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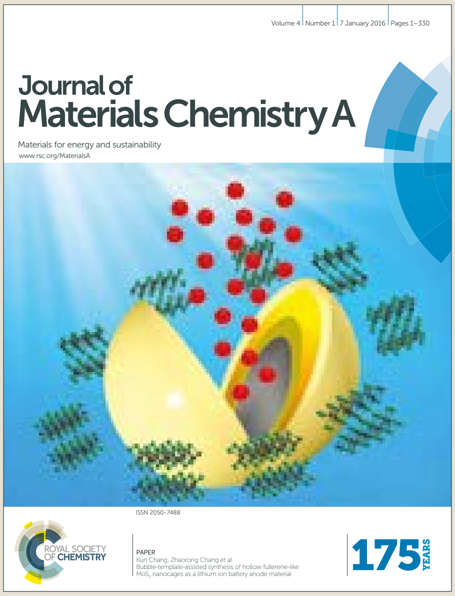

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PAPER
Kun Chang, Zhaorong Chang *et al.*
Bubble-template-assisted synthesis of hollow fullerene-like MoS_2 nanocages as a lithium ion battery anode material

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Journal of Materials Chemistry A

PAPER

High-performing and Thermally Stable Energetic 3,7-Diamino-7*H*-[1,2,4]triazolo[4,3-b][1,2,4]triazole derivatives

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Yongxing Tang,[a] Chunlin He,[a] Gregory H. Imler,[b] Damon A. Parrish[b] and Jean'ne M. Shreeve*[a]

A family of energetic salts based on 3,7-diamino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazol-2-ium were prepared by reaction of 3,7-diamino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazole (**3**) with corresponding energetic acids. The nitration product, 7-nitroimino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazole (**4**), was synthesized by using 100% nitric acid. The calculated detonation performance shows that compound **10**, composed of 3,7-diamino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazol-2-ium and 3,3'-dinitramino-4,4'-azoxyfurazanate, has good density (1.830 g cm^{-3}), high decomposition temperature (201 ^{o}C) and detonation performance (9077 m s^{-1}, 34.4 GPa) as well as acceptable sensitivities (10 J, 240 N), which is superior to those of 1,3,5-trinitroperhydro-1,3,5-triazine (RDX).

Introduction

Developing energetic compounds with high performance and low sensitivity is an important and challenging research topic in design and synthesis of high energy density materials.[1] One of the efficient ways to achieve such targeted properties is the formation of energetic salts given various combinations with tunable cations and anions.[2] Favorite cores are five-membered heterocycles, such as tetrazole, triazole, pyrazole and furazan and their derivatives. Beneficial examples of aromatic nitrogen-rich cations in energetic compounds are mono-, di- or triamino-triazolium and tetrazolium cations[3] (Fig. 1) with high nitrogen content, high positive heat of formation, ring strain, and high density.

Compared to single ring heterocycles reported previously, nitrogen-rich fused heterocyclic compounds have been gaining interest gradually as building blocks for construction of energetic compounds due to chemical stability and high positive heat of formation.[4] A typical example, 3,6,7-triamino-7*H*-[1,2,4]triazolo[4,3-*b*] [1,2,4]triazole (TATOT),[5] which arises from the combination of 3-amino-1,2,4-triazole with 3,4-diamino-1,2,4-triazole through a shared C-N bond, exhibits good thermal stability and high detonation performance. 3,7-Diamino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazole (**3**),[6] which consists of 3-amino-1,2,4-triazole and 4-amino-1,2,4-triazole fused through a shared C-N bond, should contribute positively to the heats of formation and to enhanced densities thus exhibiting promising properties.

