-nitrogen gas generator regarding its large nitrogen content and suitable overall sensitivity.

The high-nitrogen energetic ionic salt (2CH₇N₄⁺·C₄H₂N₁₄²⁻·2H₂O, **TAG₂AzTF**) of 3,6-bis([1*H*-1,2,3,4-tetrazol-5-yl)-amino]-1,2,4,5-tetrazine (**BTATz**) could be prepared and determined through Fourier transform IR spectrometry, x-ray analysis, NMR and elemental analysis (Scheme 13). The authors also studied thermal decomposition of **TAG₂AzTF** via TGA and DSC. The temperature of the exothermic peak was 509.72 K, which demonstrated that hydrated salt showed excellent thermostability. The authors also found that **TAG₂AzTF** displayed good thermal safety compared with other salts of **BTATz** [82].

The high-nitrogen ionic compound, uranyl(VI), was produced successfully from sodium salt (Scheme 14). The structure of UO₂(ZT)·5H₂O was measured by x-ray analysis and vibrational spectroscopy. UO₂(ZT)·5H₂O displayed an uncommonly

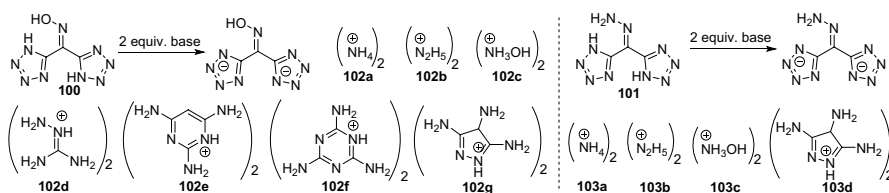
Scheme 14 Synthesis of $\text{UO}_2(\text{ZT}) \cdot 5\text{H}_2\text{O}$ [83]

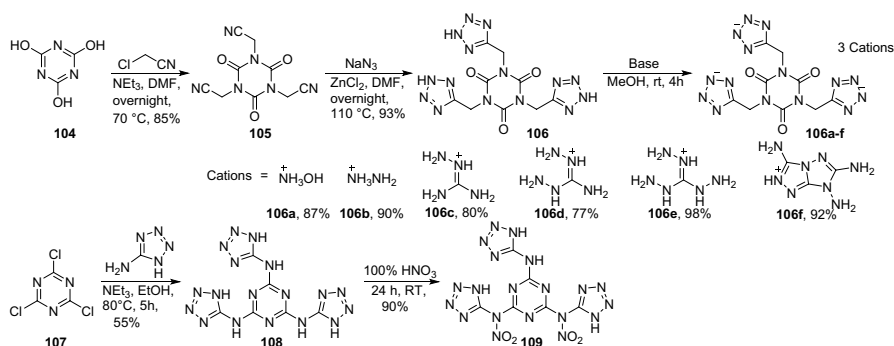
distorted angle of 172.4° for $\text{O}=\text{U}=\text{O}$. The authors showed that this molecule was one of the highest nitrogen uranium molecules (26.72% N per weight). In the presence of neutron bombardment, this compound did not decompose, indicating its exceptional stability [83]. Notably, this work provided significant access to obtaining high-nitrogen uranium compounds with radiation stability.

A series of novel high-nitrogen energetic tetrazole salts, **102a–102g** and **103a–103d**, were obtained successfully according to the reported procedure (Scheme 15) [84–89]. These energetic tetrazoles salts showed large nitrogen content, pressure density, good thermostabilities, excellent properties of detonation, acceptable sensitivities of friction and impact. Particularly, salts **103c** and **103b** possessed large formation heats, good velocities of detonation ($8839 \text{ m}\cdot\text{s}^{-1}$ and $9050 \text{ m}\cdot\text{s}^{-1}$) and pressures (28.8 GPa and 28.7 GPa) and attractive sensitivities (20 J and 35 J) [90]. These novel molecules showed potential to take place of current nitrogen-rich EMs like TATB, TNT and RDX.

