

The reaction of a variety of amino-furazans with chlorosulfonyl isocyanate was carried out to synthesize ureido-furazans. The nitration to nitro-ureido-furazan was successful in the case of 3-nitro-4-nitroureido-furazan and 3,4-dinitroureido-furazan. Furthermore, furazan derivatives linked to a second amino-oxadiazole were synthesized. All compounds were intensively characterized by X-ray diffraction measurements, NMR spectroscopy, vibrational spectroscopy (IR, Raman), BAM sensitivity tests and differential thermal analysis. The energetic properties were calculated using EXPLO5 6.03.

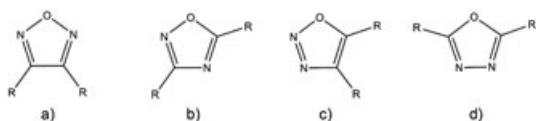
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## INTRODUCTION

Research towards new high-energy dense materials (HEDM) is still required for future applications in industrial, military, and civil sectors [1,2]. Particularly, toxicity and safety problems that need to be solved to meet current regulations, for example, REACH [3]. These new energetic materials must also be equal or better in performance compared with their traditional predecessors. Many nitrogen and oxygen containing heterocyclic compounds have been shown to exhibit good energetic properties because of high densities and high positive heat of formations [4]. Particularly, triazoles and oxadiazoles have been intensively investigated thus far [5–10]. They differ only by the replacement of a nitrogen atom with an oxygen atom. Different regioisomeric oxadiazole derivatives are depicted in Scheme 1. The great interest in these oxadiazoles can also be seen in the amount of patents in the last decade [11]. The main use of oxadiazoles in the industrial sector is for medical devices, pesticides, or polymers [12]. Oxadiazole

derivatives are also used as alternatives for carbonyl containing compounds, such as carbamates, amides, esters, and hydroxamic esters [13,14].

In the past decades, the furazan group has thoroughly been investigated, and it was proven that the furazan ring and its energetic properties are perfect building blocks for energetic materials [15–18]. Amino furazans are not only known for their high heat of formation but also their thermal and chemical stability. Selected furazans such as potassium 4,5-bis(dinitromethyl)furoxanate have been described as green replacements for lead-based primary explosives, which require a high sensitivity toward impact, friction and electrostatic discharge [16]. In terms of synthesizing oxygen-rich compounds (solid state oxidizers), furazans are useful backbones because of their ring oxygen atom. Oxidizers are compounds with a positive oxygen balance. The oxygen balance is defined as oxygen excess during combustion. This excess is used to oxidize the propellant's fuel. Oxidizers usually burn without residues, because all carbon atoms are converted into carbon monoxide or dioxide, hydrogen atoms into

**Scheme 1.** Structures of oxadiazole derivatives: (a) 1,2,5-oxadiazole (furazan), (b) 1,2,4-oxadiazole, (c) 1,2,3-oxadiazole, and (d) 1,3,4-oxadiazole.

water, and nitrogen into dinitrogen [19]. Through the introduction of nitro groups, the oxygen balance can be further tuned to positive values. In order to synthesize energetic compounds with outstanding performance, *N*-NO<sub>2</sub> groups play an important role. This functional group improves the oxygen and nitrogen balance and also yields to an improvement of the high heat of formation and density [20,21]. Nitro ureido compounds are known to have good explosive performances and high densities [22]. In order to combine the benefits of oxadiazoles and nitro ureido, new energetic compounds were synthesized and described herein. According to our literature research, only carbon chains, phenyl, and nitrated phenyl nitro ureidos were synthesized so far [23–25]. Ureido-furazanes have not been synthesized so far. To the best of our knowledge, in this paper, the first ureido 1,2,5-oxadiazolyl derivatives are described.

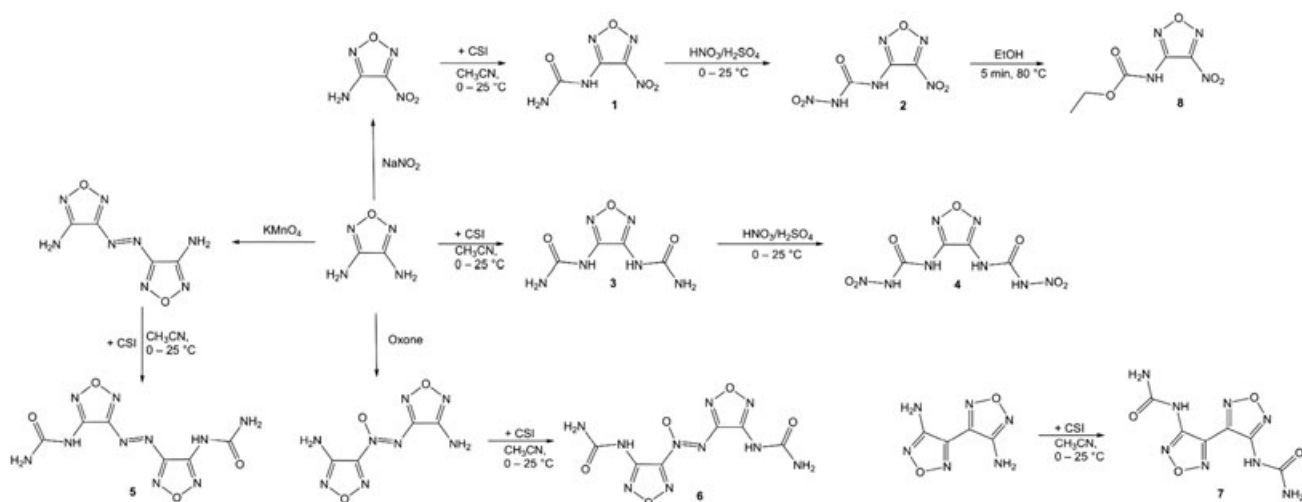
## RESULTS AND DISCUSSION

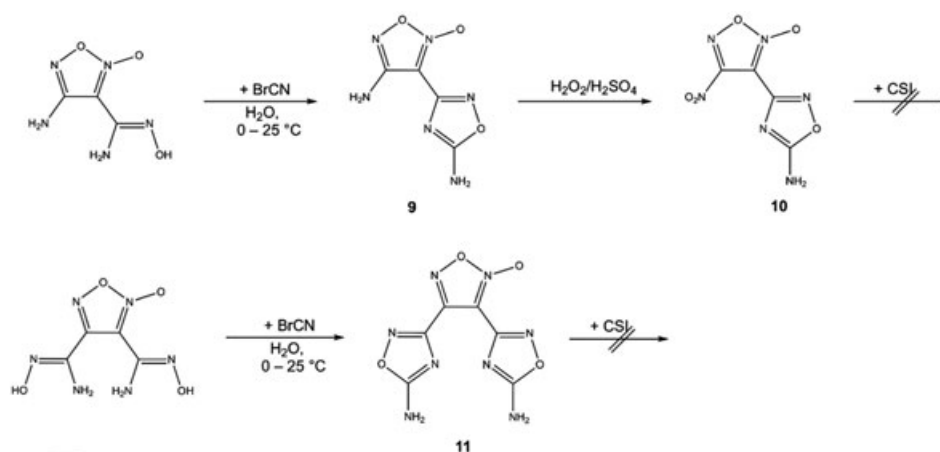
**Synthesis and characterization.** The synthesis of the starting materials, 3,4-diaminofurazan, 3-amino-4-nitrofurazan, 3,3'-diamino-4,4'-azofurazan, 3,3'-diamino-4,4'-azoxyfurazan, and C–C coupled 3,3'-dinitro-4,4'-bifurazan, was performed according literature [26–31]. The starting materials were reacted with chlorosulfonyl isocyanate (CSI) under anhydrous conditions. The reaction of amines with CSI leads to ureido moieties

(Scheme 2), which further could be nitrated to a nitro ureido derivative. The CSI reaction conditions and mechanisms have been investigated in our research group to synthesize carbamates from alcohols [32,33].

