Supplementary Information

Contents

Experimental Section

Caution

The reported compounds are all energetic materials and tend to explode under physical stress, and trifluoroacetic acid is used in the synthesis process. Laboratories and personnel must be properly grounded, and safety equipment such as protective gloves and coats, face shields and explosion-proof baffles is recommended.

Equipment and conditions

Elemental analyses (C, H and N) were performed on a PE-2400 Elemental Analytical Instrument (Perkin-Elmer, USA). IR spectra were measured with an EQUINOX-550 spectrometer via KBr pellets for solids (Bruker, Germany). NMR spectra were recorded with an AV500 NMR spectrometer (Bruker, Germany). Differential scanning calorimetry (DSC) experiments were determined by DSC200 F3 (NETZSCH, Germany) in a dynamic atmosphere of nitrogen with a flow rate of 100 mL min^{-1}. Constant-volume combustion energy was determined by oxygen bomb calorimetry (IKA C5000). Densities were measured at 25 °C using a Micromeritics AccuPyc II 1340 gas pycnometer. Impact sensitivity was evaluated by 50% points using a ZBL-B impact sensitivity instrument (Nachen, China) with a 2.0 kg fall-hammer. The pH values of aqueous solutions were measured by a PHS-3C pH meter (REX, China).

Crystal structure determination

Crystal data collection was performed on a Bruker Smart Apex CCD X-ray diffractometer (Bruker, Germany) with highly oriented graphite crystal monochromated Mo-Kα radiation (λ = 0.071073 nm) using ω and φ scans mode at room temperature. Unit cell dimensions were obtained with least-squares refinements, and semi-empirical absorption corrections were applied using the SADABS program [1]. The structures were solved by direct methods and refined by full-matrix least squares techniques based on F^2 with the SHELXTL-97 program [2]. All atoms were obtained from difference Fourier maps, and non-hydrogen atoms were refined with atomic anisotropic thermal parameters.

Synthesis methods

All chemicals used were of analytical grade and commercially available.

2,4,6-Triamino-1,3,5-triazine-1,3-dioxide (1). Melamine (1.50 g) was added to a mixed solution of trifluoroacetic acid (15.0 mL) and aqueous hydrogen peroxide (30%, 7.5 mL), and the mixture was heated at 50 °C with refluxing and stirring for 90 min. Then white precipitate was filtered and dried to give 2,4,6-triamino-1,3-dihydroxy-1,3,5-triazine-1,3-diium trifluoroacetate. ^{1}H NMR (500 MHz, D$_2$O): δ ppm: 8.47 (s, 1H, OH), 8.39 (s, 1H, OH), 7.27 (s, 2H, NH), 7.17 (s, 2H, NH), 7.06 (s, 2H, NH). ^{13}C NMR (125 MHz, D$_2$O): δ ppm: 162.9, 155.0, 146.8, 116.3. IR (KBr): 3410, 3335, 3150, 1670, 1609, 1508, 1464, 1420, 1250, 1175, 1121, 824, 795, 716, 677, 600, 518, 457, 420 cm^{-1}. Elemental analysis calcd (%) for C$_7$H$_8$N$_6$O$_6$F$_6$ (386.17): C 21.77, H 2.09, N 21.76, found: C 21.69, H 2.173, N 21.62. Then all the 2,4,6-triamino-1,3-dihydroxy-1,3,5-triazine-1,3-diium trifluoroacetate was dissolved in water (30 mL). When the solution was neutralized to pH around 7 with NaOH, a lot of white precipitate formed and was filtered, washed with water and dried at 110 °C to yield 1.32 g (70%) of **1**. ^{13}C NMR (125 MHz, D$_2$O): δ ppm: 152.0, 150.9. IR (KBr): 3439, 3061, 1609, 1483, 1234, 1173, 885, 708, 583, 440 cm^{-1}. Elemental analysis calcd (%) for C$_3$H$_6$N$_6$O$_2$ (158.12): C 22.79, H 3.82, N 53.15, found: C 22.70, H 3.926, N 53.01.

Sodium 4,6-diamino-2-imino-3-oxido-2,3-dihydro-1,3,5-triazine-1-oxide (1a). NaOH (0.25 g) and **1** (1.00 g) were dissolved in water (10 mL). When anhydrous ethanol (100 mL) was added to the solution, a lot of white precipitate formed and was filtered and dried to yield 0.82 g (72%) of **1a**. ^{13}C NMR (125 MHz, D$_2$O): δ ppm: 153.7, 151.3. IR (KBr): 3391, 3314, 3277, 2968, 1686, 1585, 1489, 1323, 1202, 1163, 1020, 926, 885, 708, 687, 613, 496, 422 cm^{-1}. Elemental analysis calcd (%) for C$_3$H$_5$N$_6$O$_2$Na (180.10): C 20.01, H 2.80, N 46.66, found: C 19.90, H 2.914, N 46.55.

Potassium 4,6-diamino-2-imino-3-oxido-2,3-dihydro-1,3,5-triazine-1-oxide (1b). KOH (0.35 g) and **1** (1.00 g) were dissolved in water (10 mL). When anhydrous ethanol (100 mL) was added to the solution, a lot of white precipitate formed and was filtered and dried to yield 0.99 g (80%) of **1b**. ^{13}C NMR (125 MHz, D$_2$O): δ ppm: 153.8,

151.3. IR (KBr): 3441, 3379, 3281, 2970, 1672, 1616, 1558, 1483, 1319, 1225, 1202, 1159, 926, 851, 710, 671, 586, 505, 419 cm^{-1}. Elemental analysis calcd (%) for $C_3H_5N_6O_2K$ (196.21): C 18.36, H 2.57, N 42.83, found: C 18.29, H 2.667, N 42.71.

2,4,6-Triamino-3-hydroxy-1,3,5-triazin-3-ium-1-oxide nitrate (1c). 1 (1.00 g, 6.32 mmol) was dissolved in nitric acid (6.32 mmol, 30 mL) at 80 °C. Then the solution was cooled to room temperature and maintained for 24 h. White precipitate was filtered, washed with water and dried to yield 0.64 g (46%) of **1c**. ^{13}C NMR (125 MHz, D$_2$O): δ ppm: 155.0, 146.9. IR (KBr): 3426, 3096, 2990, 2901, 1670, 1636, 1489, 1395, 1304, 1241, 1180, 1047, 891, 826, 723, 665, 517, 405 cm^{-1}. Elemental analysis calcd (%) for $C_3H_7N_7O_5$ (221.13): C 16.29, H 3.19, N 44.34, found: C 16.23, H 3.256, N 44.22.

2,4,6-Triamino-1,3-dihydroxy-1,3,5-triazine-1,3-diium dinitrate (1d). 1 (1.00 g) was dissolved in nitric acid (68%, 20 mL) at 80 °C. Then the solution was cooled to room temperature and maintained for 12 h. White precipitate was filtered, washed with water and dried at 150 °C to yield 0.34 g (19%) of **1d**. ^{13}C NMR (125 MHz, D$_2$O): δ ppm: 155.0, 146.9. IR (KBr): 3366, 3127, 2990, 1636, 1495, 1315, 1250, 1179, 1115, 1040, 966, 891, 826, 716, 660, 565, 528, 413 cm^{-1}. Elemental analysis calcd (%) for $C_3H_8N_8O_8$ (284.15): C 12.68, H 2.84, N 39.44, found: C 12.57, H 2.892, N 39.35.

4,6-Diamino-3-hydroxy-2-oxo-2,3-dihydro-1,3,5-triazine-1-oxide **(2).** Melamine (1.50 g) was added to a mixed solution of trifluoroacetic acid (15.0 mL) and aqueous hydrogen peroxide (30%, 7.5 mL), and the mixture was heated at 70 °C with refluxing and stirring for 60 min. After that, the mixture was cooled to 2 °C and maintained for 24 h, and white precipitate was filtered and dissolved in water (30 mL). When the solution was neutralized to pH around 7 with NaOH, a lot of white precipitate formed and was filtered, washed with water and dried at 140 °C to yield 0.92 g (49%) of **2**. ^{1}H NMR (500 MHz, DMSO-d_6): δ ppm: 8.39 (s, 2H, NH), 7.89 (s, 2H, NH). IR (KBr): 3439, 3375, 3210, 1724, 1612, 1514, 1275, 1240, 1179, 991, 781, 716, 669, 583, 515, 474, 417 cm^{-1}. Elemental analysis calcd (%) for $C_3H_5N_5O_3$ (159.11): C 22.65, H 3.17, N 44.02, found: C 22.57, H 3.221, N 43.91.

Sodium 4,6-diamino-3-oxido-2-oxo-2,3-dihydro-1,3,5-triazine-1-oxide (2a). NaOH (0.25 g) and **2** (1.00 g) were dissolved in water (10 mL). When anhydrous

ethanol (100 mL) was added to the solution, a lot of white precipitate formed and was filtered and dried to yield 1.09 g (96%) of **2a**. ^{13}C NMR (125 MHz, D$_2$O): δ ppm: 153.8, 150.8. IR (KBr): 3292, 3098, 1616, 1524, 1356, 1223, 1167, 978, 835, 714, 671, 581, 515, 501, 409 cm^{-1}. Elemental analysis calcd (%) for C$_3$H$_4$N$_5$O$_3$Na (181.09): C 19.90, H 2.23, N 38.67, found: C 19.82, H 2.242, N 38.54.

**Potassium 4,6-diamino-3-oxido-2-oxo-2,3-dihydro-1,3,5-triazine-1-oxide (2b).** KOH (0.35 g) and **2** (1.00 g) were dissolved in water (10 mL). When anhydrous ethanol (100 mL) was added to the solution, a lot of white precipitate formed and was filtered and dried to yield 1.13 g (91%) of **2b**. ^{13}C NMR (125 MHz, D$_2$O): δ ppm: 153.8, 150.7. IR (KBr): 3424, 2970, 1707, 1605, 1533, 1458, 1227, 1207, 1167, 978, 775, 716, 671, 592, 507, 459, 419, 405 cm^{-1}. Elemental analysis calcd (%) for C$_3$H$_4$N$_5$O$_3$K (197.20): C 18.27, H 2.04, N 35.52, found: C 18.19, H 2.103, N 35.41.