4 Nitrogen-Rich EMs Based on Tri- and Tetra-Tetrazole Skeleton

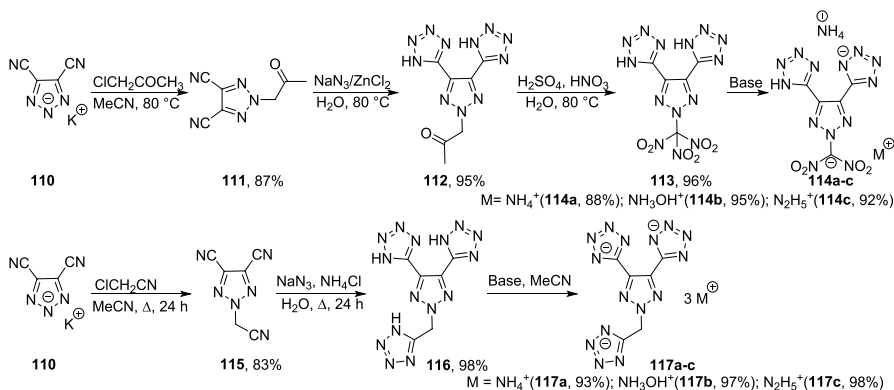
Nitrogen-rich salts (**106a–f**) were prepared from intermediate **106**, and product **109** was produced from cyanuric chloride through an efficient, simple two-step synthetic procedure (Scheme 16). All of these salts (**106a–f**) displayed positive formation heats ($205–1889 \text{ kJ}\cdot\text{mol}^{-1}$), high densities ($1.65–1.83 \text{ g}\cdot\text{cm}^{-3}$), high pressures of detonation ($20.73–27.34 \text{ GPa}$) and velocities ($7876–8832 \text{ m}\cdot\text{s}^{-1}$) and acceptable thermal stabilities ($TD=165–269 \text{ }^\circ\text{C}$). Compound **109** showed better detonation properties ($DP=30 \text{ GPa}$, $VOD=8660 \text{ m}\cdot\text{s}^{-1}$) and the highest density ($1.85 \text{ g}\cdot\text{cm}^{-3}$) [91]. Based on their facile synthesis, good detonation properties, high content of nitrogen and suitable thermal stabilities, these molecules had potential applications as nitrogen-rich EMs.

**Scheme 15** Synthesis of tetrazole salts **102a–102g**, **103a–103d** [90]



Scheme 16 Synthesis of **106a–106f**, **108–109** [91]

In 2022, Shreeve and co-authors described the synthesis of nitrogen-rich azoles, which were derived from the combination of triazole and tetrazoles. Treatment of **110** [92] with chloroacetone in MeCN under reflux formed the product **111** in 87% yield. Using ZnCl_2 as a catalyst, nitriles of **111** reacted with sodium azide to produce bis-tetrazole **112** in good yield. In the presence of mixed acids, nitration of **112** occurred to yield **113**. Treatment of bases like hydroxylamine, hydrazine and ammonia with **113** generated the target energetic salts **114a–c** in good yield. Potassium salt **110** reacted with chloroacetonitrile to produce acetonitrile **115**, which was then transformed into tri-tetrazole **116** by treatment with NaN_3 in the presence of NH_4Cl . Neutralization of the three tetrazole rings in **116** obtained the target tri-ionic salts **117a–c** (Scheme 17). Interestingly, the salts **114b** and **114c** showed good detonation velocities ($D_v=9376 \text{ m}\cdot\text{s}^{-1}$ and $D_v=9418 \text{ m}\cdot\text{s}^{-1}$), while the detonation velocities of **117c**- $0.5\text{H}_2\text{O}$ ($D_v=9058 \text{ m}\cdot\text{s}^{-1}$) and **117b**- H_2O ($D_v=8998 \text{ m}\cdot\text{s}^{-1}$) were better than that of RDX ($D_v=8795 \text{ m}\cdot\text{s}^{-1}$). From the theoretical analyses, the authors deduced that almost all these compounds were insensitive to stimuli for the present hydrogen bond interactions [93]. Importantly, this work was the first case of



Scheme 17 Synthesis of salts **114**, **117** [93]

insensitive tri-cationic nitrogen-rich salts with good performance and suitable stability to our knowledge.

