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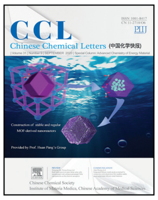

Review

# Energetic materials based on poly furazan and furoxan structures

Junlin Zhang[a,b], Jing Zhou[a], Fuqiang Bi[a], Bozhou Wang[a,*]

[a] *Xi'an Modern Chemistry Research Institute, Xi'an 710065, China*
[b] *Department of Chemistry, Technische Universität München, Garching bei München 85748, Germany*

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ABSTRACT

Furazan and furoxan represent fascinating explosophoric units with intriguing structures and unique properties. Compared with other nitrogen-rich heterocycles, most poly furazan and furoxan-based heterocycles demonstrate superior energetic performances due to the higher enthalpy of formation and density levels. A large variety of advanced energetic materials have been achieved based on the combination of furazan and furoxan moieties with different kinds of linkers and this review provides an overview of the development of energetic poly furazan and furoxan structures during the past decades, with their physical properties and detonation characteristics summarized and compared with traditional energetic materials. Various synthetic strategies towards these compact energetic structures are highlighted by covering the most important cyclization methods for construction of the hetercyclic scaffolds and the following modifications such as nitrations and oxidations. Given the synthetic availabilities and outstanding properties, energetic materials based on poly furazan and furoxan structures are undoubtedly listed as a promising candidate for the development of new-generation explosives, propellants and pyrotechnics.

## 1. Introduction

Energetic materials, a class of energetically unstable material that can release high amount of the stored chemical energy, have contributed enormously to the progress and prosperity of mankind [1–4]. Since black powder, the first known explosive discovered by ancient Chinese in the seventh century [5,6], pursuing new structures to achieve better physicochemical properties, thermodynamic behaviours and detonation performances is always regarded as the most important goal in the research of energetic materials [7–29]. Most traditional energetic materials, such as 2,4,6-trinitrotoluene (TNT) [30–32], 1,3,5-trinitro-1,3,5-triazinane (RDX) [33–35], 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) [36–38] as well as the energetic powerhouse 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) [39–43], are based on the aromatic hydrocarbon or cycloaliphatic amine scaffolds bearing explosophoric groups like nitro (-$NO_2$) and nitramine (-$NNO_2$) [44–48]. Meanwhile, new energetic materials based on nitrogen-rich heterocycles like pyrazole, imidazole, triazole, tetrazole, and their related derivatives, have received a tremendous thrust in recent years [49–62]. From an energetic standpoint, distinct advantages are achieved from nitrogen-rich heterocycles, including enhancement of the densities, increasement of the gas production and improvement of the oxygen balance [63–66]. Moreover, the large numbers of N—N and C—N bonds also contribute to a positive amount to the overall heats of formation [67].

Both furazan and its *N*-oxide derivative furoxan (Fig. 1) are $\pi$-excessive heterocycles with six electrons distributed over five atoms, however, the $\pi$-electron density on the heteroatoms in furazan and furoxan is so great that the values for left C-atoms are smaller than normal ones, which has significant influence on their reactivities [68]. Compared with furoxan, furazan is much more stable when treated with nucleophiles, possibly because the heterocyclic structure of furoxan exists in the forms of 2-oxide and 5-oxide tautomer with an interconversion mechanism believed to go through an active *cis*-1,2-dinitroethene intermediate. Dehydrative cyclization of 1,2-dioximes and oxidative cyclization of 1,2-dioximes are the most accessible approaches for the synthesis of furazan and furoxan structures. Besides that, Boulton-Katritzky rearrangement from some other heterocycles is also applied in the synthesis of furazan while dimerization of nitrile oxides and dehydration of a-nitroketoximes are alternative methods for the synthesis of furoxan. Under reductive conditions, furoxan can be converted to furazan, in contrast, furazan is extremely difficult to be oxidized to its *N*-oxide derivative [69,70].

It is noteworthy that the furazan and furoxan themselves are explosophoric structures. With high positive heats of formation of

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[*] Corresponding author.
*E-mail address:* wbz600@163.com (B. Wang).