Similar to literature known reactions using CSI, the yields of ureido derivatives reported in this investigation were about 90%. In order to synthesize more energetic compounds, attempts were carried out to nitrate the ureido moieties. In this investigation, different acids (fuming HNO<sub>3</sub>, mixed acid, and Ac<sub>2</sub>O/HNO<sub>3</sub>) and nonacidic conditions such as N<sub>2</sub>O<sub>5</sub> were employed. The nitration was successful for 3-nitro-4-nitroureido-furazan (**2**) and 3,4-dinitroureido-furazan (**4**). In the case of 3,3'-diureido-4,4'-azoxyfurazan (**5**), 3,3'-diureido-4,4'-azofurazan (**6**), and 3,3'-diureido-4,4'-bifurazan (**7**), the nitration in acidic and nonacidic conditions led to the amines, under loss of the CO–NH<sub>2</sub> moiety. The corresponding nitramine compounds have already been characterized by our research group [15]. Upon heating of **2** in ethanol for the purpose of recrystallization, a replacement of the nitramino moiety to 3-nitro-4-ethoxycarbamoyl furazan (**8**) occurred.

Furthermore, two different attempts to synthesize more complex ureido derivatives with two different oxadiazols were investigated (Scheme 3). The reaction of 4-amino-3-amino(hydroxyimino)methyl-furoxan [34] with cyanogen bromide in aqueous conditions led to 4-amino-3-(5-amino-1,2,4-oxadiazolyl) furoxan (**9**). In order to increase the energetic properties, further oxidation in peroxymonosulfuric acid (Caro's acid) yielded 4-nitro-3-(5-amino-1,2,4-oxadiazolyl) furoxan (**10**). Similar to the synthesis of **9**, 3,4-bis-amino(hydroxyimino)methyl furoxane [35] was reacted with cyanogen bromide to 3,4-bis-(5-amino-1,2,4-oxadiazolyl) furoxan (**11**). Further reactions of **9**, **10**, and **11** with CSI were unsuccessful. This result leads to the assumption that the reactivity of

**Scheme 2.** Synthesis of ureido (**1**, **3**, **5**, **6**, and **7**) and nitro ureido furazans (**2** and **4**).

**Scheme 3.** Synthesis of amino-1,2,4-oxadiazol furazan derivatives.

the amino group of the 1,2,4-oxadiazoles is not high enough for the reaction with CSI. Another important reason for their low reactivity is the very low solubility of the 1,2,4-oxadiazole derivatives in common organic solvents.

**Spectroscopy.** The vibrational analysis of **2** and **4** showed the characteristic antisymmetric  $\nu_{as}(\text{NO}_2)$  and the symmetric  $\nu_s(\text{NO}_2)$  stretching vibrations in the range of  $1620\text{--}1506\text{ cm}^{-1}$  and  $1385\text{--}1251\text{ cm}^{-1}$ , respectively. The C–N, C–O, and C–C vibrations of **1–11** are observed in the typical ranges for heterocycles and CHNO based aliphatic compounds.

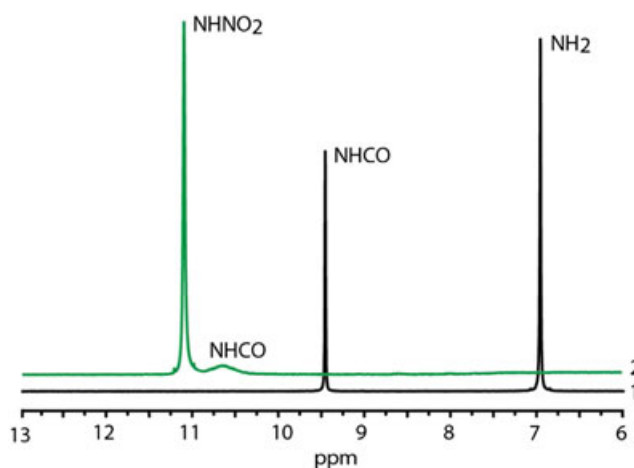
Comparing the  $^1\text{H}$  NMR spectra, a trend for the ureido hydrogen atoms can be observed. All  $\text{NH}_2$  resonances of the ureido moieties are found in the range between 7 and 5 ppm as broadened signals, because of the keto–enol tautomerism and restricted rotation [36,37]. Due to the higher acidity of the  $\text{NHNO}_2$  hydrogen atom, the resonances of the nitro ureidos are shifted downfield below 10 ppm. This is shown in Figure 1, where the  $^1\text{H}$

resonances of **1** and **2** are displayed. The carbonyl resonance, in the range of  $140\text{--}150\text{ ppm}$  of the ureido and nitro ureido moiety, is the most significant resonance in the  $^{13}\text{C}$  NMR spectra. The nitro groups of the nitro ureidos (**2** and **4**) are observed at around  $-40\text{ ppm}$  and additionally the nitro moiety of **2** at  $-33\text{ ppm}$  in the  $^{14}\text{N}$  NMR spectrum.

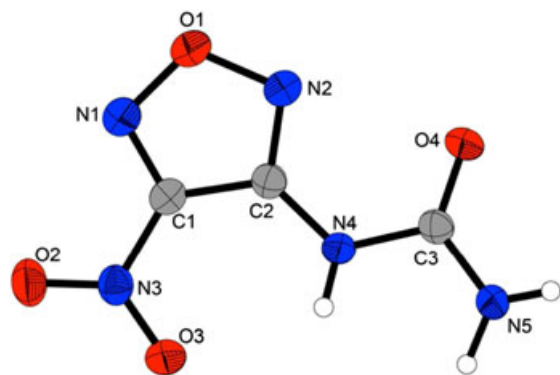
**Crystal structures.** The structures of **1**, **4**, **8**, and **10** in the solid state were determined by low temperature X-ray diffraction.

The highest density at 173 K was measured for compound **4** in the triclinic space group  $P\bar{1}$  ( $1.91\text{ g cm}^{-3}$ , Fig. 3) compared with **10** in the monoclinic space group  $P2_1/c$  ( $1.87\text{ g cm}^{-3}$  Fig. 5), and the orthorhombic space groups, **1**  $P2_12_12_1$  ( $1.72\text{ g cm}^{-3}$ , Fig. 2) and **8**  $Pbca$  ( $1.61\text{ g cm}^{-3}$ , Fig. 4).