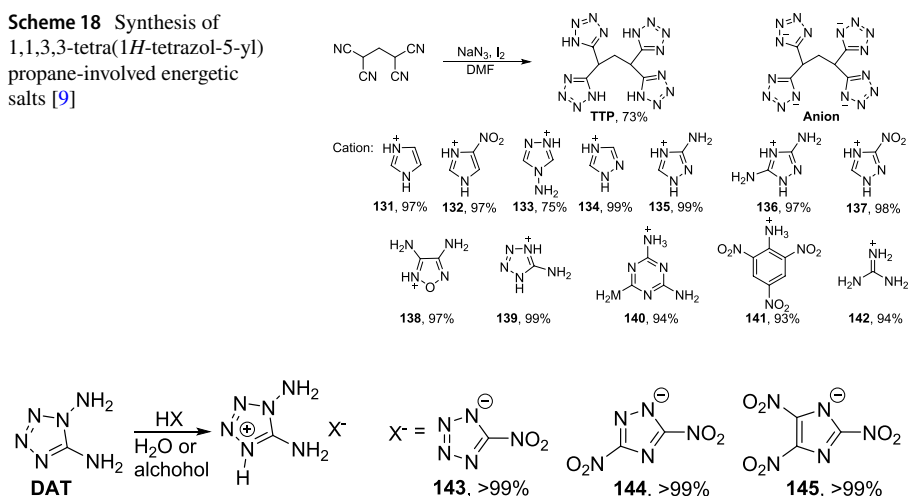
Deprotonation of a novel high-nitrogen compound, 2,3,5,6-tetra(1*H*-tetrazol-5-yl)pyrazine (H_4 TTP), with various bases resulting in a series of salts: aminoguanidinium (**130**), guanidinium (**129**), hydroxylammonium (**128**), hydrazinium (**127**), ammonium (**126**), caesium (**125**), rubidium (**124**), potassium (**123**) and sodium (**122**) (Table 8). Among these salts, the guanidinium (297 °C) and caesium (300 °C) salts showed the highest decomposition temperature, while hydroxylammonium salt displayed the lowest temperature of decomposition (207 °C). Hydroxylammonium

Table 8 Physiochemical properties of compounds **122**–**130** [94]

Cation:	Na^+ K^+ Rb^+ Cs^+ NH_4^+ $H_2N-NH_3^+$ $HO-NH_3^+$ $H_2N-C(=NC)-NH_2^+$ $H_2N-C(=NC)-NH_2^+$
(Yield)	122 (78%) 123 (84%) 124 (94%) 125 (96%) 126 (94%) ^A 127 (93%) ^{Hy} 128 (94%) ^{HA} 129 (91%) ^{GoH} 130 (94%) ^{AGoH}
Formula	$(A)_4TTP$ $(Hy)_4TTP$ $(HA)_4TTP$ $(GuH)_4TTP$ $(AGuH)_4TTP$ H_4TTP ^[8]
Formula	$C_8H_{16}N_{22}$ $C_8H_{20}N_{26}$ $C_8H_{16}N_{22}O_4$ $C_{12}H_{24}N_{30}$ $C_{12}H_{28}N_{34}$ $C_8H_4N_{18}$
N^a (%)	73.31 75.80 63.62 71.40 73.43 71.58
$- \Omega^b$ (%)	91.34 86.58 66.06 97.86 93.73 81.75
T_{dec}^c (°C)	286 247 207 297 267 260
ρ^d (g·cm ⁻³)	1.65 1.66 1.75 1.55 1.70 1.945
$\Delta_f H^o_{(s)}$ (kJ·mol ⁻¹)	320 989 625 523 926 1383
$\Delta_f H^o_{(s)}$ (kJ·kg ⁻¹)	760 2058 1290 889 1428 3926
EXPLOS 6.04 ^[15]	
$- \Delta_E U^{o(f)}$ (kJ·kg ⁻¹)	1161 2450 3166 1314 1840 3530
T_{C-J}^e (K)	1278 1910 2350 1376 1600 2692
P_{C-J}^h (GPa)	15.5 23.7 24.9 14.3 22.4 28.0
V_{C-J}^i (m·s ⁻¹)	7229 8364 8360 6873 8248 8655
Gas vol.^j (dm³·kg⁻¹)	830 852 833 829 839 678
I_{sp}^k (s)	141 184 193 147 167 203