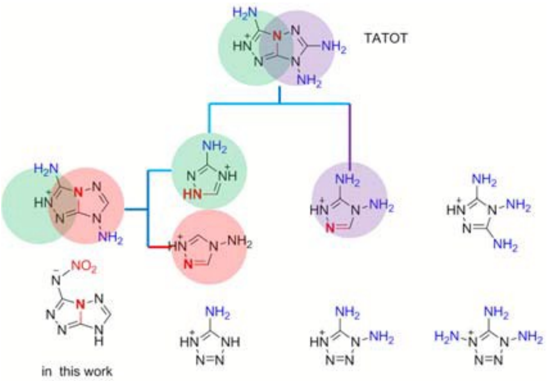

Fig. 1 Mono-, di- or triamino-triazolium and tetrazolium cations and fused heterocyclic ions.

In this study, a series of energetic salts (**5**-**10**), based on the 3,7-diamino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazol-2-ium cation, was synthesized. In addition, the nitration product (**4**) and its hydrazinium salt (**11**) were also prepared. All of the compounds are fully characterized and their energetic properties including thermal stabilities, impact sensitivities, as well as calculated detonation performances were determined. The structures of **4** and **7** were further confirmed by single-crystal X-ray diffraction.

Results and discussion

Synthesis

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Electronic Supplementary Information (ESI) available: [Crystal refinements, calculation detail, X-ray crystallographic files in CIF format for **4** and **7** [CCDC number: 1526400, and 1526401]. See DOI: 10.1039/x0xx00000x

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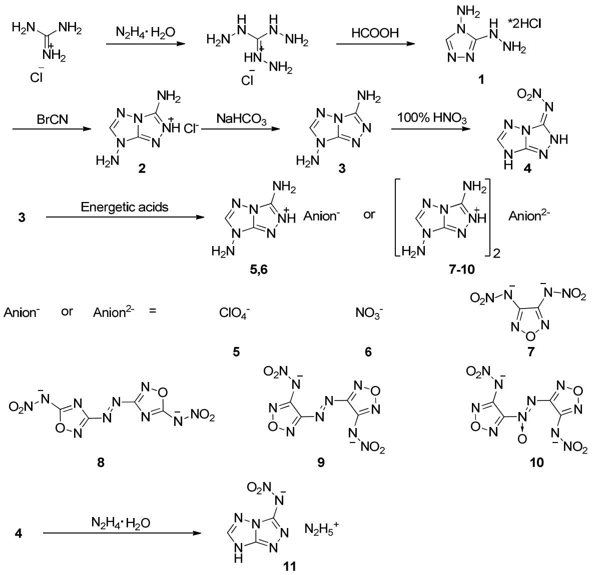
With commercially available guanidium hydrochloride and hydrazine monohydrate to form triaminoguanidium hydrochloride, **1** was obtained by heating at reflux in formic acid for 2 h (Scheme 1).[7] Reaction of **1** with cyanogen bromide in dilute HCl led to the formation of **2** in moderate yield which upon further treatment with sodium bicarbonate generated **3**. The energetic salts (**5**-**10**) were synthesized by reacting **3** with energetic acids directly. In case of **5** and **6**, they could be prepared by adding **3** in dilute nitric acid or perchlorate acid. Due to their good solubility in water, the pure product could be obtained from slow evaporation of the mother liquid. For **7**-**10**, ethanolic solutions of energetic acids were prepared and **3** (two equivalents) was added. All the compounds were obtained in high yield and high purity. When **3** was stirred with 100% nitric acid at 0 °C for 1 h, **4** was prepared by concomitant breaking of the *N*-NH_2 bond. Additionally, the hydrazinium salt (**11**) was obtained by reaction of **4** with hydrazine monohydrate in ethanol.

^{15}N NMR Spectroscopy

As shown in Fig. 2, the ^{15}N NMR spectra of selected compounds (**3**-**5** and **7**) were determined in d_6-DMSO. The signals were assigned by comparison with similar structures,[5] and analysis of ^1H-^{15}N heteronuclear multiple bond correlation (HMBC). The spectrum of **3** has only six signals at δ = -106.1 (N5), -136.5 (N2), -150.1 (N4), -243.9 (N3), -318.2 (N6), -341.2 ppm (N7). The missing signal (N1) was observed at -179.7 ppm in the HMBC spectrum (Fig. S19, ESI). Similarly, only six signals are seen in the spectrum of **4**, (Fig. S20, ESI) while the missing signal (N1) at δ = -179.3 ppm is in the HMBC spectrum. For **5** and **7**, all signals are seen. Due to the effect of the two different anions, the chemical shifts (N4, N5 and N1) in **5** are found at higher field than those in **7**. Additionally, both N6 and N7 can be seen (N6: -317.0 ppm; N7: -323.77 ppm) in the spectrum of **5** while only one peak (-317.1 ppm) was observed in **7**.



