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ARTICLE

Energetic Alliance of Tetrazole-1-oxides and 1,2,5-Oxadiazoles

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

The connection of highly endothermic heterocycles with high nitrogen but also 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 (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 tetrazoleoxides[2,3,4]. The purpose of this study was to combine furazanes (1,2,5-oxadiazoles) and furoxanes (1,2,5-oxadiazole-2-oxides) with tetrazoleoxides. The connection of highly endothermic heterocycles with high nitrogen but also oxygen content is a recent trend in the development of new energetic materials in order to obtain powerful materials with great density and proper oxygen balance on the one hand side but also perfect stability on the other hand side. 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 Figure 1.

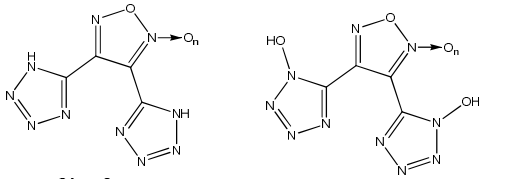

Figure 1: Compounds **9** and **10** and the literature known compounds **24** [5] and **25** [6].

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.

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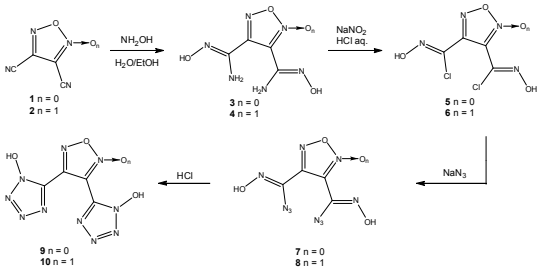
Results and Discussion

Synthesis

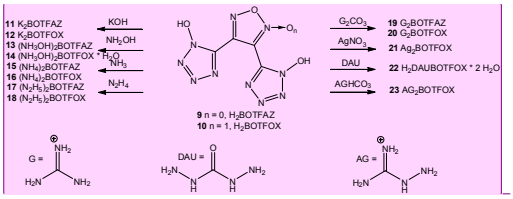
Compounds **9** and **10** were synthesised using a similar protocol from dicyanofurazane[7] and dicyanofuroxane[8] as depicted in Scheme 1.



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

The hydroximoylamines **3** and **4** are made from the nitriles by exothermic addition of aqueous hydroxylamine in ethanol in about 85% yield. The hydroximoylchlorides **5** and **6** were synthesized from **3** and **4** by diazotization in 15% HCl and subsequently extracted into diethyl ether. Reaction of **5** and **6** with sodium azide in aqueous ethanol affords hydroximoylazides **7** and **8,** which are also extracted into diethyl ether. The dried ether phase was saturated with gaseous HCl at 0°C and stirred for 24h 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 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.



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

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 supplementary information. The cif files were deposited at the Cambridge Crystallographic Data Centre (CCDC).

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 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 100K) of **3** is significantly smaller than that of the corresponding furazane **7** (1.780 g cm^{-3} at 173K). **4** crystallizes in the monoclinic space group $P2_1/n$. The molecular moieties are depicted in Figure 2.

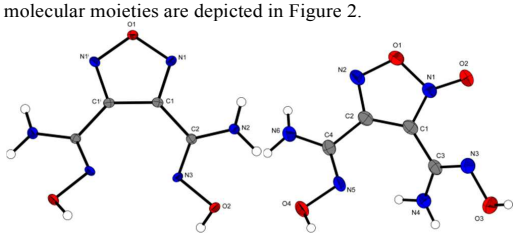


Figure 2. Molecular moieties of **3** and **4** Thermal ellipsoids are drawn at the 50% probability level. **3**: Symmetry code: 1−x, y, 1.5−z. Selected bond lengths (Å): O2–N3 1.4194(18), N3–C2 1.291(2), N2–C2 1.351(2); **4**: Selected bond lengths (Å): O2–N1 1.224(2), N4–C3 1.354(3), N4–C3 1.354(3),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

The hydroximoylchlorides **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. Molecular units are shown in Figure 3. The density of the furazane (1.909 g cm^{-3} at 100K) again is slightly lower than that of the furoxane (1.949 g cm^{-3} at 100K).

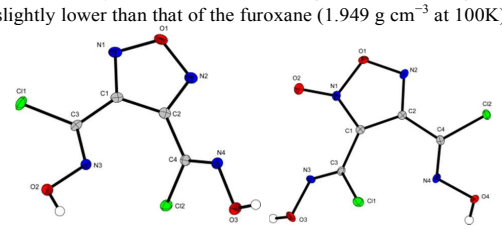


Figure 3. Molecular moiety of **5** and **6**. Thermal ellipsoids are drawn at the 50% probability level.