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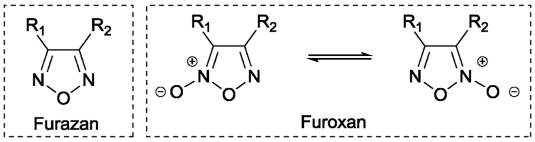


**Fig. 1.** Furazan and furoxan structures.

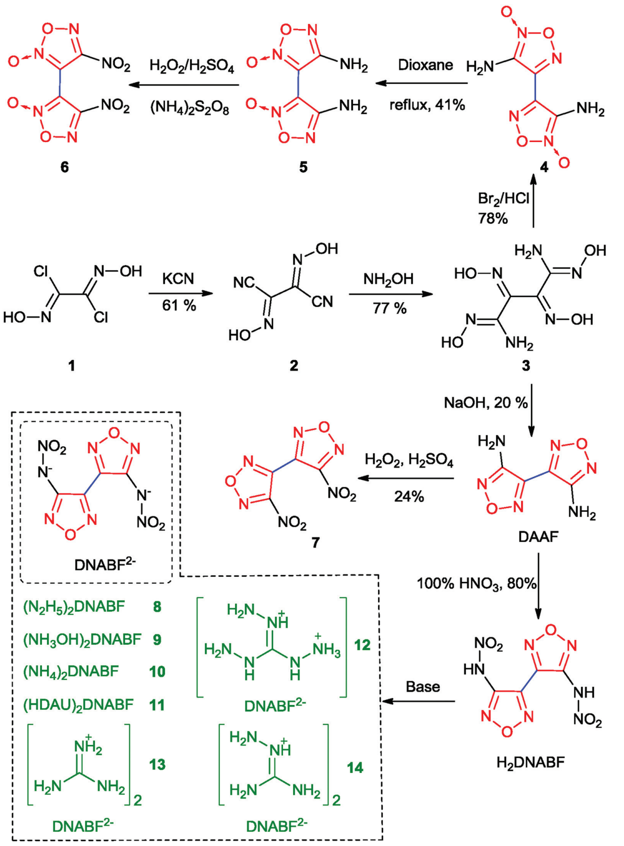
196.8 and 198.5 kJ/mol, nitrogen and oxygen contents of 62.8% and 69.7%, respectively, furazan and furoxan are important energetic units which have been widely applied in the synthesis of advanced energetic materials. Compared with other nitrogen-rich heterocycles, most poly furazan and furoxan based-heterocycles demonstrate superior energetic properties and better modifiabilities, making them as a most successful class of structures for design and synthesis of energetic materials. A large variety of mono-furazan or furoxan structures have been developed and applied, however, most of these structures suffer poor stabilities and limited varieties. In contrast, energetic materials based on poly furazan and furoxan structures have demonstrated fascinating properties including good thermal stabilities, low mechanical sensitivities and excellent detonation performances.

The present review is focus on energetic materials with high energy density levels based on poly furazan and furoxan structures during the past decades. Furazan and furoxan moieties are linked directly *via* carbon-carbon bonds or through linkers constructed by heteroatoms as oxygen and nitrogen, or in combined manners. Various synthetic strategies towards these compact energetic structures are highlighted by covering the most important synthetic cyclization methods for the heterocyclic scaffolds and the following modifications such as nitrations and oxidations, meanwhile, the physical and detonation properties, such as density (d), heat of formation ($\Delta H_f$), detonation pressure (P), detonation velocity (D), impact sensitivity (IS), friction sensitivity (FS) and thermal behaviors, are summarized and compared with some traditional energetic materials.

