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Synthesis and Promising Properties of a New Family of High-Nitrogen Compounds: Polyazido- and Polyamino-Substituted *N*,*N*′-Azo-1,2,4-triazoles

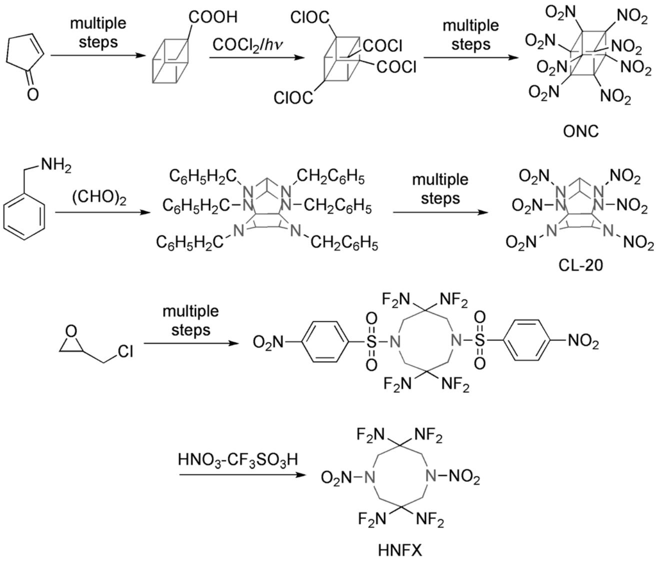
Cai Qi,[a] Sheng-Hua Li,[a] Yu-Chuan Li,[a] Yuan Wang,[a] Xiu-Xiu Zhao,[a] and Si-Ping Pang*[a, b]

Abstract: A new family of high-nitrogen compounds, that is, polyazido- and polyamino-substituted *N*,*N*′-azo-1,2,4-triazoles, were synthesized in a safe and convenient manner and fully characterized. The structures of 3,3′,5,5′-tetra(azido)-4,4′-azo-1,2,4-triazole (**15**) and 3,3′,5,5′-tetra(amino)-4,4′-azo-1,2,4-triazole (**23**) were also confirmed by X-ray diffraction. Differential scanning calorimetry (DSC) was performed to determine their thermal stability. Their heats of formation and density, which were calculated by using Gaussian 03, were used to determine the detonation performances of the related compounds (EXPLO 5.05). The heats of formation of the polyazido compounds were also derived by using an additive method. Compound **15** has the highest heat of formation (6933 kJ kg^{-1}) reported so far for energetic compounds and a detonation performance that is comparable to that of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), while compound **23** has a decomposition temperature of up to 290 °C.

Keywords: azo compounds • energetic materials • heats of formation • heterocycles • nitrogen

Introduction

Energetic materials represent an important class of materials because they can store large amounts of chemical energy that can be released by rapid decomposition, accompanied by the production of large quantities of hot gaseous products; as such, the design and synthesis of new energetic materials has been a long-standing tradition in the chemical sciences.[1] New energetic materials must meet increasing performance requirements, that is, propellants must transport ever-increasing payloads and explosives must become more powerful; therefore, energetic compounds with higher energy are a keen concern of many researchers.[1f,2] The amount of energy that is contained in a compound is directly determined by its chemical structure. In general, the structure of classical energetic compounds, such as octanitrocubane (ONC),[2c] hexanitrohexaazaisowurtzitane (CL-20),[2a] and 3,3,7,7-tetrakis(difluoramino)octahydro-1,5-dinitro-1,5-diazocine (HNFX, Scheme 1),[3] is composed of two parts, backbones (or skeletons) and functional groups, which always act as fuels and oxidizers, respectively. By combining the right backbone with the right functional groups, the energetic properties of these compounds could be tuned and improved. Strained backbones are appreciated because of their increased energy and density that is derived from ring and cage strain; for example, cubane is an exceptionally dense (1.29 g cm^{-3}) energetic molecule that has a surprising-



Scheme 1. Examples of the synthesis of some classical energetic compounds.

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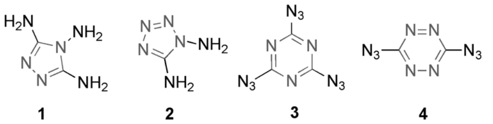
[a] Dr. C. Qi, Dr. S.-H. Li, Dr. Y.-C. Li, Dr. Y. Wang, Dr. X.-X. Zhao, Prof. Dr. S.-P. Pang
School of Materials Science & Engineering
Beijing Institute of Technology
5 South Zhongguancun Street, Haidian District
Beijing 100081 (P. R. China)
Fax: (+86) 010-68913038
E-mail: pangsp@bit.edu.cn

[b] Prof. Dr. S.-P. Pang
State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology
5 South Zhongguancun Street, Haidian District
Beijing 100081 (P. R. China)

Supporting information for this article, including the ^{1}H and ^{13}C spectra of compounds **17**–**19**, is available on the WWW under http://dx.doi.org/10.1002/chem.201202428.

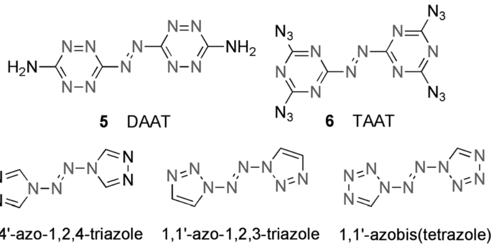
ly kinetic stability in spite of its tremendous strain energy of 161 kcal mol^{-1}.[1e] By introducing eight nitro groups onto this backbone, ONC can be obtained, which has improved energy performance (the predicted performance of ONC is 15–30% better than HMX).[1e] Compared with traditional simple energetic compounds like TNT, new energetic compounds have relatively complicated molecular structures that make them difficult to synthesize in a simple and straightforward manner. As shown in Scheme 1, their backbone must usually be synthesized first and then the energetic functional groups are introduced by multi-step functional-group transformations. On the other hand, many energetic compounds with astonishingly high predicted energy, such as 2,4,6,8-tetranitro-1,3,5,7-tetraazacubane, have not yet been synthesized, even though its structure was first predicted a long time ago,[4] partly owing to the difficulties in building up the backbone in the initial stage of the synthesis. Therefore, a good backbone is of paramount importance for the synthesis of new energetic compounds.