Crystal structures of both potassium salts were obtained. The structure of the 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 100K). For the furoxane **12** (triclinic, $P\bar{1}$) a density of 2.156 g cm^{-3} at 100K 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 Figures 2 and 3.

Comment [U1]: Hx was replaced by NH3OH

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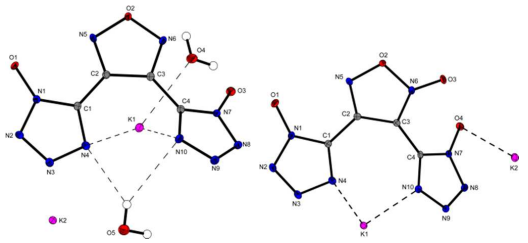

Figure 4. Molecular moiety of **11** and **12**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths of **11**/**12** (Å): O1 N1 1.297(2), N1 N2 1.340(2), N1 C1 1.360(2), N2 N3 1.321(2), N3 N4 1.344(2) O2 N5 1.3822(19), O2 N6 1.430(2), O3 N6 1.2343(19)

14·H_2O could only be obtained crystalline with inclusion of one crystal water molecule (Figure 5). It crystallizes in the monoclinic space group $P2_1$ with a density of 1.794 g cm^{-3} at 173 K.

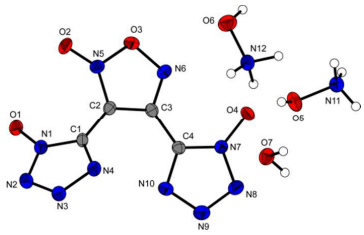

Figure 5. Molecular moiety of **14**·H_2O. Thermal ellipsoids are drawn at the 50% probability level.

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

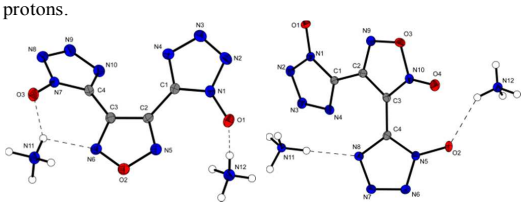

Figure 6. Molecular moiety of ammonium salts **15** and **16**. Thermal ellipsoids are drawn at the 50% probability level. **15**: Selected bond lengths (Å): C1–C2 1.455(3), C2–C3 1.432(3), C3–C4 1.457(3), O1–N1 1.327(2), O3–N7 1.327(2); **16**: Selected bond lengths (Å): C1–C2 1.450(3), C3–C2 1.423(3),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

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

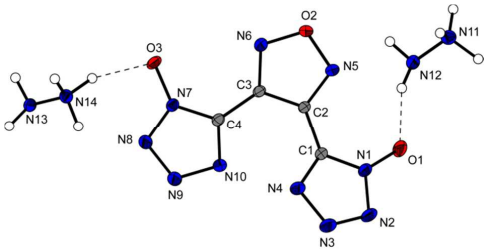

Figure 7. Molecular moiety of hydrazinium salt **17**. Thermal ellipsoids are drawn at the 50% probability level.

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

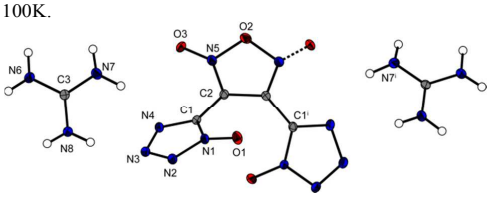

Figure 8. Molecular moiety of guanidinium salt **20**. Thermal ellipsoids are drawn at the 50% probability level. Symmetry code: (i) 1–x, y, 0.5–z.

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 Figure 14.

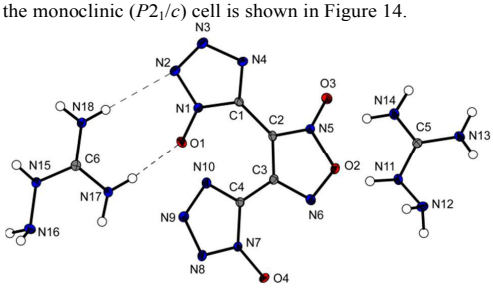

Figure 9. Molecular moiety of aminoguanidinium salt **23**. Thermal ellipsoids are drawn at the 50% probability level.