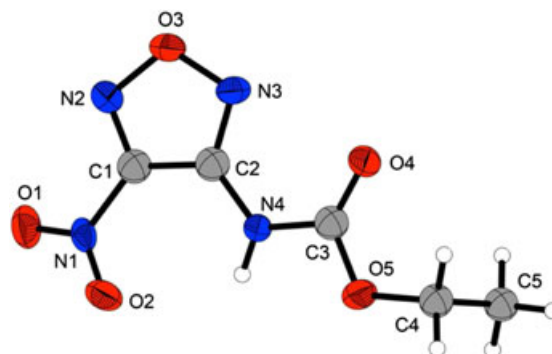
The bond lengths and angles are in the range of literature reported  $N,O$ -heterocyclic compounds [15,38]. Selected bond lengths and angles are given in Figures 2–5. Details on the measurements and refinements are listed in Table 1.



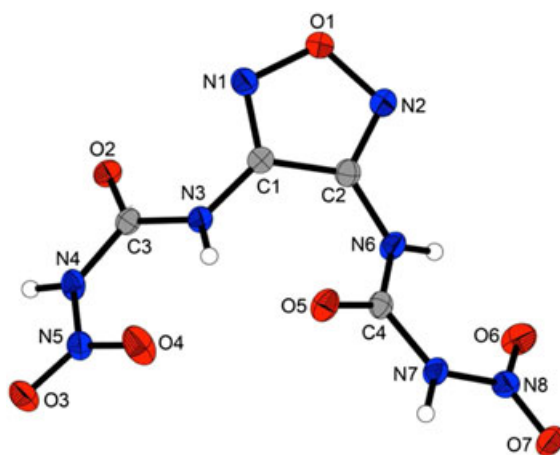
**Figure 1.**  $^1\text{H}$  NMR spectra of 3-nitro-4-ureido-furazan (**1**) and 3-nitro-4-nitroureido-furazan (**2**) in  $\text{DMSO-}D_6$ . [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



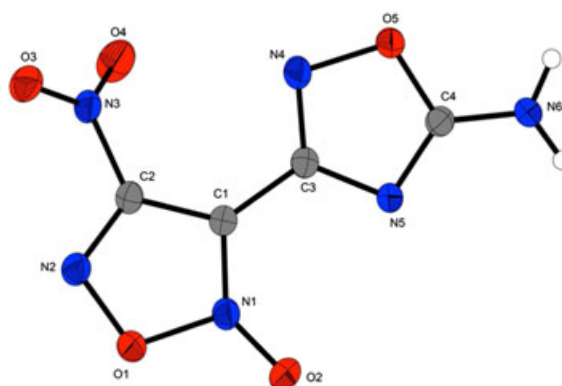
**Figure 2.** Molecular structure of 3-nitro-4-ureido-furazan (**1**). Selected bond lengths (Å) and angles (deg.): C3–N1 1.45(2), C2–N4 1.363(2), C3–N3 1.328(2), C2–C1–N3 129.04(14), C1–C2–N4 126.93(14), N4–C3–N5 113.80(14), N1–C1–C2–N4 179.67(14), N2–C2–C1–N3 0.49(18). [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



**Figure 4.** Molecular structure of 3-nitro-4-ethoxycarbonyl furazan (**8**). Selected bond lengths (Å) and angles (deg.): C1–N2 1.460(4), C2–N4 1.362(4), O5–C4 1.454(4), C2–C1–N1 107.6(3), C1–C2–N4 126.1(3), C3–O5–C4 117.1(3), N1–C2–C1–N3 176.9(3), N2–C1–C2–N4 178.7(3), O4–C3–O5–C4 2.8(5). [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



**Figure 3.** Molecular structure of 3,4-dinitroureido-furazan (**4**). Selected bond lengths (Å) and angles (deg.): C1–N3 1.388(2), C2–N6 1.391(2), C3–N4 1.395(2), C4–N7 1.390(2), N4–N5 1.369(2), N7–N8 1.370(2), C2–C1–N3 127.47(17), C1–C2–N6 129.81(17), N2–C2–C1–N3 177.44(17), N1–C1–C2–N6 176.56(18), N6–C4–N7–N8 4.4(3), N3–C3–N4–N5 3.1(3). [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



**Figure 5.** Molecular structure of 4-nitro-3-(5-amino-1,2,4-oxadiazolyl) furoxan (**10**). Selected bond lengths (Å) and angles (deg.): C2–N3 1.451(2), N1–O2 1.217(2), N4–O5 1.430(2), C4–N6 1.312(2), N2–C2–N3 117.8(1), C2–C1–C3 132.0(1), O5–C4–N6 118.1(1), O1–N2–C2–N3 173.9(1), C2–C1–C3–N5 170.9(2). [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

**Energetic properties.** The calculated physicochemical and energetic properties of **1–4** are listed in Tables 2 and 3. In terms of energetic properties, the most interesting compounds are **2** and **4**, due to their functional nitro ureido groups and positive oxygen balance. The sensitivities were measured with respect to BAM standards. The sensitivities of compounds **5–11** were determined but not listed in Table 3, because of their expected complete insensitivity. Compounds **1–4** are not sensitive towards friction (360 N). Furthermore, compounds **1** and **3** show no sensitivity towards impact or electrical discharge. Compared with this, **2** and **4** show higher sensitivities towards impact (4 and 7 J) and moderate sensitivity towards electrical discharge

(0.75 and 1.5 J), respectively. The positive oxygen balances of **2** (+14.7) and **4** (+5.8) causes a residue-free burning. Additionally, the positive oxygen balance has a direct influence on the specific impulse. The specific impulse of **2** was calculated to be 260 s for the water-free compound. In mixtures with aluminum and binder, the optimized specific impulse is 244 s. In comparison, **4** has a specific impulse of 239 s for the neat compound and 230 s for the optimized formulation. These values are slightly lower than that (264 s) for the widely used oxidizer ammonium perchlorate in mixtures.

The nitration of the ureido functional group leads to an improvement of about 70 kJ mol<sup>−1</sup> (63 kJ mol<sup>−1</sup> **1**, 136 kJ mol<sup>−1</sup> **2**) according to the calculated enthalpies. The same trend is observed for compound **4**, where the

