N,N'-Methylenebis(N-(1,2,5-oxadiazol-3-yl)nitramide) Derivatives as Metal-free Green Primary Explosives

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N,N'-Methylenebis(N-(1,2,5-oxadiazol-3-yl)nitramide) Derivatives as Metal-free Green Primary Explosives

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A series of new energetic salts based on N,N'-methylenebis(N-(4-(dinitromethyl)-1,2,5-oxadiazol-3-yl)nitramide) was synthesized and fully characterized by NMR and IR spectroscopy, and elemental analysis. Their excellent v_D (7995-8885 m s^{-1}) and acceptable sensitivities (IS, 1-5 J; FS, 40-120 N) make them good candidates as metal-free green primary explosives (with the exception of 3).

Lead azide and lead styphnate as primary explosives are the most commonly used materials in civilian and military operations. Their use suffers from leaving lead residues in the air and soil.[1] Therefore, the search for lead-free substitutes is a keen concern of many researchers. Some potassium-based primary explosives have been synthesized (Fig. 1), such as potassium 1,1'-dinitramino-5,5'-bistetrazolate (K$_2$BDNAT),[2] potassium 1,1'-di-nitramino-5,5'-bis-(tetrazolate) (K$_2$DNABT),[3] dipotassium 3,4-bis(3-dinitromethylfurazan-4-oxy)furazan (K$_2$BDFOF),[4] potassium 4,5-bis(dinitromethyl)-furoxanate (K$_2$BDNMF).[5] These potassium salts show high sensitivity towards impact and friction derived from explosophore groups such as nitramine and dinitromethyl. However, the initiation performance and priming ability of potassium-based primary explosive still cannot compete with those of lead azide.

Recently, scientists have focused their attention on the development of metal-free primary explosives with high-
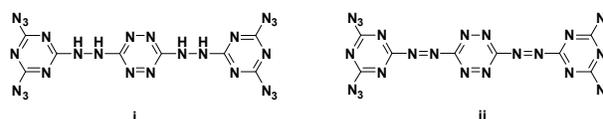

Fig. 1. Potassium-based primary explosives.

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Fig. 2. Metal-free primary explosives.

performance. Two metal-free polyazido compounds 3,6-bis-(2-(4,6-diazido-1,3,5-triazin-2-yl)-hydrazinyl)-1,2,4,5-tetrazine (i) and 3,6-bis(2-(4,6-diazido-1,3,5-triazin-2-yl)-diazenyl)-1,2,4,5-tetrazine (ii) were synthesized which have extremely high heats of formation (2114 kJ mol^{-1} and 2820 kJ mol^{-1}) and excellent detonation performance (D, 8365 m s^{-1} and 8602 m s^{-1}; P, 26.8 GPa and 29.4 GPa) (Fig. 2).[6] The results indicate that compound **i** is an environmentally friendly, potential candidate as a lead-free-primary explosive.

Energetic compounds containing the furazan ring often show good thermal stability arising from higher heats of formation (furazan, 215 kJ mol^{-1}) than other nitrogen oxygen heterocyclic rings. It has been shown that densities and explosive properties of energetic compounds could be improved when the furazan ring is substituted with other energetic groups.[7] Dinitromethyl and nitramide fragments as explosophore groups can enhance the oxygen balance values and density of the resulting compounds which improve their detonation velocities and pressures.[8] Therefore, we synthesized a series of energetic salts where furazan rings were chosen as the backbone and dinitromethyl and nitramide groups were chosen as the explosive sources. These salts have high densities, and high heats of formation, and therefore excellent detonation properties. The calculated properties coupled with the acceptable heats of formation and comparable low sensitivities suggest these high nitrogen materials as attractive candidates for metal-free green primary explosives.