4,6-Diamino-1,3-dihydroxy-2-oxo-2,3-dihydro-1,3,5-triazin-1-ium nitrate (2c). 2 (1.00 g) was dissolved in nitric acid (68%, 10 mL) at 80 °C. Then the solution was cooled to 2 °C and maintained for 24 h. Colorless crystals were filtered, washed with water and dried to yield 0.88 g (63%) of **2c**. ^{1}H NMR (500 MHz, DMSO-d_6): δ ppm: 12.22 (s, 1H, OH), 8.95 (s, 2H, NH), 8.54 (s, 2H, NH). ^{13}C NMR (125 MHz, DMSO-d_6): δ ppm: 154.6, 145.4. IR (KBr): 3410, 3281, 2556, 1771, 1630, 1560, 1533, 1425, 1290, 1269, 1236, 1198, 1175, 1045, 989, 966, 814, 714, 662, 573, 486 cm^{-1}. Elemental analysis calcd (%) for C$_3$H$_6$N$_6$O$_6$ (222.12): C 16.22, H 2.72, N 37.84, found: C 16.15, H 2.790, N 37.73.
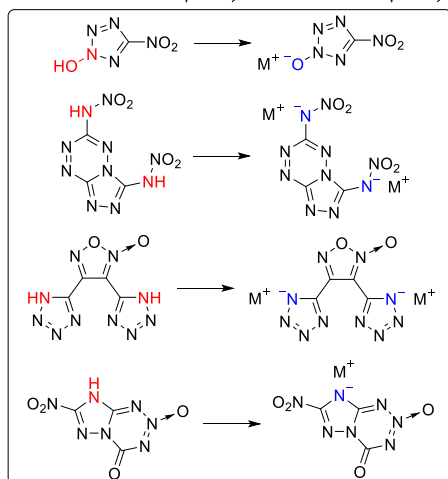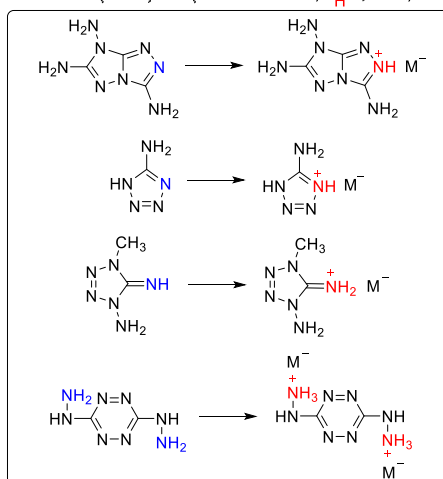
Scheme S1 Reported ionization of nitrogen-rich EMs
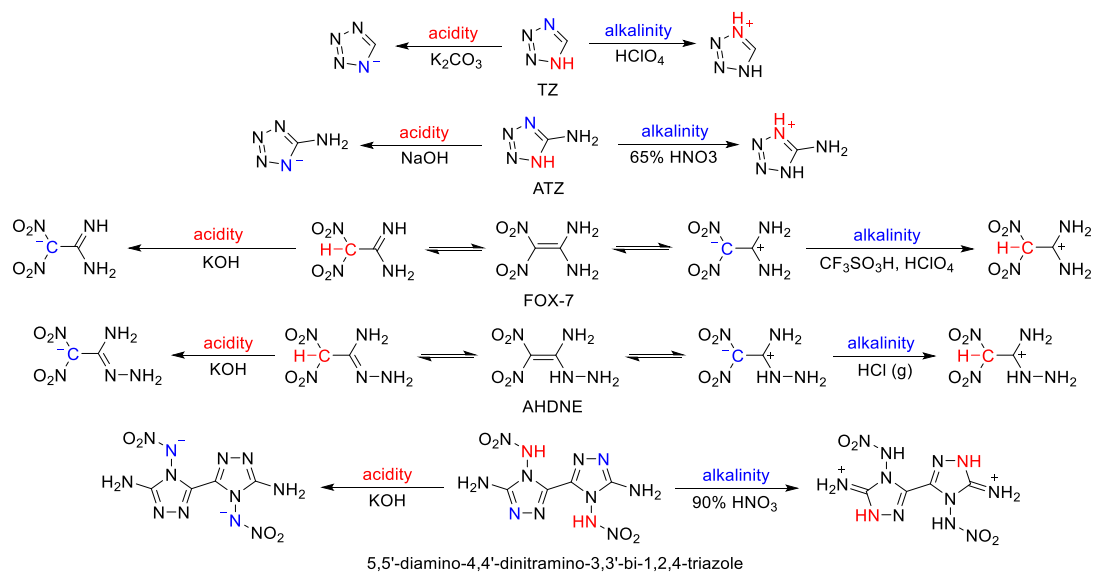
Scheme S2 Five reported amphoteric energetic compounds
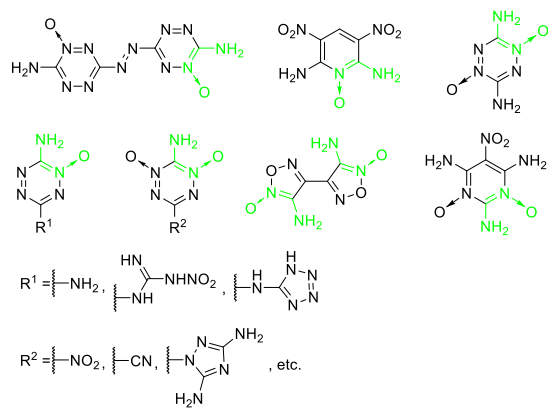
Scheme S3 Examples of synthesized nitrogen-rich EMs containing the O←N=C−NH$_2$ structure
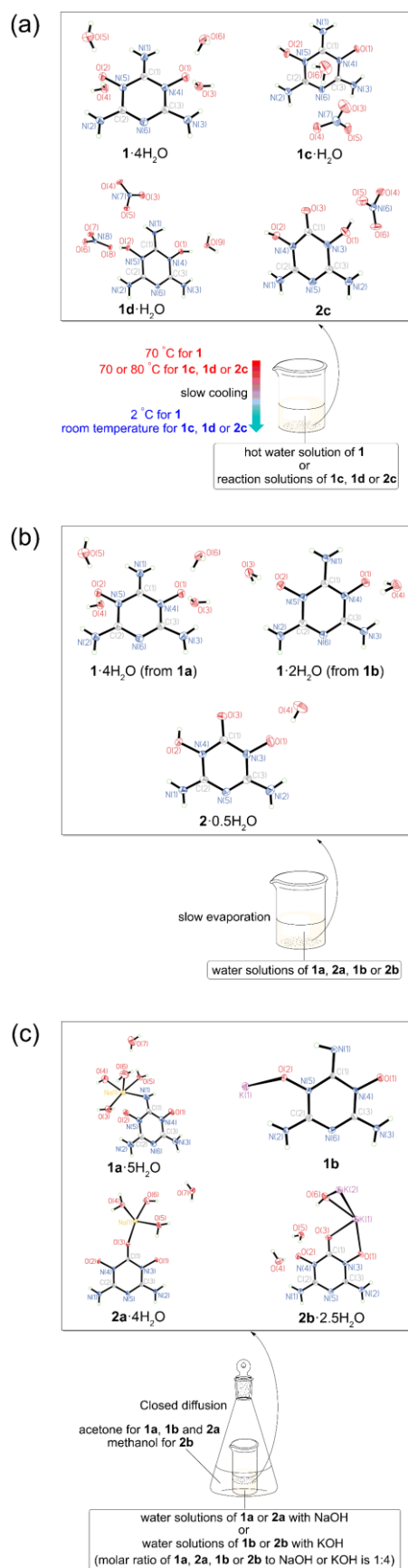
Figure S1 Strategies for crystallizing all the compounds