**Table 1**  
X-ray parameters of **1**, **4**, **8**, and **10**.

	<b>1</b>	<b>4</b>	<b>8</b>	<b>10</b>
Empirical formula	C <sub>3</sub> H <sub>3</sub> N <sub>5</sub> O <sub>4</sub>	C <sub>4</sub> H <sub>4</sub> N <sub>8</sub> O <sub>7</sub>	C <sub>5</sub> H <sub>6</sub> N <sub>4</sub> O <sub>5</sub>	C <sub>4</sub> H <sub>2</sub> N <sub>6</sub> O <sub>5</sub>
Formula mass (g mol <sup>-1</sup> )	173.09	276.13	202.13	214.12
Temperature (K)	173	173	173	173
Crystal size (mm <sup>3</sup> )	0.40 × 0.18 × 0.18	0.49 × 0.28 × 0.20	0.40 × 0.30 × 0.01	0.40 × 0.35 × 0.30
Crystal description	Colorless block	Colorless block	Colorless block	Colorless block
Crystal system	Orthorhombic	Triclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> - 1	<i>Pbca</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	5.4926(5)	7.8096(7)	10.9296(15)	6.0943(4)
<i>b</i> (Å)	8.6852(7)	8.0528(6)	8.1385(10)	8.2913(6)
<i>c</i> (Å)	14.0098(13)	8.1807(8)	18.7783(18)	15.1764(12)
<i>α</i> (°)	90	110.746(8)	90	90
<i>β</i> (°)	90	92.503 (8)	90	97.097(7)
<i>γ</i> (°)	90	93.290(7)	90	90
<i>V</i> (°)	668.33(10)	479.20(8)	1670.30(3)	760.98(10)
<i>Z</i>	4	2	8	4
$\rho_{calc}$ (g cm <sup>-3</sup> )	1.72	1.91	1.71	1.87
$\mu$ (mm <sup>-1</sup> )	0.158	0.181	0.145	0.172
<i>F</i> (000)	352	280	832	432
$\theta$ range (°)	4.39–27.86	4.437–25.996	4.72–21.32	4.255–26.495
Index range	–7 ≤ <i>h</i> ≤ 7 –8 ≤ <i>k</i> ≤ 11 –18 ≤ <i>l</i> ≤ 17	–9 ≤ <i>h</i> ≤ 9 –9 ≤ <i>k</i> ≤ 9 –9 ≤ <i>l</i> ≤ 10	–13 ≤ <i>h</i> ≤ 13 –10 ≤ <i>k</i> ≤ 10 –23 ≤ <i>l</i> ≤ 12	–6 ≤ <i>h</i> ≤ 7 –10 ≤ <i>k</i> ≤ 8 –19 ≤ <i>l</i> ≤ 18
Reflection collected	5706	3434	11251	6020
Reflection observed	1597	1871	1697	1569
Reflection unique	1415	1536	850	1241
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (2σ data)	0.0328/0.0811	0.0385/0.0890	0.0655/0.0903	0.0322/0.0757
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0392/0.0859	0.0495/0.0968	0.1547/0.1132	0.0456/0.0842
Parameters	121	172	133	144
GOOF an F <sup>2</sup>	1.058	1.055	0.998	1.057
Larg. diff. Peak/hole (e Å <sup>-3</sup> )	–0.181/0.150	–0.252/0.251	–0.241/0.255	–0.204/0.244
CCDC entry	1533343	1533341	1533342	1566030

**Table 2**  
Physicochemical properties of compounds **1–11**.

	1	2	3	4	5	6	7	8	9	10	11
Formula	C <sub>3</sub> H <sub>3</sub> N <sub>3</sub> O <sub>4</sub>	C <sub>3</sub> H <sub>2</sub> N <sub>6</sub> O <sub>6</sub>	C <sub>4</sub> H <sub>6</sub> N <sub>6</sub> O <sub>3</sub>	C <sub>4</sub> H <sub>4</sub> N <sub>8</sub> O <sub>7</sub>	C <sub>6</sub> H <sub>6</sub> N <sub>10</sub> O <sub>4</sub>	C <sub>6</sub> H <sub>6</sub> N <sub>10</sub> O <sub>5</sub>	C <sub>6</sub> H <sub>6</sub> N <sub>8</sub> O <sub>4</sub>	C <sub>5</sub> H <sub>6</sub> N <sub>4</sub> O <sub>5</sub>	C <sub>4</sub> H <sub>4</sub> N <sub>6</sub> O <sub>3</sub>	C <sub>4</sub> H <sub>2</sub> N <sub>6</sub> O <sub>5</sub>	C <sub>4</sub> H <sub>4</sub> N <sub>8</sub> O <sub>4</sub>
FW (g mol <sup>-1</sup> )	173.09	218.09	186.13	276.13	282.13	298.18	254.17	202.13	184.12	214.10	252.15
<i>T</i> <sub>dec</sub> onset <sup>a)</sup>	182	122	239	140	250	260	240	153	188	198	273
<i>N</i> (%) <sup>b)</sup>	40.5	38.5	45.2	40.6	49.6	46.9	44.1	27.7	45.7	39.3	44.4
<i>O</i> (%) <sup>c)</sup>	36.9	44.0	25.8	40.6	22.7	26.8	25.2	39.6	26.1	37.4	25.4
<i>N</i> + <i>O</i> (%) <sup>d)</sup>	77.4	82.5	71.0	81.2	72.3	73.7	69.3	67.3	71.8	76.7	69.8
<i>Q</i> <sub>CO</sub> (%) <sup>e)</sup>	-4.6	+14.7	-25.8	+5.8	-28.3	-21.5	-31.5	-23.7	-26.0	0	-12.7
<i>IS</i> (J) <sup>f)</sup>	40	4	40	7	*	*	*	*	*	*	*
<i>FS</i> (N) <sup>g)</sup>	360	360	360	360	*	*	*	*	*	*	*
<i>ESD</i> (J) <sup>h)</sup>	1.5	0.75	1.5	1.5	*	*	*	*	*	*	*

<sup>a)</sup>Decomposition temperature from DSC measurements carried out at a heating rate of 5°C min<sup>-1</sup>.

<sup>b)</sup>Nitrogen content.

<sup>c)</sup>Oxygen content.

<sup>d)</sup>Combined oxygen and nitrogen content.

<sup>e)</sup>Oxygen balance *Q* assuming the formation of CO at the combustion.

<sup>f)</sup>Impact sensitivity.

<sup>g)</sup>Friction sensitivity.

<sup>h)</sup>Sensitivity toward electrostatic discharge.

\*Insensitive.



Table 3

Calculated (EXPLO5 6.03) detonation, combustion parameters, and sensitivity data of **1–4**.

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>RDX</b>	<b>PETN</b>
density (g cm <sup>-3</sup> ) <sup>a</sup>	1.68	1.85 <sup>k</sup>	1.95 <sup>k</sup>	1.87	1.80 [38,39]	1.75
$\Delta_f H^0$ (kJ mol <sup>-1</sup> ) <sup>b</sup>	63	136	-162	-22	86	480
$\Delta_f U^0$ (kJ kg <sup>-1</sup> ) <sup>c</sup>	41	420	-1196	-227	489	1423
$\Delta_{ex} U^0$ (kJ kg <sup>-1</sup> ) <sup>d</sup>	-4323	-5692	-2037	-4626	-5743	-5995
$P_{CJ}$ (kbar) <sup>e</sup>	236	348	245	322	380	316
$V_{Det}$ (m s <sup>-1</sup> ) <sup>f</sup>	7759	8930	8283	8685	8983	8525
$T_{ex}$ (K) <sup>g</sup>	3317	4189	1767	3405	4232	3959
$I_s$ (s) <sup>h</sup>	225	260	161	239	258	257
$I_s$ (s) (15% Al, binder) <sup>i</sup>	225	241	201	229	249	257
$I_s$ (s) (Al, binder) <sup>j</sup>	225	244	203	230	249	251

<sup>a</sup>Densities at room temperature.<sup>b</sup>Enthalpy calculated by the atomization method and CBS-4 M electronic enthalpies from Gaussian 09 [40,41].<sup>c</sup>Energy of formation.<sup>d</sup>Heat of detonation.<sup>e</sup>Detonation pressure.<sup>f</sup>Detonation velocity [42].<sup>g</sup>Detonation temperature.<sup>h</sup>Specific impulse (EXPLO5 6.03: 70 bar chamber pressure, 10 bar expansion conditions equilibrium expansion).<sup>i</sup>Specific impulse (15% Al, 6% polybutadiene acrylic acid, 6% polybutadiene acrylonitrile and 2% bisphenyl A ether, EXPLO5 6.03: 70 bar chamber pressure, 1 bar expansion conditions equilibrium expansion).<sup>j</sup>Optimized specific impulse [Al (%): **1**: 15, **2**: 11, **3**: 17, **4**: 13; 6% polybutadiene acrylic acid, 6% polybutadiene acrylonitrile, and 2% bisphenyl A ether).<sup>k</sup>Density measured by pycnometry.

increase in enthalpy is twice ( $2 \times 70$  kJ mol<sup>-1</sup>) (-162 kJ mol<sup>-1</sup> **3**, -22 kJ mol<sup>-1</sup> **4**).

