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ARTICLE

Chemistry of 2,5-Diaminotetrazole

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1,5-Diaminotetrazole is one of the most prominent high-nitrogen tetrazole compounds described in literature. Interestingly the isomer 2,5-diaminotetrazole is nearly undescribed due to its challenging synthetic routes. 2,5-Diaminotetrazole (**1**) was successfully synthesized via amination of 5-aminotetrazole followed by various purification steps to separate it from isomeric 1,5-diaminotetrazole. In addition to the extensive characterization of 2,5-DAT further derivates by protonation, methylation and amination on the tetrazole ring were also synthesized and characterized. The resulting tri-functionalized, ionic tetrazolium derivatives were combined with energetic anions (nitrate, perchlorate, azide, 5,5'-bistetrazole-1,1'-diolate ($BTO2^-$)) to adjust and tune the properties of each compound. All compounds were intensively characterized including IR and multinuclear NMR spectroscopy, thermal analysis through DTA, X-ray diffraction and sensitivity testing. The purity was verified by CHNO elemental analysis and the energetic properties were calculated using the EXPLO5 code and the calculated enthalpy of formation (CBS-4M).

Introduction

Aminotetrazoles have great influence in the chemical repertoire for explosive materials.[1-2] 5-Aminotetrazole (5-AT), probably the most obvious representative, is produced on a large scale by diazotization of aminoguanidine followed by base-induced cyclization. Its commonly used as a gas generating agent in airbags, since it has some major advantages (untoxic, chemical robustness, higher nitrogen content) compared to the long-used sodium azide.[3-4] Furthermore, 5-AT provides a great platform for a variety of functionalized tetrazoles, which find wide application in almost all areas of energetic materials. DBX-1[5-8] (copper-(I)-nitrotriazolone, a green primary explosive), produced through diazotization of 5-aminotetrazole with excess of sodium nitrite and subsequent precipitation of the copper salt and bisguanidinium 5,5'-azobistetrazole[9] (ingredient in halogen-free pyrotechnics) synthesized through oxidative azo-coupling of 5-aminotetrazole are only two examples for energetic materials starting from 5-AT. 1- and 2-Aminotetrazoles and their derivatives are used primarily as powerful primary explosives. For example, the two N-substituted aminotetrazoles form a variety of promising energetic coordination compounds (ECCs)[10], and the potassium salts of the nitriminotetrazoles as heavy metal-free detonants[11].

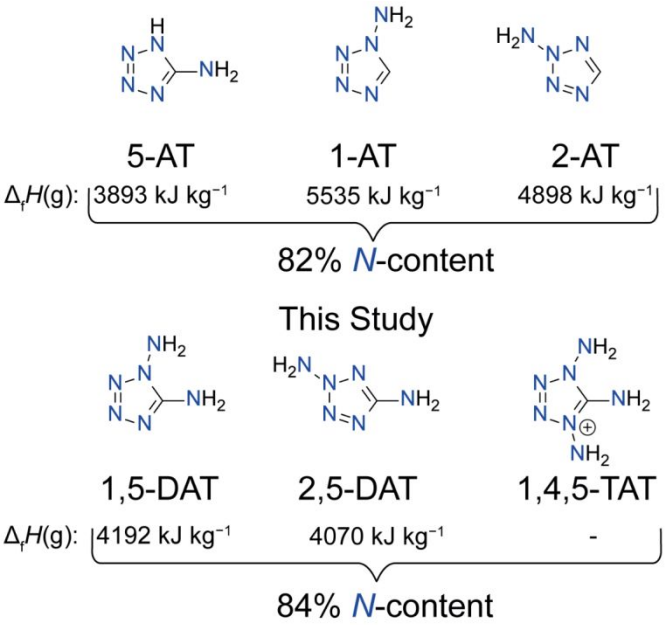

Figure 1. Compounds with exclusively aminotetrazole functionalities, the gas phase heats of formation (calculated on CBS-4M level of theory) and their respective nitrogen content: 5-aminotetrazole, 1-aminotetrazole, 2-aminotetrazole, 1,5-diaminotetrazole, 2,5-diaminotetrazole (**1**) and 1,4,5-triaminotetrazolium.

In addition to the exotic, trisubstituted 1,4,5-triaminotetrazolium cation, which is described as a thermally labile nitrate and nitrotetrazol-2-olate[12], 1,5-diaminotetrazole is the most versatile aminotetrazole representative and is highly recommended in energetic materials chemistry community.[13-16] It is synthetically available through at least four different reaction protocols (e.g. diazotization of diaminoguanidin, amination of 5-AT, oxidation of semicarbazide and reaction of hydrazine with cyanogen azide).[17-20] The further increased nitrogen content and

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associated positive environmentally properties make 1,5-DAT an interesting candidate as a next-generation gas generator.

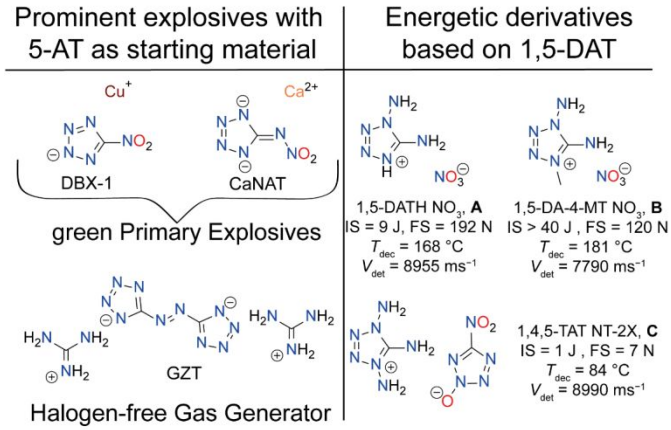
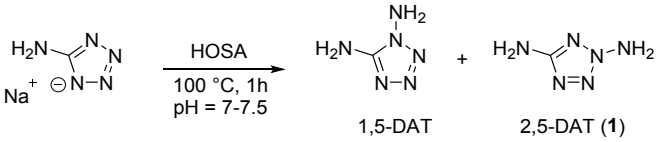


Figure 2. Prominent energetic materials requiring 5-AT as starting materials (left) and energetic derivatives of 1,5-DAT (right).