^aNitrogen content. ^bOxygen balance. ^cTemperature of decomposition. ^dDensity at 298 K. ^eStandard molar enthalpy of formation. ^fHeat of detonation. ^gDetonation temperature. ^hDetonation pressure. ⁱDetonation velocity. ^jVolume of detonation gases at standard temperature and pressure conditions. ^kSpecific impulse

Scheme 18 Synthesis of 1,1,3,3-tetra(1*H*-tetrazol-5-yl)propane-involved energetic salts [9]



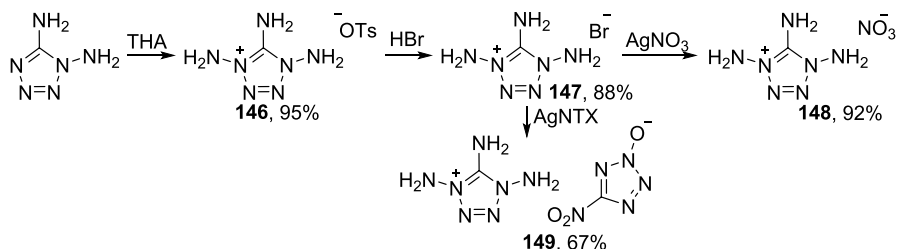
Scheme 19 Synthesis of DAT nitro-substituted azolate salts [95]

(HA)₄TTP (**128**; 23.7 GPa, -2450 kJ·kg⁻¹, 183.5 s, 8364 m·s⁻¹) and hydrazinium (Hy)₄TTP (**127**; 24.9 GPa, -3166 kJ·kg⁻¹, 192.5 s, 8360 m·s⁻¹) salts possessed remarkable datas of performance characteristics [94].

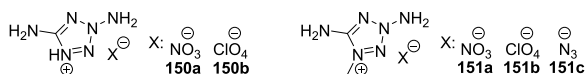
1,1,3,3-Tetra(1*H*-tetrazol-5-yl)propane-involved high-nitrogen salts **131–142** could be prepared through a straight and convenient method. The target tetraanionic salts **131–142** were obtained from TTP (Scheme 18). The enthalpy of formation of **133**, **137** and **139** were large (>1900 kJ mol⁻¹). The authors also found that the introduction of a nitro to the imidazole cycle increased the HOF. The salts **141** ($D=7.51$ km·s⁻¹, $P=24.13$ GPa) and **137** ($D=7.53$ km·s⁻¹, $P=24.41$ GPa) showed good performance of detonation [9]. This investigation gave some important information to understand the effect of nitro, amino and heterocycles in the manufacture of EMs with improved performance.