High-nitrogen compounds, which derive their energy from their inherently high heats of formation, have attracted significant recent attention from many researchers.[1d,2g,5] Together with their high positive heats of formation and high thermal stability, nitrogen-rich heterocycles, such as triazole,[6] tetrazole,[1f,2g,7] triazine,[8] and tetrazine,[9] offer good backbones for the development of new energetic compounds. Such heterocycles are often modified by functional groups, like NH_2 and N_3, which further increase the overall nitrogen content (Scheme 2). The incorporation of amino groups is one of the simplest routes to enhance the thermal stability of such compounds,[1a] while the introduction of azido groups can rapidly increase their energy level. Covalent polyazido heteroaromatic compounds have recently been extensively studied for their use in applications in either materials science or as high-density energetic materials,[2f,6e,10] and this family of compounds is famous for their extremely high heats of formation and nitrogen content. For example, 3,6-diazido-1,2,4,5-tetrazine (**4**, DiAT, N 85.36%) has the highest reported heat of formation of about 6709 kJ kg^{-1} (1101 kJ mol^{-1}).[5a,11] In addition, both the amino and azido heteroaromatic compounds are valuable precursors or intermediates in the pharmaceutical industry.[12]



Scheme 2. Examples of high-nitrogen compounds with amino and azido groups.

By combining an azo group with nitrogen-rich heteroaromatic rings in which the azo group is bonded to a carbon atom (*C*,*C*′-azo linkage), a new kind of high-nitrogen backbone is obtained. Moreover, it has been shown that the azo linkage not only desensitizes but also dramatically increases the heats of formation of high-nitrogen compounds.[13] For example, in Scheme 3, 3,3′-azobis(6-amino-1,2,4,5-tetrazine) (**5**, DAAT, N 76.35%) is thermally stable up to 252 °C and insensitive to mechanical stimulus,[14] while 4,4′,6,6′-tetra(azido)azo-1,3,5-triazine (**6**, TAAT, N 79.55%) has a high heat of formation of 6168 kJ kg^{-1} (2171 kJ mol^{-1}).[13]

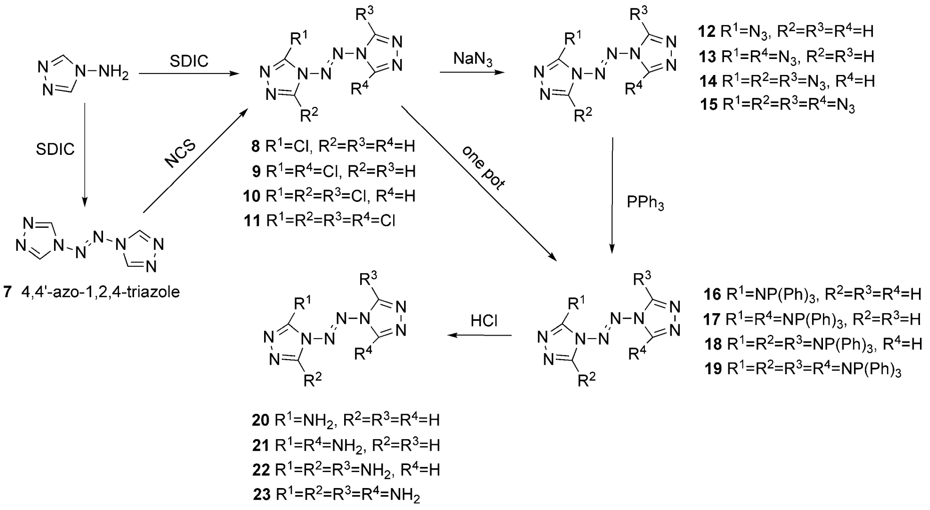


Scheme 3. Examples of high-nitrogen compounds with an azo linkage.

In a continuing effort to seek more powerful high-nitrogen compounds with good stability, we expanded *C*,*C*′-azo linkages to include a new *N*,*N*′-azo linkage.[15] Compared with the *C*,*C*′-azo linkage, the *N*,*N*′-azo linkage results in high-nitrogen compounds with a long chain of catenated nitrogen atoms, which will increase the energy more effectively and result in compounds with higher densities.[15b,c,16] These new compounds are also potential backbones, owing to their more tunable ring positions of the carbon atoms. In particular, 4,4′-azo-1,2,4-triazole (**7**) is very thermally stable, with a decomposition temperature of up to 313 °C, and its heat of formation (878 kJ mol^{-1}) is also relatively high. In addition, there are four carbon atoms in the molecule that can be modified; therefore, it is possible to further control the properties of compound **7** by judicious selection of the substituent on the carbon atoms, as in analogues **5** and **6**. These above-mentioned properties make compound **7** an ideal backbone for the development of new energetic compounds. Energetic compounds that contain a *N*,*N*′-azo moiety are uncommon in scientific literature. Although Bottaro et al. reported some *N*,*N*′-azobisnitroazoles in a patent,[17] no physical properties or proof of structure were given for these compounds. Energetic derivatives that are based on a *N*,*N*′-azo heteroaromatic backbone are practically nonexistent and the effect of functional groups, such as NH_2 and N_3, on *N*,*N*′-azo moiety, as well as the reactivity of the *N*,*N*′-azo heteroaromatic backbone are also unknown.

Beyond applications as energetic materials, *N*,*N*′-azo heteroaromatic derivatives also have great synthetic potential, for example, as building blocks in spin-crossover systems.[18]

Herein, we report the synthesis of a series of polyazido- and polyamino-substituted *N*,*N*′-azo-1,2,4-triazoles (Scheme 4), as well as their significant physical and energetic properties. By comparison of these new compounds with their analogues **5** (DAAT) and **6** (TAAT), we have demonstrated the capability of *N*,*N*′-azo heteroaromatic backbones to form high-performance energetic compounds.



Scheme 4. Synthesis of polysubstituted derivatives based on the *N,N'*-azo linkage.

Results and Discussion

To prepare their corresponding high-nitrogen derivatives, compound **7** must be prefunctionalized, because it is difficult to introduce azido or amino groups onto heterocycles in a straightforward manner. Therefore, the necessary chlorides **8–11** were produced by either using *N*-chlorosuccinimide (NCS) or sodium dichloroisocyanurate (SDIC). The solutions of compounds **8–11** in DMF were treated with excess amounts of sodium azide. When the reactions were complete, the residues were washed with acetone to obtain compounds **12–14** after the removal of the solvent under reduced pressure. In the case of compound **15**, owing to its poor solubility in water and extremely high sensitivity, the reaction mixture was poured into water and filtered to obtain the product. The introduction of the amino group was achieved by a mild Staudinger reaction. The combination of compounds **12–15** with a common reducing agent, triphenylphosphine (PPh_3), in acetone afforded iminophosphorane intermediates **16–19** that were then hydrolyzed in 1 M HCl to prepare amino derivatives **20–23**. Meanwhile, a one-pot method to synthesize compounds **16–19** was also developed. The reactions of compounds **8–11** with sodium azide in DMF were monitored by TLC, and triphenylphosphine was added when the chlorides had been completely consumed. In this way, the iminophosphorane intermediates **16–19** could be obtained more easily, without the need to handle the dangerous azido compounds **12–15**, thus enabling the development of safer procedures for the preparation of valuable molecules through halogenated heterocycles and avoiding the need for the isolation, purification, and handling of azido-heterocycles. Experimental details are summarized in the Experimental Section.