$1\cdot4H_2O$
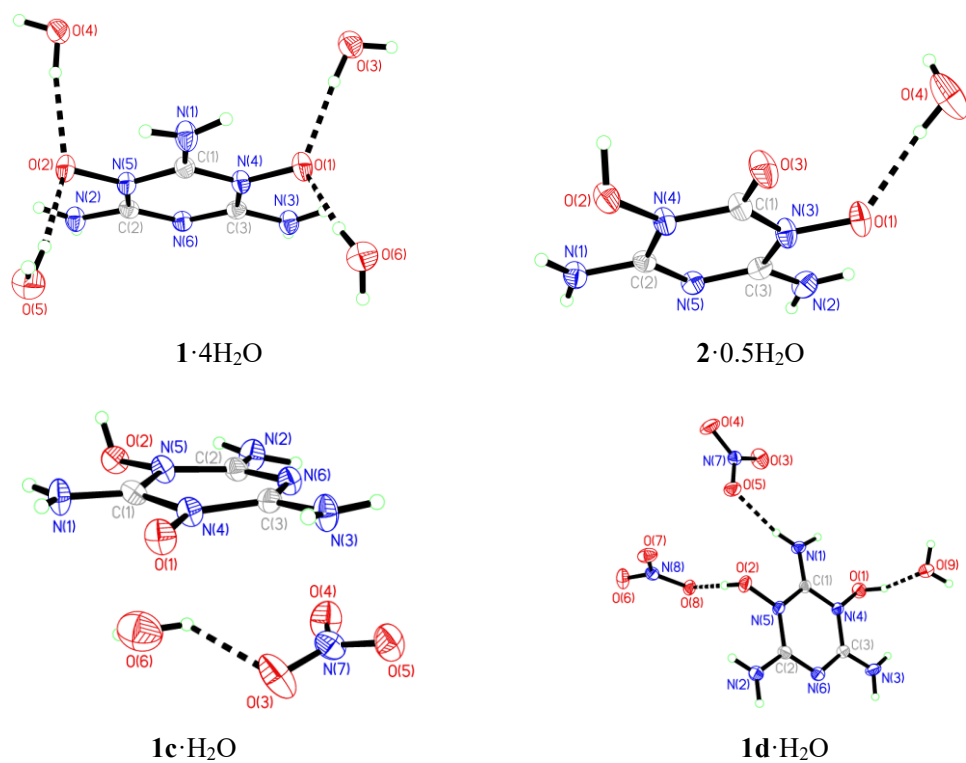
$2\cdot0.5H_2O$

$1c\cdot H_2O$

$1d\cdot H_2O$

Figure S2 Hydrogen bonds (the dashed lines) between lattice water and O atoms of N→O bonds and nitrate ions in crystals of $1\cdot4H_2O$, $2\cdot0.5H_2O$, $1c\cdot H_2O$ and $1d\cdot H_2O$
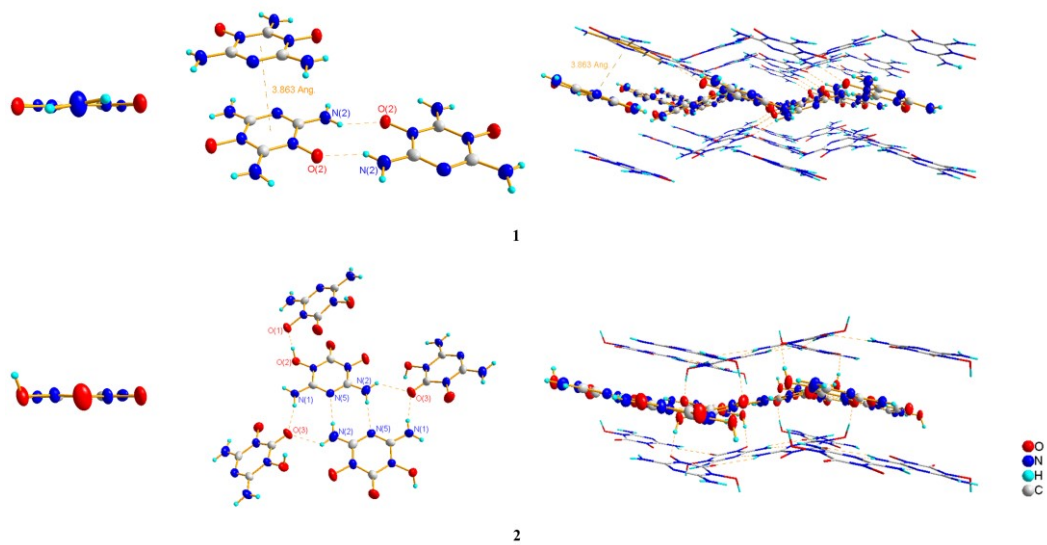
Figure S3 Horizontal views and packing (lattice water is removed for clarity) of **1** and **2** showing hydrogen bonds and π-π stacking (the dashed lines)
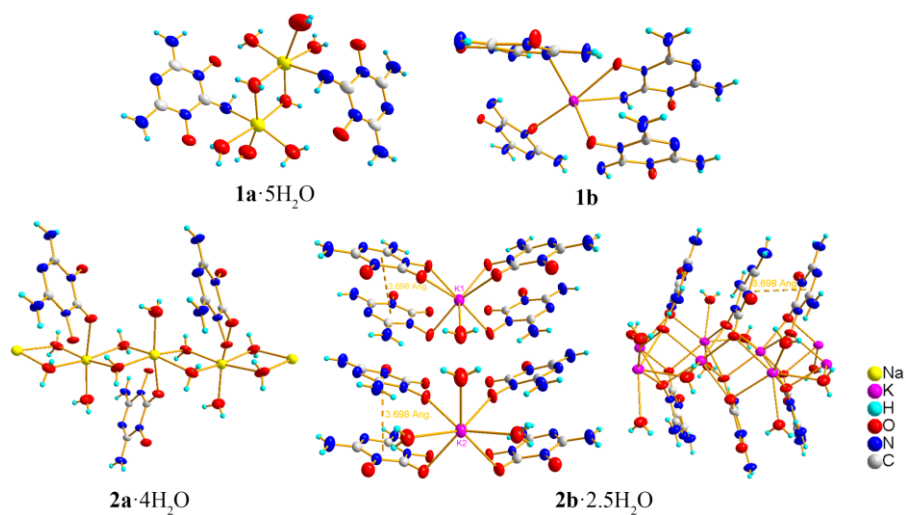
Figure S4 Coordination modes of metal ions in crystals **1a**·5H₂O, **2a**·4H₂O, **1b** and **2b**·2.5H₂O showing π-π stacking (the dashed lines)
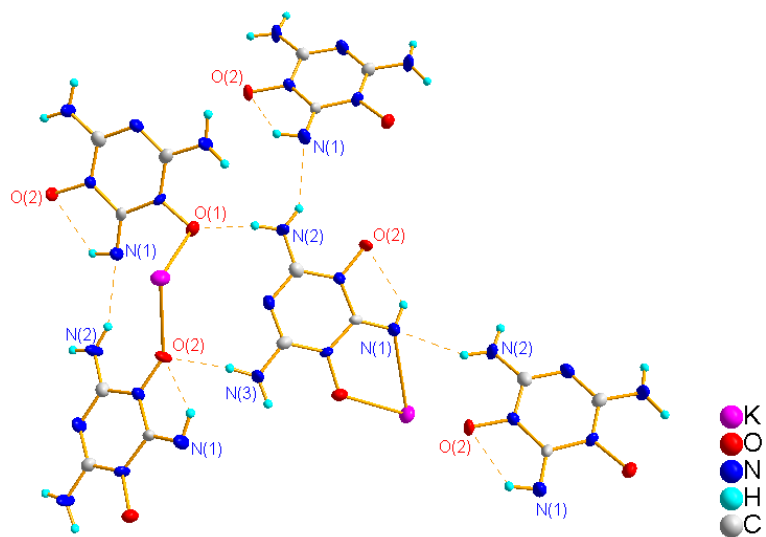
Figure S5 Hydrogen bonds (the dashed lines) in **1b**

Note 1. Molecular Total Energies of Compounds 1 and 2 and Their Tautomeric Isomers

Theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of programs [3]. Molecular total energies were characterized by the sum of electronic and thermal energies. The geometric optimization and frequency analyses were completed by using the B3LYP functional with the 6-31+G** basis set. The optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. Molecular total energies of **1**, **1′**, **2** and **2′** were calculated to be -1567378.23, -1567337.46, -1619580.13 and -1619550.44 kJ mol^{-1}, respectively.

Note 2. Electron Transfer Analysis

The Gaussian input file of compound **1** (geometry has been optimized by using the B3LYP functional with the 6-31+G** basis set based on the single crystal structure of **1**) for electron density calculation is as follows [3]:

B3LYP/6-31+G** out=wfn nosymm

0 1

O	-2.32560100	1.07624800	0.00003100
N	-0.00007700	2.40837700	-0.00011100
H	-0.89998400	2.87012200	-0.00046200
H	0.89968000	2.87036600	-0.00050500
C	0.00002100	1.08100700	0.00004800
N	2.34460000	-1.55830200	0.00035700
H	2.41161300	-2.56176900	-0.00139400
H	3.15198100	-0.94647700	-0.00100500
O	2.32560800	1.07625800	-0.00012600
C	1.14098200	-0.96513300	0.00005300
N	-2.34454900	-1.55839000	0.00005100
H	-3.15205300	-0.94680500	-0.00049200
H	-2.41134900	-2.56190700	-0.00088900
C	-1.14098500	-0.96509800	-0.00002500
N	-1.17759300	0.40547100	0.00024200
N	1.17759400	0.40551300	0.00027200
N	0.00001800	-1.65241700	-0.00008900

The Gaussian input files of melamine and coordination O for electron density calculation were obtained by respectively deleting coordination O and melamine parts from the above Gaussian input file of compound **1**. Then, the grid data of electron density difference were generated by Multiwfn [4,5].

Note 3. NMR Spectra

Heavy water was used for the NMR characterization of most compounds because of the solubility, resulting in the invisibility of signals of active hydrogen (-NH and -OH). In addition, because $1'^-$ and 1^+ can combine with H^+ and OH^- ionized from H_2O to re-form **1**, there are signals of **1** in the ^{13}C NMR spectra of its salts.
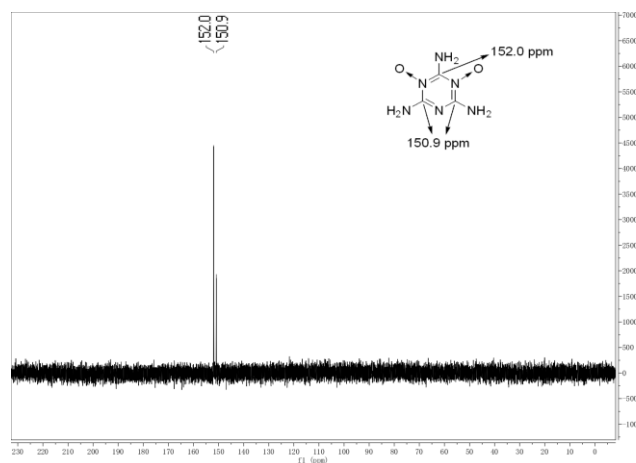
Figure S6 ^{13}C NMR (D_2O) spectrum of **1**
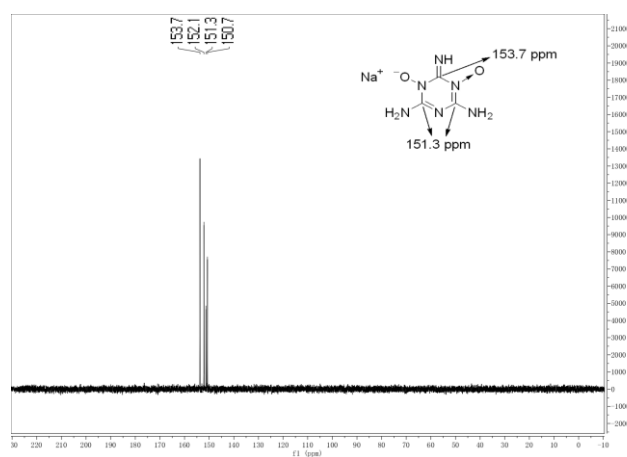
Figure S7 ^{13}C NMR (D_2O) spectrum of **1a** (signals at 152.1 and 150.7 ppm are those of **1** which comes from $1'^-$ combining with H^+ ionized from H_2O)