5 Other Nitrogen-Rich EMs Based on Tetrazole Skeleton

The nitro-azolate DAT salts **143–145** could be prepared and determined via NMR, IR, thermal stability, elemental analysis, density and phase behavior (Scheme 19). The calculated detonation pressure (P) data of **143–145** were located between 28.05 to 29.88 GPa, and the velocities (D) were 8343 to 8655 m·s⁻¹, making them promising EMs. These compounds possessed a balance of oxygen near zero (-23.8 to -33.5%). All these salts showed suitable thermal stabilities (T_d from 176 to 187 °C) and large energy densities (1.65 to 1.74 g·cm⁻³). The impact sensitivities of **143–145** were <1 J, 28 J and >60 J, respectively. Thus, salt **143** could be applied as a potential detonator or initiator, and **145** had a potential application as an impact insensitive EM [95].



Scheme 20 Synthesis of 1,4,5-triaminotetrazolium salts [96]

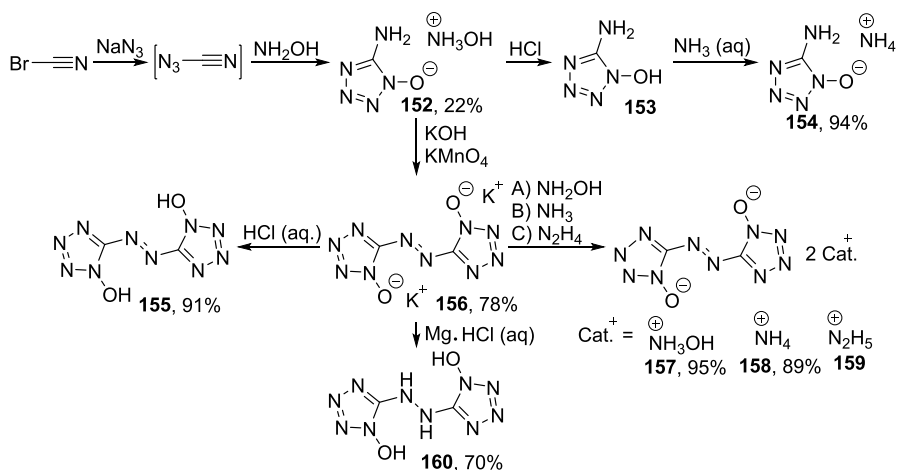


Scheme 21 Structure of high-nitrogen salts **150a-b**, **151a-c**[97]

High-nitrogen energetic compounds 1,4,5-triaminotetrazolium tosylate **146** and salts **147**–**149** were synthesized through amination of diamino-1,2,3,4-tetrazole and metathesis reactions (Scheme 20). For the dramatically large content of nitrogen, the formation heats, thermal and explosive sensitivities of these compounds were very high. Tosylate salt **146** showed the lowest sensitivity with 240 J and 10 N of impact and friction sensitivities. For all compounds **147**–**149**, friction sensitivities were < 10 N and impacts were ≤ 2 J. The velocities of detonation (V_{det}) of **148** and **149** were 8779 m·s⁻¹ and 8872 m·s⁻¹. Regarding a potential application as propellant ingredients, **148** and **149** exhibited large specific impulses (260 s for **148** and 259 s for **149**). All salts **147**–**149** decomposed at 78 to 102 °C, indicating the limited practical use as Ems [96]. This study did offer the insight that limited thermal stability appeared when the nitrogen content and formation heats were enhanced.

The energetic performances of high-nitrogen salts **150a–c**, **151a–c** were also investigated (Scheme 21). The calculated detonation velocity for **150a** was very high (9127 m s⁻¹). The author found that the decomposition temperature of the methylated nitrate and perchlorate salts **151a–b** was significantly higher than that of the corresponding protonated species **150a** and **150b**, while the explosive performances decreased because of the methylation. Compared to **150a** and **150b** with the corresponding methylated salts **151a** and **151b**, the impact sensitivity offered the same data (IS (**150b**, **151b**)=2 J, IS (**150a**, **151a**)=3 J) [97]. This study did offer the insight that limited thermal stability appeared when the nitrogen content and formation heats were enhanced.