Due to its two differently reactive amino groups and the basicity of the tetrazole ring, a variety of different derivatives can be synthesized using this molecule.[12, 21-24] Many scientific papers in the past years have dealt with the energetic derivatization of 1,5-DAT, where the parent compound could be extensively functionalized (selected examples are shown in Figure 2).[6, 8-9, 25] Surprisingly, the isomer of 1,5-DAT (2,5-DAT) has not yet been described in detail. The reason for this is the more difficult accessibility of 2-substituted tetrazoles and need to separate the isomers. It can be expected that the chemistry carried out on the 1,5-isomer can be completely transferred to 2,5-DAT.

Results and Discussion

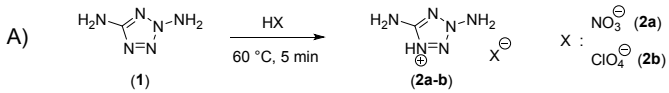
The synthetic route for the synthesis of diaminotetrazoles was already described 1969 by Raap et al..[18] However, the analytical data of 2,5-DAT in this publication do not agree with the values measured within this work. This is mainly due to the fact that the elemental analysis listed in the article gives the same values for both isomers of diaminotetrazole and we therefore suspect that 2,5-diaminotetrazole was not obtained pure. So probably an isomeric mixture of 1,5 and 2,5-diaminotetrazole was characterized.



Scheme 1. Amination of sodium 5-aminotetrazolate to yield the isomers 1,5-DAT and 2,5-DAT (**1**).

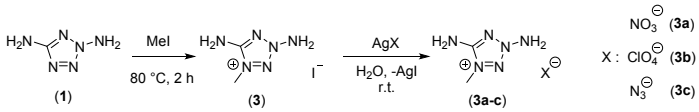
All isomeric mixture of 1,5-DAT and 2,5-DAT is synthesized through the amination of in situ generated sodium 5-aminotetrazolate in a Na_2CO_3 buffered aqueous solution at 100 °C. As amination agent hydroxylamine-O-sulfonic acid (HOSA) is used. The main products of the reaction are 1,5-DAT and 2,5-DAT. The majority of the 1,5-DAT can easily be separated by trituration with water. The purification of the remaining isomeric mixture is a time-consuming process including several recrystallization steps as well as column chromatography for the final purification. The reaction results in a yield of 46% 1,5-DAT and 16% 2,5-DAT giving a total yield of 62%.

2,5-DAT (**1**), like 1,5-DAT, is an electron-rich heterocycle due to the electron-pushing effect of the two amino groups and is therefore suitable for reactions with several electrophiles. Therefore, derivatization reactions including the protonation, methylation and amination were investigated.



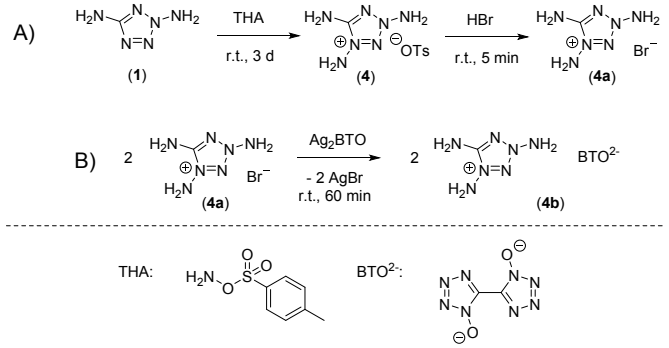
Scheme 2. A) Preparation of energetic 2,5-diaminotetrazolium salts based on the protonation of 2,5-DAT with respective acids.

The synthesis of the energetic salts **2a** and **2b** was performed by dissolving 2,5 diaminotetrazole (**1**) in a minimal amount of the respective acid (65% nitric acid for **2a**; 60% perchloric acid for **2b**) and by heating of the solution until a clear solution was obtained. Ionic derivatives **2a**-**2b** could be obtained in form of colorless crystalline products after slow evaporation of the solvent.



Scheme 3. Methylation of 2,5-DAT (**1**) using methyl iodide in MeCN and metathesis reaction with the respective silver salts.

The methylation of 2,5-DAT was performed using an excess of methyl iodide as methylation agent. The reaction yields only one isomer (2,5-diamino-4-methyltetrazolium) due to the electronic effects of the two amino groups as its iodide salt (**3**). 2,5-Diamino-4-methyltetrazolium iodide (**3**) could be collected by slow evaporation of the solvent. The subsequent metathesis reactions of the iodide with the respective silver salts yielded 2,5-diamino-4-methyltetrazolium as nitrate (**3a**) and perchlorate (**3b**) and azide (**3c**) derivatives, while silver iodide was precipitated and detached.



Scheme 4. A) Amination of 2,5-DAT (**1**), conversion to its bromide salt. B) Metathesis reaction using $AgNO_3$.

Similar to the methylation reaction, amination of 2,5-DAT using THA (O-tosylhydroxylamine) only yields one product (1,3,5-triaminotetrazolium), which precipitated as its tosylate salt **4**. Next to the 1,4,5-triaminotetrazolium derivative and 1,5-diaminotetrazole-4N-oxide, our compounds are only the third scaffold containing triple heterosubstituted tetrazoles.[12, 26] Through the amination at the position next to the C-NH_2 group, the nomenclature changes and therefore a 1,3,5-triaminotetrazolium derivative is obtained. The conversion to the 1,3,5-triaminotetrazolium bromide (**4a**) was necessary to be able to perform metathesis reactions with silver salts and precipitate silver bromide. The reaction with silver nitrate and silver perchlorate yielded the respective pure and clean 1,3,5-triaminotetrazolium nitrate and perchlorate derivative but unfortunately the products were too hygroscopic for further investigations since they liquified immediately upon exposure to air. Therefore, we pushed for another energetic anionic moiety and chose BTO2$^-$ (5,5'-bistetrazole-1,1'-diolate), the anion of TKX-50, since it affords good thermal stability and high heat of formation as well as enough sterically demand so the compound should be easy to mollify and crystallize. As expected the metathesis reaction of **4b** with Ag_2BTO in water yielded compound **4b** in quantitative yields while silver bromide precipitates. Compound **4b** is the BTO derivative with the highest overall nitrogen content.