3-Amino-4-chloroximinofurazan (ACOF) was synthesized in two steps using a known procedure starting from the commercially available malononitrile.[9] (3Z,3'Z)- 4,4'-(Methylenebis(azanediyl)) bis(N -hydroxy-1,2,5- oxadiazole-3-carbimidoyl chloride) (**1**) was easily obtained by the reaction of
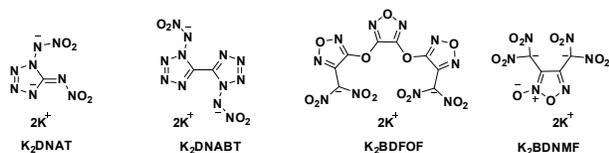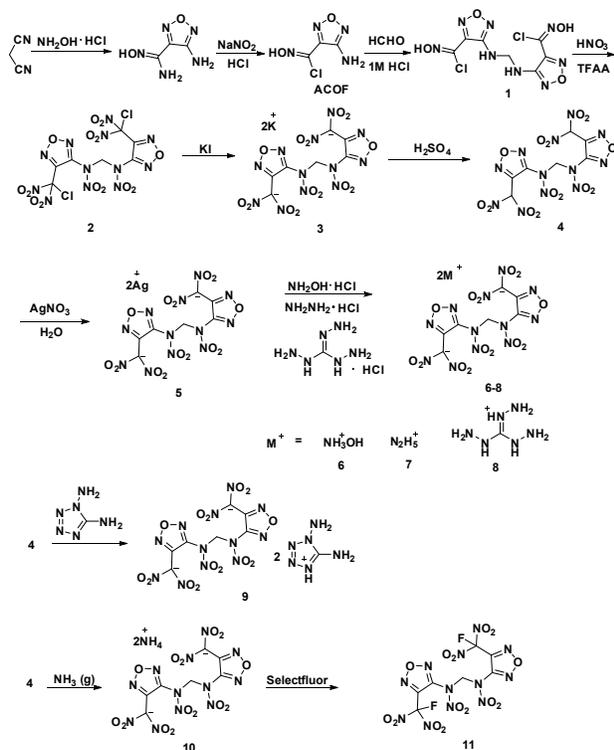
Scheme 1. Synthesis of compounds **6-11**.

formaldehyde and ACOF in 1M hydrochloric acid. Compound **1** was treated with a mixture of 100% nitric acid and trifluoroacetic anhydride (TFAA) at 0 °C to form **2** (Scheme 1). Compound **2** was extracted from the reaction mixture using dichloromethane. The nitration reaction process of **1** was monitored by TLC (ethyl acetate/hexane, 1:1). Compound **2** is a yellow oil which was treated with KI in methanol. A yellow solid **3** precipitated from the reaction mixture and was found to be stable under ambient conditions. The neutral compound **4** was obtained by acidification of the potassium salt **3** with sulfuric acid. Compound **4** was obtained as a white solid which became a liquid when exposed to moist air since it is hygroscopic. The silver salt (**5**) was synthesized by the metathesis reaction of **4** and silver nitrate. The corresponding energetic salts **6 – 8** were realized by reactions of **5** and hydrochloride salts in methanol. Salts **9** and **10** were synthesized by acid-base neutralization reactions in which **4** reacted with 1,5-diaminotetrazole or gaseous ammonia. Compound **11** was obtained by fluorination of **10** using Selectfluor® in anhydrous acetonitrile in moderate yields (59%)

In this work, all of the newly prepared compounds were fully characterized by using IR, ^{1}H and ^{13}C NMR spectra, and elemental analyses. Compound **11** was further characterized by ^{19}F NMR spectra. The ^{15}N NMR spectra were recorded for **6–10** in [D₆]DMSO (Fig. 2). They were assigned based on the literature values of resonance peaks in similar compounds[10] and GIAO NMR calculations by using the Gaussian 03 program.[11] There are five nitrogen signals associated with the