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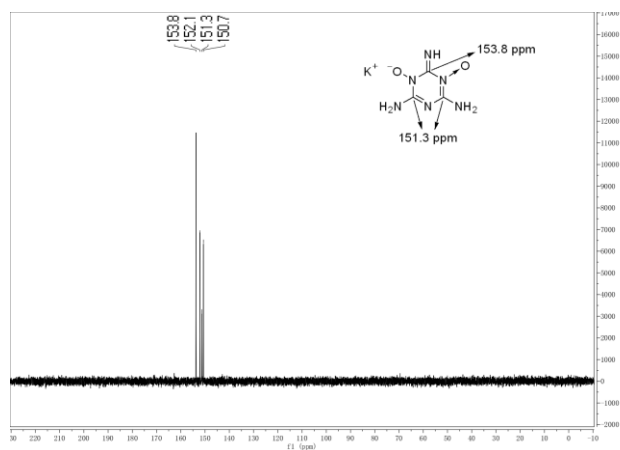
Figure S8 ^{13}C NMR (D$_2$O) spectrum of **1b** (signals at 152.1 and 150.7 ppm are those of **1** which comes from **1′**$^-$ combining with H$^+$ ionized from H$_2$O)
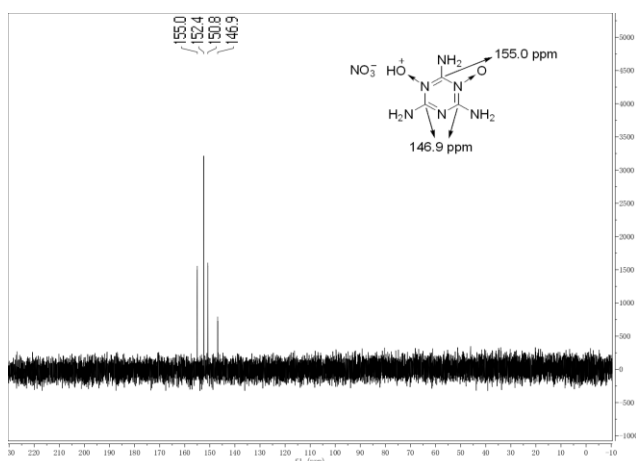
Figure S9 ^{13}C NMR (D$_2$O) spectrum of **1c** (signals at 152.4 and 150.8 ppm are those of **1** which comes from **1**$^+$ combining with OH$^-$ ionized from H$_2$O)
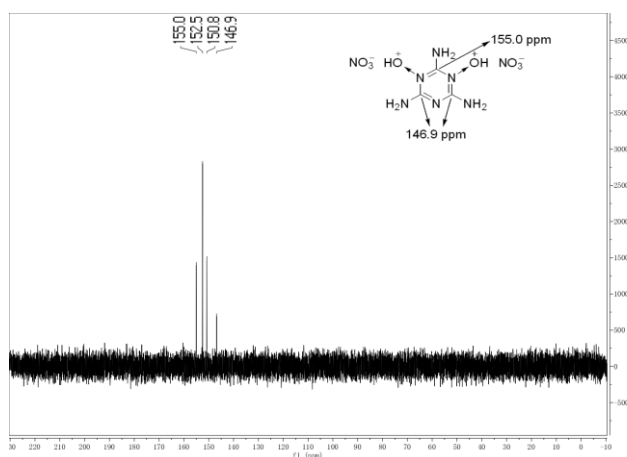
Figure S10 ^{13}C NMR (D$_2$O) spectrum of **1d** (signals at 152.5 and 150.8 ppm are those of **1** which comes from **1**$^+$ combining with OH$^-$ ionized from H$_2$O)
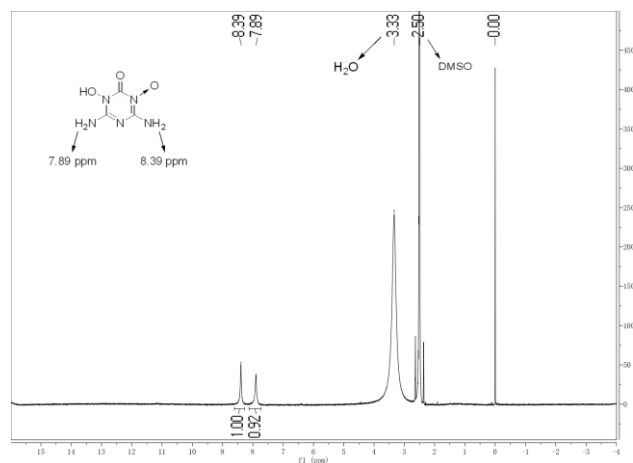
Figure S11 ^{1}H NMR (DMSO-d_6) spectrum of **2**
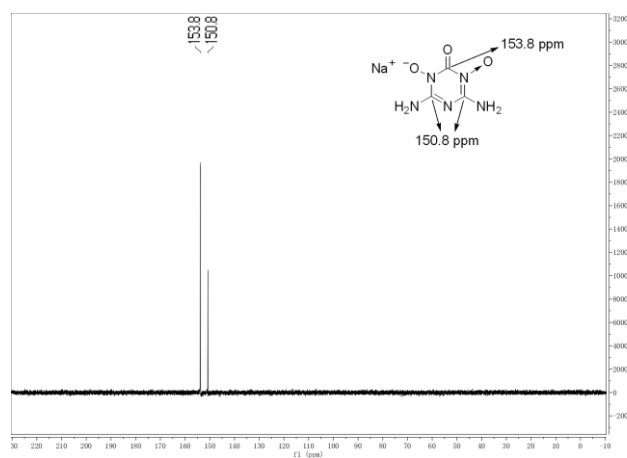
Figure S12 ^{13}C NMR (D$_2$O) spectrum of **2a**
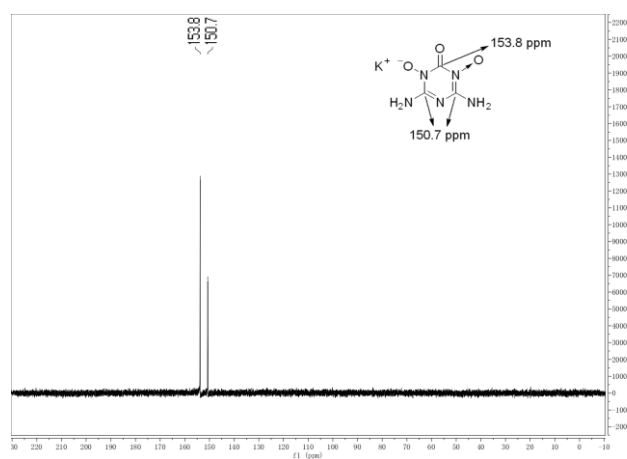
Figure S13 ^{13}C NMR (D$_2$O) spectrum of **2b**
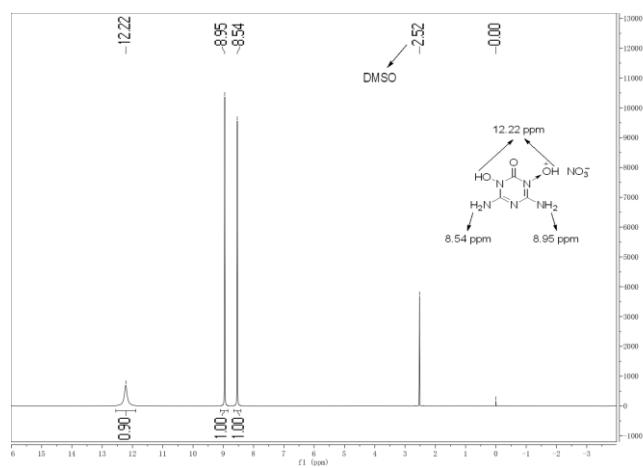
Figure S14 ^{1}H NMR (DMSO-d_6) spectrum of **2c**
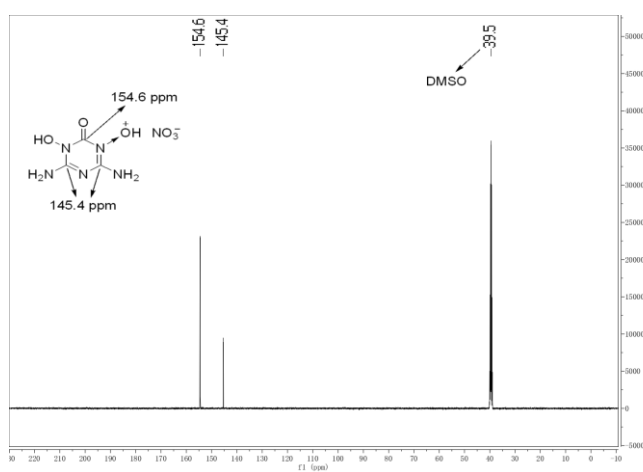
Figure S15 ^{13}C NMR (DMSO-d_6) spectrum of **2c**

Note 4. Determination of the Acidic Dissociation Constant (K_a) of 1′ and the First Basic Dissociation Constant (K_{b1}) of 1

Potassium salt **1b** can undergo hydrolysis as shown below:
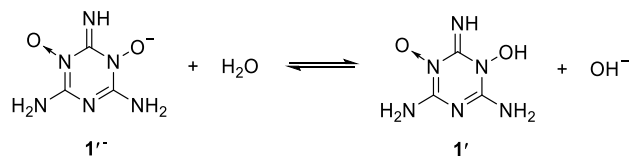
The hydrolysis constant (K_h) of **1b** satisfies the following equation:

$$K_h(\mathbf{1'^-}) = \frac{c(\mathbf{1'})c(\mathrm{OH}^-)}{c(\mathbf{1'^-})} = \frac{c(\mathbf{1'})c(\mathrm{OH}^-)c(\mathrm{H}^+)}{c(\mathbf{1'^-})c(\mathrm{H}^+)} = \frac{K_w}{K_a(\mathbf{1'})} \qquad (1)$$

where K_w is the ionization constant of water and $K_a(\mathbf{1'})$ is the acidic dissociation constant of **1′**.

