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Energetic alliance of tetrazole-1-oxides and 1,2,5-oxadiazoles†‡

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The connection of highly endothermic heterocycles with high nitrogen as well as oxygen content is a recent trend in the development of new energetic materials in order to increase densities and stabilities. Bis(1-hydroxytetrazolyl)furazane (**9**) and bis(1-hydroxytetrazolyl)furoxane (**10**) were synthesized for the first time from dicyanofurazane and dicyanofuroxane, respectively. Several nitrogen-rich compounds (*e.g.* ammonium and hydroxylammonium) and metal salts thereof were prepared. Most compounds were characterized by single crystal X-ray diffraction. In addition all compounds were analyzed by vibrational spectroscopy (IR and Raman), multinuclear NMR spectroscopy, elemental analysis and DSC measurements. The heats of formation of **4**, **5**, **15–16**, **20** and **24** were calculated using the atomization method based on CBS-4M enthalpies. With these values and the experimental (X-ray) densities several detonation parameters such as the detonation pressure, velocity, energy and temperature were computed using the EXPLO5 code (V.5.05). In addition, the sensitivities towards impact, friction and electrical discharge were tested using the BAM drop hammer and friction tester as well as a small scale electrical discharge device.

Introduction

Research towards insensitive replacements for hexogen (RDX), octogen (HMX) and nitropenta (PETN) is still of particular interest in our and many other research groups worldwide. RDX has been identified as toxic and possibly carcinogenic.[1] Several attempts to synthesize appropriate replacements for RDX have been made in the recent past using tetrazole oxides.[2–4] The purpose of this study was to combine furazanes (1,2,5-oxadiazoles) and furoxanes (1,2,5-oxadiazole-2-oxides) with tetrazole oxides. The connection of highly endothermic heterocycles with high nitrogen as well as oxygen content is a recent trend in the development of new energetic materials in order to obtain powerful materials with great density and appropriate oxygen balance on the one hand, and perfect stability on the other hand. Tetrazoles (without N-oxide) have already been attached to furazanes[5] and furoxanes.[6] The resulting literature known compounds **24** and **25** as well as the new ones **9** and **10** are displayed in Fig. 1.

Various nitrogen rich salts of **9** and **10** as well as metal salts were synthesized to investigate their properties as potential energetic ingredients. The resulting 3,4-(1-oxidotetrazolyl)-furoxanes and furazanes are capable and fairly stable compounds in their deprotonated form.

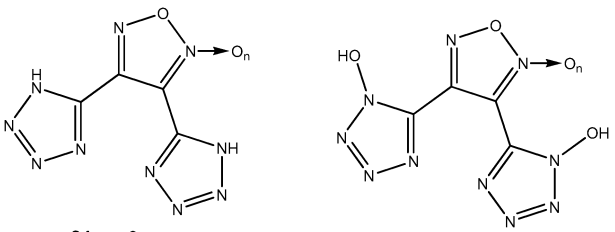

Fig. 1 Compounds **9** and **10** and the literature known compounds **24**[5] and **25**.[6]

Results and discussion

Synthesis

Compounds **9** and **10** were synthesised using a similar protocol from dicyanofurazane[7] and dicyanofuroxane[8] as depicted in Scheme 1.

Hydroximoylamines **3** and **4** are made from the nitriles by exothermic addition of aqueous hydroxylamine in ethanol in about 85% yield. Hydroximoyl chlorides **5** and **6** were synthesized from **3** and **4** by diazotization in 15% HCl and subsequently

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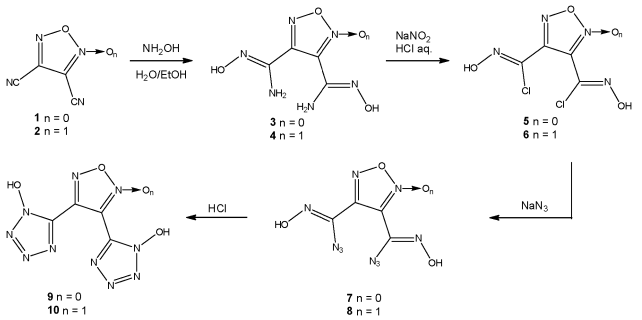
† Dedicated to Dr. Klaus Römer on the occasion of his 75th birthday.

‡ Electronic supplementary information (ESI) available: X-ray diffraction data, computations, and general experimental methods. CCDC 988403–988414. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4nj01351d



Scheme 1 Synthetic protocol for **9** and **10**.

extracted into diethyl ether. The reaction of **5** and **6** with sodium azide in aqueous ethanol affords hydroximoylazides **7** and **8**, respectively, which are also extracted into diethyl ether. The dried ether phase was saturated with gaseous HCl at 0 °C and stirred for 24 h in order to close the desired aromatic tetrazole-oxide rings. Compounds **9** and **10** are obtained as slightly yellow sticky oils after removal of the ethereal HCl solution.

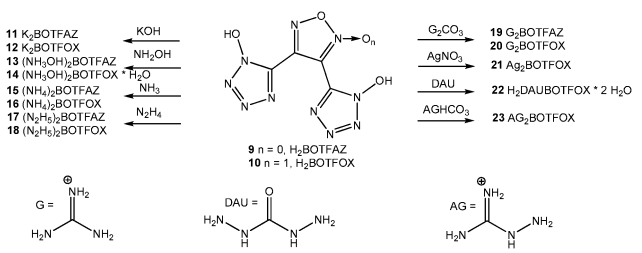
Salts of compounds **9** and **10** could be easily prepared by the addition of a base or the corresponding carbonates/bicarbonates to aqueous solutions of **9** and **10**. The silver salt of **10** precipitated upon the addition of aqueous silver nitrate. An overview of the salts prepared in this work is given in Scheme 2.

Crystal structures

Single crystals for XRD of compounds **3–6**, **11**, **12**, **14–17**, **20** and **23** could be obtained during this work. Crystallographic data and parameters as well as CCDC numbers are given in Tables S1 and S2 in the ESI.‡

In general, all bond lengths and angles were observed as expected and are comparable to similar crystal structures of furazanes,[9] furoxanes,[10] and tetrazole-oxides[11] in the literature. Compound **3** crystallizes in the monoclinic space group $C2/c$ with four molecules in the unit cell. The molecular unit is generated by C_2 symmetry through atom O1 and bond C1–C1^{i}. The density (1.667 g cm^{-3} at 100 K) of **3** is significantly smaller than that of the corresponding furazane **7** (1.780 g cm^{-3} at 173 K). Compound **4** crystallizes in the monoclinic space group $P2_1/n$. The molecular moieties are depicted in Fig. 2.

Hydroximoyl chlorides **5** and **6** crystallize in the monoclinic ($P2_1/n$) and orthorhombic ($P2_12_12_1$) crystal systems with four molecules in the unit cell. The molecular units are shown in Fig. 3. The density of furazane (1.909 g cm^{-3} at 100 K) again is slightly lower than that of furoxane (1.949 g cm^{-3} at 100 K).



Scheme 2 Synthesis of salts **11–23**.

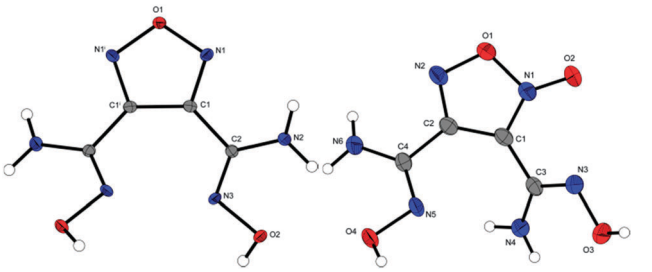


Fig. 2 Molecular moieties of **3** and **4** thermal ellipsoids are drawn at the 50% probability level. **3**: Symmetry code: 1 − *x*, *y*, 1.5 − *z*. Selected bond lengths (Å): O2–N3 1.4194(18), N3–C2 1.291(2), N2–C2 1.351(2); **4**: Selected bond lengths (Å): O2–N1 1.224(2), N4–C3 1.354(3), N4–C3 1.354(3), O3–N3 1.418(3).