Table 1. Crystallographic data for compounds **15**, **17**, **18**·4 CH_3OH, and **23**·2 H_2O.

	15	17	18·4 CH_3OH	23·2 H_2O
formula	C_4N_{20}	$C_{40}H_{32}N_{10}P_2$	$C_{62}H_{62}N_{11}O_4P_3$	$C_4H_{12}N_{12}O_2$
M_W	328.24	714.70	1118.14	260.26
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*P*2$_1$/*n*	*P*2$_1$/*n*	*P*2$_1$/*c*
size [mm]	0.58×0.10×0.07	0.50×0.40×0.20	0.55×0.18×0.12	0.43×0.27×0.13
T [K]	153(2)	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
a [Å]	19.407(14)	10.317(2)	13.735(3)	9.874(3)
b [Å]	4.211(3)	14.406(3)	19.111(4)	15.901(4)
c [Å]	14.910(10)	13.106(3)	22.320(5)	6.7279(17)
α [°]	90	90	90	90
β [°]	94.625(10)	105.60(3)	91.42(3)	95.750(4)
γ [°]	90	90	90	90
V [Å^3]	1214.4(14)	1876.1(7)	5857(2)	1051.0(5)
Z	4	2	4	4
ρ [$g cm^{-3}$]	1.795	1.265	1.268	1.645
μ [mm^{-1}]	0.144	0.159	0.159	0.135
F(000)	656	744	2352	544
R_1 [$I>2\sigma(I)$]	0.0409	0.0486	0.0594	0.0384
wR_2 [$I>2\sigma(I)$]	0.0949	0.1193	0.0726	0.0905
refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
CCDC number	875776	673984	673985	875777

All of the products were isolated and characterized by IR and NMR spectroscopy, MS, and elemental analysis. Compounds **15**, **17**, **18**·4 CH_3OH, and **23**·2 H_2O[19] were also characterized by X-ray crystallography; selected data and parameters from their X-ray structures are given in Table 1.

Crystals of compound **15** that were suitable for crystal-structure analysis were obtained from a mixture of CH_2Cl_2 and petroleum ether. Compound **15** crystallizes in a monoclinic crystal system (space group *C*2/*c*, Figure 1) and has a density of 1.795 $g cm^{-3}$ (at 153 K). Only one conformation of compound **15** is observed, although its analogue (TAAT) was previously reported to be polymorphous.[13] Both compounds **17** and **18** crystallize in the monoclinic space group *P*2$_1$/*n* (Figures 2 and 3). Crystals of compound **23**, which were obtained from water, contain two molecules of water. Compound **23**·2 H_2O crystallizes in the monoclinic space group *P*2$_1$/*c* (Figure 4) and has a density of 1.645 $g cm^{-3}$ (at 293 K). Both compounds **15** and **23**·2 H_2O have two almost planar triazole rings and a planar N_4 chain, which is the same as that in compound **7**. Moreover, the two triazole rings are coplanar in compounds **7** and **15**, while the dihedral angle of C1−C2−C3−C4 (167.52°) indicates that the structure of compound **23**·2 H_2O is slightly twisted. The four azido groups in

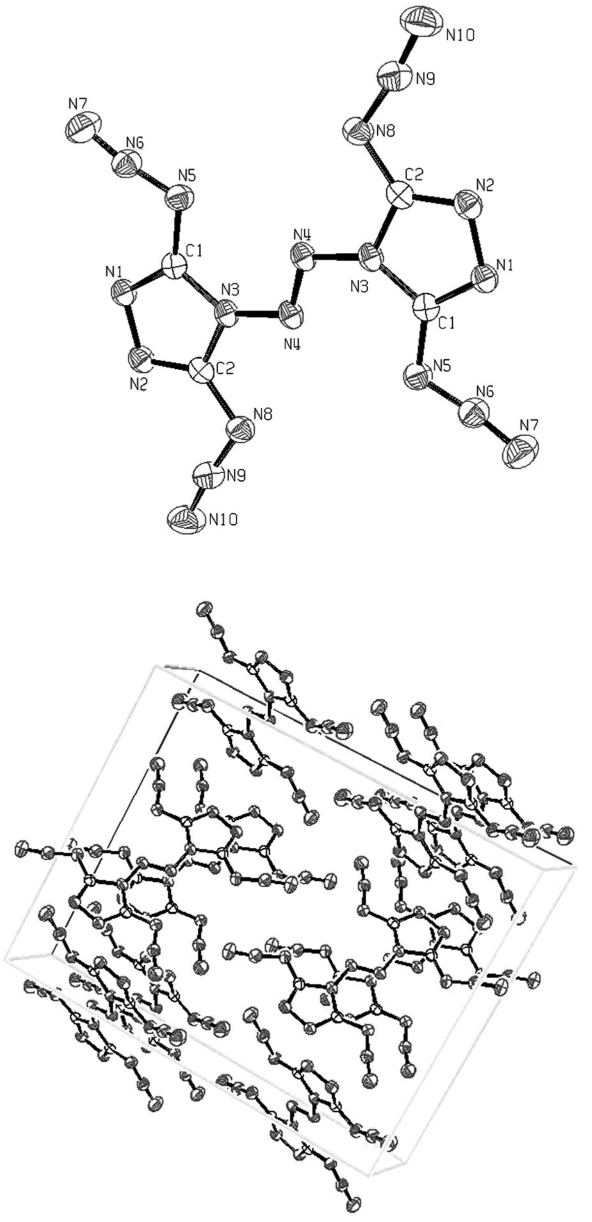


Figure 1. ORTEP of the molecular structure of compound **15**; thermal ellipsoids are set at 50 % probability.