All compounds presented in this study were intensively studied by low-temperature X-ray diffraction experiments. Herein, we present the crystal structure of 2,5-DAT (**1**) and all energetic derivatives (**2a**, **2b**, **3a**-**3c** and **4b**). The crystal structures of the precursor compounds **3**, **4** and **4a** can be found in the Supporting Information. Deposition Numbers 2172089 (for **1**), 2172088 (for **2a**), 2172090 (for **2b**), 2172091 (for **3**), 2172087 (for **3a**), 2172093 (for **3b**), 2172084 (for **3c**), 2172092 (for **4**), 2172086 (for **4a**) and 2172085 (for **4b**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre .and Fachinformaitonszentrum Karlsruhe Access Structures service. Crystals for the respective compounds were obtained directly by slow evaporation of the respective solvent or by simple recrystallization from popular solvents. All compounds crystallize in common space groups (P–1, $P2_1/c$, $P2_1/n$, $P2_12_12_1$).

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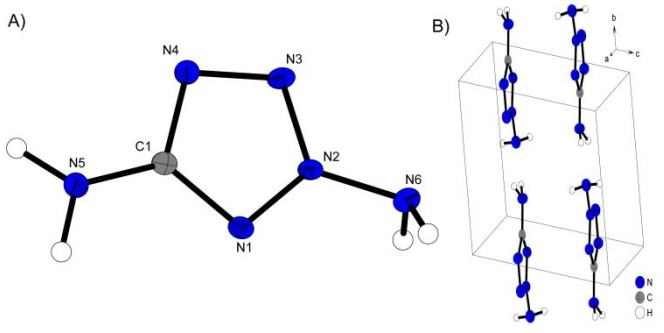

Figure 3. Representation of the molecular unit of 2,5-diaminotetrazole (**1**), showing the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. B) Elemental cell. Selected bond distances [Å] and angles [°]: C1-N5 1.3530(2), N2-N6 1.3877(2), N6-N2-N1 124.81(2), N6-N2-N3 120.31(1), N5-C1-N1 123.93(2).

2,5-Diaminotetrazole (**1**) crystallizes in the triclinic space group P–1 and comes up with a density of 1.577 g cm^{-3} at 298 K. The density is nearly the same as for 1,5-diaminotetrazole (1.571 g cm^{-3})[27]. **1** contains two amino groups, which show varying reactivities due to their different hybridization. Based on the orientation of the protons, it can be seen that the amino group on the carbon (C-NH_2) is sp^2 hybridized, since the free electron pair is donated into the tetrazole ring. The hydrazine amino group at N2 (N-NH_2) is sp^3 hybridized and accordingly still has its free electron pair located on the amine nitrogen atom and is thus the more reactive amino group. Accordingly, the two amino groups also have different bond lengths, with the carbon-bonded amino group having a shorter bond distance (C1-N5 1.353(3) Å) than the nitrogen-bonded one (N2-N6 1.388(3) Å). 2,5-Diaminotetrazole forms a layered structure along the b axis, forming pairs of alternating molecular units that form strong intermolecular interactions between the protons of the C-bonded amino group and N4 (H5B-N4 2.18(2) Å). Additional hydrogen bonds are formed by the protons of the N-amino group and N1 (H6A-N1 2.46(2) Å, H6B-N1 3.14(2) Å).

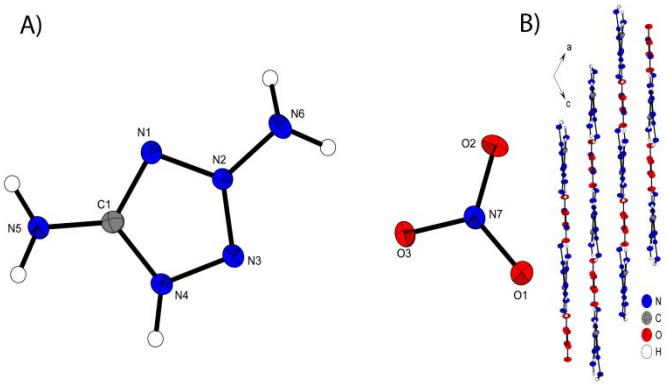

Figure 4. Representation of the molecular unit of 2,5-diaminotetrazolium nitrate (**2a**), showing the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. Selected bond distances [Å] and angles [°]: C1-N5 1.328(3), N2-N6 1.365(3), H4-O2^i 1.83(3), H5A-N1^i 2.26(2), H5B-O3^i 2.14(2), H6A-O2^i 1.98(2), N6-N2-N3 121.63(2), N5-C1-N1 124.93 (2), N4-H4-O 172(2), O3^i-H5B-N5 156(2), N5-H5A-N7 163(2); B) 3D layer pattern of **2a** along the b axis.

2,5-Diaminotetrazolium nitrate (**2a**) crystallizes in the monoclinic space group $P2_1/n$ and has a density of 1.737 g cm^{-3} at 298 K. The density is slightly higher than for the 1,5 diaminotetrazolium nitrate isomer **A** (1.726 g cm^{-3} @ 298K).[24] **2a** forms a layered structure along the b-axis, with both the 2,5-diaminotetrazolium cations and the nitrate anions in the same layer. The distance between the layers is 3.07 Å. A large number of strong interactions are formed both between two molecular cation units and between anions and cations. Similar to neutral compound **1**, the interactions of the aminotetrazole units origins from the carbon-bonded amine. In this case, however, the interaction is established with N1, since the most electron-rich site N4 is of the tetrazole system is blocked through the protonation (N1-H5A 2.24(2) Å). The oxygen

atoms of the nitrate interact strongly with the protons of both amino groups and with the hydrogen on the aromatic ring. This results in an arrangement within the plane in which four tetrazolium cations are arranged around one nitrate anion (O3-H6A 1.98(2) Å, O3-H4 1.76(3) Å, O1-H5B 2.13(2) Å).