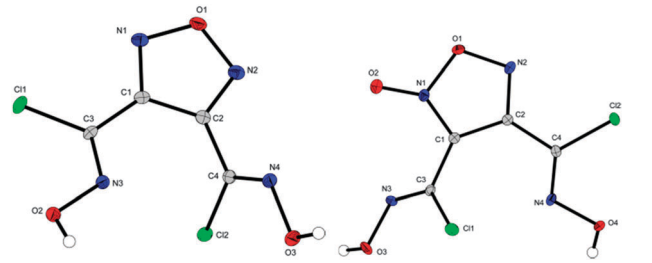


Fig. 3 Molecular moiety of **5** and **6**. Thermal ellipsoids are drawn at the 50% probability level.

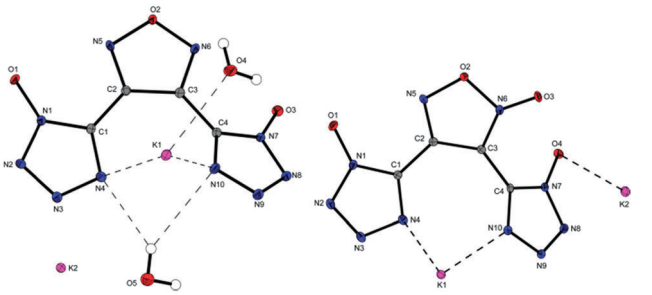


Fig. 4 Molecular moiety of **11** and **12**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths of **11**/**12** (Å): O1 N1 1.297(2), N1 N2 1.340(2), N1 C1 1.360(2), N2 N3 1.321(2), N3 N4 1.344(2) O2 N5 1.3822(19), O2 N6 1.430(2), O3 N6 1.2343(19)

Crystal structures of both potassium salts were obtained. The structure of furazane **11**, which crystallizes in the monoclinic space group $P2_1/c$, contains two crystal water molecules resulting in a lower density of 1.926 g cm^{-3} (at 100 K). For furoxane **12** (triclinic, $P\bar{1}$) a density of 2.156 g cm^{-3} at 100 K has been calculated. In both structures two rings (containing atoms C1 and C2/C3) are almost in plane while the third one is significantly deviated. Molecular moieties of **11** and **12** are depicted in Fig. 4.

Compound **14**·H_2O could only be obtained in the crystalline form with inclusion of one crystal water molecule (Fig. 5).

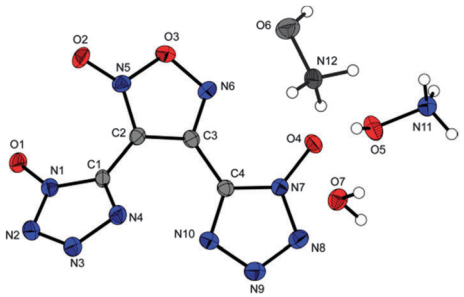


Fig. 5 Molecular moiety of **14**·H_2O. Thermal ellipsoids are drawn at the 50% probability level.

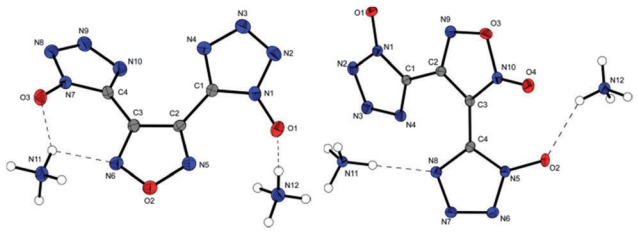


Fig. 6 Molecular moiety of ammonium salts **15** and **16**. Thermal ellipsoids are drawn at the 50% probability level. **15**: Selected bond lengths (Å): C1–C2 1.455(3), C2–C3 1.432(3), C3–C4 1.457(3), O1–N1 1.327(2), O3–N7 1.327(2); **16**: Selected bond lengths (Å): C1–C2 1.450(3), C3–C2 1.423(3), C3–C4 1.449(3), O1–N1 1.3187(19), O2–N5 1.323(2), O4–N10 1.231(2).

It crystallizes in the monoclinic space group $P2_1$ with a density of 1.794 g cm^{-3} at 173 K.

Bisammonium salt **15** crystallizes in the orthorhombic space group *Pbca* with a calculated density of 1.686 g cm^{-3} at 298 K. The corresponding bisammonium furoxane salt **16** crystallizes with a higher density of 1.748 g cm^{-3} (at 293 K) in the monoclinic space group $P2_1/c$. Both structures shown in Fig. 6 are dominated by strong hydrogen bonds involving all NH_4^+ protons.

The products of deprotonation of **9** with hydrazine and different guanidinium bases have not been obtained as single crystals. The hydrazinium salt of **9** crystallizes in the triclinic ($P\bar{1}$) crystal system and with a density of 1.727 g cm^{-3} at 236 K without inclusion of crystal water. The molecular moiety is shown in Fig. 7.

The bisguanidinium salt **20** (Fig. 8) crystallizes in the monoclinic space group $C2/c$ and with a density of 1.739 g cm^{-3} at 100 K (Fig. 8).

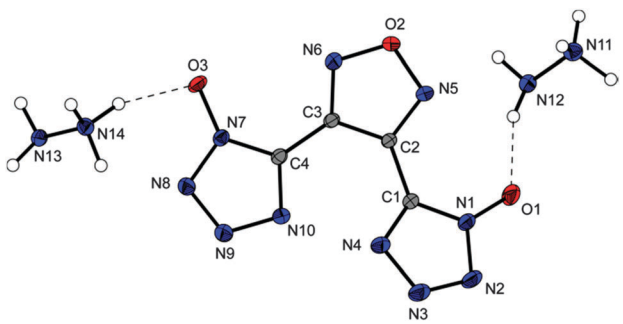


Fig. 7 Molecular moiety of hydrazinium salt **17**. Thermal ellipsoids are drawn at the 50% probability level.

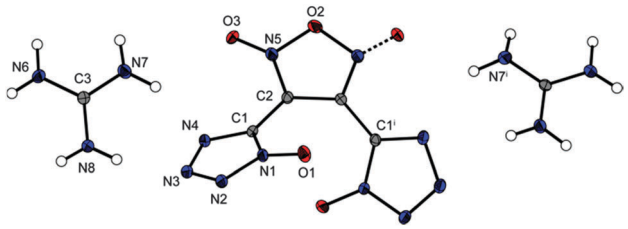


Fig. 8 Molecular moiety of guanidinium salt **20**. Thermal ellipsoids are drawn at the 50% probability level. Symmetry code: (i) $1 - x, y, 0.5 - z$.

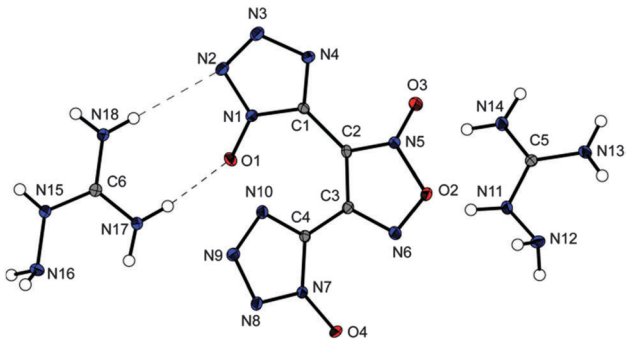


Fig. 9 Molecular moiety of aminoguanidinium salt **23**. Thermal ellipsoids are drawn at the 50% probability level.