Scheme 1 Synthesis of 3,7-diamino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazole (**3**) and its derivatives

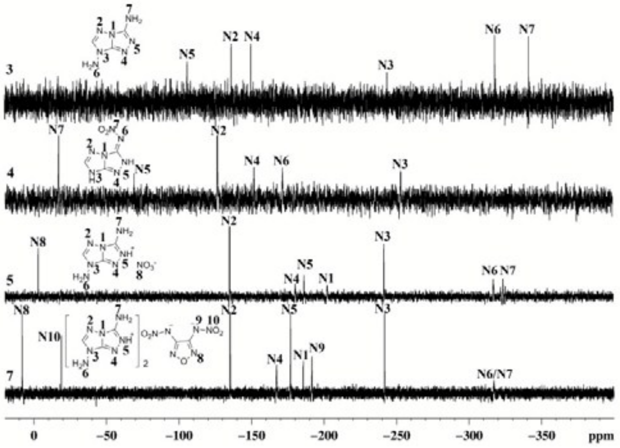


Fig. 2 ^{15}N NMR spectra of compounds **3**-**5** and **7.**

Crystal structures

Compound **4** crystallizes as a monohydrate in the monoclinic space group $P2_1/c$ with a calculated density of 1.774 g cm^{-3} at 150 K. As can be seen in Fig. 3a, it has a zwitter ionic structure with a negative charge at N4 and a protonated nitrogen atom N6. All of the atoms lie in the same plane with an N7-C8-N12-N11 torsion angle of 178.94(16)°. As shown in Fig. 3b, there are several hydrogen bonds and short interactions (C⋯N, C⋯O, C⋯C and N⋯O) in the crystal structure. Additionally, the crystal structure of **4**·H_2O consists of parallel layers along the *b* axis. The layers are stacked above each other with a layer distance of *d* = 3.135 Å.

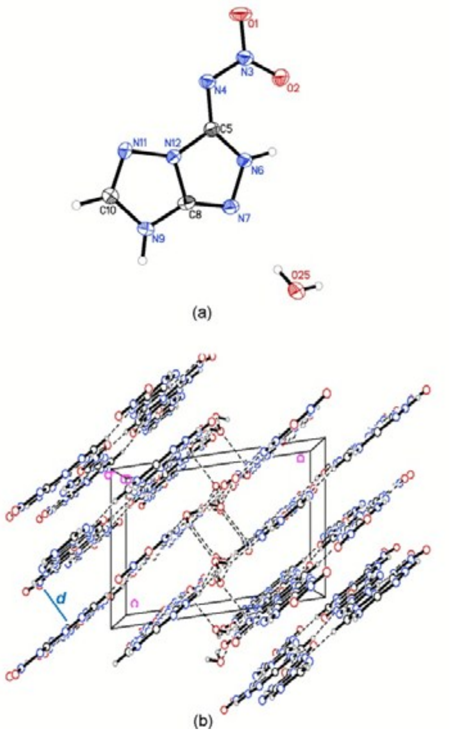


Fig. 3 (a) Molecular structure of **4**. Thermal ellipsoids are drawn at the 50% probability level. (b) Packing diagram of **4** viewed along the *b* axis. Dashed lines represent hydrogen bonding.