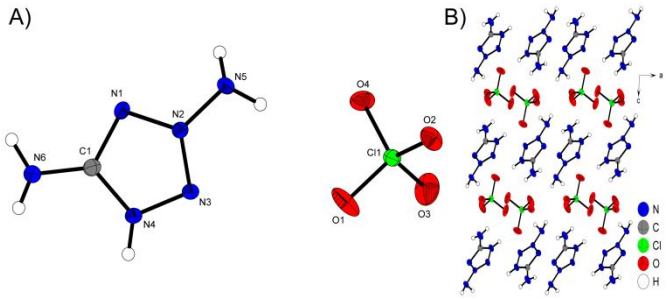

Figure 5. A) Representation of the molecular unit of 2,5-diaminotetrazolium perchlorate (**2b**), showing the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. Selected bond distances [Å] N6-C1 1.316(3), N5-N2 1.372(3), Cl1-O1 1.470(2), N2-N3 1.284(2), H4-O1 2.27(3), H5A-O4 2.25(2), H5B-O4 2.24(2), H6B-O3 2.60(3), H4-N3^{i} 2.52(2), H6A-N1 2.26(3) and angles [°]: N4-H4-O1 134(3), N5-H5A-O4 151(2), N5-H5B-O4 150(2), N6-H6B-O3 160(3), N4-H4-N3 119(2), N6-H6A-N1 163(3); B) 3D layer pattern of **2b** along the b axis.

2,5-Diaminotetrazolium perchlorate (**2b**) crystallizes in the monoclinic space group $P2_1/c$ and shows a density of 1.870 g cm^{-3} at 298 K. Compared with the isomeric 1,5-diaminotetrazolium perchlorate, hardly any difference in density (ρ(1,5-DATH^{+} ClO_4^{-}) = 1.872 g cm^{-3} at 298 K)[24] is observed. Strong interactions are formed between the perchlorate anion and the protons of the amino groups of the cationic unit. These attractive interactions lead to the formation of a layer-like arrangement of anions and cations in the ac plane. In addition, strong interactions are formed between pairs of two cationic units in a plane, favouring the present structure.

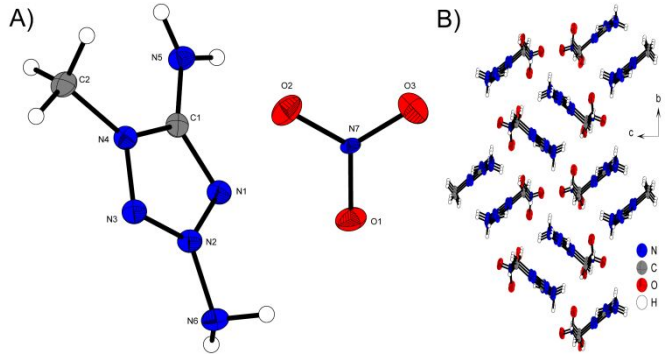

Figure 6. A) Representation of the molecular unit of 2,5-diamino-4-methyltetrazolium nitrate (**3a**), showing the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. Selected bond distances [Å] C1-N5 1.328(2), N2-N6 1.390(2), C2-N4 1.466(3), N7-O2 1.257(2), O1-H6B 2.28(3), O1-H6B^{i} 2.18(3), O2-H6A 2.11(3), O3-H5A 2.23(3), O3-H5B 2.16(3) and angles [°]: N1-N2-N6 124.5(2), C1-N4-C2 129.1(2), O1-H6B-O1 143(2), O1-H6B^{i}-N6^{i} 140(2), O2-H6A-N6 157(2), O3-H5A-N5 164(2), O3-H5B-N5 159(3); B) 3D layer pattern of **3a** along the a axis.

2,5-Diamino-4-methyltetrazolium nitrate (**3a**) crystallizes in the monoclinic space group P21/c and shows a density of 1.649 g cm^{-3} at 298 K. The density drops about 0.08 g cm^{-3} in comparison to **2a**. Compared with its isomer 1,5-diamino-4-methyltetrazolium nitrate **B** (ρ(1,5-DA-4-MT NO_3) = 1.487 g cm$_{-3}$ at 298 K)[24] the density of **3a** is clearly higher. The big difference in density between the two isomers is quite unusual. Various intermolecular interactions are formed between the protons of the amino group and the nitrate anion. The methyl group does not take place in these interactions.

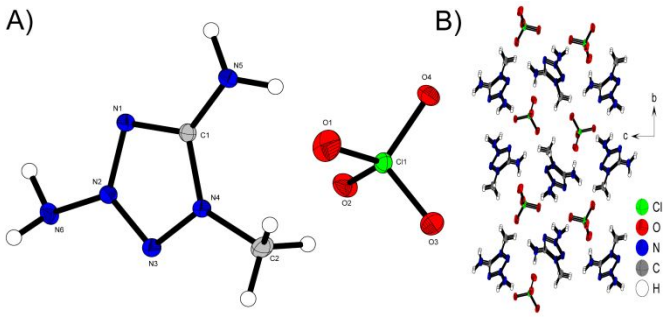

Figure 7. A) Representation of the molecular unit of 2,5-diamino-4-methyltetrazolium perchlorate (**3b**), showing the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. Selected bond distances [Å] and angles [°]: C1-N5 1.337(2), N2-N6 1.379(2), C2-N4 1.454(2), C1-N4-C2 129.2(2), H5A-O3 2.15(2), H5B-O2 2.26(3), H6A-O4 2.16(2) H6B-O2 2.25(2), N5-H5A-O3 163.9(2), N5-H5B-O2 165(2), N6-H6B-O4 168(2), N6-H6B-O2 149(2); B) 3D layer pattern of **3b** along the a axis.

2,5-Diamino-4-methyltetrazolium perchlorate (**3b**) crystallizes in the monoclinic space group $P2_1/n$ and has a room temperature density of 1.770 g cm^{-3}. The methylation results in a decrease of the density by 0.1 g cm^{-3} compared to 2,5-diaminotetrazolium perchlorate (**2b**). This is mainly due to the fact that the 2,5-diaminotetrazolium units also interact with the proton on the tetrazolium ring and are therefore more densely packed. The methyl group in **3b** does not form hydrogen bonds. Only three oxygen atoms are involved in the formation of hydrogen bonds with the cationic moiety. No intermolecular interactions can be observed for O1. Each of the four amino hydrogen atoms form strong interactions with one perchlorate anion (O2-H6B 2.25(2) Å, O4-H6A 2.16(2) Å, O3-H5A 2.15(2) Å, O2-H5B 2.26(3) Å). This results in an environment for each cation structure consisting of four perchlorate anions interacting with the NH_2 protons and one additional anionic unit located with O1 above the centre of the tetrazolium ring (plane of C1-N2-N3) with a distance of 3.023(2) Å. Due to the low polarization of the protons of the methyl group, they do not participate in the formation of intermolecular interactions.