In contrast to **20**, the aminoguanidinium salt **23** shows a slightly lower crystal density of 1.692 g cm^{-3}. The asymmetric unit of the monoclinic ($P2_1/c$) cell is shown in Fig. 9.

NMR spectroscopy

All ^{1}H NMR and ^{13}C NMR shifts of compounds **1–23** are gathered in Table 1. The ^{1}H NMR spectra of **9** and **10** exhibit both a broad singlet at around 7 ppm although **10** has no

Table 1 ^{1}H NMR and ^{13}C NMR shifts of all compounds

C	^{1}H NMR shift [ppm]	^{13}C NMR shift [ppm]
1	—	136.3, 106.7
2	—	134.7, 106.8, 105.0, 99.5
3	10.33, 6.20	148.7, 142.1
4	10.64, 10.08, 6.98, 6.08	151.6, 142.5, 139.8, 109.9
5	13.61	148.7, 122.9
6	13.78, 13.58	150.6, 124.8, 120.3, 110.2
7	12.85	147.1, 132.6
8	13.00, 12.75	149.4, 133.7, 130.4, 107.7
9	9.02	142.1, 136.6
10	6.67	143.4, 136.8, 134.4, 103.4
11	—	145.0, 132.8
12	—	147.7, 133.2, 130.3, 106.5
13	10.22	144.2, 133.9
14	10.27	146.4, 134.3, 131.5, 105.6
15	7.18	144.8, 133.1
16	7.22	147.2, 133.5, 130.7, 106.1
17	7.09	144.8, 133.1
18	7.16	147.1, 133.7, 130.9, 106.1
19	6.63	158.1, 144.2, 132.9
20	6.99	158.5, 146.9, 133.8, 130.9, 105.9
21	—	146.2, 133.2, 130.4, 105.4
22	6.36	158.4, 145.6, 135.1, 132.5, 105.0
23	8.70, 7.26, 6.90, 4.51	159.4, 147.0, 133.8, 130.9, 106.0

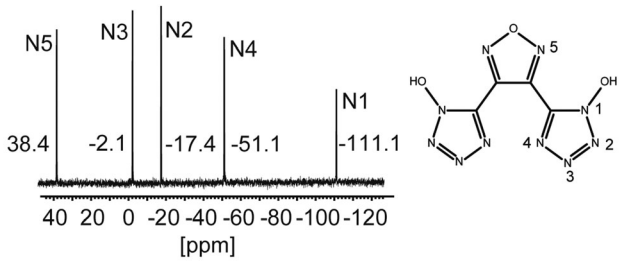


Fig. 10 $^{15}N\{^{1}H\}$ NMR spectrum of **9**.

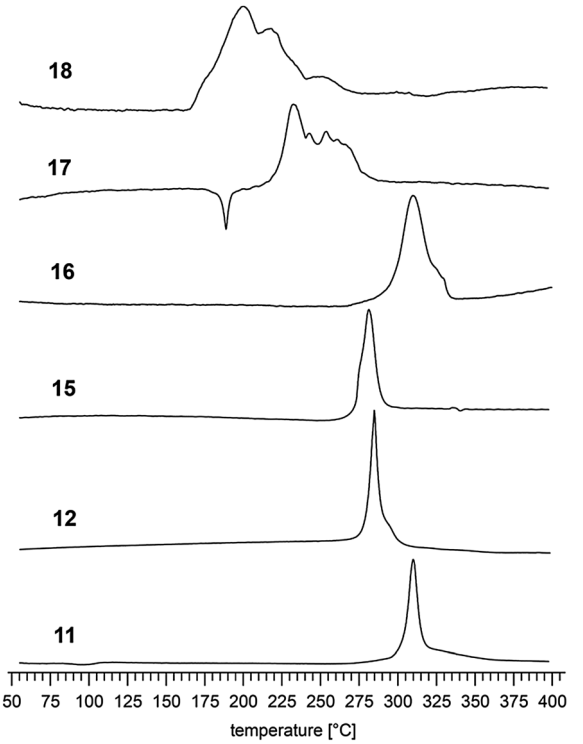


Fig. 11 DSC plots of compounds **11**, **12**, **15**, **16**, **17** and **18** at 5 °C min^{-1}.

C_{2V} symmetry anymore. The oximes in compounds **3–8** are observed in low field regions from 10.33 to 13.00 ppm. In the case of the oxime and amide protons splitting of the signals of the furoxane compounds can be observed because of the lower symmetry. In the ^{13}C NMR spectrum **9** exhibits two resonances at 142.1 ppm caused by furazane and 136.6 ppm caused by 1-hydroxytetrazole. **10** shows four resonances in the ^{13}C NMR spectra because of the lower symmetry at 136.8 and 134.4 ppm for the tetrazole oxides and at 143.4 and 103.4 ppm for the furoxane ring. Upon deprotonation the furazane signal of **9** is shifted towards lower fields up to 148.7 ppm and the tetrazole-oxide signal is shifted towards higher fields down to 132.8 ppm. The same trend was observed for **10**. Deprotonation led to a shift towards lower fields up to 149.4 and 107.7 ppm for furoxane but to a shift towards higher fields down to 133.2 and 130.3 ppm for the tetrazole-oxide resonances. The ^{15}N NMR spectrum of **9** is depicted in Fig. 10. The chemical shifts are assigned to the particular nitrogen atoms.

The carbon signals of the salts **11–23** are shifted to lower fields in comparison with their acids. No irregularities in the ^{1}H NMR and ^{13}C NMR shifts of the nitrogen-rich cations were observed.

Energetic properties

Thermal behavior (DSC). The thermal behaviour of the most important salts (with respect to their energetic behavior) of **9** and **10** is depicted in Fig. 11. The highest thermal stabilities of bis(1-oxidotetrazolyl)furaz(ox)anes are reached by the potassium salts at 277 °C (**11**) and 265 °C (**12**), respectively.

Heats of formation, sensitivities and detonation parameters. Gas phase heats of formation ($\Delta_f H^\circ_{(g,M,298)}$) were calculated theoretically using the atomization eqn (1) and CBS-4M electronic enthalpies. Details of the computations and the conversion of gas phase values into solid state values are given in the ESI.‡

$$\Delta_f H^\circ_{(g,M,298)} = H_{(M,298)} - \Sigma H^\circ_{(atoms,298)} + \Sigma \Delta_f H^\circ_{(atoms,298)} \quad (1)$$

Sensitivities were measured using a BAM drop hammer, a BAM friction tester[12] and a OZM electrostatic discharge device[13] (see also the Experimental part, General methods).

Detonation parameters were calculated using the computer code EXPLO5.05[14] using X-ray densities which were converted to room temperature values according to eqn (2). A coefficient of volume expansion[15] α_v of 1.5×10^{-4} K^{-1} was used. The structures of **15** and **16** were already measured at room temperature. Further explanations are gathered in the ESI.‡

$$\rho_{298K} = \rho_T/(1 + \alpha_v(298 - T_0)) \quad (2)$$

Only the physicochemical properties of compounds **4**, **5**, **15–16**, **20** and **23** are discussed since (i) they consist only of CHNO atoms and (ii) anhydrous crystal structures were obtained. The energetic parameters in comparison with RDX (cyclotrimethylene-trinitramine) are summarized in Table 2. All compounds investigated show improved sensitivities to RDX (IS 7.4 J, FS 120 N). Especially **20** is classified as insensitive towards impact and friction. The highest heat of formation was calculated for hydrazinium salt **17** ($\Delta_f H^\circ_{(s)}$ = 947.5 kJ mol^{-1}). For energetic materials it is more convenient to look for mass based enthalpies or energies. Also the highest mass based energy of formation value ($\Delta_f U^\circ$ 3245.4 kJ kg^{-1}) was calculated for **17**. The most important detonation parameters (heat of detonation, detonation temperature, pressure, velocity of detonation, and volume of detonation gases) were calculated with the EXPLO5.05 code and are summarized in Table 2. Based on these computations, compound **17** (8843 m s^{-1}) has higher velocity of detonation than RDX (8763 m s^{-1}). However, with respect to the synthetic expenditures and the assessment of all important energetic properties (sensitivities, stabilities and performance) probably none of the compounds will be used as an explosive filler by itself.