anion. Interestingly, the hydroxylammonium and ammonium cations did not give ^{15}N signals.
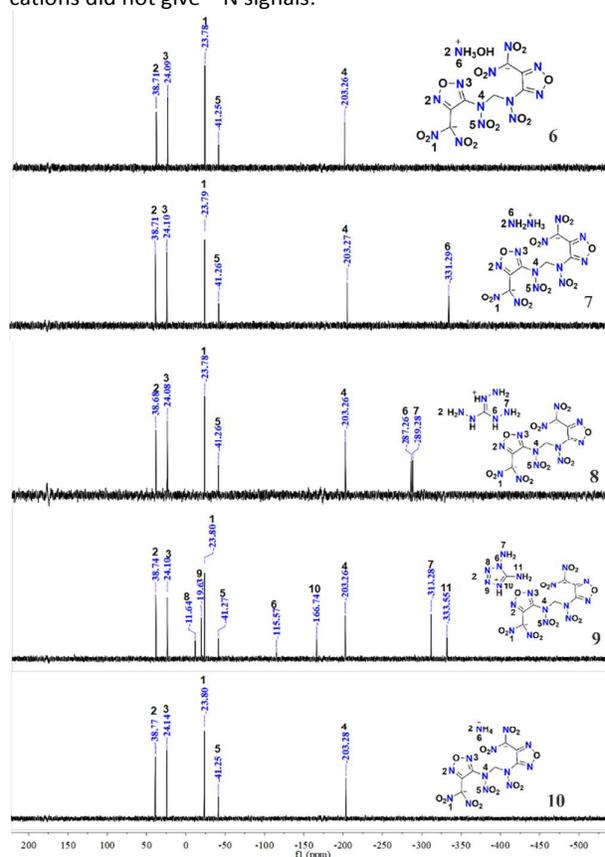
Figure 3. ^{15}N NMR spectra of compounds **6–10**.
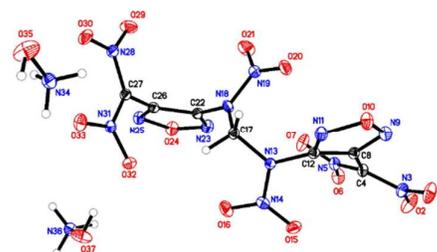
Fig. 4. Thermal ellipsoid plot (50%) and labeling scheme for **6**.

A suitable crystal of **6** was obtained by slow evaporation of its saturated solution in methanol. The crystal structure of **6** is given in Fig. 4. Crystallographic data and data collection parameters, bond lengths, and bond angles are in the Supporting Information. The unit cell of **6**, which crystallizes in the monoclinic space group P2₁/n, contains four formula moieties. The crystal density is 1.917 g cm⁻³ at 170 K (1.886 g cm⁻³ at 20 °C). The furazan ring of the anion of **6** is planar which is supported by the torsion angles: O10-N11-C12-C8, 1.36(14); C8-N9-O10-N11, 0.33(14); C12-C8-N9-O10, 0.49(14); N9-C8-C12-N11, -1.21(15); N9-O10-N11-C12, -1.08(14); N23-O24-N25-C26, 0.91(14); C22-N23-O24-N25, -1.09(14); N23-C22-C26-N25, -0.32(16); O24-N25-C26-C22, -0.36(14); and C26-C22-N23-O24, 0.84(15). However, the dinitromethyl group is

twisted out of the plane of the furazan ring which is indicated by a dihedral angle of 41.383(34)°. Hydrogen bonding interactions occur between

Table 1. Properties of energetic compounds (**3** and **6**·H_2O-**11**).

Comp.	T_d^a [°C]	d^b [g cm^{-3}]	ΔH_f^c [kJ g^{-1}]	v_D^d [m s^{-1}]	P^e [GPa]	IS^f [J]	FS^g [N]	OB^h [%]	I_{sp}^i [s]
3	125	2.03	-1.61	7955	28.1	1	120	17.3	205
6·H_2O	133	1.84	-0.97	8606	32.2	1	60	11.3	248
7·H_2O	141	1.78	-0.58	8371	30.3	2	60	2.9	241
8	120	1.65	0.05	7996	24.5	5	60	-8.8	227
9	119	1.75	0.83	8422	29.8	3	40	-2.4	246
10	123	1.77	-1.22	8121	28.0	3	80	6.2	231
11	128	1.87	0.58	8885	37.8	2	80	18.6	268
ADN^j	159	1.81	-	-	-	3-5	64-72	25.8	202^k
RDX^l	210	1.82	0.36	8748	34.9	7.4^m	120	0	-
TNT^n	300	1.65	-0.26	6881	19.5	15	-	-24.7	-

^{a} Decomposition temperature (onset) under nitrogen gas (DSC, 5 °C/min). ^{b} Density measured by gas pycnometer (25 °C). ^{c} Heat of formation. ^{d} Detonation pressure (calculated with Explo5 v6.01). ^{e} Detonation velocity (calculated with Explo 6.01). ^{f} Impact sensitivity. ^{g} Friction sensitivity. ^{h} Oxygen balance (based on CO) for $C_aH_bO_cN_d$, $1600(c-a-b/2)/M_W$, M_W = molecular weight. ^{i} Specific impulse (values obtained from Explo5 v6.01 and calculated at an isobaric pressure of 70 bar and initial temperature of 3300 K). ^{j} Ref. 15. ^{k} Calculated with Explo 5 v6.01. ^{l} Ref. 16. ^{m} Idaho expt'l value. ^{n} Ref. 17.

the nitrogen atom of the hydroxylammonium cation and the nitro groups and the furazan ring of the anion.