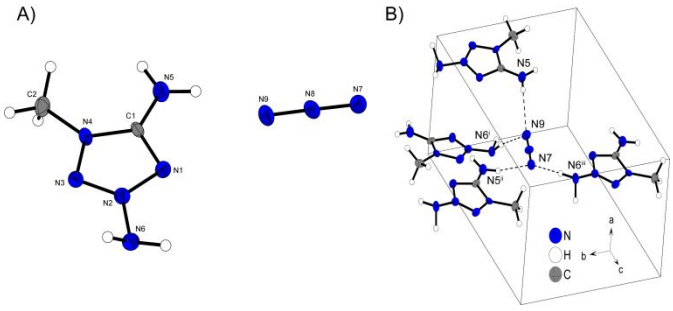

Figure 8. Representation of the molecular unit of 2,5-diamino-4-methyltetrazolium azide (**3c**), showing the atom-labeling scheme. Thermal ellipsoids represent the 50%

probability level and hydrogen atoms are shown as small spheres of arbitrary radius. Selected bond distances [Å] and angles [°]: C1-N5 1.310(6), N2-N6 1.366(6), N4-C2 1.468(7), N7-N8 1.181(6), N8-N9 1.168(6), H5B-N9 2.156(4), N5-N9 2.947(6), H6B^{i}-N9 1.97(9), N6^{i}-N9 2.953(7), H5A^{ii}-N7 2.048(4), N5^{ii}-N7 2.912(6), H6A^{iii}-N7 1.96(7), N6^{iii}-N7 2.889(6), N7-N8-N9 178.1(5); B) Embedding of the azide anion and representation of the main amine-azide interactions. Symmetry codes: i: 0.5+x, 0.5−y, 1−z; ii: 1−x, 0.5+y, 0.5−z; iii: 1−x, −0.5+y, 0.5−z.

Compound **3c** crystallizes in the orthorhombic space group $P2_12_12_1$ and comes up with a density of 1.447 g cm^{-3} at 298 K. Thus, **3c** is the least dense, energetic compound in the study as a whole. The anionic azide moiety is almost linear (N7-N8-N9 178.1(5) °) and coordinated by four cations, which form strong intramolecular interactions. As in the structures of **3a** and **3b** only the more polarized protons of the amino groups act as action site.

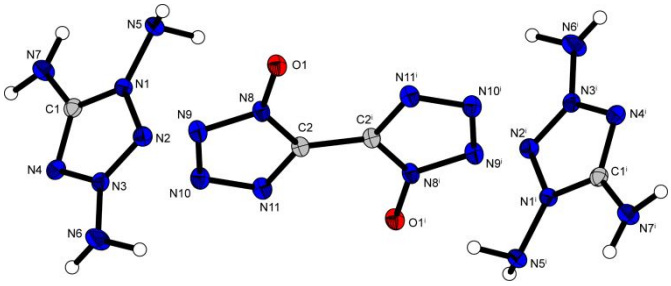

Figure 9. Representation of the molecular unit of di-(1,3,5-triaminotetrazolium)-5,5'-bistetrazole-1,1'-diolate (**4b**), showing the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. Selected bond distances [Å] N1-N5 1.390(4), N3-N6 1.365(5), C1-N7 1.329(4), O1-N8 1.311(4), O1-H5A 1.91(4), O1-H5B 1.89(4), O1-H6A 1.92(5), N4-H6B 2.41(5), N10-H7B 1.93(6) and angles [°]: N2-N3-N4 117.7(3), C1-N4-N3 101.4(3), O1-H5A-N5 174(3), O1-H5B-N5 162(4), O1-H6A-N6 152(3), N4-H6B-N6 176(3), N7-H7B-N10 173(3). Symmetry codes i: 1−x, −y, 2−z.

Compound **4b** crystallizes in the monoclinic space group $P2_1/n$ and has a density of 1.713 g cm$_{-3}$ recalculated to 298 K. The BTO2^{-} di-anion is presented as expected from other ionic derivatives as a planar bis-heterocycle with the two oxygen functions being in the same plane (N11-C2-C2^{i}-N11^{i} 180.0(5)°, O1-N8-C2-N11 179.7(3)°, O1-N8-N9-N10 179.5(3)°).[28-29] The N-NH$_2$ and C-NH$_2$ distances are all in the range between single and double bonds with C1-N7 being the shortest one (C1-N7 1.329(4) Å). Compared to the precursor compounds **4** and **4a**, the N-amino group N6 seems to be sp^2 hybridized as N7. Having a closer look at the intermolecular interactions, it becomes clear that the orientation of the protons' origins from the performed interactions to O1 and N4. Therefore, the direction of the amino protons results from the crystal packing of the compound and not from the different hybridization. A complex network of interactions is formed in which short and thus strong hydrogen bridges occur. Many of these hydrogen bonds have a length D-H···A of less than 2.00 Å (O1-H5A 1.91(4) Å, O1-H5B 1.89(4) Å, O1-H6A 1.92(5) Å, N10-H7B 1.93(6) Å,) or slightly more (H6B-N4 2.41(5) Å, N10-H7A 2.39(4) Å) and are formed by all protons of the amino groups to the oxygen atoms of the anion unit as well as to N4 of a neighbouring cation unit and N10 of the BTO anion, which has the highest interaction affinity there.