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 around 7 ppm although **10** has no C_{2V} Symmetry any more. 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 a 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 the furazane and 136.6 ppm caused by the 1-hydroxytetrazole. **10** shows four resonances in the ^{13}C NMR because of the lower symmetry at 136.8 and 134.4 ppm for the tetrazoleoxides and at 143.4 and 103.4 ppm for the

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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 field up to 149.4 and 107.7 ppm for the furoxane but to a shift towards higher field down to 133.2 and 130.3 ppm for the tetrazole-oxide resonances. A ^{15}N NMR spectrum of **9** is depicted in figure 10. The chemical shifts are assigned to the particular Nitrogen atoms.

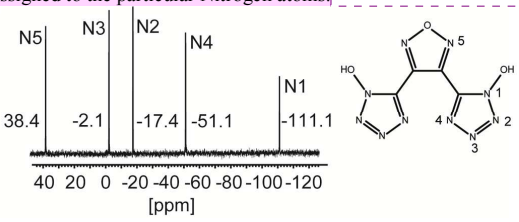

Figure 10. ^{15}N{^{1}H} NMR spectrum of **9**.

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.

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

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 Figure 11. The highest thermal stabilities of the bis(1-oxidotetrazolyl)furaz(ox)anes are reached by the potassium salts with 277°C (**11**) and 265°C (**12**), respectively.

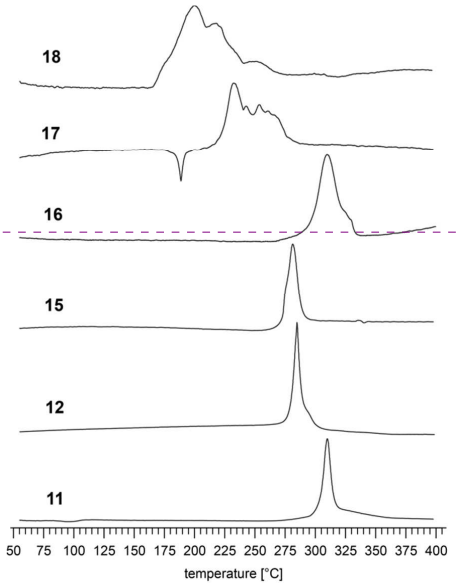

Figure 11. DSC plots of compounds **11**, **12**, **15**, **16**, **17** and **18** at 5 °C min^{-1}.

Comment [U2]: This sentence was added

Heats of formation, Sensitivities and Detonation parameters

Gas phase heats of formation ($\Delta_f H°_{(g,M,298)}$) were calculated theoretically using the atomization equation 1 and CBS-4M electronic enthalpies. Details for the computations and the conversion of gas phase values into solid state values are given in the supplementary information.

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

Sensitivities were measured using a BAM drophammer, BAM friction tester[12] and a OZM electrostatic discharge device[13] (see also experimental part, general methods).

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

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

Only the physicochemical properties of compounds **4**, **5**, **15**–**16**, **20** and **23** are discussed since they (i) 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** ($\Delta_f H°_{(s)}$ = 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

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energy of formation value ($\Delta_f U°$ 3245.4 kJ kg^{-1}) was calculated for **17**. The most important detonation parameters (heat of detonation, detonation temperature, pressure, velocity of detonation, volume of detonation gases) were calculated with the EXPLO5.05 code and are summarized in Tables 2 and 3. Based on these computations, compound **17** (8843 m s^{-1}) has a higher velocitiy of detonation than RDX (8763 m s^{-1}) However, with respect to 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 a 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_{CO2} / % [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(100K) 1.64(298K)	1.781(173K) 1.75 (298K)	1.686(293K)	1.748(293K)	1.727(236K) 1.71(298K)	1.739(100K) 1.69(298K)	1.692 (100K) 1.64(298K)	1.858 (90 K)[17] 1.806 (298K)[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 (Ω = (xO–2yC–1/2zH)M/1600); f start of decomposition temperature from DSC (β = 5 °C); g from X-ray diffraction, values for 298 K were calculated with $\rho_{298K} = \rho_T/(1+\alpha_v(298\text{-}T)$, [15] $\alpha_v = 1.5 \cdot 10^{-4}$ 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 proper 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 tetrazoleoxide anions attached to a furoxane or furazane ring is sufficient to reach decomposition temperatures above 200°C.

Experimental Part

For general methods, please see SI.

Syntheses

Bisaminohydroximoylfurazane (**3**): 10.8 g (90 mmol) **1** were dissolved in 45 mL ethanol and added within 15 min to 22.2 g (336 mmol) 50% hydroxylamine solution, which was diluted with 90 mL ethanol. The solvent was removed under reduced pressure until crystallization started. 9.3 g (50 mmol, 55%) of **3** were obtained by filtering 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 dicyanofuroxane (10 mmol) were dissolved in 30 mL of ethanol and 1.3 g 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 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.