compound **15** lie perfectly within the plane of the parent ring. However, the hydrogen atoms of the amino groups in compound **23**·2 H_2O are slightly twisted out of the triazole plane, with a maximum torsion angle of 37°. Notably, there is a difference in the N3–N4 distances between compounds **15** and **23**·2 H_2O (1.385 versus 1.362 Å; Table 2); the value of this same bond in compound **7** is 1.384 Å. This result is probably attributed to the different properties of the two kinds of substituents (the amino group is electron donating whereas the azido group is electron withdrawing). Nevertheless, a comparison with the bond lengths of the N_4 azo linkage in compounds **15**, **23**·2 H_2O, **7**, and N_4H_4 (2-tetrazene) indicates that the strong delocalization of the azo π-bond along the N_4 moiety is not greatly affected by the substituent. In addition, although both of the C1–N3 and C2–N3 bonds in compounds **15** and **23**·2 H_2O are stretched, owing to the effect of the substituent, all of the bond lengths of the C–N, N–N, and C=N bonds within the triazole moiety are still between the lengths of the standard single (C–N 1.47 Å, N–N 1.45 Å) and double bonds (C=N 1.28 Å, N=N 1.24 Å), which indicates that the molecule is aromatic. Moreover, nitrogen atoms from the triazole ring in compound **23**·2 H_2O are found to participate in hydrogen bonds (N_9–H_{9a}···N_7 0.957, 1.973, 2.899, 162.317°; N_9–H_{9a}···N_8 0.957, 2.723, 3.449, 133.150°), and hydrogen-bonding interactions between oxygen atoms from water and hydrogen atoms from the amino group (N_{10}–H_{10a}···O_1 0.814, 2.286, 3.018, 149.941°; N_{10}–H_{10b}···O_2 0.812, 2.107, 2.918, 176.165°) can also be observed.

Table 2. Selected bond lengths [Å] in compounds **7**, **15**, and **23**·2 H_2O.

	15	**23**·2 H_2O	**7**
N3–N4	1.385	1.362	1.384
C1–C3	1.384	1.401	1.373
C2–C3	1.376	1.389	1.369
C1–N1	1.294	1.298	1.305
C2–N2	1.292	1.294	1.298
N1–N2	1.403	1.424	1.406

The thermal stabilities of the related compounds were studied by differential scanning calorimetry (DSC) at a heating rate of 10 °C min^{-1} (Figures 5 and 6). All of the azido derivatives decomposed between 135 and 190 °C without melting, and their thermal stability decreased as the number of azido groups increased. The lowest decomposition temperature occurred at 136 °C for compound **15**, which is a little higher than the value for DiAT (130 °C). Not unexpectedly, compounds **20**–**23** are more stable than their azido derivatives, with values in the range 245–290 °C. The highest value (290 °C) for compound **23** is 40 °C higher than that of DAAT, while compounds **20**, **21**, and **22** have values of 248, 245 and 246 °C, respectively. Notably, although the decomposition temperatures of the azido and amino derivatives are lower than that of compound **7** (313 °C), the *N*,*N'*-azo linkage is still stable enough for normal operation because all of the values are higher than 135 °C, which means that the synthesis, treatment, and characterization of these high-nitrogen derivatives are possible under normal conditions, without decomposition.

The electron-withdrawing group N_3 is commonly used as an effective ligand for increasing the heat of formation of an energetic compound, because one azido group adds about 87 kcal mol^{-1} (364 kJ mol^{-1}) of endothermicity to a hydrocarbon compound, along with an increase in nitrogen content.[20] The heats of formation of compounds **12**–**15** are calculated by using the method of isodesmic reactions (Scheme 5).[21] All calculations were carried out by using the Gaussian 03 program.[22] Geometries were optimized at the B3LYP/6-31G* level by using the default convergence criteria and were confirmed to be true local-energy minima on potential-energy surfaces without imaginary frequencies. The single-point energy was calculated at the B3LYP/6-311+

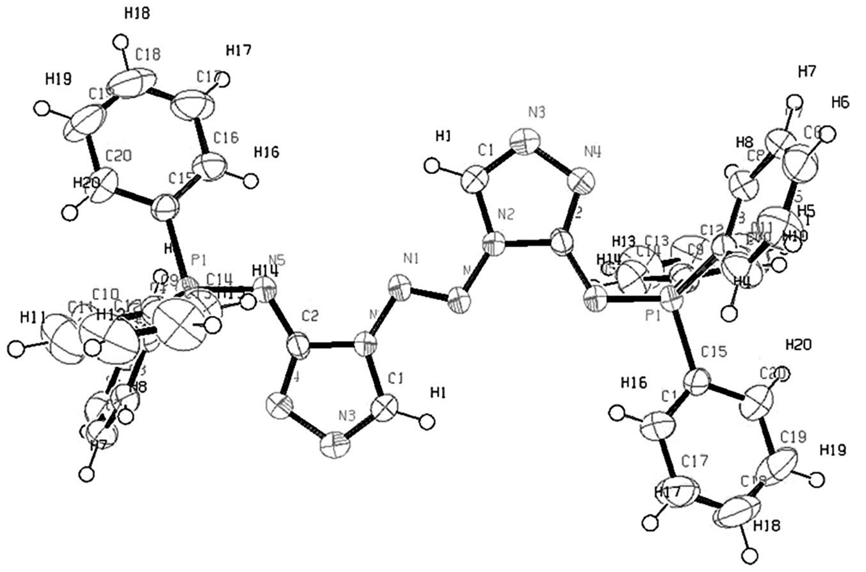


Figure 2. ORTEP of the molecular structure of compound **17**; thermal ellipsoids are set at 50 % probability.

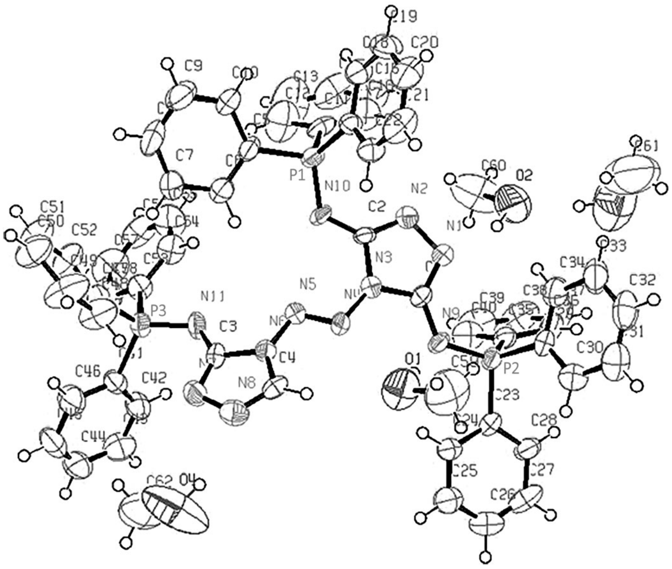
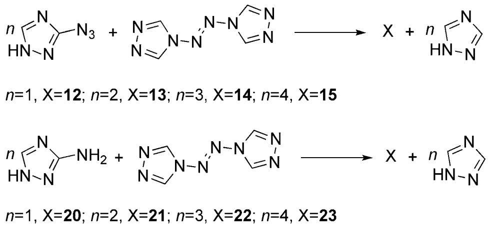


Figure 3. ORTEP of the molecular structure of compound **18**·4 CH_3OH; thermal ellipsoids are set at 50 % probability.