All compounds were intensively studies by multinuclear NMR spectroscopy. The isomeric purity of 2,5-DAT (**1**) could be easily guaranteed by ^{1}H NMR spectroscopy, since two signals at 7.38 ppm and 5.83 ppm are obtained, which are clearly different from those of 1,5-DAT (δ (ppm) = 6.38, 6.36). The signal for the carbon of **1** appears at 165.7 ppm. For protonated compounds **2a** and **2b** the proton signals for all five protons of the tetrazole occur as one broad signal because of the mixing due to the higher acidity. As expected, the methyl signals for compounds **3–3c** show singlet signals in the range of 3.80 ppm in the ^{1}H NMR and 34.5 ppm in the ^{13}C NMR spectrum.[30] The triaminotetrazolium derivatives **4**, **4a** and **4b** show three different resonances for the three different amino groups in the ^{1}H NMR. The resonanes for the N-NH$_2$ are broader then for the C-NH$_2$, which occur sharp. For both, the methylated and aminated compounds (**3–3c**, **4–4b**) the carbon signals of the tetrazoles appear about 10 ppm high-field-shifted compared to 2,5-DAT (**1**).

Compound **1** was further analyzed using proton coupled ^{15}N spectroscopy. The correct assignment could be made by the comparison with the ^{15}N shifts of 2-aminotetrazole, 1,5 diaminotetrazole and by the recording of a ^{15}N-^{1}H-HMBC spectrum.[10] The signals for the tetrazole nitrogen atoms are observed in the range of −15.8 ppm (N3) to −116.7 ppm (N1). The two nitrogen atoms representing the amino groups are detectable as triplets due to their ^{1}J coupling with the respective NH protons. They appear at higher fields at −289.7 (t, N-NH$_2$, ^{1}J = 72.3 Hz) and −338.8 (t, C-NH$_2$, ^{1}J = 84.2 Hz).

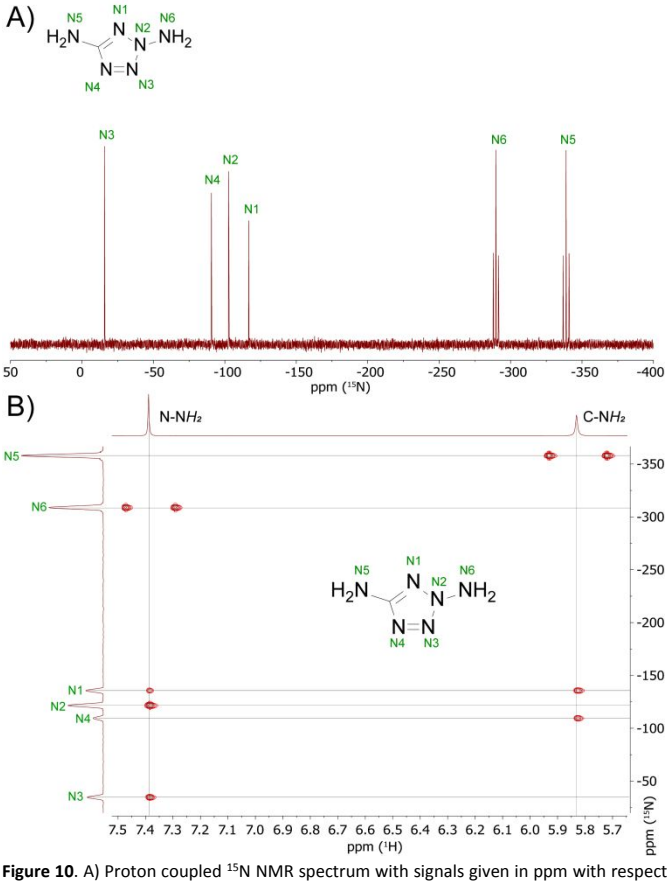

Figure 10. A) Proton coupled ^{15}N NMR spectrum with signals given in ppm with respect to MeNO$_2$. B) ^{15}N-^{1}H HMBC spectrum of **1**. Both spectra were measured in DMSO-d$_6$.

Table 1. Physic-chemical properties of investigated energetic materials **1**, **2a**-**2b**, **3a**-**3c**, **4b**, 1,5-DAT and RDX.

	1	**2a**	**2b**	**3a**	**3b**	**3c**	**4b**	1,5-DAT	RDX[25]
Formula	CH_4N_6	$CH_5N_7O_3$	$CH_5N_6O_4Cl$	$C_2H_7N_7O_3$	$C_2H_7N_6O_4Cl$	$C_2H_7N_9$	$C_4H_{12}N_{22}O_2$	CH_4N_6	$C_3H_6N_6O_6$
M [g mol^{-1}]	100.1	163.1	200.6	177.1	213.6	157.1	400.3	100.1	222.12
IS [J][a]	5	3	2	3	2	4	2	40	7.5
FS [N][b]	160	60	20	120	10	80	30	360	120
ESD [J][c]	0.20	0.13	0.10	0.14	0.10	0.07	0.08	>0.5	0.2
ρ [g cm^{-3}][d]	1.577	1.737	1.870	1.649	1.770	1.447	1.713	1.569	1.806
N [%][e]	84.0	60.1	41.9	55.4	39.2	80.2	77.0	84.0	81.0
Ω [%][f]	−48.0/−63.9	−4.9/−14.7	−4.3/−13.0	−22.6/−40.7	−7.5/−22.5	−56.0/−76.4	−32.0/−48.0	−48.0/−63.9	0/−21.6
T_{melt}/T_{dec} [°C][g]	125/180	-/112	-/115	-/203	60/155	125/165	-/170	187	210
$\Delta_f H°$ [kJ mol^{-1}][h]	345.2	202.1	256.8	264.0	230.0	685.3	1678.1	332.4	86.3
$\Delta_f U°$ [kJ mol^{-1}][i]	357.5	220.7	276.6	285.1	252.3	705.1	1722.7	344.8	108.6
Explo5 V6.05.02									
$-\Delta_{Ex}U°$ [kJ kg^{-1}][j]	3985	5346	5976	5356	5433	4913	5515	3862	5740
T_{det} [K][k]	2628	3542	4289	3376	3800	3005	3492	2580	3745
V_0 [L kg^{-1}][l]	918	918	854	919	847	919919	890	918	784
P_{CJ} [kbar][m]	265	333	356	284	307	236	333	258	336
V_{det} [m s^{-1}][n]	8788	9127	9065	8714	8489	8440	9416	8698	8801

[a] Impact sensitivity (BAM drophammer (1 of 6)). [b] Friction sensitivity (BAM friction tester (1 of 6)). [c] Electrostatic discharge device (OZM research). [d] From X-Ray diffraction analysis recalculated to 298 K. [e] Nitrogen content. [f] Oxygen balance with respect to CO/CO_2 [g] Melting/Decomposition temperature (DTA or DSC; β = 5 °C min^{-1}). [h] Calculated enthalpy of formation. [i] Calculated energy of formation. [j] Energy of explosion. [k] Detonation temperature. [l] Volume of detonation products (assuming only gaseous products). [m] Detonation pressure at Chapman-Jouguet point. [n] Detonation velocity.