Compounds **2** and **4** also show interesting calculated detonation values. The values of **2** and **4** are comparable with RDX. Comparing the energetic properties of **2** and **4** with RDX and PETN, the heat of detonation [-5692 (**2**), -4626 (**4**) and -5743 (RDX), -5995 kJ kg<sup>-1</sup> (PETN)], detonation pressure [348 (**2**), 322 (**4**), and 380 (RDX), 316 kbar (PETN)], detonation velocity [8930, 8685, and 8983 (RDX), 8525 m s<sup>-1</sup> (PETN)] and detonation temperature [4189 (**2**), 3405 (**4**), and 4232 (RDX), 3959 K (PETN)] are in a similar range or slightly better. Responsible for the good detonation values is the nitro ureido moiety and the energetic furazan backbone. This also is supported by the high nitrogen and oxygen content, such as for RDX. This is also displayed by comparing the detonation values of **1** and **3**, which are significantly lower.

The mentioned properties of **1–4**, make them not only green explosives, in a sense of being free of heavy metals, but also useful precursors for potential energetic polymers, for example, if they would be reacted with dihalide compounds such as phosgene.

## CONCLUSION

In this article, various heterocyclic ureido derivatives were synthesized in order to meet current requirements for safer and more powerful energetic materials. The synthetic

routes to the heterocyclic compounds **1–11** are relatively easy. IR and NMR spectroscopy are valuable methods for identification. Two ureido moieties were converted successfully (**2**, **4**) to the corresponding nitro ureido derivatives. Comparison of the enthalpy calculations showed, that nitration of an ureido functional group leads to an improvement of the enthalpy (~70 kJ mol<sup>-1</sup> per ureido group) but also leads to a decrease in thermal stability. Except for **2** and **4**, all compounds are low sensitive toward impact and friction and have moderate thermal stabilities. As expected, the ureidos show higher thermal stabilities than the corresponding nitro ureido derivatives. Compound **2** is very sensitive toward impact. The physicochemical and explosive properties of **1–4** make them potential energetic materials and furthermore potential precursors for energetic polymers.

## EXPERIMENTAL SECTION

**General methods.** The low-temperature single-crystal X-ray diffraction measurements were performed on an Oxford XCalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector operating with MoK $\alpha$  radiation ( $\lambda = 0.7107$  Å). Data collection was performed using the CRYSLIS CCD software [43]. The data reduction was carried out using the CRYSLIS RED software [44]. The solution of the structure was performed by direct methods (SIR97) [45] and refined by full-matrix least-squares on F2

(SHELXL) [46] implemented in the WINGX software package [47] and finally checked with the PLATON software [48]. All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were located in a difference Fourier map. DIAMOND plots are shown with thermal ellipsoids at the 50% probability level. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. All chemicals were used as supplied. Raman spectra were recorded in a glass tube with a Bruker MultiRAM FT-Raman spectrometer (Bruker, Germany) with Nd:YAG laser excitation up to 1000 mW (at 1064 nm). Infrared spectra were measured with a PerkinElmer Spectrum BX-FTIR spectrometer (PerkinElmer, Germany) equipped with a Smiths Dura/SamplIR II ATR device (Smiths, UK). All spectra were recorded at ambient (25°C) temperature. NMR spectra were recorded with a JEOL/Bruker instrument (JEOL, Japan) and chemical shifts were determined with respect to external  $\text{Me}_4\text{Si}$  ( $^1\text{H}$ , 399.8 MHz,  $^{13}\text{C}$ , 100.5 MHz) and  $\text{MeNO}_2$  ( $^{14}\text{N}$ , 28.9 MHz). Analyses of C/H/N were performed with an Elemental Vario EL Analyzer (Elementar, Germany). Melting and decomposition points were measured using differential scanning calorimetry (DSC) at a heating rate of  $5^\circ\text{C min}^{-1}$  with an OZM Research differential thermal analysis 552-Ex instrument. The sensitivity data were explored using a BAM drop hammer and a BAM friction tester (Reichert & Partner, Germany) [49]. The energetic properties were calculated using the computer code EXPLO6.03. It is based on the chemical equilibrium, a steady state model of detonation. It uses Becker–Kistiakowsky–Wilson's equation of state (BKW EOS) for gaseous detonation products and Cowan–Fickett's equation of state for solid carbon. The input is based on the sum formula, calculated heats of formation, and the maximum densities according to their crystal structures (Table 1). All calculations were carried out using the Gaussian G09 W (revision A.02) program package. The heats of formations were calculated by the atomization method based on CBS-4M electronic enthalpies [50]. All calculations affecting the detonation parameters were carried out using the program package EXPLO5 6.03 [42,51].

#### General synthesis of ureido derivatives (1, 3, 5, 6, and 7).

The 0.50 g of the corresponding amino furazan was poured to 20 mL dry acetonitrile in a round bottom flask and placed in an ice bath. CSI (1.10 molar equivalent for **1**, 2.10 molar equivalent for **3**, **5**, **6**, and **7**) was added slowly at  $0^\circ\text{C}$ . The mixture was stirred at ambient temperature for 30 min and then cooled again to  $0^\circ\text{C}$ . Fifteen milliliter of water was added very slowly at this temperature. After warming the mixture to room temperature, it was stirred for 1 h, while a precipitate was generated. The organic solvent was removed under vacuum. The precipitate formed was filtered off and washed with ice water.

**3-Nitro-4-ureido-furazan (1).** After drying in vacuum 0.58 g (88%), 1-nitro-4-ureido-furazan was obtained as a pale green powder. DSC ( $5^\circ\text{C min}^{-1}$ ):  $179^\circ\text{C}$  (m.p.),  $182^\circ\text{C}$  (dec.); IR (ATR,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3319$  (w), 3124 (w), 1593 (s), 1558 (m), 1484 (w), 1439 (m), 1291 (s), 1262 (s), 1134 (m), 1092 (s), 1040 (s), 975 (m), 846 (m), 816 (m), 783 (m), 754 (m), 720 (m); Raman (1064 nm, 500 mW,  $25^\circ\text{C}$ ,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3302$  (2), 1693 (6), 1614 (3), 1583 (4), 1554 (7), 1469 (49), 1411 (6), 1365 (29), 1321 (7), 1122 (3), 1052 (2), 976 (6), 836 (20), 793 (3), 765 (3), 656 (5), 465 (2), 402 (5), 332 (6), 218 (6), 146 (16), 85 (100);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta = 9.46$  (NH), 6.9 (br,  $\text{NH}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta = 154.8$  ( $\text{CNO}_2$ ), 153.1 (CNH), 146.6 (CO); EA ( $\text{C}_3\text{H}_3\text{N}_5\text{O}_4$ ,  $173.09 \text{ g mol}^{-1}$ ) Calc.: C 20.82; H 1.75; N 40.46%; Found: C 20.97; H 1.84; N 40.36%; Sensitivity ( $100 \mu\text{m} \geq \text{g.s.} \geq 50 \mu\text{m}$ ) IS: 40 J; FS: 360 N; ESD: 1.5 J.