Table 2 Energetic properties of **3**, **4**, **15–17**, **20** and **23**

	3	**4**	**15**	**16**	**17**	**20**	**23**	RDX
Formula	$C_4H_6N_6O_3$	$C_4H_6N_6O_4$	$C_4H_8N_{12}O_3$	$C_4H_8N_{12}O_4$	$C_4H_{10}N_{14}O_3$	$C_6H_{12}N_{16}O_4$	$C_6H_{14}N_{18}O_4$	$C_3H_6N_6O_6$
FW/g mol^{-1}	186.13	202.13	272.18	288.18	302.21	372.26	402.29	222.12
IS/J[a]	>40	10	9	10	7	30	8	7.4[16]
FS/N[b]	>360	240	>360	240	>360	>360	>360	120[16]
ESD/J[c]	>1.5	0.25	1.5	1	1.5	n.d.	n.d.	0.2
N/%[d]	45.15	41.58	61.75	58.32	64.89	60.20	62.67	37.84
Ω_{CO_2}/%[e]	−68.76	−55.40	−52.90	−44.41	−52.94	−60.17	−59.65	−21.61
$T_{Dec.}$/°C[f]	198	180	259	234	211	197	165	205
ρ/g cm^{-3} [g]	1.668(100 K)	1.781(173 K)			1.727(236 K)	1.739(100 K)	1.692(100 K)	1.858(90 K)[17]
	1.64(298 K)	1.75(298 K)	1.686(293 K)	1.748(293 K)	1.71(298 K)	1.69(298 K)	1.64(298 K)	1.806(298 K)[18]
$\Delta_f H_m°$/kJ mol^{-1} [h]	150.2	159.3	625.6	621.7	947.5	638.3	885.4	66.6[16]
$\Delta_f U°$/kJ kg^{-1} [i]	907.1	886.4	2402.8	2260.2	3245.4	1820.8	2311.2	400.2[16]
EXPLO5.05:								
$-\Delta_{Ex}U°$/kJ kg^{-1} [j]	4713	5323	5122	5530	5779	4532	4884	6110
T_{det}/K[k]	3286	3631	3582	3841	3813	3193	3340	4224
P_{CJ}/kbar[l]	229	287	279	313	318	261	261	351
$V_{Det.}$/m s^{-1} [m]	7727	8312	8364	8671	8843	8161	8224	8763
V_o/L kg^{-1} [n]	720	719	769	772	793	764	782	739

[a] Impact sensitivity (BAM drophammer (1 of 6)). [b] Friction sensitivity (BAM friction tester (1 of 6)). [c] Electrostatic discharge device (OZM research). [d] Nitrogen content. [e] Oxygen balance ($\Omega = (x\mathrm{O} - 2y\mathrm{C} - 1/2z\mathrm{H})\mathrm{M}/1600$). [f] Start of decomposition temperature from DSC (β = 5 °C). [g] From X-ray diffraction, values for 298 K were calculated with $\rho_{298K} = \rho_T/(1 + \alpha_v(298 - T))$,[15] $\alpha_v = 1.5 \times 10^{-4}$ K^{-1}. [h] Calculated enthalpy of formation. [i] Calculated energy of formation. [j] Energy of explosion. [k] Explosion temperature. [l] Detonation pressure. [m] Detonation velocity. [n] Volume of detonation gases (assuming only gaseous products).

Conclusions

From this combined experimental and theoretical study the following conclusions can be drawn.

– The combination of furazanes or furoxanes with tetrazole-1-oxides is a suitable strategy in order to generate new triheterocyclic high-performing energetic materials due to their large positive heats of formation and appropriate densities.

– Generally the investigated furoxanes show mostly higher densities but lower thermal stabilities than the corresponding furazanes. Therefore, furazanes mostly are the better choice as energetic backbone heterocycles.

– The thermal stability of the tetrazole oxide anions attached to a furoxane or furazane ring is sufficient to reach decomposition temperatures above 200 °C.

Experimental part

For general methods, please see the ESI.‡

Syntheses

Bisaminohydroximoylfurazane (3). 10.8 g (90 mmol) of **1** was dissolved in 45 mL of ethanol and added within 15 min to 22.2 g (336 mmol) of 50% hydroxylamine solution, which was diluted with 90 mL of ethanol. The solvent was removed under reduced pressure until crystallization started. Upon filtering 9.3 g (50 mmol, 55%) of **3** were obtained as a yellowish powder. DSC (5 °C min^{-1}): 193 (mp.), 198 °C (dec.). Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 3162 (6), 1651 (71), 1592 (17), 1535 (35), 1513 (100), 1374 (43), 1282 (6), 1126 (6), 1040 (16), 984 (32), 956 (9), 923 (8), 826 (4), 761 (6), 488 (14) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 10.33, 6.20 ppm. ^{13}C{^{1}H} NMR (270 MHz, DMSO-d_6, 25 °C), δ: 148.7, 142.1 ppm.

Bisaminohydroximoylfuroxane (4). 1.4 g of dicyanofuroxane (10 mmol) was dissolved in 30 mL of ethanol and 1.3 g of 50% hydroxylamine solution in 10 mL of ethanol was added. After stirring for 30 min the solvent was removed and the residue was suspended in 20 mL of diethyl ether. The solid was filtered yielding 1.7 g (8.4 mmol, 84%) of the yellowish product. DSC (5 °C min^{-1}): 180 (dec.)°C. IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3463 (w), 3371 (w), 3309 (w), 1668 (m), 1647 (s), 1579 (s), 1539 (w), 1504 (m), 1418 (m), 1360 (m), 1311 (m), 1229 (w), 1082 (w), 1021 (w), 951 (s), 929 (s), 858 (w), 810 (m), 744 (vs), 688 (s) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 3372 (12), 1671 (39), 1651 (34), 1582 (13), 1542 (100), 1507 (12), 1421 (20), 1310 (14), 1232 (14), 1107 (10), 1066 (10), 1021 (10), 956 (9), 933 (11), 860 (6), 756 (10), 639 (6), 480 (24), 370 (5), 330 (11), 299 (5), 263 (6) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 10.64, 10.08, 6.98, 6.08 ppm. ^{13}C{^{1}H} NMR (270 MHz, DMSO-d_6, 25 °C), δ: 151.6, 142.5, 139.8, 109.9 ppm. EA ($C_4H_6N_6O_4$, 202.13 g mol^{-1}) calc. (found): C 23.77 (23.99), H 2.99 (2.86), N 41.58 (41.45)%. IS: 10 J (<100 μm). FS: 240 N. ESD: 0.25 J.

Bischlorohydroximoylfurazane (5). 6.9 g (37 mmol) of **3** was dissolved in 200 mL of semi-conc. hydrochloric acid. A solution of 6.3 g (92 mmol) of sodium nitrite in 30 mL of water was added dropwise within one hour while maintaining the temperature below 0 °C. The solution was stirred for one hour, allowed to come to ambient temperature, diluted with 200 mL of water and was extracted with 4 × 35 mL of diethyl ether. The organic phase was dried over magnesium sulfate and the solvent was removed under reduced pressure to obtain 7.97 g (35 mmol, 96%) of **5** as an oily liquid which partially started to crystallize.