Scheme 5. Isodesmic reactions of polyazido and polyamino derivatives.

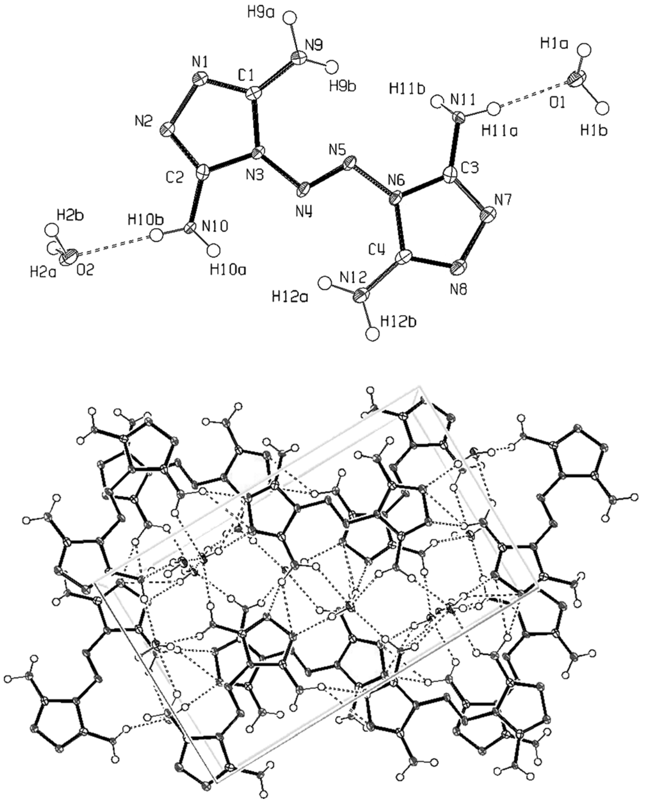


Figure 4. ORTEP of the molecular structure of compound **23**·2 H_2O; hydrogen atoms are shown as spheres and thermal ellipsoids are set at 50 % probability.

+G** level. The enthalpy of the isodesmic reaction was obtained by combining the B3LYP/6-311++G** energy difference for the reaction with thermodynamic parameters, including the zero-point energy (ZPE) and the thermal correction to the enthalpy (H_T). As shown in Table 3, the heats of formation of compounds **12**–**15** are remarkably higher than that of compound **7** and they increase linearly with the number of azido groups. The incremental contribution of each additional azido group to the heat of formation in the sequence **7**→**12**, **12**→**13**, **13**→**14**, and **14**→**15** is 344, 344, 340, and 356 $kJ\,mol^{-1}$, respectively.

The high energy of high-nitrogen compounds is derived from the larger number of inherently energetic N–N and C–N bonds that are contained within the molecule;[13] thus, nitrogen content and the heat of formation are important parameters in high-nitrogen compounds. The higher the nitrogen content is, the higher the heat of formation, and, concurrently, the better the energetic performance. Unfortunately, such increased perform-

Table 3. Physical properties of azido and amino derivatives.

	N [%][a]	T_{decomp}[b] [°C]	ρ[c] [g cm^{-3}]	HOF[d] [kJ mol^{-1}]	HOF[d] [kJ kg^{-1}]	D[e] [km s^{-1}]	P[f] [GPa]	IS[g] [J]
12	75.1	189.7	1.63	1205 (1227)	5878 (5985)	8.28	27.18	12
13	79.7	185.7	1.66	1549 (1576)	6297 (6407)	8.54	29.62	8
14	82.9	136	1.74 (1.76)	1889 (1925)	6582 (6707)	8.95	34.09	<3
15	85.4	136	1.76 (1.79)	2245 (2274)	6845 (6933)	9.37	38.43	<3
20	70.4	248	1.53	829.8	4636	7.64	21.52	>40
21	72.1	245	1.59 (1.68)	799.0	4119	7.84	23.04	>40
22	73.7	246	1.57	774.3	3705	7.73	22.08	>40
23	75.0	290	1.57 (1.64)	748.9	3343	7.70	21.70	>40
7[h]	68.3	313.4	1.60	861 (878)	5250 (5354)	7.97	24.42	14
RDX[i]	37.8	230	1.82	93	419	8.97	35.20	7.4
HMX[i]	37.8	287	1.91	105	361	9.32	39.60	7.4

[a] The percentage of nitrogen content. [b] Temperature of thermal decomposition under a nitrogen atmosphere (heating rate: 10 °C min^{-1}). [c] Calculated density based on the method reported in reference [25]; measured value is given in parentheses. [d] Theoretical heat of formation (HOF) and derived heat of formation (in parentheses) based on the method reported in reference [5a]. [e] Detonation velocity. [f] Detonation pressure. [g] Impact sensitivity (IS). [h] Data taken from reference [15c]. [i] Data from reference [6c].

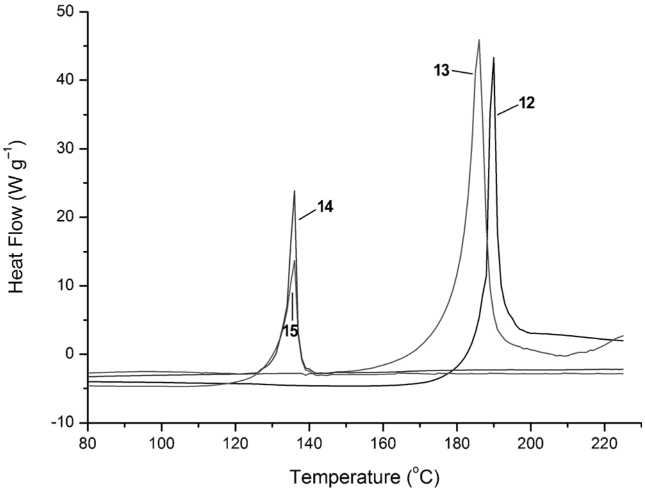


Figure 5. DSC thermograms of compounds **12**–**15** (heating rate: 10 °C min^{-1}); T_{decomp}: **12** = 190 °C, **13** = 186 °C, **14** = 136 °C, **15** = 136 °C.