**3-Nitro-4-nitroureido-furazan (2).** A mixture of fuming nitric and sulfuric acid (each 2 mL) was cooled to  $0^\circ\text{C}$ . **1** (0.25 g; 1.44 mmol) was added slowly to this mixture. The reaction was stirred at  $0^\circ\text{C}$  for 30 min, then allowed to warm up to room temperature and stirred additionally for 1 hr. Afterwards the mixture was poured on 30 g of ice and extracted three times with 50 mL ethyl acetate. The organic phases were washed twice with water and one time with brine. Subsequently, the organic phases were dried with magnesium sulfate and the solvent removed on the rotary evaporator to obtain a pale yellow powder. After recrystallization from acetonitrile, 0.28 g (90%) of colorless pure **2** was obtained. DSC ( $5^\circ\text{C min}^{-1}$ ):  $122^\circ\text{C}$  (dec.); IR (ATR,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3469$  (w), 3446 (m), 3336 (m), 1710 (w), 1633 (s), 1520 (s), 1498 (m), 1435 (m), 1368 (s), 1347 (m), 1209 (m), 1107 (w), 1040 (m), 870 (w), 763 (w), 726 (w); Raman (1064 nm, 500 mW,  $25^\circ\text{C}$ ,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 2247$  (3), 1748 (16), 1722 (10), 1629 (9), 1611 (10), 1567 (10), 1532 (16), 1467 (73), 1415 (13), 1366 (76), 1051 (6), 973 (25), 894 (6), 843 (20), 765 (8), 597 (3), 567 (4), 458 (4), 372 (9), 328 (12), 239 (14), 96 (102);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta = 11.08$  ( $\text{NHNO}_2$ ), 10.67 (br,  $\text{NHCO}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta = 154.2$  ( $\text{CNO}_2$ ), 145.0 (CNH), 144.8 (CO);  $^{14}\text{N}$  NMR ( $\text{CDCl}_3$ )  $\delta = -33$  ( $\text{CNO}_2$ ),  $-42$  ( $\text{NHNO}_2$ ); EA ( $218.09 \text{ g mol}^{-1}$ ) Calc.: C 16.52, H 0.92, N 38.54%; Found: C 16.73, H 1.04, N 38.31%; Sensitivity ( $100 \mu\text{m} \geq \text{g.s.} \geq 50 \mu\text{m}$ ) IS: 4 J; FS: 360 N; ESD: 0.75 J.

**3,4-Diureido-furazan (3).** Drying in vacuum yielded 0.87 g (94%) of **3** as a powder. DSC ( $5^\circ\text{C min}^{-1}$ ):  $239^\circ\text{C}$  (dec.); IR (ATR,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3418$  (m), 3334 (m), 3129 (m), 1716 (s), 1694 (s), 1632 (w), 1576 (m), 1553 (s), 1477 (m), 1397 (m), 1360 (m), 1251 (m), 1131 (m), 1056 (m), 992 (w), 923 (w), 887 (w), 856 (m), 778 (m), 717 (m), 660 (w); Raman (1064 nm, 500 mW,  $25^\circ\text{C}$ ,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3231$  (4), 1699 (3), 1570 (3), 1342 (16), 1305 (4), 1279 (3), 1136 (4), 1057 (5), 1016 (100), 889 (4), 857



(3), 681 (9), 556 (7), 537 (13), 362 (16), 179 (10), 123 (17).  $^1\text{H}$  NMR (DMSO- $\text{D}_6$ )  $\delta$  = 9.38 (NH), 6.8 (br,  $\text{NH}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (DMSO- $\text{D}_6$ )  $\delta$  = 154.8 (CNH), 146.6 (CO); EA ( $\text{C}_4\text{H}_6\text{N}_6\text{O}_3$ , 186.13 g mol $^{-1}$ ) Calc.: C 25.81, H 3.25, N 45.15%; Found: C 25.72, H 3.32, N 44.74%; IS: 40 J; FS: 360 N; ESD: 1.5 J.

**3,4-Dinitroureido-furazan (4).** Into a mixture of 2 mL of fuming nitric acid and 2 mL of sulfuric acid, **3** (0.25 g; 1.30 mmol) was added slowly at 0°C. The mixture was stirred at this temperature for 30 min and an additional hour at room temperature. Then, the reaction was poured on 20 g of ice and extracted three times with 30 mL of ethyl acetate. The combined organic layers were washed twice with water and once with brine. After drying the organic phases with magnesium sulfate, the solvent was removed in vacuum to yield a colorless powder. After recrystallization from acetonitrile, 0.32 g (90%) of colorless pure **4** was obtained. DSC (5°C min $^{-1}$ ): 140°C (dec.); IR (ATR, cm $^{-1}$ ):  $\tilde{\nu}$  = 3308(w), 2358 (w), 1746 (s), 1601 (s), 1432 (s), 1377 (m), 1311 (m), 1280 (m), 1234 (s), 1156 (m), 1085 (m), 982 (m), 932 (w), 871 (w), 839 (w), 771 (m), 744 (m), 704 (m); Raman (1064 nm, 500 mW, 25°C, cm $^{-1}$ ):  $\tilde{\nu}$  = 1739 (41), 1702 (37), 1618 (36), 1565 (84), 1523 (28), 1410 (50), 1339 (90), 1065 (6), 1036 (12), 986 (100), 938 (11), 884 (54), 850 (18), 771 (20), 724 (9), 600 (12), 502 (23), 470 (22), 456 (18), 418 (17), 381 (9), 308 (22), 229 (18), 204 (23);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 13.5 (br,  $\text{NHNO}_2$ ), 10.93 (2H, CNH);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 147.2 (CNH); 146.4 (CO),  $^{14}\text{N}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = -42 ( $\text{NHNO}_2$ ); EA ( $\text{C}_4\text{H}_4\text{N}_8\text{O}_7$ , 276.13 g mol $^{-1}$ ) Calc.: C 17.40, H 1.46, N 40.58%, Found: C 17.98, H 1.81, N 40.48%; Sensitivity (100  $\mu\text{m}$   $\geq$  g.s.  $\geq$  50  $\mu\text{m}$ ) IS: 7 J; FS: 360 N; ESD: 0.7 J.