DSC (5 °C min^{-1}): 115 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3502 (m), 3388 (m), 2991 (w), 2877 (w), 1731 (w), 1607 (m), 1561 (w), 1507 (w), 1499 (w), 1397 (m), 1390 (m), 1376 (m), 1359 (m),

1343 (m), 1265 (m), 1193 (w), 1094 (vw), 1057 (s), 1032 (s), 999 (s), 962 (s), 900 (s), 887 (vs), 863 (s), 818 (m), 795 (w), 749 (vw), 664 (m) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 3397 (6), 2944 (9), 2245 (3), 1626 (9), 1611 (100), 1563 (14), 1509 (89), 1396 (16), 1374 (3), 1361 (2), 1273 (3), 160 (8), 1002 (3), 968 (4), 889 (18), 864 (2), 666 (29), 655 (6), 616 (5), 601 (7), 499 (7), 430 (13), 413 (3), 366 (4), 325 (7), 296 (9), 241 (19), 226 (10), 182 (8), 151 (10), 102 (55), 76 (11), 67 (6) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 13.61 ppm. $^{13}C\{^{1}H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 148.7, 122.9 ppm. EA ($C_4H_2N_4O_3Cl_2$, 224.99 g mol^{-1}) calc. (found): C 21.35 (23.19), H 0.90 (1.53), N 24.90 (22.76)%.

Bischlorohydroximoylfuroxane (6). **4** (34.8 g, 0.2 mol) was dissolved in 500 mL of 34% hydrochloric acid (595 g, 6.0 mol). The solution was cooled with a salt-ice bath and additionally 500 g of ice was added to the solution. Sodium nitrite (31.1 g, 0.5 mol) was dissolved in little water and added dropwise over 1 h while keeping the temperature below 0 °C. Afterwards the solution was allowed to warm to ambient temperature and diluted by addition of 1 L of ice water. The product was extracted three-times with 200 mL of diethyl ether and dried over magnesium sulfate. **6** was obtained as a slightly yellow oily liquid which partially started to crystallize to give a total yield of 41.1 g (170 mmol, 81%). ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 13.78, 13.58 ppm. $^{13}C\{^{1}H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 150.6, 124.8, 120.3, 110.2 ppm.

Bisazidohydroximoylfurazane (7). 7.96 g (35 mmol) of **5** was dissolved in 50 mL of ethanol and 6.53 g (100 mmol) of sodium azide in 50 mL water was added at 0–5 °C. The suspension was stirred for 1 h on ice, diluted with 100 mL of water and brought to pH 2 using 2 M hydrochloric acid. The product was extracted with 5 × 30 mL of diethyl ether. The organic phase was dried over magnesium sulfate. The product does not need to be isolated for the continuing steps. If the solvent is removed a yellowish oil is obtained in approx. 80% yield which partially starts to crystallize on standing. IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3258 (m), 3035 (w), 2981 (w), 2855 (w), 2361 (vw), 2325 (vw), 2132 (s), 1733 (w), 1614 (m), 1558 (vw), 1516 (w), 1445 (w), 1389 (m), 1340 (s), 1272 (s), 1223 (m), 1108 (vw), 1093 (w), 1026 (s), 976 (vs), 936 (s), 899 (m), 855 (s), 819 (w), 781 (vw), 753 (w), 668 (vw) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 12.85 ppm. $^{13}C\{^{1}H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 147.1, 132.6 ppm.

Bisazidohydroximoylfuroxane (8). **6** (3.9 g, 16 mmol) was dissolved in 20 mL of ethanol and cooled with an ice bath while an aqueous solution of sodium azide (2.6 g, 40 mmol) was added in small portions. After the addition of sodium azide, the mixture was stirred for 1 h. The yellowish solution was diluted with 70 mL of ice water, adjusted to pH 1 by addition of concentrated hydrochloric acid and extracted with 3 × 30 mL and 1 × 10 mL of diethyl ether. The organic phase was dried over magnesium sulfate and the solvent was removed under reduced pressure. **8** was obtained as a yellowish oil in approx. 80% yield. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 13.00, 12.75 ppm. $^{13}C\{^{1}H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 149.4, 133.7, 130.4, 107.7 ppm.

Bis(1-hydroxytetrazolyl)furazane (9). The ethereal solution of **7** was saturated with gaseous HCl below 5 °C, the reaction flask was sealed and was then allowed to come to ambient temperature and stirred overnight. The solvent was removed under reduced pressure and bis(1-hydroxytetrazolyl)furazane was obtained as a yellowish oily liquid. DSC (5 °C min^{-1}): 91 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3404 (w), 2255 (w), 2128 (w), 1713 (w), 1660 (m), 1463 (m), 1344 (m), 1246 (m), 1197 (m), 1103 (m), 1053 (s), 1022 (s), 1005 (s), 982 (s), 922 (s), 895 (s), 819 (vs), 758 (s), 729 (s), 709 (m), 686 (m), 673 (m) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 2982 (8), 2940 (70), 2878 (14), 1618 (100), 1453 (10), 1387 (7), 1261 (30), 1205 (6), 1111 (5), 1011 (8), 907 (10), 764 (5), 736 (15), 711 (5), 455 (10), 92 (38) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 9.02 ppm. $^{13}C\{^{1}H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 142.1, 136.6 ppm. $^{15}N\{^{1}H\}$ NMR (400 MHz, DMSO-d_6, 25 °C), δ: 38.39, −2.1, −17.4, −51.1, −111.1 ppm.

Bis(1-hydroxytetrazolyl)furoxane (10). The oily compound **8** (3.3 g, 13 mmol) was dissolved in 100 mL of diethyl ether. Gaseous HCl was passed through the reaction mixture until saturation was reached at 0–5 °C and the reaction flask was sealed. After stirring overnight at room temperature the solvent was removed and bis(1-hydroxytetrazolyl)furoxane remained as a yellowish resinous substance. IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3423 (w), 2460 (w), 1607 (vs), 1461 (w), 1402 (w), 1369 (m), 1301 (m), 1259 (m), 1223 (m), 1194 (w), 1135 (w), 1091 (w), 1000 (m), 965 (s), 816 (s), 762 (w), 744 (w), 728 (w), 696 (w) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 2997 (2), 2990 (2), 2982 (7), 2943 (44), 1612 (100), 1463 (12), 1309 (14), 1265 (35), 1227 (31), 1201 (6), 1138 (6), 1003 (12), 820 (8), 765 (9), 747 (13), 733 (14), 700 (7), 526 (7), 453 (10), 414 (6), 388 (6), 358 (8) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 6.67 ppm. $^{13}C\{^{1}H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 143.4, 136.8, 134.4, 103.4 ppm.

Dipotassium bis(1-oxidotetrazolyl)furazane (11). An aqueous solution of **9** was brought to pH 8 with 2 M potassium hydroxide solution. The solution was left for crystallization and the dihydrate of **11** was obtained as a crystalline solid. The anhydrous compound was obtained by pouring a hot concentrated aqueous solution of **11** into the five-fold volume of ethanol and filtering. DSC (5 °C min^{-1}): 87 °C (dehy), 277 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3552 (w), 3357 (m), 3242 (w), 1665 (w), 1635 (m), 1592 (m), 1574 (w), 1542 (w), 1471 (s), 1437 (m), 1407 (s), 1372 (m), 1362 (m), 1286 (s), 1239 (s), 1173 (w), 1118 (m), 1084 (w), 1033 (m), 1015 (w), 1000 (s), 983 (vs), 912 (s), 896 (m), 834 (w), 803 (w), 771 (m), 751 (w), 727 (w), 692 (w), 664 (w) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 1594 (26), 1575 (100), 1473 (6), 1374 (13), 1240 (11), 1176 (12), 1145 (8), 1121 (4), 1085 (3), 1017 (5), 1004 (3), 774 (5), 457 (5), 98 (13), 79 (5) cm^{-1}. $^{13}C\{^{1}H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 145.0, 132.8. EA ($K_2C_4H_4N_{10}O_5$, 386.37 g mol^{-1}) calc. (found): C 12.43 (13.60), H 1.04 (1.22), N 36.25 (36.72)%. MS (FAB^+) m/z: 39.0 [K^+], (FAB^-) m/z: 237.2 [$C_4HN_{10}O_3^-$]. IS: 35 J (<100 μm), FS: >360 N. ESD: 1.5 J.