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The dihydrate of **7** crystallizes in the monoclinic space group $P2_1/c$ with a density of 1.749 g cm^{-3} at 150 K and four molecules per unit cell (Fig. 4a). In the cations, the two heterocyclic rings are in the same plane with torsion angles N32-C28-N29-C25 of -179.93(15)^{o} and N(17)-C(18)-N(19)-N(20) of 179.15(15)^{o}, respectively. In the anion, the parameters involving the bond lengths and bond angles are consistent with those in the literature.[3a] The torsion angle N(3)-N(4)-C(5)-N(6) is -1.0 (3)^{o}, indicating that the anion is also in the same plane. The nitrogen fused cations, the 3,4-dinitraminofurazanate anion and the water molecule are linked through hydrogen bonds (Fig. 4b). The details can be found in the ESI.

Physicochemical and energetic properties

The physiochemical and energetic properties are given in Table 1. The density is an important parameter which plays an important role in calculation of energetic performance. Densities were measured by using a gas pycnometer at 25 ^{o}C. Compound **10** is the densest of these compounds at 1.83 g cm^{-3}, while the others exhibit moderate densities of ≥1.70 g cm^{-3}. The thermal behavior was determined by differential scanning calorimetric (DSC) measurements at a rate of 5 ^{o}C min^{-1}. The parent compound **3** shows a decomposition temperature of 219 ^{o}C, while the nitration product **4** decomposes at 169 ^{o}C, which is the highest of the neutral nitroimino compounds.[8] After deprotonation of **4**, the hydrazinium salt **11** exhibits a low decomposition temperature of 132 ^{o}C. The energetic salts **5**-**10** formed from the monocation of **3** and corresponding nitrogen rich anions show good thermal stabilities with decomposition temperatures over the range of 167 ^{o}C (**7**) to 222 ^{o}C (**9**).

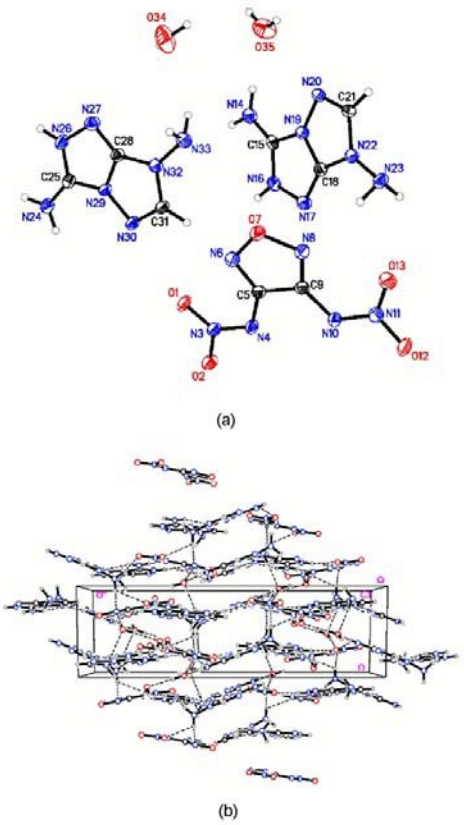

Fig. 4 (a) Molecular structure of **7**. Thermal ellipsoids are drawn at the 50% probability level. (b) Packing diagram of **7** viewed along the *a* axis. Dashed lines represent hydrogen bonding.

Table 1 Physicochemical and energetic properties of compounds **3–11** in comparison with RDX.

Comp	$\rho^{[a]}$ (g·cm^{-3})	Dv [b] (m s^{-1})	$P^{[c]}$ (GPa)	$\Delta H_f^{[d]}$ (kJ mol^{-1}/kJ g^{-1})	$T_{dec}^{[e]}$ (^{o}C)	$IS^{[f]}$ (J)	$FS^{[g]}$ (N)
3	1.712	8461	25.4	480.3/3.45	219	40	360
4·H₂O	1.732	8271	26.6	174.9/0.93	169	6	120
5	1.777	8250	29.0	364.4/1.52	220	4	120
6·H₂O	1.744	8590	28.4	83.9/0.38	191	15	360
7	1.742	8715	29.5	1411.6/3.01	167	8	240
8	1.773	8694	30.1	1682.9/2.98	221	8	160
9	1.761	8732	30.3	1853.2/3.28	222	12	240
10	1.830	9077	34.4	1882.0/3.24	201	10	240
11	1.751	9121	32.1	618.1/3.07	132	12	360
RDX	1.800	8795	34.9	70.3/0.32	204	7.5	120