Treatment of cyanogen azide with aqueous hydroxylamine afforded **152**. Using **152** as a precursor, various energetic salts (**156**–**160**) were obtained successfully (Scheme 22). Compound **152** and its salt (**156**) showed high detonation velocities (8609 m·s⁻¹ and 9056 m·s⁻¹), with friction sensitivities of 108 and 360 N and an impact sensitivity of 10 J. The monoclinic configuration of compound **153** showed a higher velocity of detonation (9312 m s⁻¹) for the higher density. Salt **157** displayed

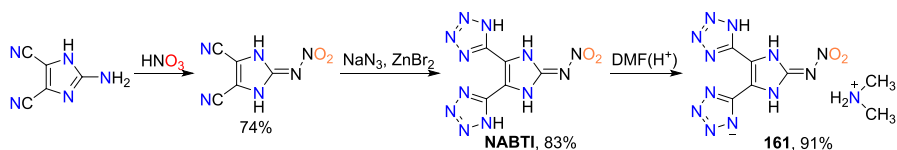


Scheme 22 Synthesis of energetic salts **156–159** [98]

remarkably high performance (338 kbar and 9032 m·s⁻¹). The authors also suggested that salts **157–159** could be applied as propellant or explosive ingredients [98].

A new high-nitrogen molecule (**NABTI**) bearing bis(tetrazole)imidazole and salt (**161**) was prepared successfully (Scheme 23). The authors also demonstrated that both of these two compounds had layer-by-layer packing models and regular planar configurations, and the sensitivity to mechanical stimuli could be weakened by the interactions of π - π and 3D hydrogen-bonding network inside the crystals. **NABTI** also displayed positive formation heat (916.8 kJ·mol⁻¹), large nitrogen content (63.6%), high density (1.80 g·cm⁻³) and good detonation performance ($P=31.4$ GPa and $D=8329$ m·s⁻¹) [99]. These two energetic compounds based on bis(tetrazole)imidazole were good candidates for EMs.

The coordination compounds based on tetrazole were also developed as high-nitrogen energetic complexes. For example, the high-nitrogen complex [Cd(DAT)₆](NO₃)₂ was obtained via treatment of DAT with Cd(NO₃)₂·6H₂O. The structure of this complex was determined by FT-IR, elemental and x-ray analysis. The Cd²⁺ cation chelated with six N atoms in the ligand of DAT to give a hexacoordinating distorted octahedral molecule. The [Cd(DAT)₆](NO₃)₂ molecules were connected by two kinds of hydrogen bonds, giving a stable structure with a three-dimensional net. The authors also found that the exothermic activation energy of this complex was 121.7 kJ·mol⁻¹ [100]. Other complexes like copper(II) dicyanamide compounds based on *N*-substituted tetrazole



Scheme 23 Synthesis of **NABTI** and its salt **161** [99]

were also synthesized. These complexes displayed good energetic performance as well as moderate sensitivities ($FS > 80N$, $IS > 6$) [101].

Two environmental-friendly high-nitrogen energetic metal–organic frameworks (MOFs), $[(AG)_3(Co(btm)_3)]$ (Fig. 3) and $\{[(AG)_2(Cu(btm)_2)]\}_n$, in which H_2btm was bis(tetrazole)methane and AG was aminoguanidinium (Fig. 4), were manufactured and determined through x-ray analysis. The authors also demonstrated that the two energetic MOFs exhibited abundant hydrogen bonding with very large content of nitrogen, suitable insensitivities, favorable thermal stabilities and good detonation performances [102]. Compared to other known high-energy MOFs [103, 104], these two anionic MOFs also showed some advantages like good detonation performances and environment friendly.