The thermal stabilities of these new energetic salts were determined by differential scanning calorimetric (DSC) measurements at a heating rate of 5 °C min^{-1}. All compounds decomposed between 119 and 141 °C (onset temperature) without melting (Table 1). The heats of formation of **11** and the anion of compounds **6**−**10** were calculated by using the isodesmic reaction approach with the Gaussian 03 (Revision E.01) suite of programs (Supporting Information).[11] The solid-phase heats of formation of energetic salts were calculated on the basis of the Born-Haber energy cycle.[12] Compounds **8**, **9** and **11** have positive heats of formation which range from 0.05 kJ g^{-1} to 0.83 kJ g^{-1}

With the values of the heats of formation and measured densities (gas pycnometer), detonation properties were calculated by using EXPLO5 (version 6.01).[13] The neutral compound **11** has the highest detonation velocity (8885 m s^{-1}) and detonation pressure (37.8 GPa), which is superior to RDX (8748 m s^{-1}, 34.9 GPa) (Table 1). Of all the energetic salts, the hydroxylammonium salt **6**·H_2O has superior detonation properties (8606 m s^{-1}, 32.2 GPa). The I_{sp} values range from 205 to 268 s, which are higher than that of ADN.

Impact and friction sensitivities of **11** and the energetic salts were measured using a BAM drop hammer apparatus and a BAM friction tester, respectively.[14] All the compounds are sensitive towards impact and friction, thereby highlighting their potential for application as primary explosives. Compound **6**·H_2O is the most sensitive with an impact sensitivity of 1 J and a friction sensitivity of 60 N.

Conclusions

In summary, a new family of energetic compounds of *N,N'*-methylenebis(*N*-(1,2,5-oxadiazol-3-yl)nitramide) featuring the dinitromethyl and fluorodinitromethyl groups were designed, synthesized and characterized. The potassium salt **3** has a density of 2.03 g cm^{-3}, positive oxygen balance and detonation properties (*D*, 7955 km s^{-1}; *P*, 28.1 GPa), which indicates that it might be useful as a green primary explosive. Of all the energetic salts, the hydroxylammonium salt **6**·H_2O exhibits the highest density of 1.84 g cm^{-3} and best detonation properties (*D*, 8606 km s^{-1}; *P*, 32.2 GPa). The calculated detonation parameters of other salts are in the range of TNT and RDX, respectively. The high sensitivities and remarkable detonation performance of these energetic salts as well as the green detonation products make them competitive candidates as metal-free green primary explosives.

Experimental section

Caution!!! Although we have encountered no difficulties in preparing these new compounds (**3**, **6**·H_2O-**11**) herein, manipulations must be carried out by using appropriate standard safety precautions. Eye protection and leather gloves must be worn. Mechanical actions of these energetic materials involving scratching or scraping must be avoided.

General methods: Reagents were purchased from Aldrich and Acros Organics and were used as received. ^1H and ^{13}C spectra were recorded on a 300 MHz (Bruker AVANCE 300) NMR spectrometer operating at 300.13 and 75.48 MHz, respectively. [D_6]DMSO and CDCl$_3$ were used as solvent and locking solvent. Chemical shifts in the ^1H and ^{13}C NMR spectra are reported relative to Me$_4$Si. ^{15}N spectra were obtained on a 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 50.69 MHz. The melting and decomposition (onset temperature) points were obtained on a differential scanning calorimeter (TA Instruments Co., model Q2000) at a heating rate of 5 °C min^{-1}. IR spectra were recorded on a FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films by using KBr plates. Densities were determined at 25 °C by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses were carried out by using a Vario Micro cube Elementar Analyser. Impact and friction sensitivity measurements were made by using a standard BAM Fall hammer and a BAM friction tester.

Computational methods: The gas-phase enthalpies of formation were calculated using the G2 method. For energetic salts, the solid-phase enthalpies of formation were obtained

by using a Born-Haber energy cycle.[18] The details are given in the Supporting Information.