[a] Density measured by a gas pycnometer at 25 °C; [b] Calculated detonation velocity; [c] Calculated detonation pressure; [d] Calculated molar enthalpy of formation in solid state; [e] Decomposition temperature (onset); [f] Impact sensitivity; [g] Friction sensitivity.

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The heats of formation were obtained by using the Gaussian 03 suite of programs. As expected, all of them show positive heats of formation. Compounds **7**-**10** with large anions exhibit high positive heats of formation. The calculated formation together with the measured densities were used to derive the detonation performances with EXPLO 5 version 6.01 code.[10] Compound **10** has a higher detonation velocity than RDX and a comparable detonation pressure (**10**: *D*: 9077 m s^{-1}; *P*: 34.4 GPa; RDX: *D*: 8795 m s^{-1}; *P*: 34.9 GPa). In addition, the detonation velocity of **11** (9121 m s^{-1}) also exceeds that of RDX, although the detonation pressure is slightly lower (32.1 GPa). For the other compounds **3**-**9**, the calculated detonation velocities lie in the range between 8250 and 8732 m s^{-1} and detonation pressures between 25.4 and 30.3 GPa.

The sensitivities toward friction and impact were measured by using standard BAM methods. The neutral nitramino compound **4** and nitrate salt **5** are sensitive towards impact (**4**: 6 J; **5**: 4 J), and their friction sensitivities are similar to RDX. The other compounds **3** and **6**-**11** show acceptable impact and friction sensitivities, which are less sensitive than those of RDX.

Conclusions

In conclusion, 3,7-diamino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazole (**3**) was synthesized and utilized as a precursor to the energetic salts (**5**-**10**) composed of anions from energetic acids formed in a straightforward manner by neutralization. In addition, the nitration product **4** which results from the breaking of the *N*-NH_2 bond was prepared by nitration of **3** using 100% nitric acid. All the compounds are well characterized including the single crystal X-ray diffraction structures for **4** and **7**. Most of them exhibit good thermal stability except the nitroimino compound (**4**) and its hydrazinium salt (**11**). Calculations show that these compounds have high detonation performance; especially **10** which displays promising properties with a density of 1.830 g cm^{-3}, detonation velocity of 9077 m s^{-1}, detonation pressure of 34.4 GPa, impact sensitivity of 10 J and friction sensitivity of 240 N, which suggests it could be used as a high energy dense material as a replacement for RDX.

Experimental Section

General methods

All reagents were purchased from AK Scientific or Alfa Aesar in analytical grade and were used as received. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz (Bruker AVANCE 300) NMR spectrometer operating at 300.13 and 75.48 MHz, respectively, and a 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 50.69 MHz for ^{15}N spectra. Chemical shifts for ^1H, and ^{13}C NMR spectra are reported relative to $(CH_3)_4Si$. [D_6]DMSO was used as a locking solvent. IR spectra were recorded using KBr plates with an AVATAR 370 FT-IR (Thermo Nicolet) spectrometer. Density was determined at room temperature by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Decomposition temperatures (onset) were recorded on a differential scanning calorimeter (DSC, TA Instruments Q2000) at a scan rate of 5 °C min^{-1}. Elemental analyses (C, H, N) were performed on a CE-440 Elemental Analyzer. Impact and friction sensitivity measurements were made using a standard BAM Fallhammer and a BAM friction tester.

Computational Methods

The gas phase enthalpies of formation were calculated by G2 method. For energetic salts, the solid-phase enthalpies of formation were obtained using a Born−Haber energy cycle.[11] The details are found in the ESI.