## 2. Poly furazan and furoxan structures linked by carbon-carbon bonds

### *2.1. Bi-furazan/furoxanyl structures*

3,3'-Diamino-4,4'-bifurazan (DAAF) [71] and 3,3'-diamino-4,4'-bisfuroxan [72] are most readily accessible precursors for many poly furazan and furoxan energetic structures. DAAF is available from dichloroglyoxime through dicyanoglyoxime and tetraoximodiaminobutane with a low yield cyclization process but can also be prepared in a one-pot synthesis from isocyanilic acid [73–75]. In contrast, the structure of 4,4'-diamino-3,3'-bisfuroxan is afforded from the intermediate tetraoximodiaminobutane by treating with $Br_2$/HCl mixture [72]. Although DAAF can be oxidised by peroxytrifluoroacetic acid [76] or $H_2O_2$/$H_2SO_4$ [73] to give 3,3'-dinitro-4,4'-bifurazan, similar oxidation of 3,3'-diamino-4,4'-bisfuroxan has been proved to be much more difficult with 3,3'-dinitro-4,4'-bisfuroxan crystals only obtained from a yellowish reaction mass in low yield due to the electron deficient properties of furoxan moieties [72]. Despite all that, 3,3'-dinitro-4,4'-bisfuroxan is still recognized as one of the most powerful energetic structures obtained, with an impressive high density of 2.007 g/cm$^3$ (Scheme 1). Based on the structure of DAAF, 3,3'-dinitramino-4,4'-bifurazan ($H_2$DNABF) and its metal and nitrogen-rich salts are prepared and experiment results show salt formation successfully lead to an increase of the thermal stability up to 280 °C [73] (Table 1).



**Scheme 1.** Synthesis of 3,3'-dinitro-4,4'-bifurazan, 3,3'-dinitramino-4,4'-bifurazan and 3,3'-dinitro-4,4'-bisfuroxan.

Bifuroxanyl systems containing the 3-nitrobifuroxanyl core are established through a novel one-pot transformation with a proposed mechanism which includes a cascade of the following one-pot reactions: acylation of dinitromethane sodium salt (NaDNM) with (chlorohydroxamoyl)furoxan **15** leading to the formation of 2-furoxanyl-2-oximino-1,1-dinitroethane sodium salt **16**, nitrosation of the dinitromethyl anion derived from this salt with $NaNO_2$/AcOH/AcONa mixture to afford a dinitro nitroso derivative with simultaneous formation of the sodium salt of the oxime fragment (intermediate **17**), and intramolecular attack of the oxime anion in this intermediate on the nitroso-group nitrogen atom, followed by $NaNO_2$ elimination giving the 3-nitrofuroxanyl moiety [77]. The synthetic approach has been successfully applied in the construction of impressive energetic bifuroxanyl structures bearing nitro or azido groups (Scheme 2).

Treatment of 4-aminofurazan-3-carbohydroximamide with $NaNO_2$/HCl followed by the addition of KCN affords a nitrile derivative **19**. 1-Amino-2-(4-aminofurazan-3-yl)glyoxime is smoothly obtained by treating compound **19** with hydroxylamine hydrochloride and $NaHCO_3$ in boiling aqueous methanol, which can be converted to the structure of 3-amino-4-(4-amino-1,2,5-oxadiaz-ol-3-yl)-1,2,5-oxadiazole-2-oxide *via* an oxidative cyclization process of the glyoxime fragment into a furoxan ring with bromine or $K_3Fe(CN)_6$. This furazan-furoxan diamine structure is completely isomerized into its isomer in boiling dioxane [74], meanwhile, the diamino groups can also be nitrated and further turned into corresponding salts [78] (Scheme 3). From a performance point of view, compound **22** has a high detonation velocity of 9351 m/s and the detonation pressure of **23** is 38.3 GPa, which is only slightly lower than that of HMX, but much higher than that of RDX (Table 2).

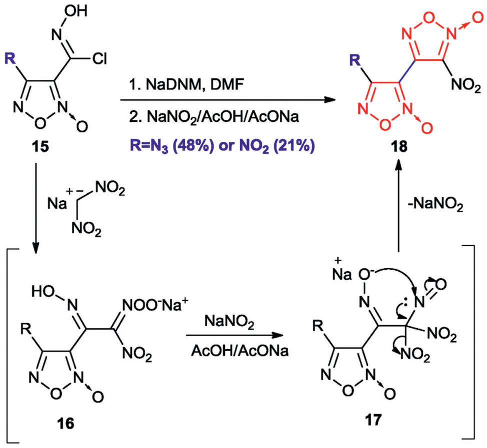
**Table 1**
Physiochemical properties and detonation parameters of $H_2$DNABF and compounds **8-14**.