Dipotassium bis(1-oxidotetrazolyl)furoxane (12). The total amount of **10** was suspended in 50 mL of ethanol and an aqueous solution of potassium hydroxide was added until pH 7 was reached. The potassium salt started to precipitate. After

addition of 20 mL of diethyl ether more precipitate could be obtained. Filtration of the mixture and air drying led to 4.9 g (15 mmol, 94% based on step **6**) of a white powder. DSC (5 °C min^{-1}): 265 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3376 (w), 3142 (w), 3087 (w), 2841 (w), 2799 (w), 2652 (w), 2449 (w), 2357 (w), 2343 (w), 2167 (w), 2000 (w), 1799 (w), 1703 (w), 1670 (w), 1648 (w), 1609 (s), 1575 (s), 1546 (s), 1464 (m), 1450 (s), 1427 (s), 1421 (s), 1396 (s), 1370 (s), 1297(m), 1231 (vs), 1195 (w), 1167 (m), 1156 (w), 1144 (w), 1115 (w), 1095 (m), 1035 (w), 1017 (m), 988 (s), 964 (s), 879 (w), 836 (s), 792 (w), 767 (s), 754 (m), 731 (m), 711 (m), 705 (w), 693 (m), 682 (m), 654 (w) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 1616 (22), 1576 (100), 1549 (35), 1449 (11), 1403 (11), 1372 (3), 1299 (5), 1235 (24), 1195 (29), 1170 (19), 1158 (6), 1147 (6), 1098 (6), 1021 (6), 992 (18), 838 (8), 769 (16), 734 (3), 713 (3), 696 (7), 685 (3), 595 (4), 558 (5), 511 (13), 456 (13), 442 (5), 411 (5), 368 (6), 341 (3), 297 (2), 260 (4), 240 (4), 166 (34), 137 (46), 122 (24), 101 (36), 77 (27) cm^{-1}. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 147.7, 133.2, 130.3, 106.5. MS (FAB^+): 39.0 [K^+], (FAB^-): 253.1 [$C_4HN_{10}O_4^-$]. EA ($K_2C_4N_{10}O_4$, 330.30 g mol^{-1}) calc. (found): C 14.55 (14.64), H 0.00 (0.00), N 42.41 (41.38)%. Found: C 14.64, H 0.00, N 41.38%. IS: 10 J (<100 μm). Friction tester: 48 N (<100 μm).

Dihydroxylammonium bis(1-oxidotetrazolyl)furazane (13). 3.2 g (10 mmol) of **11** was dissolved in 20 mL of 2 M hydrochloric acid. The solution was extracted with 5 × 30 mL of diethyl ether and the solvent was removed under reduced pressure. The residue was dissolved in 20 mL of ethanol. 2.2 eq. of 50% hydroxylamine solution was added under vigorous stirring. The solution was stirred for additional 30 min, the solvent was then removed under reduced pressure and the precipitate was filtered off. 2.9 g (9.6 mmol, 95%) of **13** was obtained as a white crystalline powder. DSC (5 °C min^{-1}): 170 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3210 (w), 3043 (w), 2885 (w), 2663 (m), 1992 (w), 1623 (w), 1602 (w), 1497 (m), 1473 (s), 1434 (m), 1429 (m), 1404 (s), 1376 (w), 1361 (s), 1285 (s), 1245 (s), 1230 (s), 1197 (m), 1180 (m), 1126 (w), 1035 (w), 1009 (m), 1000 (s), 986 (vs), 894 (m), 878 (w), 773 (m), 748 (w), 694 (w) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 1606 (15), 1588 (100), 1477 (5), 1439 (2), 1376 (14), 1289 (2), 1249 (13), 1236 (4), 1183 (16), 1147 (8), 1128 (4), 1089 (5), 1012 (16), 903 (7), 776 (4), 750 (6), 686 (2), 556 (4), 462 (10), 46 (2), 349 (2), 309 (2), 98 (14) cm^{-1}. ^1H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 10.22 ppm. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 144.2, 133.9 ppm. EA ($C_4H_8N_{12}O_5$, 304.18 g mol^{-1}) calc. (found): C 15.79 (16.39), H 2.65 (2.67), N 55.26 (54.23)%. IS: 7 J (<100 μm). FS: 216 N (<100 μm). ESD (<100 μm): 1 J.

Dihydroxylammonium bis(1-oxidotetrazolyl)furoxane monohydrate (14). 1.7 g of **12** (5 mmol) was dissolved in 20 mL of 2 M hydrochloric acid and extracted with 4 × 20 mL of diethyl ether. The ether was removed under reduced pressure and the residue was dissolved in a few milliliters of water. Hydroxylamine (661 mg of 50% solution in H_2O, 0.61 mL, 10 mmol) was added while stirring. The solution was left for crystallisation. Compound **14** crystallized to give 1.7 g (4.9 mmol, 98%) yield. DSC (5 °C min^{-1}): 135 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 2976 (m), 2709 (m), 1696 (w), 1625 (s), 1591 (s), 1559 (s), 1461 (s), 1426 (m), 1399 (m), 1376 (m), 1300 (m), 1232 (vs), 1187 (m), 1020 (m), 996 (s), 964 (s), 822 (m), 757 (m), 704 (w) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 2986 (13), 1630 (27), 1590 (100), 1567 (29), 1495 (6), 1463 (8), 1398 (14), 1300 (8), 1235 (15), 1212 (44), 1186 (6), 1137 (10), 1102 (5), 1018 (14), 1001 (33), 833 (4), 756 (8), 707 (3), 684 (3), 506 (4), 460 (7). ^1H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 10.27 ppm. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 146.4, 134.3, 131.5, 105.6 ppm. EA ($C_4H_{10}N_{12}O_7$, 338.20 g mol^{-1}) calc. (found): C 14.21 (14.30), H 2.98 (2.90), N 49.70 (48.43)%. IS: 10 J (100–500 μm). FS: 240 N (100–500 μm).

Diammonium bis(1-oxidotetrazolyl)furazane (15). 3.1 g (10 mmol) of **11** was dissolved in 20 mL of 2 M hydrochloric acid. The solution was extracted with 5 × 30 mL of diethyl ether and the solvent was removed under reduced pressure. The residue was dissolved in 20 mL of water. 2.2 eq. of ammonium hydroxide was added under vigorous stirring. The solvent was then removed under reduced pressure. The crude product was recrystallized from methanol, 2.66 g (8.8 mmol, 87%) of **11** was obtained as colorless crystals. DSC (5 °C min^{-1}): 259 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3134 (w), 3000 (w), 2881 (w), 2796 (w), 1665 (w), 1604 (w), 1594 (w), 1469 (m), 1440 (s), 1405 (s), 1366 (s), 1283 (s), 1229 (vs), 1181 (w), 1133 (w), 1122 (m), 1031 (m), 1014 (w), 1003 (m), 983 (s), 905 (s), 889 (m), 765 (w), 748 (s), 731 (w), 716 (w), 696 (w) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 1606 (31), 1594 (100), 1482 (4), 1373 (11), 1235 (20), 1182 (16), 1136 (12), 1123 (4), 1015 (6), 1005 (3), 906 (7), 767 (4), 750 (7), 612 (3), 461 (10), 305 (2), 163 (5), 129 (6), 102 (42). ^1H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 7.18 ppm. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 144.8, 133.1 ppm. EA ($C_4H_8N_{12}O_3$, 272.19 g mol^{-1}) calc. (found): C 17.65 (17.93), H 2.96 (2.95), N 61.75 (61.00)%. IS: 9 J (<100 μm). FS: >360 N (<100 μm). ESD (<100 μm): 1.5 J.