**3,3'-Diureido-4,4'-azoxyfurazan (5).** Compound **5** (0.63 g) was obtained as yellow powder (88%). DSC (5°C min $^{-1}$ ): 250°C (dec.); IR (ATR):  $\tilde{\nu}$  = 3367 (w), 3314 (w), 3208 (w), 2357 (w), 1737 (w), 1700 (s), 1637 (m), 1594 (w), 1533 (s), 1477 (w), 1695 (s), 1347 (m), 1260 (m), 1133 (w), 1051 (m), 993 (w), 942 (w), 886 (w), 819 (m), 776 (w), 749 (w), 701 (w), 660 (w); Raman (1064 nm, 500 mW, 25°C, cm $^{-1}$ ):  $\tilde{\nu}$  = 2859 (16), 2083 (4), 2028 (3), 1485 (5), 1450 (100), 1427 (13), 1355 (18), 1296 (5), 1259 (7), 999 (4), 948 (3), 929 (7), 806 (4), 538 (3), 466 (2);  $^1\text{H}$  NMR (DMSO- $\text{D}_6$ )  $\delta$  = 9.43 (s, NH), 6.9 (br,  $\text{NH}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (DMSO- $\text{D}_6$ )  $\delta$  = 156.8 (CNN), 153.0 (CNH), 146.4 (CO); EA ( $\text{C}_6\text{H}_6\text{N}_{10}\text{O}_4$ , 282.06 g mol $^{-1}$ ) Calc.: C 24.75, H 2.42, N 48.10%; found: C 24.94, H 2.25, N 47.37%.

**3,3'-Diureido-4,4'-azofurazan (6).** Compound **6** (0.37 g) was obtained as orange powder (89%). DSC (5°C min $^{-1}$ ): 260°C (dec.); IR (ATR):  $\tilde{\nu}$  = 3432 (m), 3291 (m), 3220 (w), 1717 (m), 1690 (vs), 1614 (m), 1538 (s), 1468 (m), 1392 (s), 1342 (m), 1302 (w), 1251 (w), 1169 (w), 1112 (w), 1049 (w), 975 (w), 820 (m), 771 (w), 712 (m); Raman

(1064 nm, 500 mW, 25°C, cm $^{-1}$ ):  $\tilde{\nu}$  = 2859 (26), 2084 (6), 2028 (3), 1692 (5), 1616 (5), 1497 (100), 1448 (75), 1397 (28), 1354 (42), 1308 (9), 1108 (6), 1053 (6), 980 (7), 949 (5), 912 (9), 875 (13), 808 (7), 642 (4), 538 (4), 432 (4), 404 (4);  $^1\text{H}$  NMR (DMSO- $\text{D}_6$ )  $\delta$  = 9.80 (s, NH), 9.60 (s, NH), 6.9 (br,  $\text{NH}_2$ ), 6.8 (br,  $\text{NH}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (DMSO- $\text{D}_6$ )  $\delta$  = 154.2 (N(NO)C), 153.2 (ONNC), 152.9 (CNH), 149.2 (CNH), 148.4 (CO), 146.6 (CO); EA ( $\text{C}_6\text{H}_6\text{N}_{10}\text{O}_5$ , 298.05 g mol $^{-1}$ ) Calc.: C 22.79, H 2.55, N 44.30%; found: C 23.10, H 2.45, N 43.75%.

**3,3'-Diureido-4,4'-bifurazan (7).** Compound **7** (1.39 g) was obtained as colorless powder (91%). DSC (5°C min $^{-1}$ ): 240°C (dec.); IR (ATR):  $\tilde{\nu}$  = 3502 (w), 3283 (m), 3183 (w), 2360 (w), 1694 (s), 1599 (m), 1519 (s), 1455 (w), 1377 (m), 1289 (m), 1103 (m), 1038 (m), 990 (s), 921 (m), 871 (m), 795 (m), 716 (m); Raman (1064 nm, 500 mW, 25°C, cm $^{-1}$ ):  $\tilde{\nu}$  = 3286 (10), 2858 (11), 2553 (6), 2407 (6), 1700 (28), 1632 (100), 1601 (31), 1548 (52), 1525 (74), 1427 (75), 1365 (8), 1251 (9), 1117 (40), 1051 (8), 1038 (8), 969 (13), 883 (17), 815 (55), 660 (24), 585 (6), 544 (10), 530 (9), 463 (21), 443 (5), 367 (20), 286 (17), 221 (11);  $^1\text{H}$  NMR (DMSO- $\text{D}_6$ )  $\delta$  = 9.63 (s, NH), 6.5 (br,  $\text{NH}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (DMSO- $\text{D}_6$ )  $\delta$  = 154.3 (CNN), 151.9 (CNH), 140.3 (CO); EA ( $\text{C}_6\text{H}_6\text{N}_8\text{O}_4$ , 254.17 g mol $^{-1}$ ) Calc.: C 28.35, H 2.38, N 44.09%; found: C 28.05, H 2.70, N 43.37%.

**3-Nitro-4-ethoxycarbamoyl furazan (8).** Compound **2** (0.50 g, 2.30 mmol) was dissolved in 10 mL ethanol. The mixture was heated 5 min to reflux and cooled to room temperature. The solvent was evaporated slowly yielding **8** (0.43 g) as colorless crystals (91%). DSC (5°C min $^{-1}$ ): 126°C (melt), 153°C (dec.); IR (ATR):  $\tilde{\nu}$  = 3280 (w), 2984 (w), 1757 (m), 1728 (s), 1616 (m), 1565 (m), 1536 (s), 1466 (m), 1408 (m), 1371 (m), 1338 (s), 1303 (m), 1227 (s), 1197 (s), 1092 (m), 1058 (s), 1040 (m), 993 (m), 942 (m), 854 (m), 831 (s), 773 (m), 724 (w). Raman (1064 nm, 500 mW, 25°C, cm $^{-1}$ ):  $\tilde{\nu}$  = 3748 (6), 3008 (7), 2981 (23), 2964 (10), 2841 (23), 1753 (6), 1729 (14), 1580 (7), 1548 (7), 1538 (11), 1472 (100), 1409 (22), 1391 (17), 1372 (18), 1341 (36), 1306 (7), 1099 (10), 1067 (7), 1042 (12), 1010 (7), 995 (14), 947 (9), 899 (7), 854 (17), 832 (17), 763 (10), 594 (8), 558 (8), 465 (15), 450 (12), 440 (14), 425 (14), 414 (13), 309 (20), 287 (16), 177 (23), 84 (63).  $^1\text{H}$  NMR (DMSO- $\text{D}_6$ )  $\delta$  = 9.73 (NH), 4.28 (q, 7.1 Hz,  $\text{CH}_2$ ), 1.31 (t, 7.1 Hz,  $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (DMSO- $\text{D}_6$ )  $\delta$  = 154.8 (CNO $_2$ ), 151.9 (CNH), 145.7 (CO), 62.9 ( $\text{CH}_2$ ), 13.6 ( $\text{CH}_3$ );  $^{14}\text{N}$  NMR (DMSO- $\text{D}_6$ )  $\delta$  = -26 (CNO $_2$ ); EA ( $\text{C}_5\text{H}_6\text{N}_4\text{O}_5$ , 202.13 g mol $^{-1}$ ) Calc.: C 29.71, H 2.99, N 27.72%, found: C 29.41, H 3.75, N 28.08%.