X-ray crystallography of 6·H$_2$O: A yellow needle (0.330 x 0.145 x 0.117 mm^3) for **6·H$_2$O** was mounted on a MiteGen MicroMesh by 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 by using graphite monochromated MoKa radiation (λ = 0.71073). 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 by using APEX2 [v2014.3-0].[19] Data reduction was performed using SAINT [v7.68A][20] and XPREP [v2014/2].[21] Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS [v2008/1].[22] The structure was solved and refined with the aid of the programs SHELXL-2014/7 within WingX.[23] The full matrix least-squares refinement on F2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms.

(3Z,3'Z)-4,4'-(methylenebis(azanediyl))bis(N-hydroxy-1,2,5-oxadiazole-3-carbimidoyl chloride) (1): 25 °C, 1.63 g (10 mmol) 3-amino-4-chloroximinofurazan (ACOF)[9] was added to a solution of 1M HCl (30 mL) and 0.41 g (5 mmol) 37% formaldehyde was dropped in. Then the mixture was stirred for 3 h. The precipitate was filtered, washed with water, and dried in air to yield **1** (3.07 g) as a white solid, yield 91.1 %. $T_{(decomp; onset)}$ = 156 °C. ^{1}H NMR: δ = 4.86 (t, 2H), 6.64 (t, 2H), 13.47 (s, 2H) ppm; ^{13}C NMR: δ = 153.5, 141.8, 126.5, 53.7 ppm; IR (KBr pellet): ṽ = 3390, 3255, 3044, 2942, 2867, 2148, 1830, 1686, 1617, 1596, 1556, 1475, 1438, 1410, 1379, 1259, 1123, 1108, 1076, 1036, 1000, 947, 913, 868, 764, 712, 645, 564, 519, 485, 408 cm^{-1}; elemental analysis (%) calcd for C$_7$H$_6$Cl$_2$N$_8$O$_4$ (337.08): C 24.94, H 1.79, N 33.24; found: C 25.06, H 1.84, N 33.63.

Dipotassium N,N'-dinitro-N,N'-bis[3-dinitromethyl-furazanate-4-yl] methylenediamine (3): Compound **1** (3.37 g, 10 mmol) dissolved in CH$_2$Cl$_2$ (30 mL) was added dropwise into a stirred mixture of trifluoroacetic acid anhydride (14 mL) and 100% HNO$_3$ (8 mL), while maintaining the reaction temperature below 0 °C . After the addition was complete, the ice bath was removed, and the mixture was allowed to warm slowly to room temperature. It was stirred for another 3 h, and then poured into ice water (100 mL) and extracted with CH$_2$Cl$_2$ (3 x 20 mL). The organic phases were combined, washed with water and brine, dried over sodium sulfate, and then concentrated under vacuum to provide the intermediate **2** as a colorless oil. Compound **2** was dissolved in methanol (20 mL), potassium iodide (6 g, 36 mmol) in methanol (30 mL) was dropwise added, and the mixture was stirred overnight at room temperature. The precipitate formed was collected by filtration and washed with cold water (10 mL) and then

methanol (10 mL) and ethyl ether (10 mL) to give **3 (**4.06 g) as a yellow solid, yield 73%. $T_{(decomp; onset)}$ = 124.8 °C. ^{1}H NMR: δ = 6.29 (s, 2H) ppm; ^{13}C NMR: δ = 151.0, 146.3, 120.6, 64.4 ppm; IR (KBr pellet): ṽ = 3448, 1605, 1593, 1556, 1526, 1483, 1401, 1380, 1281, 1238, 1144, 1090, 1029, 999, 895, 821, 780, 748, 652 cm^{-1}; elemental analysis (%) calcd for C$_7$H$_2$K$_2$N$_{12}$O$_{14}$ (556.36): C 15.11, H 0.36, N 30.21; found: C 15.13, H 0.65, N 30.69.