Diammonium bis(1-oxidotetrazolyl)furoxane (16). 1.7 g of **12** (5 mmol) was dissolved in 20 mL of 2 M hydrochloric acid and extracted with 4 × 20 mL of diethyl ether. The solvent was removed under reduced pressure and the residue was dissolved in a few milliliters of water. The solution was adjusted to pH 7 by addition of 2 M NH_3. The solvent was removed under reduced pressure and **16** precipitated as a colorless solid to give 1.2 g (4.2 mmol, 84%) yield. Crystals of **16** were obtained from water. DSC (5 °C min^{-1}): 230 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3166 (w), 3010 (w), 2892 (w), 2801 (w), 1622 (s), 1583 (m), 1555 (m), 1462 (s), 1426 (s), 1399 (s), 1374 (m), 1297 (m), 1228 (vs), 1181 (w), 1020 (w), 996 (m), 964 (s), 832 (s), 760 (m), 744 (w), 733 (w), 706 (w), 688 (w) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 3031 (3), 1622 (29), 1585 (100), 1556 (20), 1398 (10), 1297 (4), 1229 (14), 1207 (28), 1182 (4), 1134 (9), 1102 (4), 1025 (4), 999 (8), 832 (3), 761 (4), 711 (2), 687 (2), 553 (2), 500 (4). ^1H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 7.22 ppm. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 147.2, 133.5, 130.7, 106.1 ppm. EA ($C_4H_8N_{12}O_4$, 288.18 g mol^{-1}) calc. (found): C 16.67 (16.88), H 2.80 (2.82), N 58.32 (56.18)%. IS: 10 J (<100 μm). FS: 240 N (<100 μm). ESD (<100 μm): 1 J.

Dihydrazinium bis(1-oxidotetrazolyl)furazane (17). 3.2 g (10 mmol) of **11** was dissolved in 20 mL of 2 M hydrochloric acid.

The solution was extracted with 5 × 30 mL of diethyl ether and the solvent was removed under reduced pressure. The residue was dissolved in 20 mL of ethanol and 2.2 eq. of hydrazine hydrate was added under vigorous stirring. The solution was stirred for additional 30 min, the solvent was then concentrated under reduced pressure and the precipitate was filtered off. The crude product was recrystallized from methanol, 2.9 g (9.4 mmol, 94%) of **17** was obtained as yellowish crystals. DSC (5 °C min^{-1}): 175 °C (mp.), 211 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3323 (w), 3187 (w), 2839 (m), 2710 (m), 2640 (m), 1604 (m), 1537 (m), 1471 (m), 1422 (w), 1402 (s), 1374 (w), 1361 (m), 1285 (s), 1232 (m), 1222 (s), 1173 (w), 1141 (m), 1115 (s), 1093 (s), 1078 (s), 1009 (w), 999 (m), 982 (s), 962 (vs), 897 (s), 874 (m), 768 (w), 758 (m), 747 (m), 731 (w), 716 (w), 697 (w), 689 (w) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 3326 (3), 3188 (4), 1609 (57), 1587 (100), 1473 (8), 1376 (15), 1235 (16), 1174 (18), 1150 (9), 1137 (5), 1087 (7), 1004 (7), 963 (10), 901 (9), 772 (7), 749 (5), 620 (3), 464 (14), 171 (4), 141 (5), 104 (9), 92 (16). ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 7.09 ppm. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 144.8, 133.1 ppm. EA ($C_4H_{10}N_{14}O_3$, 302.21 g mol^{-1}) calc. (found): C 15.90 (16.36), H 3.34 (3.27), N 64.89 (64.45)%. IS: 7 J (<100 μm). FS: >360 N (<100 μm). ESD (<100 μm): 1.5 J.

Dihydrazinium bis(1-oxidotetrazolyl)furoxane (18). 1.7 g of **12** (5.6 mmol) was dissolved in 20 mL of 2 M hydrochloric acid and extracted four-times with 20 mL of diethyl ether. The solvent was removed under reduced pressure and the residue was dissolved in a few milliliters of water. Hydrazinium hydroxide (0.5 g, 0.5 mL, 10 mmol) was added to the colorless solution, the solvent was removed under reduced pressure and **18** precipitated as a colorless solid to give 1.5 g (4.8 mmol, 96%) yield. DSC (5 °C min^{-1}): 160 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3563 (w), 3461 (w), 3344 (m), 3331 (m), 3285 (m), 2833 (m), 2725 (m), 2606 (m), 2105 (m), 1613 (s), 1580 (s), 1551 (s), 1512 (s), 1455 (s), 1426 (s), 1413 (s), 1391 (s), 1371 (s), 1345 (m), 1292 (m), 1230 (s), 1108 (m), 1088 (s), 1018 (m), 984 (s), 956 (s), 942 (vs), 820 (s), 773 (m), 760 (s), 746 (m), 732 (m), 704 (m), 688 (m), 679 (m) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 1613 (19), 1583 (100), 1554 (12), 1457 (4), 1396 (9), 1295 (3), 1237 (11), 1209 (30), 1181 (7), 1152 (7), 1137 (7), 1096 (7), 1018 (4), 989 (11), 946 (4), 764 (10), 734 (3), 707 (3), 692 (3), 556 (4), 500 (7), 456 (11), 439 (5), 366 (3), 324 (6), 295 (2), 159 (14), 110 (46), 88 (45) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 7.16 ppm. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 147.1, 133.7, 130.9, 106.1 ppm. MS (FAB^+): 33.0 [$N_2H_5^+$], (FAB^-): 253.1 [$C_4HN_{10}O_4^-$]. EA ($C_4H_{10}N_{14}O_4$, 318.21 g mol^{-1}) calc. (found): C 15.10 (15.56), H 3.17 (3.24), N 61.62 (59.96)%. IS: 5 J (<100 μm). FS: 96 N (<100 μm). ESD (<100 μm): 0.5 J.

Diguanidinium bis(1-oxidotetrazolyl)furazane (19). 3.1 g (10 mmol) of **11** was dissolved in 20 mL of 2 M hydrochloric acid. The solution was extracted with 5 × 30 mL of diethyl ether and the solvent was concentrated under reduced pressure. The residue was dissolved in 5 mL of water. 1.1 eq. of a solution of guanidinium carbonate in water was added under vigorous stirring. The solution was stirred for additional 30 min, the solvent was then removed under reduced pressure and the precipitate was filtered off. The crude product was recrystallized from methanol, 3.4 g of **19** was obtained as pale yellow crystal rods. DSC (5 °C min^{-1}): 124 (mp.), 264 (dec.) °C. IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3360 (s), 3206 (m), 3119 (s), 2813 (w), 1691 (w), 1656 (vs), 1591 (m), 1582 (m), 1469 (s), 1432 (w), 1404 (s), 1363 (m), 1291 (s), 1237 (s), 1140 (m), 1126 (m), 1040 (m), 1001 (m), 987 (s), 899 (m), 882 (m), 770 (w), 750 (w), 696 (w) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 3370 (2), 3229 (9), 1597 (9), 1578 (100), 1470 (5), 1368 (19), 1243 (9), 1180 (16), 1151 (6), 1128 (4), 1099 (7), 1010 (24), 906 (5), 777 (6), 752 (2), 542 (6), 462 (10), 293 (6), 136 (2), 106 (2) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 6.63 ppm. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 158.1, 144.2, 132.9 ppm. EA ($C_6H_{12}N_{16}O_3$, 356.27 g mol^{-1}) calc. (found): C 20.23 (19.56), H 3.40 (3.63), N 62.90 (59.68)%. IS: >40 J (<100 μm). FS: >360 N (<100 μm). ESD (<100 μm): 1.5 J.