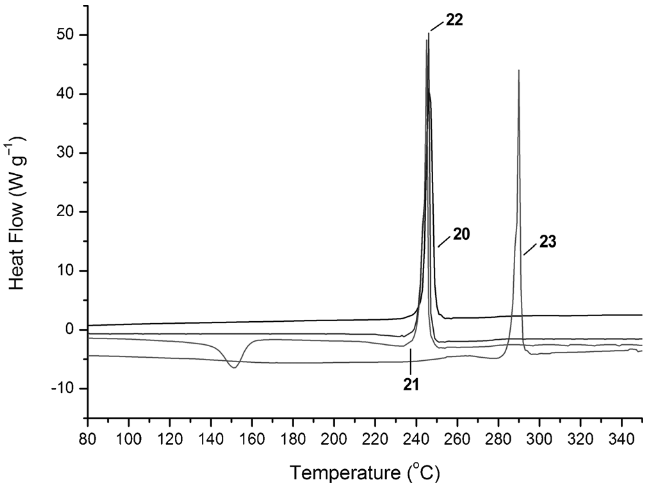
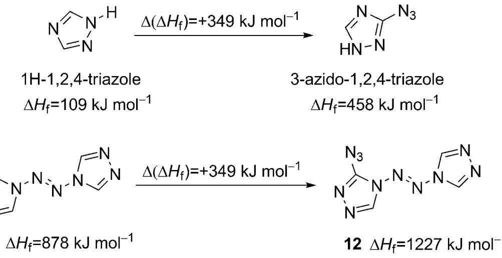


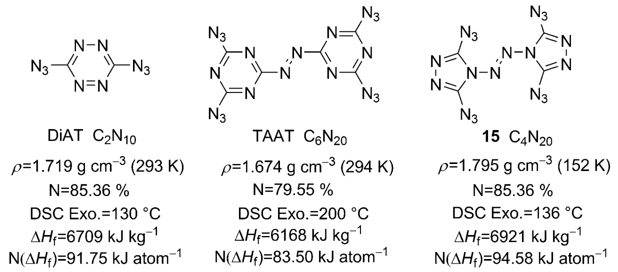
Figure 6. DSC thermograms of compounds **20**–**23** (heating rate: 10 °C min^{-1}); T_{decomp}: **20** = 248 °C, **21** = 245 °C (T_{melt}: 152 °C), **22** = 246 °C, **23** = 290 °C.

ance is always accompanied by poor stability, both thermally and mechanically.[6c,10f,g] Studies on unstable high-nitrogen compounds that are on the borderline of existence and non-existence allows the elucidation of the fundamental properties that affect their chemical stability and bonding.[2f,16,23] Therefore, it is of particular interest to compare the heat of formation of 3,3′,5,5′-tetra(azido)azo-1,2,4-triazole (**15**) with those of DiAT and TAAT, because of their relatively high nitrogen content and similar polyazido structures. Thus, a similar method to that used to derive the heat of formation of DiAT was applied (Scheme 6).[5a] The heat of formation of 3-azido-1,2,4-triazole is 349 kJ mol^{-1} larger than that of 1*H*-1,2,4-triazole.[24] Therefore, the change in the heat of formation of compound **7** is predicted to be +349 kJ mol^{-1} following the first introduction of N_3. This value is also confirmed by the theoretical predictions, as mentioned above. According to the additive method, the value of compound **15** is estimated to be 6933 kJ kg^{-1}(2274 kJ mol^{-1}), which is 224 kJ kg^{-1} higher than that of DiAT and is the highest reported heat of formation. Moreover, the NΔH_f value (94.75 kJ atom^{-1}) is also higher than that of other known organic molecules (Scheme 7). Compound **15** is superior to TAAT in terms of both the heat of formation and the nitrogen content. Furthermore, it is probably a good precursor to carbon-nitride nanomaterials, like DiAT and TAAT, owing to its high nitrogen content (N 85.36 %) and binary C/N component.[5a,11]

The theoretical densities of compounds **7** and **12**–**23** (Table 3) were obtained by using the statistical averaging method reported by Xiao and co-workers.[25] By using the calculated densities and heats of formation of compounds **12**–**15**, their detonation performances were calculated with EXPLO program (version 5.05). However, in the case of com-



Scheme 6. Additive method that was used to derive the heats of formation of compounds **12**–**15**.



Scheme 7. Polyazido energetic compounds with high heats of formation.

pound **15**, owing to the limitations of the program, the performances of compounds with a binary CN form could not be predicted. By using the formula of compound **14**, the parameters of compound **15** were derived with its own calculated density and heat of formation. Although the detonation performance of compound **15** that is derived in this way must be lower than the actual value, the increasing trend is still obvious, as shown in Table 3. Owing to the increased density and heat of formation, the detonation parameters of compound **15** are superior to those of RDX and comparable to those of HMX. Impact-sensitivity measurements were performed according to the Bruceton method on a type-12 tooling. The values of compounds **12–15** ranged from sensitive (**12**: 12 J, **13**: 8 J) to very sensitive (**14**, **15**: < 3 J).[26] Considering the hydrogen-bonding interactions that are formed between the nitrogen atoms of the triazole rings and the hydrogen atoms of the amino groups in compounds **20–23**, it is no surprise that the impact sensitivities of these compounds are greater than 40 J. Although the impact sensitivity can be decreased by replacing the azido groups with amino groups, the corresponding detonation performance is negatively impacted. The calculated performances of compounds **20–23** are not excellent, but their good stability, especially for compound **23**, enable them to be further modified into their N-oxide derivatives, like DAAT.[9b]

Conclusion

In summary, a series of polyazido- and polyamino-substituted high-nitrogen compounds that are based on a new backbone have been synthesized and fully characterized. The physical and detonation properties of these polyazido and polyamino compounds were also determined. 3,3′,5,5′-Tetra(azido)azo-1,2,4-triazole (**15**, N 85.36 %) was found to have a relatively high decomposition temperature (136 °C) and the highest positive heat of formation of 6933 kJ kg^{-1} (2274 kJ mol^{-1}) reported so far for energetic materials. Moreover, its detonation values are comparable to those of HMX. Meanwhile, the decomposition temperature of 3,3′,5,5′-tetra(amino)azo-1,2,4-triazole (**23**, N 74.97 %) is up to 290 °C. The ease of these reactions, together with the high stability of the *N*,*N*′-azo linkage, make this family of *N*,*N*′-azo heteroaromatic compounds potential precursors for many interesting subsequent transformations and may give access to many new high-nitrogen compounds. We hope that this work might also inspire others in shedding additional light on this fundamental class of compounds.