X-Ray crystallography

A clear colorless plate crystal of dimensions 0.258 × 0.215 × 0.029 mm^3 (**4**), and a clear colorless block crystal of dimensions 0.295 × 0.081 × 0.030 mm^2 (**7**) were mounted on a MiteGen MicroMesh using a small amount of Cargille immersion oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK_α radiation (λ = 0.71073 Å). An Oxford Cobra low temperature device was used to keep the crystals at a constant 150(2) K during data collection.

Data collection was performed and the unit cell was initially refined using *APEX3* [v2015.5-2].[12] Data reduction was performed using *SAINT* [v8.34A][13] and *XPREP* [v2014/2][14]. Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2014/2].[15] The structure was solved and refined with the aid of the program SHELXL-2014/7.[16] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model.

Syntheses

Caution! Although we have encountered no difficulties during preparation and handling of these compounds, they are potentially explosive energetic materials, which are very sensitive to impact and friction. Mechanical actions of these energetic materials, involving scratching or scraping, must be avoided. Manipulations must be carried out by using appropriate standard safety precautions.

3,7-Diamino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazole hydrochloride (2)[6] 3-Hydrazinium-4-amino-1*H*-1,2,4-triazolium dichloride[3e, 7] (**1**, 2.28 g, 20.0 mmol) was dissolved in dilute hydrochloric acid (50 mL, 2 M), cyanogen bromide (4.24 g, 40 mmol) was added, and the solution was heated to 60 °C for 2 h. After stirring another 3 h at reflux, the solution was cooled and stored in the refrigerator overnight. The precipitate was collected as a white solid and dried in air. White solid (1.93 g, 55% yield). $T_{d\ (onset)}$: 221 °C. ^1H NMR: δ 8.83 (s, 1H), 8.61 (s, 2H), 6.24 (br) ppm. ^{13}C NMR: δ 152.5, 147.6, 142.1 ppm. IR (KBr): $\tilde{\nu}$ 3327, 3281, 3157, 3072, 1964, 1661,

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1615, 1530, 1427, 1224, 1186, 1088, 1027, 949, 759, 703, 589, 580 cm^{-1}.

3,7-Diamino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazole (3)[6] Compound **2** (1.76 g, 10.0 mmol) was dissolved in distilled water (20 mL). Sodium bicarbonate (0.84 g, 10.0 mmol) was added, and after stirring 15 min at 25 °C, the white solid (1.15 g, 83% yield) was filtered, washed with water (15 mL × 2) and dried in air. $T_{d\ (onset)}$: 219 °C. ^{1}H NMR: δ 8.31 (s, 1H), 5.99 (s, 2H), 5.78 (s, 2H) ppm. ^{13}C NMR: δ 149.7, 149.5, 143.6 ppm. IR (KBr): $\tilde{\nu}$ 3313, 3271, 3221, 3104, 1645, 1622, 1589, 1538, 1430, 1231, 1215, 1117, 1080, 1000, 960, 751 cm^{-1}. *IS*: 40 J. *FS*: 360 N.

7-Nitroimino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazole monohydrate (4) Compound **3**[6] (1.0 g, 7.19 mmol) was added slowly to nitric acid (3 mL, 100%) at 0 °C. The solution was stirred for 1 h at 0 °C. The reaction mixture was poured into ice-water (50 mL), the yellow solid was precipitated and collected by filtration, washed with cold water (30 mL) and dried in air. Yellow solid (0.66 g, 49% yield). $T_{d\ (onset)}$: 169 °C. ^{1}H NMR: δ 8.78 (s, 1H) ppm. ^{13}C NMR: δ 149.1, 148.5, 141.6 ppm. IR (KBr): $\tilde{\nu}$ 3136, 1655, 1589, 1518, 1465, 1420, 1292, 1248, 1148, 1113, 1070, 1012, 951, 870, 815, 775 cm^{-1}. Elemental analysis for $C_3H_5N_7O_3$ (187.12): Calcd C 19.26, H 2.69, N 52.40 %. Found: C 19.14, H 2.41, N 51.24 %. *IS*: 6 J. *FS*: 120 N.