**4-Amino-3-(5-amino-1,2,4-oxadiazolyl) furoxan (9).** Potassium bicarbonate (2.07 g, 20.72 mmol) was dissolved in 40 mL water and 4-amino-3-aminooxim furoxan (1.00 g, 6.28 mmol) was added. The reaction

mixture was heated until a clear solution is obtained. After cooling to room temperature cyanogen bromide (0.73 g, 6.91 mmol) was added in portions. The reaction mixture was stirred overnight and then acidified with 2 M hydrochloric acid. The precipitate was filtered off and washed extensively with water and diethyl ether. A 0.62 g (54%) of **9** was obtained as yellowish brown powder. DSC (5°C min<sup>-1</sup>): 198°C (dec.). IR (ATR):  $\tilde{\nu}$  = 3436 (w), 3334 (w), 3168 (w), 1689 (m), 1635 (m), 1574 (w), 1537 (s), 1494 (m), 1422 (w), 1350 (w), 1236 (w), 1161 (m), 1078 (w), 1034 (m), 948 (m), 913 (w), 857 (m), 760 (m), 687 (m), 666 (m). Raman (1064 nm, 500 mV, 25°C)  $\tilde{\nu}$  = 1757 (6), 1609 (82), 1571 (46), 1558 (4), 1455 (12), 1254 (5), 1219 (16), 1069 (8), 1053 (3), 955 (36), 827 (6), 751 (16), 669 (6), 556 (4), 504 (5), 449 (19), 406 (4), 375 (26), 308 (3), 264 (10), 242 (2), 205 (16), 124 (3), 96 (100). <sup>1</sup>H NMR (DMSO-D<sub>6</sub>)  $\delta$  = 8.4 (br, NH<sub>2</sub>), 6.5 (br, NH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-D<sub>6</sub>)  $\delta$  = 172.3 (CNO), 157.6 (C<sub>ring</sub>), 156.3 (CN(O)O), 101.7 (CNH<sub>2</sub>). EA (C<sub>4</sub>H<sub>4</sub>N<sub>6</sub>O<sub>3</sub>, 184.12 g mol<sup>-1</sup>): Calc.: C 26.09, H 2.19, N 45.65%; found: C 25.84, H 2.38, N 43.93%.

**4-Nitro-3-(5-amino-1,2,4-oxadiazolyl) furoxan (10).** For the preparation of Caro's acid, 10 mL of conc. sulfuric acid was added slowly to 30% hydrogen peroxide at 0°C. Compound **9** (0.5 g, 1.36 mmol) was dissolved in 5 mL conc. sulfuric acid and slowly added to Caro's acid, while keeping the temperature between 0°C and 10°C. The reaction mixture was heated slowly to 40°C and stirred for 30 min. After cooling to ambient temperature, the mixture was quenched with ice and water. After extracting with ethyl acetate (3 × 30 mL), the combined organic phases were washed with water (2 × 20 mL), brine (1 × 20 mL) and dried over magnesium sulfate. The solvent was removed under reduced pressure and recrystallized from acetone. A 0.20 g (66%) of **10** was obtained as yellow crystals. DSC (5°C min<sup>-1</sup>): 188°C (dec.). IR (ATR):  $\tilde{\nu}$  = 3443 (m), 3363 (m), 3268 (m), 3188 (m), 3143 (m), 2963 (w), 2927 (w), 2855 (w), 1678 (s), 1634 (s), 1572 (s), 1503 (s), 1386 (s), 1342 (s), 1314 (s), 1261 (m), 1229 (s), 1141 (m), 1097 (s), 1070 (s), 1049 (s), 991 (s), 960 (s), 908 (s), 847 (m), 790 (s), 760 (s), 730 (s), 692 (s), 663 (s). Raman (1064 nm, 500 mV, 25°C)  $\tilde{\nu}$  = 1682 (18), 1625 (16), 1556 (24), 1540 (100), 1508 (23), 1492 (59), 1358 (20), 1315 (13), 1231 (31), 1073 (12), 992 (14), 964 (24), 749 (27), 489 (12), 458 (37), 398 (25), 358 (12), 259 (11), 204 (10), 132 (13), 88 (83). <sup>1</sup>H NMR (DMSO-D<sub>6</sub>)  $\delta$  = 8.2 (br, NH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-D<sub>6</sub>)  $\delta$  = 173.4 (CNO), 161.5 (C<sub>ring</sub>), 155.9 (CN(O)O), 102.6 (CNH<sub>2</sub>). <sup>14</sup>N NMR (DMSO-D<sub>6</sub>)  $\delta$  = -35 (NO<sub>2</sub>) ppm. EA (C<sub>4</sub>H<sub>2</sub>N<sub>6</sub>O<sub>5</sub>, 214.10 g mol<sup>-1</sup>): Calc.: C 22.44, H 0.94, N 39.25%, found: C 23.32, H 1.19, N 37.98%.

**3,4-Bis-(5-amino-1,2,4-oxadiazolyl) furoxan (11).** Into an aqueous solution of sodium hydroxide (0.72 g,

17.9 mmol) 3,4-bis-aminooxime furoxan (1.44 g, 7.1 mmol) was added. The reaction mixture was heated under reflux for 10 min forming a clear solution. After cooling to 40°C cyanogen bromide (1.89 g, 17.85 mmol) was added in portions. The reaction mixture was stirred overnight at ambient temperature and subsequently acidified with 2 M hydrochloric acid to pH 2. The precipitate was filtered off and washed extensively with water. A 0.93 g (54%) of **11** was obtained as brownish powder. DSC (5°C min<sup>-1</sup>): 273°C (dec.). IR (ATR):  $\tilde{\nu}$  = 3472 (w), 3340 (w), 3249 (w), 3177 (w), 1662 (s), 1608 (s), 1566 (m), 1529 (m), 1449 (m), 1416 (m), 1359 (w), 1259 (w), 1220 (w), 1112 (m), 1073 (w), 1050 (m), 1008 (w), 976 (w), 946 (m), 910 (w), 824 (s), 761 (m), 724 (m), 683 (m). Raman (1064 nm, 500 mV, 25°C)  $\tilde{\nu}$  = 2859 (20), 1661 (19), 1606 (7), 1569 (77), 1530 (24), 1509 (42), 1455 (8), 1425 (25), 1378 (22), 1220 (58), 1108 (16), 1099 (3), 1010 (8), 977 (59), 911 (11), 827 (13), 757 (42), 546 (6), 498 (12), 464 (11), 421 (18), 362 (28), 314 (3), 304 (4), 283 (9), 272 (3), 244 (2), 214 (21), 126 (100), 95 (8). <sup>1</sup>H NMR (DMSO-D<sub>6</sub>)  $\delta$  = 8.4 (br, NH<sub>2</sub>), 8.3 (br, NH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-D<sub>6</sub>)  $\delta$  = 173.0 (CNH<sub>2</sub>), 159.6 (CNH<sub>2</sub>), 156.9 (C<sub>ring</sub>), 155.9 (C<sub>ring</sub>), 144.7 (CNO), 106.7 (CN(O)O). EA (C<sub>6</sub>H<sub>4</sub>N<sub>8</sub>O<sub>4</sub>, 252.15 g mol<sup>-1</sup>) Calc.: C 28.58, H 1.60, N 44.44%, found: C 27.73, H 2.03, N 42.28%.

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