Experimental Section

All materials were commercially available and used as received. Melting points were determined on an XT4 microscope melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet Magna IR 560 spectrophotometer (KBr pellets). NMR spectroscopy was performed on an ARX-400 instrument with TMS as an internal standard. MS EI were recorded on a GCTMS Micromass UK spectrometer and MS ESI were recorded on an Agilent 6120 LCMS spectrometer. Elemental analysis was performed on an Elementar Vario EL(Germany). Crystal structures were determined on a Rigaku RAXIS IP diffractometer with the SHELXTL crystallographic software package of molecular structure. To determine the thermal stability of the described compounds, a TA-DSC Q2000 differential scanning calorimeter (heating rate: 10 °C min^{-1}) was used.

Safety precautions: We encountered several unintended explosions were we were working with these materials, so standard safety precautions (leather gloves, face shield, and ear plugs) should be used at all times!

Preparation of compounds 8–11: The necessary chlorides (**8–11**) were produced by either using NCS or, in a more direct way in which the oxidation and chlorinated reactions occurred simultaneously, by the treatment of 4-amino-1,2,4-triazole with SDIC under different reaction conditions.[15a,27] The latter route afforded the chlorides products more efficiently and in higher yields. This route is important, because it enabled us to tune the properties of these compounds by controlling the number of functional groups on their backbones.

General method for the preparation of compounds 8–11 from compound 7: Compound **7** was added to a solution of NCS in THF with molar ratios of 1:1, 1:2, 1:3, and 1:4 for compounds **8--11**, respectively. The mixture was stirred at RT and, when the reaction was complete, the solvent was removed under reduced pressure. The residue was washed successively with CH_2Cl_2 and acetone. The acetone solution was collected and evaporated slowly to afford the corresponding products (Yield: 30 % for compound **8**, 25 % for compound **9**, 15 % for compound **10**, and 8 % for compound **11**).

3-Azido-4,4′-azo-1,2,4-triazole (12): NaN_3 (0.25 g, 3.8 mmol) was added to a solution of compound **8** (0.5 g, 2.5 mmol) in DMF (15 mL) at RT and the reaction mixture was stirred for 2 h. After evaporation of the solvent, the residue was dissolved in acetone, filtered, concentrated, and purified by recrystallization from acetone/petroleum ether. Yield: 0.26 g, 50 %; T_{decomp}: 190 °C (DSC, 10 °C min^{-1}); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 9.17$ (s, 1 H), 9.29 ppm (s, 2 H); ^{13}C NMR (400 MHz, [D$_6$]DMSO): $\delta = 135.0$, 138.0, 147.2 ppm; IR (KBr): $\tilde{\nu} = 2921$, 2172, 1553, 1469, 1423, 1167, 1031 cm^{-1}; MS (ESI): *m*/*z*: 206 [*M*+H]$^+$.

3,3′-Di(azido)-4,4′-azo-1,2,4-triazole (13): NaN_3 (0.18 g, 2.75 mmol) was added to a solution of compound **9** (0.25 g, 1.1 mmol) in DMF (15 mL) at RT and the reaction mixture was stirred for 4 h. After evaporation of the solvent, the residue was dissolved in acetone, filtered, concentrated, and purified by recrystallization from acetone. Yield: 0.12 g, 44 %; T_{decomp}: 186 °C (DSC, 10 °C min^{-1}); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 9.90$ ppm (s, 2 H); ^{13}C NMR (400 MHz, [D$_6$]DMSO): $\delta = 135.1$, 153.8 ppm; IR (KBr): $\tilde{\nu} = 3090$, 2145, 1500, 1417, 1180, 1095 cm^{-1}; MS (ESI): *m*/*z*: 247 [*M*+H]$^+$.

3,3′,5-Tri(azido)-4,4′-azo-1,2,4-triazole (14): NaN_3 (0.45 g, 8 mmol) was added to a solution of compound **10** (0.53 g, 2 mmol) in DMF (15 mL) at RT and the reaction mixture was stirred for 12 h. After evaporation of the solvent, the residue was dissolved in acetone, filtered, concentrated, and purified by recrystallization from acetone/petroleum ether, as previously reported by our group.[28]

3,3′,5,5′-Tetra(azido)-4,4′-azo-1,2,4-triazole (15): NaN_3 (0.29 g, 4.5 mmol) was added to a solution of compound **11** (0.30 g, 1.0 mmol) in DMF

(15 mL) at RT and the reaction mixture was stirred for 2 h. The mixture was poured into water, stirred for a further 1 h, and then filtered. The residue was dissolved in CH_2Cl_2 and purified by recrystallization from CH_2Cl_2/petroleum ether. Yield: 0.13 g, 40 %; T_{decomp}: 136 °C (DSC, 10 °C min^{-1}); ^{13}C NMR (400 MHz, CD_3COCD_3): $\delta = 154.3$ ppm; MS (ESI): m/z: 301 $[M{-}N_2{+}H]^+$.

3,3′-Di(iminotriphenylphosphorane)-4,4′-azo-1,2,4-triazole (17): NaN_3 (0.55 g, 8.5 mmol) was added to a solution of compound **9** (0.93 g, 4 mmol) in DMF (30 mL) at RT and the reaction mixture was stirred for 4 h. PPh_3 (2.36 g, 9 mmol) was added to the solution and the reaction mixture was stirred for a further 2 h before pouring into water. After filtration and washing with acetone, the residue was purified by recrystallization from $CHCl_3$/MeOH to obtain compound **17**. Yield: 2.37 g, 83 %; m.p. 255 °C; IR (KBr): $\tilde{\nu} = 3050$, 1578, 1534, 1482, 1437, 1339, 1173, 1112, 972, 721, 690 cm^{-1}; MS (FAB+): m/z: 715 $[M{+}H]^+$; elemental analysis calcd (%) for $C_{40}H_{32}N_{10}P_2$: C 67.23, H 4.48, N 19.27; found: C 66.96, H 4.63, N 19.27.