Disilver N,N'-dinitro-N,N'-bis[3-dinitromethyl-furazanate-4-yl] methylenediamine (5): Concentrated sulfuric acid (1 mL) was added dropwise into a stirred mixture of **3** (0.56 g, 1 mmol) and H$_2$O (0.5 mL). After the addition was complete, the mixture was stirred for another 30 minutes, and then extracted with CH$_2$Cl$_2$ (6 x 5 mL). The combined extracts were concentrated under vacuum to provide white solid **4** (0.33 g), yield 68.8%. The solid **4** should be stored under vacuum. Compound **4** (0.48 g, 1 mmol) was dissolved in chloroform (2 mL), and silver nitrate solution was added dropwise. The white solid was filtered, washed with water, and dried in air, giving **5 (**0.57 g) as a white solid, yield 83%. $T_{(decomp; onset)}$ = 105.5 °C. ^{1}H NMR: δ = 6.28 (s, 2H) ppm; ^{13}C NMR: δ =151.0, 146.3, 120.6, 64.4 ppm; IR (KBr pellet): ṽ = 3441, 1588, 1562, 1514, 1485, 1414, 1385, 133, 1268, 1156, 1128, 1101, 1028, 1004, 965, 916, 902, 821, 806, 771, 746, 735, 723, 670, 593, 462 cm^{-1}; elemental analysis (%) calcd for C$_7$H$_2$Ag$_2$N$_{12}$O$_{14}$ (693.90): C 12.12, H 0.29, N 24.22; found: C 12.11, H 0.49, N 23.69.

General procedures for salts 6– 8: Compound **5** (0.69 g, 1 mmol) was added to a methanol solution (10 mL) of hydroxylammonium chloride (0.140 g, 2 mmol), hydrazinium chloride (0.137 g, 2 mmol) or triaminoguanidinium chloride (0.281 g, 2 mmol). After stirring for 2 h at room temperature, silver chloride was removed by filtration and washed with a small amount of methanol. The filtrate was concentrated under reduced pressure and dried in vacuum to yield **6–8**.

Dihydroxylammonium N,N'-dinitro-N,N'-bis[3-dinitromethyl-furazanate-4-yl] methylenediamine hydrate (6·H$_2$O): yellow solid, 82% yield. $T_{(decomp; onset)}$ = 133.2 °C. ^{1}H NMR: δ = 6.27 (s, 2H), 9.87 (s, 2H), 10.06 (s, 6H) ppm; ^{13}C NMR: δ =151.1, 146.4, 120.7, 64.5 ppm; IR (KBr pellet): ṽ = 3416, 3057, 2696, 1610, 1593, 1563, 1526, 1483, 1430, 1384, 1346, 1326, 1292, 1242, 1144, 1087, 1029, 999, 895, 820, 779, 747, 731, 674, 651, 624, 603, 537 cm^{-1}; elemental analysis (%) calcd for C$_7$H$_{12}$N$_{14}$O$_{17}$ (564.25): C 14.90, H 2.14, N 34.75; found: C 14.65, H 2.27, N 35.14.

Dihydrazinium N,N'-dinitro-N,N'-bis[3-dinitromethyl-furazanate-4-yl] methylenediamine hydrate (7·H$_2$O): yellow solid, 80% yield. $T_{(decomp; onset)}$ = 133.2 °C. ^{1}H NMR: δ = 6.27 (s, 2H), 9.87 (s, 2H), 10.06 (s, 6H) ppm; ^{13}C NMR: δ = 151.1, 146.4, 120.7, 64.5 ppm; IR (KBr pellet): ṽ = 3346, 3150, 1596, 1523, 1475, 1384, 1285, 1233, 1141, 1088, 1025, 996, 962, 903, 820, 750, 650, 596, 464 cm^{-1}; elemental analysis (%) calcd for

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$C_7H_{14}N_{16}O_{15}$ (562.29): C 14.95, H 2.51, N 39.86; found: C 14.89, H 2.50, N 40.49.

Di(triaminoguanidinium) N,N'-dinitro-N,N'-bis[3-dinitromethyl-furazanate-4-yl] methylenediamine (8): yellow solid, 88% yield. $T_{(decomp; onset)}$ = 120.1 °C. ^{1}H NMR: δ = 4.48 (s, 12H), 6.27 (s, 2H), 8.58 (s, 6H) ppm; ^{13}C NMR: δ =159.0, 151.0, 146.3, 120.6, 64.4 ppm; IR (KBr pellet): $\tilde{u}$ = 3354, 3320, 3213, 3044, 1686, 1588, 1527, 149, 1393, 1360, 1328, 1284, 1227, 1136, 1091, 1026, 996, 953, 907, 821, 800, 751, 23, 652, 605 cm^{-1}; elemental analysis (%) calcd for $C_9H_{20}N_{24}O_{14}$ (688.41): C 15.70, H 2.93, N 48.83; found: C 15.91, H 3.00, N 49.39.