We assume that the dissociation of water can be ignored and $c(\mathbf{1'^-}) \approx c(\mathbf{1b})$. Therefore,

$$K_a(\mathbf{1'}) = \frac{K_w \cdot c(\mathbf{1'^-})}{c(\mathbf{1'})c(\mathrm{OH}^-)} = \frac{K_w \cdot c(\mathbf{1b})}{\{c(\mathrm{OH}^-)\}^2} = \frac{\{c(\mathrm{H}^+)\}^2 \cdot c(\mathbf{1b})}{K_w} \qquad (2)$$

where $c(\mathbf{1b})$ is the concentration of the aqueous solution of potassium salt **1b**.

In a similar way, the monotrifluoroacetate salt of **1** (2,4,6-triamino-3-hydroxy-1,3,5-triazine-3-ium-1-oxide trifluoroacetate) can undergo hydrolysis as shown below:
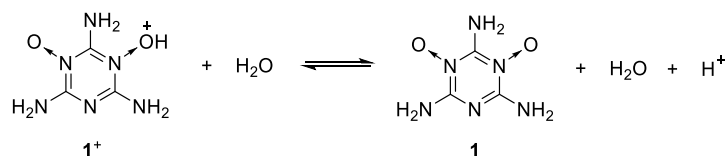
The hydrolysis constant (K_h) of the monotrifluoroacetate salt of **1** satisfies the following equation:

$$K_h(\mathbf{1^+}) = \frac{c(\mathbf{1})c(\mathrm{H}^+)}{c(\mathbf{1^+})} = \frac{c(\mathbf{1})c(\mathrm{H}^+)c(\mathrm{OH}^-)}{c(\mathbf{1^+})c(\mathrm{OH}^-)} = \frac{K_w}{K_{b1}(\mathbf{1})} \qquad (3)$$

where $K_{b1}(\mathbf{1})$ is the first basic dissociation constant of **1**.

We assume that the dissociation of water can be ignored and $c(\mathbf{1^+}) \approx c(\mathrm{salt})$. Therefore,

$$K_{b1}(\mathbf{1}) = \frac{K_w \cdot c(\mathbf{1^+})}{c(\mathbf{1})c(\mathrm{H}^+)} = \frac{K_w \cdot c(\mathrm{salt})}{\{c(\mathrm{H}^+)\}^2} \qquad (4)$$

where c(salt) is the concentration of the aqueous solution of the monotrifluoroacetate salt of **1**.

The pH values of 0.200 mol L^{-1} aqueous solutions of potassium salt **1b** and the monotrifluoroacetate salt of **1** (prepared by the equimolar mixture of NaOH and 2,4,6-triamino-1,3-dihydroxy-1,3,5-triazine-1,3-diium trifluoroacetate) were measured to be 11.61 and 2.10, respectively, at 25 °C. K_w is 1.01×10^{-14} at 25 °C [6]. Thus, according to the equations (2) and (4),

$$K_a(\mathbf{1'}) = (10^{-11.61})^2 \times 0.200 \div (1.01 \times 10^{-14}) = 1.19 \times 10^{-10}$$

$$K_{b1}(\mathbf{1}) = 1.01 \times 10^{-14} \times 0.200 \div (10^{-2.10})^2 = 3.20 \times 10^{-11}$$

Checking calculations:

According to the equations (1) and (3), we obtain

$$K_h(\mathbf{1'^-}) = 1.01 \times 10^{-14} \div (1.19 \times 10^{-10}) = 8.49 \times 10^{-5} \gg K_w$$

$$c(\mathbf{1b})/K_h(\mathbf{1'^-}) = 0.200 \div (8.49 \times 10^{-5}) > 500$$

$$K_h(\mathbf{1^+}) = 1.01 \times 10^{-14} \div (3.20 \times 10^{-11}) = 3.16 \times 10^{-4} \gg K_w$$

$$c(\text{salt})/K_h(\mathbf{1^+}) = 0.200 \div (3.16 \times 10^{-4}) > 500$$

Thus, the assumptions that the dissociation of water can be ignored, $c(\mathbf{1'^-}) \approx c(\mathbf{1b})$ and $c(\mathbf{1^+}) \approx c(\text{salt})$ are reasonable.

Note 5. Calculations of Surface Electrostatic Potentials of 1, 1′, 2 and 2′

Molecular geometries of **1**, **1′**, **2** and **2′** were optimized by using the B3LYP functional with the 6-31+G** basis set based on crystal structures to obtain their checkpoint files [3]. Then, the checkpoint files were used to calculate their surface electrostatic potentials (ESPs) and extremum values of ESPs on the 0.001 a.u. isosurfaces of electronic density by Multiwfn [4,5]. The obtained data of ESPs were visualized by VMD [7].

Note 6. Calculations about Heat of Formation for All the Newly Synthesized Energetic Compounds by Experiment

The constant-volume combustion energies of the compounds were determined by oxygen bomb calorimetry (IKA C5000). A sample of approximately 200 mg to be tested was pressed with a well-defined amount of benzoic acid (ca. 500 mg) to form a tablet to ensure better combustion. The recorded data were the average of six single tests. The calorimeter was calibrated by the combustion of certified benzoic acid in an oxygen atmosphere at a pressure of 30.5 bar.

The averaged experimental values for the constant-volume combustion energies ($\Delta_c\bar{U}$) of **1a**, **1b**, **1c**, **2**, **2a**, **2b** and **2c** were measured to be -1946.16, -1867.33, -1851.52, -1553.54, -1409.15, -1498.42 and -1421.57 kJ mol^{-1}, respectively. Their enthalpies of combustion (Δ_cH) were calculated from $\Delta_c\bar{U}$ with a gas volume correction given in the equation (5).

$$\Delta_cH(\text{sample,s}) = \Delta_c\bar{U} + \Delta nRT \qquad (5)$$

where Δn is the change in the number of gas products during the reaction process, R is 8.314 J mol^{-1} K^{-1}, and T is 298.15 K.

The combustion reactions for **1a**, **1b**, **1c**, **2**, **2a**, **2b** and **2c** are as follows:

1a: $C_3H_5N_6O_2Na$ (s) + 3.5O_2 (g) → 3CO_2 (g) + 2.5H_2O (l) + 3N_2 (g) + 0.5Na_2O (s)

1b: $C_3H_5N_6O_2K$ (s) + 3.5O_2 (g) → 3CO_2 (g) + 2.5H_2O (l) + 3N_2 (g) + 0.5K_2O (s)

1c: $C_3H_7N_7O_5$ (s) + 2.25O_2 (g) → 3CO_2 (g) + 3.5H_2O (l) + 3.5N_2 (g)

2: $C_3H_5N_5O_3$ (s) + 2.75O_2 (g) → 3CO_2 (g) + 2.5H_2O (l) + 2.5N_2 (g)

2a: $C_3H_4N_5O_3Na$ (s) + 2.75O_2 (g) → 3CO_2 (g) + 2H_2O (l) + 2.5N_2 (g) + 0.5Na_2O (s)

2b: $C_3H_4N_5O_3K$ (s) + 2.75O_2 (g) → 3CO_2 (g) + 2H_2O (l) + 2.5N_2 (g) + 0.5K_2O (s)

2c: $C_3H_6N_6O_6$ (s) + 1.5O_2 (g) → 3CO_2 (g) + 3H_2O (l) + 3N_2 (g)
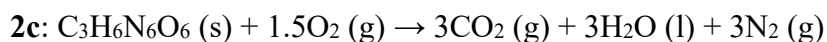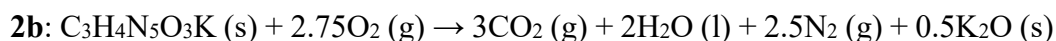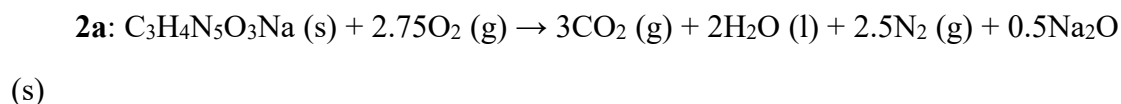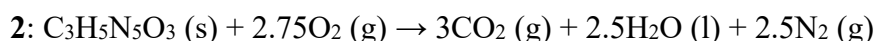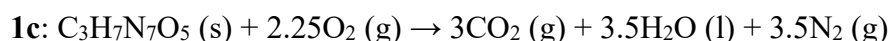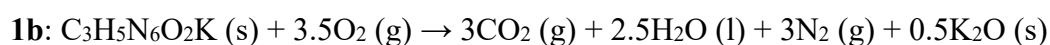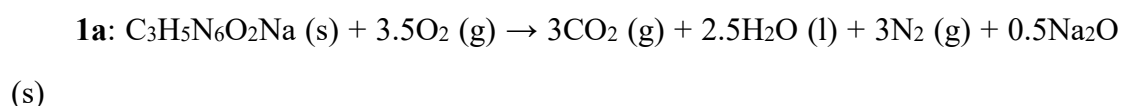
The enthalpies of combustion (Δ_cH) of **1a**, **1b**, **1c**, **2**, **2a**, **2b** and **2c** were calculated to be -1939.96, -1861.13, -1840.99, -1546.72, -1402.33, -1491.60 and -1410.42 kJ

mol^{-1}, respectively. Their standard heat of formation ($\Delta_f H$) was back-calculated from their combustion equations by the Hess's law.