3,3′,5-Tri(iminotriphenylphosphorane)-4,4′-azo-1,2,4-triazole (18): NaN_3 (0.85 g, 13 mmol) was added to a solution of compound **10** (1.07 g, 4 mmol) in DMF (30 mL) at RT and the reaction mixture was stirred for 4 h. PPh_3 (3.67 g, 14 mmol) was added to the solution and the reaction mixture was stirred for a further 2 h before pouring into water. After filtration and washing with acetone, the residue was purified by recrystallization from $CHCl_3$/MeOH to obtain compound **18**. Yield: 3.09 g, 78 %; m.p. 160 °C; IR (KBr): $\tilde{\nu} = 3055$, 1580, 1530, 1480, 1438, 1331, 1112, 925, 720, 692 cm^{-1}; MS(MALDI-TOF): m/z: 990 $[M{+}H]^+$; elemental analysis calcd (%) for $C_{58}H_{46}N_{11}P_3$: C 70.37, H 4.65, N 15.57; found: C 69.98, H 4.89, N 15.46.

3,3′,5,5′-Tetra(iminotriphenylphosphorane)-4,4′-azo-1,2,4-triazole (19): NaN_3 (1.11 g, 17 mmol) was added to a solution of compound **11** (1.21 g, 4 mmol) in DMF (30 mL) at RT and the reaction mixture was stirred for 1 h. PPh_3 (4.45 g, 17 mmol) was added to the solution and the reaction mixture was stirred for a further 2 h before pouring into water. After filtration and washing with acetone, the residue was purified by recrystallization from $CHCl_3$/MeOH to obtain compound **19**. Yield: 2.53 g, 50 %; m.p. 210 °C; IR (KBr): $\tilde{\nu} = 3054$, 1580, 1575, 1520, 1483, 1436, 1336, 1111, 942, 718 cm^{-1}; MS (FAB+): m/z: 1265 $[M{+}H]^+$; elemental analysis calcd (%) for $C_{76}H_{60}N_{12}P_4$: C 73.19, H 4.82, N 13.29; found: C 73.07, H 4.89, N 13.46.

General method for the preparation of compounds 16–19 from compounds 12–15: Triphenylphosphine (PPh_3) was added to a solution of the corresponding azido derivatives (**12**-**15**) in acetone with molar ratios of 1:1.5, 1:2.5, 1:3.5, and 1:4.5, respectively. The reaction mixture was stirred for 4 h at RT. After filtration, the residue was purified by recrystallization from $CHCl_3$/MeOH to obtain compounds **16**–**19** (Yield: 72 % for compounds **16**, 65 % for compounds **17**, 60 % for compounds **18**, and 20 % for compounds **19**).

3-Amino-4,4′-azo-1,2,4-triazole (20): Compound **16** (1.75 g, 4 mmol) was added to a stirring solution of 1 M HCl (60 mL) and then the mixture was heated at 50 °C for 3 h, until no starting material remained (by TLC). The precipitate was filtered and washed with $CHCl_3$/MeOH to obtain compound **20**. Yield: 0.54 g, 75 %; T_{decomp}: 248 °C (DSC, 10 °C min^{-1}); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 9.56$ (s, 2 H), 9.08 (s, 1 H), 8.77 ppm (s, 2 H); ^{13}C NMR (400 MHz, [D$_6$]DMSO): $\delta = 131.0$, 138.3, 149.4 ppm; IR (KBr): $\tilde{\nu} = 3039$, 2960, 1703, 1503, 1470, 1361, 1222, 1175, 1062, 889, 617 cm^{-1}; MS (EI): m/z: 179 $[M]^+$; elemental analysis calcd (%) for $C_4H_5N_9$: C 26.82, H 2.81, N 70.37; found: C 26.80, H 2.81, N 70.39.

3,3′-Di(amino)-4,4′-azo-1,2,4-triazole (21): Compound **17** (2.86 g, 4 mmol) was added to a stirring solution of 1 M HCl (80 mL) and then the mixture was heated at 50 °C for 3 h, until no starting material remained (TLC). The precipitate was filtered and washed with $CHCl_3$/MeOH to obtain compound **21**. Yield: 0.59 g, 75 %; T_{decomp}: 245 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 8.55$ (s, 4 H), 9.11 ppm (s, 2 H); ^{13}C NMR (400 MHz, [D$_6$]DMSO): $\delta = 131.2$, 148.8 ppm; IR (KBr): $\tilde{\nu} = 3292$, 3209, 3144, 3123, 2957, 1685, 1642, 1531, 1462, 1328, 1224, 1117, 1062, 967 cm^{-1}. MS (EI): m/z: 194 $[M]^+$; elemental analysis calcd (%) for $C_4H_6N_{10}$: C 24.74, H 3.09, N 72.16; found: C 24.54, H 3.30, N 71.26.

3,3′,5-Tri(amino)-4,4′-azo-1,2,4-triazole (22): Compound **18** (3.96 g, 4 mmol) was added to a stirring solution of 1 M HCl (100 mL) and then the mixture was heated at 50 °C, until no starting material remained (TLC). The precipitate was filtered and washed with $CHCl_3$/MeOH to obtain compound **22**. Yield: 0.50 g, 60 %; T_{decomp}: 246 °C; ^{13}C NMR (100 MHz, D_2O): $\delta = 131.2$, 145.9, 148.7 ppm; IR (KBr): $\tilde{\nu} = 3318$, 3249, 3167, 3129, 2963, 2796, 2723, 1515, 1456, 1365, 1265, 1140 cm^{-1}; MS (ESI): m/z: 210 $[M{+}H]^+$; elemental analysis calcd (%) for $C_4H_7N_{11}$: C 22.97, H 3.35, N 73.68; found: C 23.15, H 3.30, N 73.43.

3,3′,5,5′-Tetra(amino)-4,4′-azo-1,2,4-triazole (23): Compound **19** (5.06 g, 4 mmol) was added to stirring solution of 1 M HCl (120 mL) and then the mixture was heated to 50 °C, until no starting material remained (TLC). The precipitate was filtered and washed with $CHCl_3$/MeOH to obtain compound **23**. Yield: 0.49 g, 45 %; T_{decomp}: 290 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 9.66$ ppm (s); ^{13}C NMR (400 MHz, D_2O): $\delta = 145.2$ ppm; IR (KBr): $\tilde{\nu} = 3462$, 3295, 3265, 3174, 3112, 2943, 2658, 2742, 2695, 1515, 1456, 1365, 1265, 1140 cm^{-1}; MS (ESI): m/z: 225 $[M{+}H]^+$; elemental analysis calcd (%) for $C_4H_8N_{12}$: C 21.43, H 3.57, N 75.00; found: C 21.21, H 3.40, N 75.18.

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