Combining the advantages of furazan and tetrazole, a 2D MOF complex $[Cd(H_2O)_2(AFT)_2]_n$ (**HAFT**: 4-amino-3-(5-tetrazolate)-furazan) was prepared and measured by FTIR, elemental and x-ray analysis. In the structure of **HAFT**, Cd^{2+} was hexacoordinated by two water molecules and four AFT groups. Tetrazole showed a classic model of bidentate coordination, in which furazan did not participate. The authors also demonstrated that the decomposition temperature of **HAFT** was $> 250\text{ }^\circ\text{C}$, which indicated the thermal stability of **HAFT** [105]. This 2D coordination complex could be a foundation for the development of the 3D high-nitrogen energetic MOFs.

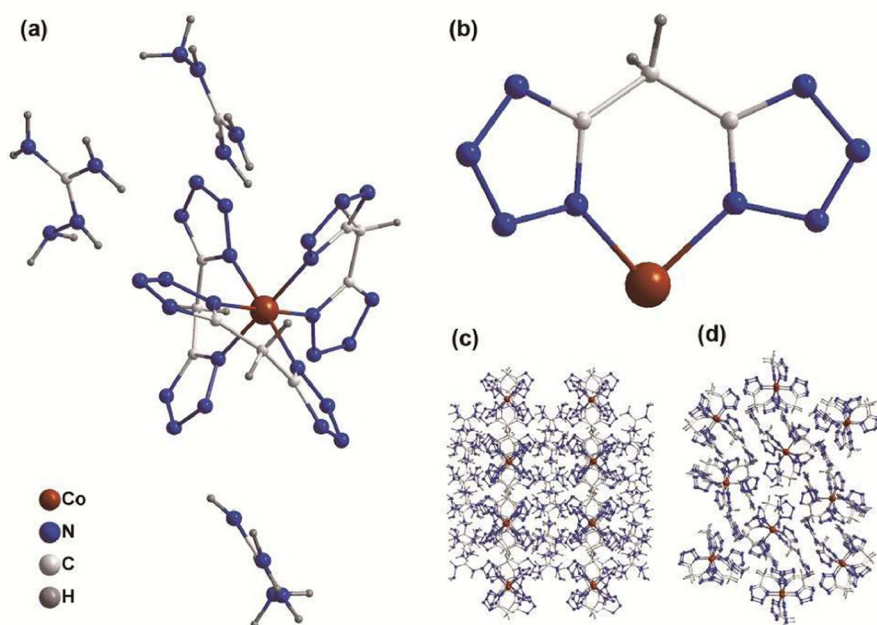


Fig. 3 **a** Coordination environment of Co(III) ions in $[(AG)_3(Co(btm)_3)]$, **b** coordination sites of btm, **c** 3D supramolecular network, **d** 3D supramolecular network. (Images reproduced from Ref. 103 with permission of Royal Society of Chemistry) [102]