$\Delta_f H$(**1a**, s) = 3$\Delta_f H$(CO$_2$, g) + 2.5$\Delta_f H$(H$_2$O, l) + 0.5$\Delta_f H$(Na$_2$O, s) − $\Delta_c H$(**1a**, s)

$\Delta_f H$(**1b**, s) = 3$\Delta_f H$(CO$_2$, g) + 2.5$\Delta_f H$(H$_2$O, l) + 0.5$\Delta_f H$(K$_2$O, s) − $\Delta_c H$(**1b**, s)

$\Delta_f H$(**1c**, s) = 3$\Delta_f H$(CO$_2$, g) + 3.5$\Delta_f H$(H$_2$O, l) − $\Delta_c H$(**1c**, s)

$\Delta_f H$(**2**, s) = 3$\Delta_f H$(CO$_2$, g) + 2.5$\Delta_f H$(H$_2$O, l) − $\Delta_c H$(**2**, s)

$\Delta_f H$(**2a**, s) = 3$\Delta_f H$(CO$_2$, g) + 2$\Delta_f H$(H$_2$O, l) + 0.5$\Delta_f H$(Na$_2$O, s) − $\Delta_c H$(**2a**, s)

$\Delta_f H$(**2b**, s) = 3$\Delta_f H$(CO$_2$, g) + 2$\Delta_f H$(H$_2$O, l) + 0.5$\Delta_f H$(Na$_2$O, s) − $\Delta_c H$(**2b**, s)

$\Delta_f H$(**2c**, s) = 3$\Delta_f H$(CO$_2$, g) + 3$\Delta_f H$(H$_2$O, l) − $\Delta_c H$(**2c**, s)

The standard heat of formation of CO$_2$ (g), H$_2$O (l), Na$_2$O (s) and K$_2$O (s) is −393.51, −285.83, −417.98 and −363.17 kJ mol^{-1}, respectively [8]. The standard heat of formation of **1a**, **1b**, **1c**, **2**, **2a**, **2b** and **2c** was calculated to be −164.17, −215.59, −339.99, −348.39, −558.88, −442.21 and −627.64 kJ mol^{-1}, respectively.

Table S1. Crystal data and structure refinement details for compounds **1**·4H$_2$O, **1a**·5H$_2$O, **1b**, **1c**·H$_2$O and **1d**·H$_2$O.

Compounds	**1**·4H$_2$O	**1a**·5H$_2$O	**1b**	**1c**·H$_2$O	**1d**·H$_2$O
Chemical formula	C$_3$H$_{14}$N$_6$O$_6$	C$_6$H$_{30}$N$_{12}$Na$_2$O$_{14}$	C$_3$H$_5$KN$_6$O$_2$	C$_3$H$_9$N$_7$O$_6$	C$_3$H$_{10}$N$_8$O$_9$
Formula weight/(g mol^{-1})	230.20	540.40	196.23	239.17	302.19
Temperature/K	296(2)	296(2)	296(2)	293(2)	296(2)
Color	Colorless	Colorless	Colorless	Colorless	Colorless
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$Pna2_1$	$P2_1/n$	$P\bar{1}$
a/Å	8.972(6)	7.055(3)	13.776(7)	6.635(3)	7.448(3)
b/Å	7.067(5)	8.868(4)	3.764(2)	13.288(6)	8.709(4)
c/Å	16.369(10)	9.776(4)	12.796(6)	10.347(2)	10.072(4)
α/º	90	86.644(7)	90	90	114.164(6)
β/º	94.273(11)	69.909(7)	90	96.915(18)	94.456(6)
γ/º	90	87.122(8)	90	90	107.497(7)
Volume/Å^3	1035.0(11)	573.1(4)	663.5(6)	905.6(6)	553.1(4)
Z	4	1	4	4	2
ρ_{calc}/(g cm^{-3})	1.477	1.566	1.964	1.754	1.814
Absorption coefficient/mm^{-1}	0.138	0.176	0.766	0.164	0.177
$F(000)$	488	284	400	496	312
θ range/º	2.495 to 26.072	2.302 to 24.999	3.184 to 26.426	2.506 to 26.497	2.278 to 26.088
Index ranges	−11≤h≤10, −8≤k≤8, −16≤l≤20	−8≤h≤8, −6≤k≤10, −10≤l≤11	−17≤h≤16, −4≤k≤4, −15≤l≤10	−8≤h≤8, −16≤k≤16, −12≤l≤6	−8≤h≤9, −9≤k≤10, −12≤l≤11
Reflections collected	5247	2942	3384	5080	2968
Reflections unique	2015 [R(int) = 0.0275]	1997 [R(int) = 0.1011]	1138 [R(int) = 0.1101]	1860 [R(int) = 0.1484]	2131 [R(int) = 0.0283]
Goodness-of-fit on F^2	1.014	0.908	0.833	0.767	1.002
Final R indices [$l>2\sigma(l)$]	R_1=0.0433, wR_2=0.1122	R_1=0.1089, wR_2=0.2548	R_1=0.0507, wR_2=0.0764	R_1=0.0627, wR_2=0.1183	R_1=0.0591, wR_2=0.1427
R indices (all data)	R_1=0.0616, wR_2=0.1237	R_1=0.1594, wR_2=0.3113	R_1=0.0911, wR_2=0.0876	R_1=0.1915, wR_2=0.1575	R_1=0.1059, wR_2=0.1732
Largest diff. peak and hole/e Å^{-3}	0.334 and −0.242	0.589 and −0.790	0.424 and −0.480	0.313 and −0.385	0.640 and −0.302
CCDC number	1967830	1972805	1972807	1968247	1968249

Table S2. Crystal data and structure refinement details for compounds $\mathbf{1}\cdot2H_2O$, $\mathbf{2}\cdot0.5H_2O$, $\mathbf{2a}\cdot4H_2O$, $\mathbf{2b}\cdot2.5H_2O$ and $\mathbf{2c}$.

Compounds	$\mathbf{1}\cdot2H_2O$	$\mathbf{2}\cdot0.5H_2O$	$\mathbf{2a}\cdot4H_2O$	$\mathbf{2b}\cdot2.5H_2O$	$\mathbf{2c}$
Chemical formula	$C_3H_{10}N_6O_4$	$C_6H_{12}N_{10}O_7$	$C_3H_{12}N_5NaO_7$	$C_6H_{18}K_2N_{10}O_{11}$	$C_3H_6N_6O_6$
Formula weight/(g mol^{-1})	194.17	336.26	253.17	484.50	222.14
Temperature/K	296(2)	293(2)	296(2)	296(2)	296(2)
Color	Colorless	Colorless	Colorless	Colorless	Colorless
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$Pbcn$	$P2_1/n$	$Pbcm$	$C2/c$
a/Å	4.0471(9)	13.067(3)	10.619(2)	9.2305(9)	15.358(6)
b/Å	11.869(3)	14.398(3)	7.1380(14)	7.0126(7)	7.426(3)
c/Å	16.879(4)	6.5342(13)	14.224(3)	27.175(2)	15.144(6)
α/º	90	90	90	90	90
β/º	91.091(4)	90	103.238(3)	90	111.743(7)
γ/º	90	90	90	90	90
Volume/Å^3	810.6(3)	1229.3(4)	1049.5(4)	1759.0(3)	1604.3(11)
Z	4	4	4	4	8
ρ_{calc}/(g cm^{-3})	1.591	1.817	1.602	1.829	1.839
Absorption coefficient/mm^{-1}	0.142	0.163	0.184	0.622	0.175
$F(000)$	408	696	528	1000	912
θ range/º	2.098 to 26.080	2.105 to 26.669	2.716 to 26.136	2.206 to 28.253	2.856 to 26.659
Index ranges	$-5\leqslant h\leqslant4$, $-10\leqslant k\leqslant14$, $-19\leqslant l\leqslant20$	$-16\leqslant h\leqslant16$, $-9\leqslant k\leqslant18$, $-8\leqslant l\leqslant8$	$-13\leqslant h\leqslant13$, $-7\leqslant k\leqslant8$, $-16\leqslant l\leqslant17$	$-11\leqslant h\leqslant11$, $-6\leqslant k\leqslant9$, $-35\leqslant l\leqslant27$	$-19\leqslant h\leqslant10$, $-8\leqslant k\leqslant9$, $-18\leqslant l\leqslant19$
Reflections collected	4213	6423	5548	10225	4324
Reflections unique	1581 [R(int) = 0.0266]	1301 [R(int) = 0.1530]	2073 [R(int) = 0.0548]	2196 [R(int) = 0.0281]	1641 [R(int) = 0.0457]
Goodness-of-fit on F^2	1.024	0.881	0.960	1.057	0.985
Final R indices [$l>2\sigma(l)$]	R_1=0.0341, wR_2=0.0873	R_1=0.0520, wR_2=0.0962	R_1=0.0382, wR_2=0.0900	R_1=0.0423, wR_2=0.1287	R_1=0.0500, wR_2=0.1118
R indices (all data)	R_1=0.0407, wR_2=0.0924	R_1=0.1057, wR_2=0.1123	R_1=0.0546, wR_2=0.0975	R_1=0.0525, wR_2=0.1360	R_1=0.1017, wR_2=0.1379
Largest diff. peak and hole/e Å^{-3}	0.132 and −0.241	0.307 and −0.387	0.217 and −0.261	0.311 and −0.996	0.216 and −0.295
CCDC number	1967836	1967846	1972810	1977527	1968244

Table S3. Hydrogen bonds in **1**·4H$_2$O, **1a**·5H$_2$O, **1b**, **1c**·H$_2$O, **1d**·H$_2$O, **2**·0.5H$_2$O, **2a**·4H$_2$O, **2b**·2.5H$_2$O and **2c**.