3,7-Diamino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazol-2-ium perchlorate (5) Compound **3**[6] (0.278 g, 2 mmol) was added to $HClO_4$ (2 mL, 10%) and the reaction was stirred at 25 °C for 1 h. The solution was allowed to evaporate in air until a white solid was formed. The solid was collected by filtration, washed with ethanol and dried in vacuum to yield **6** (0.417 g, 87% yield). T_m: 215 °C. $T_{d(onset)}$: 220 °C. ^{1}H NMR: δ 13.86 (br), 8.81 (s, 1H), 8.57 (s, 2H), 6.21 (s, 2H) ppm. ^{13}C NMR: δ 152.6, 147.7, 142.2 ppm. IR (KBr): $\tilde{\nu}$ 3343, 3167, 3135, 1701, 1667, 1628, 1590, 1541, 1463, 1430, 1336, 1349, 1271, 1231, 1218, 1120, 969, 935, 899, 760, 715, 670, 625, 589 cm^{-1}. Elemental analysis for $C_3H_6ClN_7O_4$ (239.58): Calcd C 15.04, H 2.52, N 40.92 %. Found: C 15.08, H 2.39, N 40.70 %. *IS*: 4 J. *FS*: 120 N.

3,7-Diamino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazol-2-ium nitrate monohydrate (6) Compound **3**[6] (0.278 g, 2 mmol) was added to HNO_3 (2 mL, 20%) and the mixture was stirred at 25 °C for 1 h. The solution was allowed to evaporate in air until colorless crystals formed. The crystals were collected by filtration, washed with ethanol (5 mL × 2) and dried in vacuum to yield **6** (0.396 g, 90% yield). T_m: 174 °C. $T_{d(onset)}$: 191 °C. ^{1}H NMR: δ 13.93 (br), 8.82 (s, 1H), 8.55 (s, 2H), 6.24 (s, 2H) ppm. ^{13}C NMR: δ 152.8, 147.9, 142.3 ppm. IR (KBr): $\tilde{\nu}$ 1764, 1710, 1686, 1665, 1617, 1575, 1533, 1458, 1384, 1227, 1195, 1096, 1025, 980, 762, 691, 601 cm^{-1}. Elemental analysis for $C_3H_8N_8O_4$ (220.15): Calcd C 16.37, H 3.66, N 50.99 %. Found: C 16.44, H 3.58, N 50.89 %. *IS*: 15 J. *FS*: 360 N.

General procedure for synthesis of 7-10

The energetic acid (1 mmol) was dissolved in ethanol (10 mL), then **3**[6] (0.278 g, 2 mmol) was added while stirring. The reaction mixture was stirred for 2 h at 25 °C. The precipitate formed, was collected by filtration, and washed with ethanol (5 mL × 2) and dried in vacuum to give the products **7-10**.

Bis{3,7-diamino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazol-2-ium} 3,4-dinitraminofurazanate (7) White solid (0.431 g, 92% yield). $T_{d(onset)}$: 167 °C. ^{1}H NMR: δ 8.69 (s, 1H), 7.83 (s, 2H), 6.19 (s, 2H) ppm. ^{13}C NMR: δ 151.8, 151.2, 148.2, 142.6 ppm. IR (KBr): $\tilde{\nu}$ 3300, 3209, 3126, 1697, 1655, 1617, 1537, 1476, 1420, 1374, 1281, 1217, 1097, 1059, 1009, 920, 888, 846, 808, 778, 759, 711, 601 cm^{-1}. Elemental analysis for $C_8H_{12}N_{20}O_5$ (468.31): Calcd C 20.52, H 2.58, N 59.82 %. Found: C 20.17, H 2.34, N 60.10 %. *IS*: 8 J. *FS*: 240 N.