Di(1,5-diaminotetrazolium) N,N'-dinitro-N,N'-bis[3-dinitromethyl-furazanate -4-yl] methylenediamine (9): Compound **4** (0.48 g, 1 mmol) was dissolved in 5 mL acetonitrile, and 1,5-diaminotetrazole (0.2 g, 2mmol) was added. The precipitate was filtered, washed with acetonitrile, and dried in air, giving **9** (0.54 g) as a yellow solid, yield 79%. $T_{(decomp; onset)}$ = 118.7 °C. ^{1}H NMR: δ =, 6.28 (s, 2H) ppm; ^{13}C NMR: δ =153.2, 151.1, 146.4, 120.7, 64.5 ppm; IR (KBr pellet): $\tilde{u}$ = 3355, 3264, 1718, 1596, 1522, 145, 1401, 1283, 1233, 1141, 1091, 1024, 995, 900, 818, 776, 750, 647, 600, 480 cm^{-1}; elemental analysis (%) calcd for $C_9H_{12}N_{24}O_{14}$ (680.35): C 15.89, H 1.87, N 49.40; found: C 16.44, H 2.07, N 47.12.

Diammonium N,N'-dinitro-N,N'-bis[3-dinitromethyl-furazanate-4-yl] methylenediamine (10): Compound **4** (0.48 g, 1 mmol) was dissolved in acetonitrile (5 mL), and ammonia gas was bubbled in. The precipitate was filtered, washed with acetonitrile, and dried in air, giving **10** (0.39 g) as a yellow solid, yield 76%. $T_{(decomp; onset)}$ = 123.2 °C. ^{1}H NMR: δ = 7.09 (t, 8H), 6.27 (s, 2H) ppm; ^{13}C NMR: δ = 151.0, 146.3, 120.6, 64.4 ppm; IR (KBr pellet): $\tilde{u}$ = 3224, 2856, 1607, 1589, 1562, 1527, 1475, 1425, 1356, 1332, 127, 1231, 1140, 1088, 1027, 997, 893, 820, 778, 747, 731, 674, 651, 623, 534, 479 cm^{-1}; elemental analysis (%) calcd for $C_7H_{10}N_{14}O_{14}$ (514.24): C 16.35, H 1.96, N 38.13; found: C 16.30, H 2.04, N 38.06.

N,N'-methylenebis(N-(4-(fluorodinitromethyl)-1,2,5-oxadiazol-3-yl)nitramide) (11): Compound **9** (0.51 g, 1 mmol) was dissolved in anhydrous acetonitrile (30 mL) and Selectfluor® (1.34 g, 3.79 mmol) was added at ambient temperature. The yellow mixture was stirred until decolorized (about 2 h) and the solvent was evaporated under reduced pressure. Anhydrous diethyl ether (50 mL) was added to the yellowish residue and this mixture stirred in a closed vessel for 30 min. The solid was filtered and the solvent was removed under reduced pressure giving **11** (0.37 g) as a white solid, yield 72%. T_m 83.4 °C. $T_{(decomp; onset)}$ = 127.6 °C. ^{1}H NMR: δ = 6.61 (s, 2H) ppm; ^{13}C NMR: δ = 148.7, 141.2, 140.9, 115.0, 112.7, 64.6 ppm; IR (KBr pellet): $\tilde{u}$ = 3030, 2930, 2909, 1740, 1608, 1561, 1500, 1425, 1401, 1360, 1282, 1219, 1131, 1115, 1085, 1031, 991, 960, 924, 90, 836, 818, 795, 751, 727, 696, 660, 614, 559, 465, 437 cm^{-1}; elemental analysis (%) calcd for

$C_7H_2F_2N_{12}O_{14}$ (516.16): C 16.29, H 0.39, N 32.56; found: C 16.57, H 0.41, N 31.93.

Conflicts of interest

There are no conflicts to declare.

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Metal-free green primary explosives with excellent detonation properties and acceptable sensitivities were synthesized and fully characterized.