D-H…A	Type	d(D-H) (Å)	d(H…A) (Å)	d(D…A) (Å)	∠DHA (º)
1·4H$_2$O					
N(1)-H(2)...O(4)[a]	**1**-water	0.866(17)	2.090(18)	2.892(3)	154(2)
N(1)-H(1)...O(6)[b]	**1**-water	0.878(16)	2.002(17)	2.829(3)	156(2)
N(2)-H(4)...O(3)[c]	**1**-water	0.848(16)	2.037(17)	2.861(3)	164(2)
N(2)-H(3)...O(2)[d]	**1-1**	0.897(16)	2.084(19)	2.879(3)	147.0(19)
O(3)-H(7)...O(6)[e]	water-water	0.826(16)	1.995(16)	2.813(3)	170(2)
O(3)-H(8)...O(1)	water-**1**	0.879(15)	1.833(16)	2.703(2)	170(2)
N(3)-H(6)...O(5)[f]	**1**-water	0.874(16)	2.285(18)	3.091(3)	153(2)
N(3)-H(5)...O(4)[c]	**1**-water	0.864(15)	2.097(17)	2.928(3)	161(2)
O(4)-H(9)...O(5)[g]	water-water	0.840(15)	2.104(15)	2.935(3)	170(2)
O(4)-H(10)...O(2)	water-**1**	0.876(15)	1.947(15)	2.814(3)	170(2)
O(5)-H(11)...O(2)	water-**1**	0.869(16)	1.980(16)	2.844(3)	173(3)
O(5)-H(12)...O(3)[a]	water-water	0.849(16)	2.041(16)	2.860(3)	162(2)
O(6)-H(14)...N(6)[h]	water-**1**	0.847(15)	2.30(2)	3.054(3)	148(2)
O(6)-H(13)...O(1)	water-**1**	0.861(15)	1.771(16)	2.627(3)	172(2)
1a·5H$_2$O					
O(5)-H(8)...N(6)[i]	water-**1a**	0.85(2)	2.05(2)	2.892(6)	172(5)
O(5)-H(7)...O(1)[c]	water-**1a**	0.85(2)	1.83(2)	2.674(6)	173(6)
O(3)-H(11)...O(2)	water-**1a**	0.86(2)	1.86(3)	2.695(7)	165(8)
O(3)-H(10)...O(7)[j]	water-water	0.85(2)	2.10(2)	2.934(8)	168(6)
O(4)-H(5)...O(6)[j]	water-water	0.84(2)	2.18(5)	2.892(8)	143(7)
O(4)-H(4)...O(1)[k]	water-**1a**	0.84(2)	1.87(2)	2.699(7)	171(7)
N(3)-H(9)...O(3)[l]	**1a**-water	0.90(2)	2.13(4)	2.930(8)	148(6)
N(3)-H(3)...O(7)[c]	**1a**-water	0.87(2)	2.33(4)	3.103(8)	147(6)
N(2)-H(6)...O(2)[m]	**1a-1a**	0.89(2)	2.15(5)	2.892(7)	141(6)
N(2)-H(2)...O(4)[n]	**1a**-water	0.89(2)	2.12(4)	2.922(8)	150(6)
N(1)-H(1)...O(1)	**1a** intramolecularly	0.893(19)	2.27(4)	2.744(7)	113(2)
N(1)-H(1)...O(1)[c]	**1a-1a**	0.893(19)	2.50(3)	3.153(7)	130(3)
O(7)-H(14)...O(2)[h]	water-**1a**	0.85(2)	2.01(6)	2.737(7)	143(8)
O(7)-H(15)...O(6)	water-water	0.85(2)	2.14(3)	2.962(10)	164(7)
O(6)-H(12)...O(4)[j]	water-water	0.84(2)	2.36(9)	2.892(8)	122(8)
1b					
N(1)-H(2)...O(2)	**1b** intramolecularly	0.87(3)	2.22(7)	2.752(8)	119(6)
N(3)-H(1)...O(2)[o]	**1b-1b**	0.88(3)	2.02(3)	2.888(8)	173(8)
N(2)-H(5)...O(1)[p]	**1b-1b**	0.88(3)	1.91(3)	2.776(8)	169(8)
N(2)-H(4)...N(1)[q]	**1b-1b**	0.87(3)	2.31(5)	3.075(9)	146(7)
1c·H$_2$O					
N(1)-H(6)...O(5)[e]	**1c-1c**, between layers	0.865(19)	2.14(3)	2.917(6)	150(4)
N(1)-H(5)...O(4)[r]	**1c-1c**, within layers	0.882(19)	2.18(4)	2.883(6)	137(4)
N(2)-H(4)...O(6)[s]	**1c**-water, within layers	0.875(19)	2.08(3)	2.821(6)	142(4)
N(2)-H(2)...O(4)[c]	**1c-1c**, within layers	0.890(19)	2.11(2)	2.981(6)	166(4)
O(2)-H(7)...O(1)[s]	**1c-1c**, between layers	0.852(19)	1.62(2)	2.465(5)	172(5)

N(3)-H(1)...O(5)[t]	**1c-1c**, within layers	0.872(19)	2.15(3)	2.973(5)	157(4)
N(3)-H(3)...O(2)[u]	**1c-1c**, within layers	0.872(19)	2.19(3)	2.972(6)	150(4)
O(6)-H(8)...O(3)	water-**1c**, between layers	0.91(2)	1.96(5)	2.635(8)	129(6)
O(6)-H(9)...O(1)[v]	water-**1c**, within layers	0.886(19)	2.32(5)	2.933(5)	127(5)
O(6)-H(9)...O(5)[b]	water-**1c**, within layers	0.886(19)	2.44(6)	3.056(7)	127(6)
1d·H₂O					
O(1)-H(6)...O(9)	**1d**-water, between layers	0.881(19)	1.64(2)	2.492(4)	162(4)
N(1)-H(7)...O(5)	**1d** intramolecularly	0.872(19)	1.98(2)	2.840(4)	169(4)
N(1)-H(1)...O(8)[d]	**1d-1d**, within layers	0.875(19)	2.13(3)	2.882(4)	144(3)
O(2)-H(5)...O(8)	**1d** intramolecularly	0.822(19)	1.81(2)	2.621(4)	172(4)
N(2)-H(8)...O(6)[h]	**1d-1d**, within layers	0.879(19)	2.06(2)	2.916(5)	166(4)
N(2)-H(2)...O(4)[w]	**1d-1d**, within layers	0.87(2)	2.25(3)	3.016(5)	146(4)
N(3)-H(4)...O(7)[i]	**1d-1d**, between layers	0.86(2)	2.16(3)	2.915(5)	147(4)
N(3)-H(3)...O(4)[i]	**1d-1d**, within layers	0.874(19)	2.15(2)	3.011(5)	167(4)
O(9)-H(11)...N(6)[x]	water-**1d**, within layers	0.836(18)	2.29(3)	2.941(4)	135(4)
O(9)-H(10)...O(8)[g]	water-**1d**, within layers	0.840(19)	1.97(2)	2.787(4)	165(5)
2·0.5H₂O					
N(1)-H(5)...O(3)[y]	**2-2**	0.847(16)	2.024(17)	2.859(3)	169(2)
N(1)-H(3)...O(4)[a]	**2**-water	0.866(16)	2.079(19)	2.887(2)	155(2)
N(2)-H(1)...N(5)[c]	**2-2**	0.889(16)	2.239(17)	3.128(3)	178(2)
N(2)-H(2)...O(3)[z]	**2-2**	0.892(16)	2.35(2)	2.906(3)	120(2)
O(2)-H(4)...O(1)[aa]	**2-2**	0.925(15)	1.545(16)	2.463(3)	171(2)
O(4)-H(7)...O(2)[aa]	water-**2**	0.84(2)	2.56(6)	3.253(2)	141(7)
O(4)-H(6)...O(1)	water-**2**	0.847(19)	2.07(4)	2.859(3)	154(8)
2a·4H₂O					
O(6)-H(12)...N(5)[ab]	water-**2a**	0.839(15)	2.51(2)	3.238(2)	146(2)
O(6)-H(11)...O(7)[ac]	water-water	0.855(15)	1.955(15)	2.803(2)	171(2)
N(1)-H(2)...O(1)[e]	**2a-2a**	0.865(15)	2.049(16)	2.903(2)	169(2)
N(2)-H(4)...O(1)[ad]	**2a-2a**	0.877(15)	2.099(16)	2.877(2)	147.4(18)
N(2)-H(3)...O(2)[e]	**2a-2a**	0.908(15)	2.059(16)	2.937(2)	162.3(19)
O(4)-H(8)...O(1)[a]	water-**2a**	0.847(15)	1.986(16)	2.7836(19)	157(2)
O(4)-H(7)...O(7)[b]	water-water	0.870(14)	1.934(15)	2.791(2)	168.1(19)
O(5)-H(6)...O(2)[ae]	water-**2a**	0.856(15)	1.957(16)	2.8055(18)	171(2)
O(5)-H(5)...O(1)	water-**2a**	0.859(15)	2.092(17)	2.9294(19)	165(2)
O(7)-H(10)...O(2)[a]	water-**2a**	0.821(14)	2.101(18)	2.8373(18)	149.1(19)
O(7)-H(10)...O(3)[a]	water-**2a**	0.821(14)	2.499(18)	3.0828(18)	129.1(18)
O(7)-H(9)...O(2)[ae]	water-**2a**	0.886(15)	1.890(15)	2.770(2)	172(2)
2b·2.5H₂O					
O(5)-H(7)...O(2)[af]	water-**2b**	0.82	2.28	3.062(2)	158.2
O(5)-H(8)...O(2)[ag]	water-**2b**	0.85	1.92	2.769(2)	176.2
N(1)-H(1)...O(4)[ah]	**2b**-water	0.85	2.27	2.890(2)	129.3
N(1)-H(2)...N(5)[ah]	**2b-2b**	0.89	2.12	2.997(2)	167.6
N(2)-H(3)...O(5)[ai]	**2b**-water	0.87	2.47	3.170(2)	137.8
N(2)-H(4)...O(4)	**2b**-water	0.87	2.04	2.882(2)	162.3