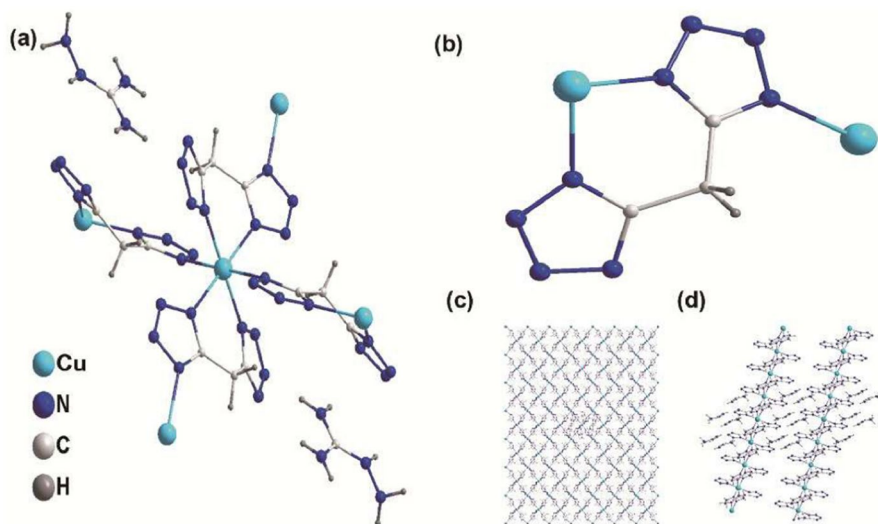


Fig. 4 **a** Coordination environment of Cu(II) ions in $\{[(AG)_2(Cu(btm)_2)]\}_n$, **b** coordination sites of btm, **c** 3D supramolecular network, **d** 3D supramolecular network. (Images reproduced from Ref. 103 with permission of Royal Society of Chemistry) [102]

The high-nitrogen energetic coordination polymers (ECPs) were manufactured using high-nitrogen ligands 5,5'-bistetrazole-1,1'-diolate dehydrate (BTO) and azotetrazole (AT) with promising thermostability but large photosensitivity. By intercalating 5 wt% graphene oxide (GO), the activation energy of decomposition (E_a) for Cu-AT was enhanced between 135.7 and 151.9 $\text{kJ}\cdot\text{mol}^{-1}$; meanwhile, the temperature of the exothermic peak (T_p) rose by 12.6 $^\circ\text{C}$. In sharp contrast to this, the E_a of decomposition for Cu-BTO reduced because of the influence of the same amount GO with little influence on T_p . This demonstrated that GO had a stabilizing influence on the crystal of Cu-AT. Moreover, when 3% GO was added, the resulting $\text{GO}_{0.03}\text{-Cu-AT}$ showed good thermostability ($T_P = 293.7\text{ }^\circ\text{C}$) and a larger density ($2.88\text{ g}\cdot\text{cm}^{-3}$). This ECP could be ignited at a wavelength of 976 nm with an energy of $< 1\text{ mJ}$ (Fig. 5). This small energy laser initiation was recognized as safer [106].

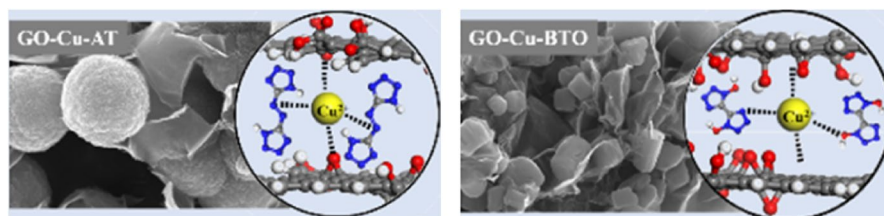


Fig. 5 High-nitrogen energetic coordination polymers GO-Cu-AT and GO-Cu-BTO. (Images reproduced from Ref. 107 with permission of ACS publications) [106]

6 Summary and Outlook

In summary, the nitrogen-rich tetrazole-based EMs have attracted increasing popularity because of their outstanding advantages such as high content of nitrogen and energy density, good thermostability, suitable sensitivity, high energetic performance, environmental-friendly, etc. The nitrogen-rich energetic EMs based on mono-, di-, tri- and tetra-tetrazole skeletons were prepared and characterized successfully; meanwhile, their energetic properties were also investigated systematically. In design and manufacture of practically useful high-nitrogen tetrazole-based EMs, the big issue of achieving the contradictory balance of excellent performance of detonation and good insensitivity still existed.

Although various nitrogen-rich tetrazole-based EMs with good performances have been manufactured, development of other kinds of nitrogen-rich EMs based on tetrazole skeleton is still urgently required. The following challenges should be focused on: (1) Since ionic liquid usually shows remarkable stability, design and preparation of ionic liquid nitrogen-rich EMs based on tetrazole should be enhanced in future research; (2) nitrogen-rich EMs with 2D coordination MOF structure were prepared; thus, 3D high-nitrogen energetic EMs require more attention.

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Declarations

Conflict of Interest The authors declare no conflict of interest.

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