Diguanidinium bis(1-oxidotetrazolyl)furoxane (20). 1.7 g of **12** (5.1 mmol) was dissolved in 20 mL of 2 M hydrochloric acid and extracted four-times with 20 mL of diethyl ether. The solvent was removed under reduced pressure and the residue was dissolved in a few milliliters of water. Guanidinium carbonate (0.9 g, 5.2 mmol) was added and the solution was heated while stirring. After filtration the mixture was cooled down to ambient temperature and **20** precipitated to give 1.8 g (4.8 mmol, 96%) of colorless, crystalline blocks. DSC (5 °C min^{-1}): 197 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3428 (s), 3342 (s), 3161 (s), 2793 (m), 2202 (w), 1999 (w), 1640 (vs), 1590 (s), 1553 (s), 1458 (m), 1423 (s), 1400 (m), 1335 (s), 1303 (s), 1243 (s), 1226 (s), 1180 (s), 1134 (m), 1106 (m), 1089 (m), 1026 (m), 1010 (m), 986 (s), 964 (s), 846 (w), 818 (s), 763 (s), 735 (s), 726 (s), 700 (m), 692 (m) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 3267 (2), 1623 (42), 1594 (100), 1558 (40), 1460 (22), 1434 (12), 1338 (3), 1307 (27), 1234 (9), 1210 (64), 1183 (7), 1136 (15), 1109 (8), 1092 (5), 1028 (7), 1009 (69), 989 (18), 967 (3), 823 (8), 761 (12), 729 (8), 704 (9), 592 (4), 564 (11), 529 (14), 494 (11), 448 (14), 421 (14), 368 (23), 286 (7), 230 (26), 163 (26) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 6.99 ppm. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 158.5, 146.9, 133.8, 130.9, 105.9 ppm. MS (FAB^+): 60.1 [$CH_6N_3^+$], 373.1 [M + H^+], (FAB^-): 253.1 [$C_4HN_{10}O_4^-$]. EA ($C_6H_{12}N_{16}O_4$, 372.26 g mol^{-1}) calc. (found): C 19.36 (19.74), H 3.25 (3.22), N 60.20 (59.93)%. IS: 30 J (100–500 μm). FS: 360 N (100–500 μm). ESD (<100 μm): 1.5 J.

Disilver bis(1-oxidotetrazolyl)furoxane (21). 0.5 g of **11** (1.5 mmol) was dissolved in 20 mL of water and an aqueous solution of silver nitrate (0.5 g, 3.0 mmol) was added, the silver salt precipitated immediately. After stirring and heating until boiling for a short time, the colorless solid was filtered off and air dried to give 0.7 g (1.4 mmol, 90%) of Ag_2BOTFOX as a monohydrate. DSC (5 °C min^{-1}): 221 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3365 (w), 3155 (w), 1628 (s), 1584 (s), 1462 (s), 1432 (s), 1397 (s), 1372 (m), 1302 (m), 1231 (vs), 1185 (m), 1092 (w), 1027 (w), 990 (m), 967 (s), 818 (s), 765 (s), 747 (m), 726 (m), 696 (m), 677 (m) cm^{-1}. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 146.2, 133.2, 130.4, 105.4 ppm. MS (DEI^+): 107.0 [Ag^+]. EA ($Ag_2C_4H_2N_{10}O_5$, 485.86 g mol^{-1}) calc. (found): C 9.89 (10.09), H 0.41 (0.41), N 28.83 (28.47)%. IS: 3 J (<100 μm). FS: 16 N (<100 μm).

Diaminouronium bis(1-oxidotetrazolyl)furoxane dihydrate (22). 1.7 g of **12** (5 mmol) was dissolved in 20 mL of 2 M

hydrochloric acid and extracted four-times with 20 mL of diethyl ether. The solvent was removed under reduced pressure and the residue was dissolved in a few milliliters of water. Diaminourea (0.9 g, 10 mmol) was added and the solution was heated while stirring. After filtration the mixture was cooled down to ambient temperature and **22** precipitated as a colorless solid to give 1.8 g (4.8 mmol, 96%) yield. DSC (5 °C min^{-1}): 156 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3288 (w), 2964 (m), 2683 (m), 2133 (w), 1693 (m), 1618 (s), 1575 (s), 1557 (s), 1454 (s), 1427 (m), 1396 (m), 1377 (m), 1297 (m), 1233 (vs), 1180 (m), 1106 (w), 1014 (w), 990 (m), 965 (s), 826 (s), 750 (s), 734 (m), 678 (m) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 1618 (20), 1586 (100), 1557 (20), 1453 (2), 1400 (11), 1298 (6), 1248 (9), 1209 (33), 1180 (5), 1145 (8), 1104 (5), 1016 (6), 993 (19), 830 (7), 769 (7), 736 (3), 711 (3), 691 (3), 591 (2), 502 (8), 453 (8), 407 (3), 670 (3), 242 (6), 154 (31), 102 (47) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 6.36 ppm. $^{13}C\{^{1}H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 158.4, 145.6, 135.1, 132.5, 105.0. MS (FAB^-): 253.1 [$C_4HN_{10}O_4^-$], EA ($C_5H_{12}N_{14}O_7$, 380.24 g mol^{-1}) calc. (found): C 15.79 (16.23), H 3.18 (2.99), N 51.57 (51.47)%. IS: 40 J (<100 μm). FS: 216 N (<100 μm). ESD (<100 μm): 1.5 J.

Di(aminoguanidinium) bis(1-oxidotetrazolyl)furoxane (23). 1.7 g of **11** (5 mmol) was dissolved in 20 mL of 2 M hydrochloric acid and extracted four-times with 20 mL of diethyl ether. The solvent was removed under reduced pressure and the residue was dissolved in a few milliliters of water. Aminoguanidinium bicarbonate (1.4 g, 10 mmol) was added and the solution was heated while stirring. After filtration the mixture was cooled down to ambient temperature and **23** crystallized to give 1.9 g (4.7 mmol, 94%) of colorless blocks. DSC (5 °C min^{-1}): 165 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3424 (w), 3359 (m), 3303 (m), 3241 (m), 3101 (w), 1668 (vs), 1620 (s), 1585 (m), 1560 (s), 1455 (m), 1428 (m), 1400 (m), 1363 (m), 1301 (m), 1238 (s), 1227 (s), 1193 (m), 1168 (m), 1095 (m), 1077 (m), 1056 (m), 1024 (w), 1009 (w), 990 (m), 961 (s), 910 (s), 823 (s), 771 (m), 758 (s), 732 (m), 710 (m) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 3363 (6), 3263 (5), 1622 (31), 1588 (100), 1562 (30), 1456 (9), 1430 (6), 1397 (7), 1365 (5), 1303 (15), 1215 (69), 1170 (10), 1138 (14), 1107 (10), 1025 (6), 1011 (5), 992 (33), 966 (14), 824 (13), 773 (8), 752 (9), 735 (5), 711 (3), 687 (2), 624 (4), 591 (4), 557 (10), 501 (16), 460 (11), 434 (6), 405 (2), 375 (12), 342 (3), 285 (3), 260 (6), 231 (20), 155 (49), 138 (64), 127 (60), 100 (77), 89 (91) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 8.70, 7.26, 6.90, 4.51 ppm. $^{13}C\{^{1}H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 159.4, 147.0, 133.8, 130.9, 106.0 ppm. MS (FAB^+): 75.1 [$CH_7N_4^+$], 403.2 [M + H^+], (FAB^-): 253.1 [$C_4HN_{10}O_4^-$]. EA ($C_6H_{14}N_{18}O_4$, 402.29 g mol^{-1}) calc. (found): C 17.91 (18.17), H 3.51 (3.47), N 62.67 (61.54)%. IS: 8 J (<100 μm). FS: 360 N (<100 μm).

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