O(4)-H(5)...O(2)[f]	water-**2b**	0.84	2	2.820(2)	167.6
O(4)-H(6)...O(2)[aj]	water-**2b**	0.88	1.88	2.735(2)	163.1
2c					
O(1)-H(5)...O(5)	**2c** intramolecularly	0.926(13)	1.682(13)	2.603(3)	173(3)
N(1)-H(2)...O(4)[ak]	**2c-2c**, within layers	0.836(18)	2.26(2)	2.999(3)	148(3)
N(1)-H(1)...O(3)[g]	**2c-2c**, within layers	0.827(16)	2.135(16)	2.862(4)	147(3)
N(2)-H(3)...O(6)[al]	**2c-2c**, within layers	0.882(16)	2.141(19)	3.015(4)	171(3)
O(2)-H(6)...O(4)[am]	**2c-2c**, between layers	0.830(17)	1.804(16)	2.627(3)	171(2)

Symmetry transformations: [a] -x+1/2, y+1/2, -z+1/2; [b] -x+1/2, y-1/2, -z+1/2; [c] -x+1, -y+1, -z+1; [d] -x, -y+1, -z+1; [e] -x+3/2, y-1/2, -z+1/2; [f] x+1, y, z; [g] x, y-1, z; [h] -x+1, -y+2, -z+1; [i] x, y, z+1; [j] -x+2, -y+2, -z+1; [k] -x+2, -y+1, -z+1; [l] -x+2, -y+1, -z; [m] -x+2, -y+2, -z; [n] x, y, z-1; [o] x+1/2, -y+3/2, z; [p] -x+3/2, y+1/2, z-1/2; [q] -x+1, -y+1, z-1/2; [r] x+1/2, -y+1/2, z-1/2; [s] x+1/2, -y+1/2, z+1/2; [t] -x+1, -y+1, -z; [u] -x+3/2, y+1/2, -z+1/2; [v] x-1/2, -y+1/2, z+1/2; [w] x+1, y+1, z+1; [x] -x+1, -y+1, -z+2; [y] -x+3/2, y+1/2, z; [z] x-1/2, -y+1/2, -z+1; [aa] -x+3/2, -y+1/2, z-1/2; [ab] x-1, y, z; [ac] -x, -y+1, -z; [ad] -x+1, -y, -z; [ae] x-1/2, -y+1/2, z-1/2; [af] x+1, y, -z-1/2; [ag] -x-1, y-1/2, -z-1/2; [ah] -x-1, -y+1, -z; [ai] x, y, -z-1/2; [aj] -x-1, y-1, -z+3/2; [ak] -x+1, y-1, -z+3/2; [al] -x+1/2, -y+1/2, -z+1; [am] x+1/2, y-1/2, z.

Table S4. Physical properties of compounds **1a-1c**, **2** and **2a-2c** and comparison with TNT and DDNP.

Compounds	T_d (°C)[a]	ρ (g cm^{-3})[b]	$-\Delta_c H_m$ (kJ mol^{-1})[c]	$\Delta_f H_m$ (kJ mol^{-1})[d]	P (GPa)[e]	v_D (m s^{-1})[e]	IS (J)[f]	OB (%)[g]
1a	325	2.06	1940.0	-164.2	20.7	6572	>23.5	-35.5
1b	293	1.95	1861.1	-215.6	14.9	5658	>23.5	-32.6
1c	226	1.73	1841.0	-340.0	24.1	7459	6.9	-10.9
2	293	1.96	1546.7	-348.4	22.8	6976	>23.5	-25.1
2a	317	2.10	1402.3	-558.9	16.3	5767	>23.5	-22.1
2b	287	1.99	1491.6	-442.2	14.9	5606	>23.5	-20.3
2c	194	1.83	1410.4	-627.6	25.3	7503	6.9	0
TNT[h]	224	1.65	-	-59.3	19.4	6915	15	-24.7
DDNP[i]	157	1.72	-	321.0	24.2	6900	1	-15.2

[a] Decomposition temperature (onset) from DSC at 10.0 °C min^{-1}. [b] Measured density (gas pycnometer). [c] Experimental molar enthalpy of combustion determined by oxygen bomb calorimetry. [d] Heat of formation calculated from enthalpy of combustion. [e] Detonation pressure and detonation velocity calculated by Kamlet-Jacobs equations for CHNO explosives and the developed Kamlet-Jacobs equations for metal-containing explosives [9,10]. [f] Impact sensitivity. [g] Oxygen balance based on CO for $C_a H_b N_c M_d O_e$ (M represents alkali metal ions) calculated by OB=1600[e-a-(b+d)/2]/M_W, where M_W is molecular weight. [h] Refs. [11-13]. [i] Ref. [14].
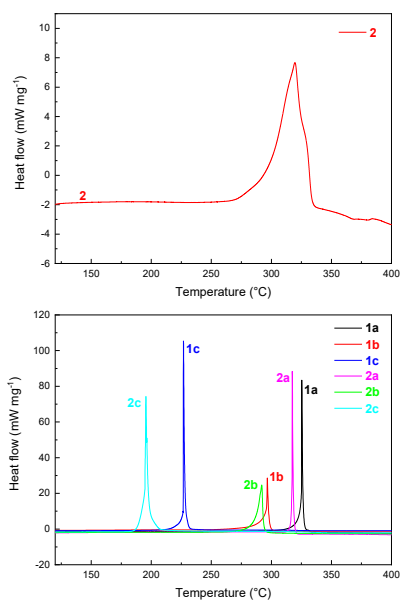
Note 7. DSC Curves

Figure S16 DSC curves of **1a-1c**, **2** and **2a-2c** at 10.0 °C min^{-1}

Table S5. Extrapolated onset temperatures (T_e), peak temperatures (T_p) and decomposition enthalpies (ΔH_d) the exothermic decomposition processes of **1a-1c**, **2** and **2a-2c** from the DSC curves.

Compounds	T_e (°C)	T_p (°C)	ΔH_d (J g^{-1})
1a	324.8	325.3	981
1b	292.8	296.6	921
1c	226.3	226.8	900
2	293.3	319.6	1479
2a	316.8	317.4	998
2b	286.7	291.9	1020
2c	193.5	195.5	1631

Supplementary References

[1] G. M. Sheldrick, SADABS, Siemens Area Detector Absorption Corrected Software, University of Göttingen, Germany, **2000**.

[2] G. M. Sheldrick, SHELXL-97, Program for X-ray Crystal Structure Refinement, University of Göttingen, Germany, **1997**.

[3] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[4] T. Lu, F. Chen, Multiwfn: A Multifunctional Wavefunction Analyzer, *J. Comput. Chem.* **2012**, *33*, 580–592.

[5] T. Lu, F. Chen, Quantitative Analysis of Molecular Surface Based on Improved Marching Tetrahedra Algorithm, *J. Mol. Graph. Model.* **2012**, *38*, 314–323.

[6] J. A. Dean, *Lange's Handbook of Chemistry (15th ed.)*, McGraw- Hill, Inc., New York, **1999**.

[7] W. Humphrey, A. Dalke, K. Schulten, VMD - Visual Molecular Dynamics, *J. Molec. Graphics* **1996**, *14*, 33–38.

[8] W. Mallard, P. Linstrom, NIST Chemistry Webbook; NIST Standard Reference Database; NIST: Gaithersburg, MD, 2000.

[9] M. J. Kamlet, S. J. Jacobs, Chemistry of Detonations. I. A Simple Method for Calculating Detonation Properties, *J. Chem. Phys.* **1968**, *48*, 23–35.

[10] Y. Wang, J. Zhang, H. Su, S. Li, S. Zhang, S. Pang, A Simple Method for the Prediction of the Detonation Performances of Metal-Containing Explosives, *J. Phys. Chem. A* **2014**, *118*, 4575–4581.

[11] S.-L. Chen, Z.-R. Yang, B.-J. Wang, Y. Shang, L.-Y. Sun, C.-T. He, H.-L. Zhou, W.-X. Zhang, X.-M. Chen, Molecular Perovskite High-Energetic Materials, *Sci. China Mater.* **2018**, *61*, 1123–1128.

[12] X. Wang, L. Wang, X. Xu, Y. Jiang, L. Zhao, Investigation on the Thermal Decomposition Behavior of TNT by TG-FTIR, *Chin. J. Energ. Mater.* **1998**, *6*, 169–172.

[13] Y. Ma, Q. Huang, H.-Z. Li, B.-S. Tan, Y.-C. Liu, Z.-W. Yang, Preparation and Characterization of TNT/TNCB Cocrystal Explosive, *Chin. J. Energ. Mater.* **2017**, *25*, 86–88.

[14] R. Matyáš, J. Pachman, *Primary Explosives Ch. 6*, Springer, Heidelberg, **2013**.