2,5-Diaminotetrazole (**1**) has an onset decomposition temperature of 180 °C, which is is in the same range as for its isomer 1,5-DAT. Additionaly, a melting point at 120 °C is observed. Its sensitivity data were measured to be 160 N for friciton sensitivity, 5 J for impact sensitivity and 0.2 J for electrical discharge, making it less sensitive than all other compounds within this study. Protonation of **1** with HNO_3 decreases the thermal resistance, with **2a** decomposing already at 112 °C. However, the detonation velocity is significantly increased compared to 2,5 DAT. The EXPLO5 calculations result in a detonation velocity of 9127 m s^{-1} for **2a**, whereas it is calculated to only 8788 m s^{-1} for **1**. For perchlorate derivative **2b**, the same trend is observed as the decomposition decreases to T_{dec} = 115 °C. The detonation velocity is also higher then for the parent compound **1** and reaches a value slightly above 9000 m s^{-1}. Compared with the protonated nitrate and perchlorate species **2a** and **2b**, the decomposition temperature for the respective methylated salts increases significantly to 203 °C for the 2,5-diamino-4-methyltetrazolium nitrate (**3a**) and 155 °C for the 2,5-diamino-4-methyltetrazolium perchlorate (**3b**). However, the explosive properties decrease significantly due to the methylation and is 400 m s^{-1} (for **3a**) and 650 m s^{-1} (for **3b**) less compared to the respective protonated compounds.

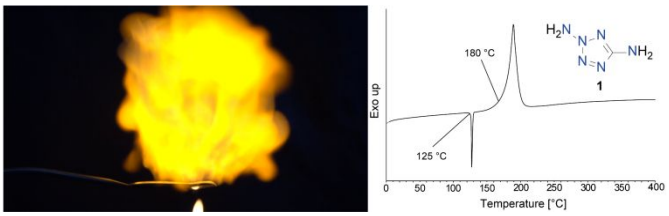

Figure 11. Flame test of approximately 20 mg 2,5-DAT (**1**)(left) and DSC curve of 1 with a heating rate of 5 °C min^{-1} (right).

The impact sensitivity in comparison to **2a** and **2b** with the respective methylated compounds **3a** and **3b** gives the same values (IS (**2a**, **3a**) = 3 J, IS (**2b**, **3b**) = 2 J). The friction sensitivities, however, vary considerably, since the value for the methylated nitrate **3a** decreases significantly to 120 N, but even increases for the methylated perchlorate **3b** to 10 N. Due to the azide moiety included in **3c**, a extremely high heat of formation could be calculated ($\Delta_f H^0$ = 685.3 kJ mol^{-1}). However, because of the low density, compound 3c has the lowest calculated performance data (P_{CJ} = 236 kbar; V_{det} = 8440 m s^{-1}) of all investigated energetic compounds. **3c** has sensitivities in the range of PETN (IS = 4 J, FS = 80 N), decomposes at 165 °C, while melting at 125 °C. 1,3,5-Triaminotetrazolium derivative **4b** shows relatively high sensitivity toward all tested external stimuli (IS = 2 J, FS = 30 N, ESD = 80 mJ). It decomposes sharply at 170 °C and has therefore the same thermal stability then 1,5-diaminotetrazolium 1-hydroxy-5,5'-bistetrazol-1'-olate.[28] The enormously high enthalpy of formation of 1678.1 kJ mol^{-1} with a room temperature density of 1.713 g cm^{-3} results in an extremely high calculated detonation velocity of 9416 m s^{-1}, which is significantly higher than that of HMX. Compared with 1,4,5-triaminotetrazolium nitrotetrazolate-2-olate (**C**), which contains a differently substituted isomer of the 1,3,5-TAT cation, **4b** achieves significantly higher decomposition temperature and explosion parameters, with lower friction and impact sensitivity. The main reason for this, however, seems to be the BTO anion, which, as expected, provided the desired stability and performance properties. Nevertheless, it should be noted that thermally robust explosives can be obtained with triaminotetrazolium cations in combination with suitable energetic anions.

Conclusions

Summarized, we report 2,5-diaminotetrazole as a missing aminotetrazole scaffold for the design of new energetic materials, with many promising properties. With a nitrogen content of 84%, a stable tetrazole backbone with a good enthalpy of formation coupled with functionalizable amino sites, 2,5-DAT, like its better-studied isomer 1,5-DAT, offers the best conditions for energetic functionalization. By HOSA amination of 5-aminotetrazole and separation of 1,5-DAT from mixture, 2,5-DAT (**1**) was synthesized for the first time in gram-scale quantities and characterized as a respectable explosive with energetic properties (IS = 5 J, FS = 160 N, V_{det} = 8788 m s^{-1}) in the range of RDX. Through targeted functionalization, we attempted to further tune the energetic properties. In this context, we focused on the protonation, methylation and amination of the tetrazole backbone and further investigated the obtained trisubstituted tetrazolium derivatives with different energetic anions, such as nitrate and perchlorate. The energetic performance could be increased by protonation and the thermal stability by methylation. The amination produces the enormously endothermic 1,3,5-tetrazolium ($\Delta_f H^0$ = 1140.3 kJ mol^{-1}) moiety, which has been characterized as 5,5'-bistetrazole-1,1'-diolate salt **4b**. Although the compound has a convincing detonation velocity of over 9400 m s^{-1}, unfortunately the sensitivity toward impact and friction is unacceptable for further applications. Nevertheless, the 2,5 diaminotetrazole derivatives investigated in this study showed they are promising building blocks for energetic materials and that greater research efforts should be devoted to study these compounds. Further, reactions used with 1,5-DAT such as nitration, protection, azo coupling, oxidation or complexation might offer great opportunities for this scaffold and could yield in very interesting energetic materials.

Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript. ‡: First author.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 a) O. T. O'Sullivan, M. J. Zdilla, *Chem. Rev.* **2020**, *120*, 5682-5744; b) J.-D. Lin, F. Chen, J.G. Xu, F.-K. Zheng, N. Wen, *ACS Appl. Nano Mater.* **2019**, *2*, 5116-5124; c) Z.-M. Li, Y.-Q. Xu, C. Wang, G.-R. Lei, R. Zhang, L. Zhang, J.-H. Chen, J.-G. Zhang, T.-L. Zhang, Q.-Y. Wang, *J. Mater. Chem. A* **2022**, *10*, 2795-2799.
2 Y.-H. Joo, J. M. Shreeve, *Org. Lett.* **2008**, *10*, 4665-4667.
3 Y. Li, Y. Yang, Z. Yi, D. Song, Y. Cheng, Y. Li, *Chem. Eng. J.* **2021**, *413*, 127442.
4 S. B. Kim, K. J. Kim, M. H. Cho, J. H. Kim, K. T. Kim, S. H. Kim, *ACS Appl. Mater. & Interfaces* **2016**, *8*, 9405-9412.
5 D. M. Smith, T. D. Manship, D. G. Piercey, *ChemPlusChem* **2020**, *85*, 2039-2043.
6 D. D. Ford, S. Lenahan, M. Jörgensen, P. Dubé, M. Delude, P. E. Concannon, S. R. Anderson, K. D. Oyler, G. Cheng, N. Mehta, J. S. Salan, *Org. Process Res. Dev.* **2015**, *19*, 673-680.
7 T. M. Klapötke, D. G. Piercey, N. Mehta, K. D. Oyler, M. Jorgensen, S. Lenahan, J. S. Salan, J. W. Fronabarger, M. D. Williams, *Z. Anorg. Allg. Chem.* **2013**, *639*, 681-688.
8 J. W. Fronabarger, M. D. Williams, W. B. Sanborn, J. G. Bragg, D. A. Parrish, M. Bichay, *Propellants Explo. Pyrotech.* **2011**, *36*, 541-550.
9 T. Küblböck, G. Angé, G. Bikelytė, J. Pokorná, R. Skácel, T. M. Klapötke, *Angew. Chem. Int. Ed.* **2020**, *59*, 12326-12330.
10 N. Szimhardt, M. H. H. Wurzenberger, L. Zeisel, M. S. Gruhne, M. Lommel, J. Stierstorfer, *J. Mater. Chem. A* **2018**, *6*, 16257-16272.
11 N. Szimhardt, M. H. H. Wurzenberger, P. Spieß, T. M. Klapötke, J. Stierstorfer, *Propellants Explo. Pyrotech.* **2018**, *43*, 1203-1209.
12 T. M. Klapötke, D. G. Piercey, J. Stierstorfer, *Eur. J. Inorg. Chem.* **2012**, *2012*, 5694-5700.
13 Y. Xu, Y. Wang, Y. Zhong, G. Lei, Z. Li, J. Zhang, T. Zhang, *Inorg. Chem.* **2021**, *60*, 5100-5106.
14 C. Jin, Y. Liu, L. Wang, W. Zhang, T. Zhang, J. Zhu, *RSC Adv.* **2020**, *10*, 30069-30076.
15 Z. Li, Y. Yuan, Y. Zhang, L. Liu, S. Zhang, *Z. Anorg. Allg. Chem.* **2017**, *643*, 647-652.
16 Y. Qian, Z. Han, Y. Zhang, Z. Du, Y. Zhao, Y. Yang, J. Zhang, *J. Heterocycl. Chem.* **2016**, *53*, 651-657.
17 J.-G. Zhang, J.-Y. Li, Y. Zang, Y.-J. Shu, T.-L. Zhang, L. Yang, Philip P. Power, *Z. Anorg. Allg. Chem.* **2010**, *636*, 1147-1151.
18 R. Raap, *Can. J. Chem.* **1969**, *47*, 3677-3681.
19 P. N. Gaponik, S. V. Voitekhovich, A. S. Lyakhov, V. E. Matulis, O. A. Ivashkevich, M. Quesada, J. Reedijk, *Inorg. Chim. Acta* **2005**, *358*, 2549-2557.
20 Y.-H. Joo, B. Twamley, S. Garg, J. M. Shreeve, *Angew. Chem. Int. Ed.* **2008**, *47*, 6236-6239.
21 T. M. Klapötke, F. A. Martin, J. Stierstorfer, *Chem. Eur. J.* **2012**, *18*, 1487-1501.
22 L. Liu, C. He, C. Li, Z. Li, *J. Chem. Crystallogr.* **2012**, *42*, 816-823.
23 F. Li, X. Cong, Z. Du, C. He, L. Zhao, L. Meng, *New J. Chem.* **2012**, *36*, 1953-1956.
24 J. C. Galvez-Ruiz, G. Holl, K. Karaghiosoff, T. M. Klapötke, K. Loehnwitz, P. Mayer, H. Noeth, K. Polborn, C. J. Rohbogner, M. Suter, J. J. Weigand, *Inorg. Chem.* **2005**, *44*, 5192-5192.
25 N. Fischer, T. M. Klapötke, J. Stierstorfer, *Journal of Energetic Materials* **2011**, *29*, 61-74.
26 S. R. Yocca, M. Zeller, E. F. C. Byrd, D. G. Piercey, *J. Mater. Chem. A* **2022**, *10*, 1876-1884.
27 A. S. Lyakhov, P. N. Gaponik, S. V. Voitekhovich, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **2001**, *57*, 185-186.
28 N. Fischer, T. M. Klapötke, M. Reymann, J. Stierstorfer, *Eur. J. Inorg. Chem.* **2013**, 2167-2180.
29 Y. Shang, B. Jin, R. Peng, Z. Guo, Q. Liu, J. Zhao, Q. Zhang, *RSC Adv.* **2016**, *6*, 48590-48598.

30 N. Szimhardt, M. H. H. Wurzenberger, A. Beringer, L. J. Daumann, J. Stierstorfer, *J. Mater. Chem. A* **2017**, *5*, 23753-23765.