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(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) **3** was dissolved in 200 mL semi-conc. hydrochloric acid. A solution of 6.3 g (92 mmol) sodium nitrite in 30 mL 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 water and was extracted with 4 × 35 mL 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 were 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 slightly yellow oily liquid which partially started to crystallize to give a total 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) **5** were dissolved in 50 mL ethanol and 6.53 g (100 mmol) sodium azide in 50 mL water were added at 0-5°C. The suspension was stirred for 1 h on ice, diluted with 100 mL water and brought to p*H* 2 using 2M hydrochloric acid. The product was extracted with 5 × 30 mL 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 p*H* 1 by addition of concentrated hydrochloric acid and extracted with 3 × 30 mL and 1 × 10 mL 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 etheral 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 0–5C 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.

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Dipotassium bis(1-oxidotetrazolyl)furazane (**11**): An aqueous solution of **9** was brought to p*H* 8 with 2M potassium hydroxide solution. The solution was left for crystallization and the dihydrate of **11** was obtained as 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}. **$^{13}C\{^1H\}$ 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 (<100µm), **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) **11** was dissolved in 20 mL 2M hydrochloric acid. The solution was extracted with 5 × 30 mL diethyl ether and the solvent were removed under reduced pressure. The residue was dissolved in 20 mL ethanol. 2.2 eq. 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%) **13** were 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 **12** (5 mmol) was dissolved in 20 mL of 2M 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 a 50% solution in H_2O, 0.61 mL, 10 mmol) was added while stirring. The solution was left for crystallisation. **14** crystallized to give 1.7 g (4.9 mmol, 98%). **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) **11** were dissolved in 20 mL 2M hydrochloric acid. The solution was extracted with 5 × 30 mL diethyl ether and the solvent was removed under reduced pressure. The residue was dissolved in 20 mL water. 2.2 eq. ammonium hydroxide were 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%) **11** were 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),

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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). **^{1}H NMR** (270 MHz, dmso-d_6, 25°C), δ: 7.18 ppm. **^{13}C{^{1}H} 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 2M hydrochloric acid and extracted 4 × with 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 2M 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%). 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). **^{1}H NMR** (270 MHz, dmso-d_6, 25°C), δ: 7.22 ppm. **^{13}C{^{1}H} 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) **11** were dissolved in 20 mL 2M hydrochloric acid. The solution was extracted with 5 × 30 mL diethyl ether and the solvent was removed under reduced pressure. The residue was dissolved in 20 mL ethanol and 2.2 eq. hydrazine hydrate were 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%) **17** were 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{^{1}H} 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 2M 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 to give 1.5 g (4.8 mmol, 96%). **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{^{1}H} 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) **11** were dissolved in 20 mL 2M hydrochloric acid. The solution was extracted with 5 × 30 mL diethyl ether and the solvent was concentrated under reduced pressure. The residue was dissolved in 5 mL water. 1.1 eq. of a solution of guanidinium carbonate in water were 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 **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{^{1}H} 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 2M hydrochloric acid

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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{^{1}H} 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 **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{^{1}H} 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 2M 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%). **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 2M 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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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: X-ray diffraction, Computations, General experimental methods. See DOI: 10.1039/b000000x/

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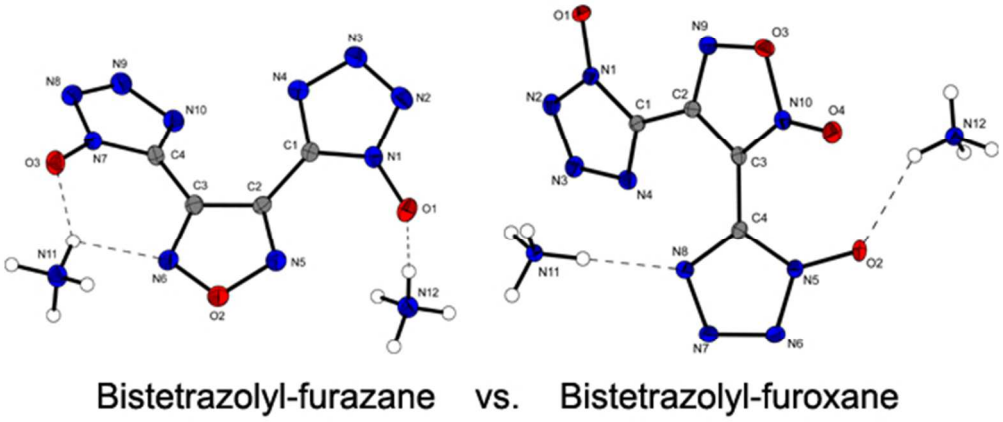

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