Bis{3,7-diamino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazol-2-ium} 5,5'-dinitramino-3,3'-azo-1,2,4-oxadiazolate (8) Yellow solid (0.508 g, 90% yield). $T_{d(onset)}$: 221 °C. ^{1}H NMR: δ 8.82 (s, 1H), 8.57 (s, 2H), 6.23 (s, 2H) ppm. ^{13}C NMR: δ 175.7, 175.1, 152.6, 147.7, 142.2 ppm. IR (KBr): $\tilde{\nu}$ 3418, 3327, 3189, 1670, 1616, 1560, 1545, 1502, 1457, 1369, 1287, 1205, 1084, 1025, 1002, 983, 970, 847, 763, 711, 605 cm^{-1}. Elemental analysis for $C_{10}H_{12}N_{24}O_6$ (564.36): Calcd C 21.28, H 2.14, N 59.57 %. Found: C 21.38, H 1.92, N 58.15 %. *IS*: 8 J. *FS*: 160 N.

Bis{3,7-diamino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazol-2-ium} 3,3'-dinitramino-4,4'-azofurazanate (9) Orange-red solid (0.497 g, 88% yield). $T_{d(onset)}$: 222 °C. ^{1}H NMR: δ 8.81 (s, 1H), 8.53 (s, 2H), 6.21 (br) ppm. ^{13}C NMR: δ 160.0, 152.6, 152.5, 147.8, 142.2 ppm. IR (KBr): $\tilde{\nu}$ 3560, 3462, 3313, 3061, 1691, 1655, 1605, 1542, 1454, 1374, 1321, 1282, 1231, 1217, 1056, 1017, 950, 806, 777, 760, 690 cm^{-1}. Elemental analysis for $C_{10}H_{12}N_{24}O_6$ (564.36): Calcd C 21.28, H 2.14, N 59.57 %. Found: C 21.16, H 1.97, N 59.62 %. *IS*: 12 J. *FS*: 240 N.

Bis{3,7-diamino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazol-2-ium} 3,3'-dinitramino-4,4'-azoxyfurazanate (10) Yellow solid (0.522 g, 90% yield??). $T_{d(onset)}$: 201 °C. ^{1}H NMR: δ 8.81 (s, 1H), 8.55 (s, 2H), 6.30 (br) ppm. ^{13}C NMR: δ 155.1, 154.9, 153.9, 152.6, 151.2, 147.7, 142.2 ppm. IR (KBr): $\tilde{\nu}$ 3542, 3500, 3434, 3381, 1708, 1685, 1637, 1535, 1518, 1459, 1406, 1394, 1565, 1321, 1282, 12262, 1234, 1191, 1034, 998, 944, 843, 829, 758, 712, 597 cm^{-1}. Elemental analysis for $C_{10}H_{12}N_{24}O_7$ (580.36): Calcd C 20.70, H 2.08, N 57.92 %. Found: C 20.56, H 2.12, N 56.79 %. *IS*: 10 J. *FS*: 240 N.

Hydrazinium 7-nitramino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazolate (11) Compound **4** (0.37 g, 2.0 mmol) was suspended in ethanol (5 mL), then hydrazine monohydrate (0.11 g, 2.1 mmol) in ethanol (2 mL) was added. After stirring 2 h at room temperature, the crude product was collected by filtration. The product was purified by recrystallization in water/ethanol. Yellow solid (0.34 g, 85% yield). $T_{d(onset)}$: 132 °C. ^{1}H NMR: δ 7.86 (s, 1H), 7.02 (br) ppm. ^{13}C NMR: δ 157.9, 157.8, 140.4 ppm. IR (KBr): $\tilde{\nu}$ 3299, 3173, 3093, 1621, 1510, 1481, 1390, 1351, 1216, 1190, 1163, 1154, 1016, 977, 962, 933, 879, 828, 764, 738, 701, 635 cm^{-1}. Elemental analysis for $C_3H_7N_9O_2$ (201.15): Calcd C 17.91, H 3.51, N 62.67 %. Found: C 17.77, H 3.39, N 61.80 %. *IS*: 12 J. *FS*: 360 N.

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