| | $H_2$DNABF | **8** | **9** | **10** | **11** | **12** | **13** | **14** |
|---|---|---|---|---|---|---|---|---|
| Formula | $C_4H_2N_8O_6$ | $C_4H_{10}N_{12}O_6$ | $C_4H_8N_{10}O_8$ | $C_4H_8N_{10}O_6$ | $C_6H_{14}N_{16}O_8$ | $C_5H_{10}N_{14}O_6$ | $C_6H_{12}N_{14}O_6$ | $C_6H_{14}N_{16}O_6$ |
| Fw [g/mol] | 258.11 | 322.20 | 324.17 | 292.17 | 438.33 | 362.22 | 376.25 | 406.28 |
| IS [J] | 1.5 | 6 | 11 | 10 | 40 | 3 | 40 | 10 |
| FS [N] | 48 | 120 | 288 | 324 | 360 | 360 | 360 | 360 |
| ESD [J][a] | 0.03 | 0.3 | 0.1 | 0.2 | 0.1 | – | – | – |
| $OB_{\langle CO_2\rangle}$ [%] [b] | −18.59 | −34.76 | −19.74 | −32.85 | −40.15 | −39.75 | −51.02 | −51.19 |
| d [g/cm$^3$] | 1.978 (173 K)<br>1.94 (298 K) | 1.812 (173 K)<br>1.78 (298 K) | 1.963 (173 K)<br>1.93 (298 K) | 1.834 (173 K)<br>1.80 (298 K) | 1.830 (100 K)<br>1.78 (298 K) | 1.811 (300 K) | 1.769 (100 K)<br>1.72 (298 K) | 1.680 (173 K)<br>1.649 (298 K) |
| $\Delta H_f$ [kJ/mol] | 526 | 637 | 417 | 306 | 615 | 584 | 323 | 580 |
| $T_{dec.}$ [°C] | 80 | 230 | 141 | 230 | 192 | 203 | 280 | 215 |
| P [GPa] | 40.3 | 35.4 | 42.5 | 33.4 | 33.3 | 33.5 | 27.1 | 26.5 |
| D [m/s] | 9086 | 9058 | 9363 | 8748 | 8848 | 8836 | 8225 | 8228 |
| $V_o$ [L/kg][d] | 646 | 794 | 738 | 759 | 788 | 769 | 769 | 790 |

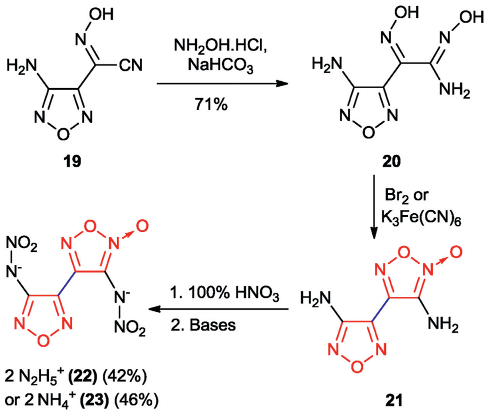
[a] ESD: electrostatic discharge (OZM research).
[b] $OB_{<CO_2>}$: oxygen balance (W = (xO-2yC-1/2 zH)M/1600).
[c] $T_{dec.}$: thermal decomposition temperature.
[d] $V_o$: volume of detonation gases.

### *2.2. Tri-furazan/furoxanyl structures*

Bis(4-nitro-1,2,5-oxadizaol-3-yl)-1,2,5-oxadiazole-*N*-oxide (DNTF) is a poly furazan-furoxan structure with impressive performances [78,79]. With a crystal density of 1.93 g/cm$^3$ and a heat of formation of 657 kJ/mol, energetic performance of DNTF is 168% better than that of trinitrotoluene (TNT), making it a promising candidate for applications in the development of multipurpose energetic formulations, especially in melt-cast explosives since its melting point is as low as 109 °C while the decomposition temperature reaches 292 °C [80–82]. 4-Amino-*N*-hydroxy-1,2,5-oxadiazole-3-carbimidoyl chloride (**24**), prepared from 4-amino-*N*'-hydroxy-1,2,5-oxadiazole-3-carboximidamide (AAOF), is often applied as the synthetic precursor in the synthesis of furazan and furoxan derivatives. The most applied synthetic strategy towards DNTF includes the synthesis of 3,4-diaminofurazanofuroxan (DAFF) followed by the oxidation of amino groups to nitro groups. A similar method involves oxidizing the amino group in **24** to corresponding nitro group, followed by a base catalyzed 1,3-dipolar cycloaddition [83,84]. Silylation of both amino and methyl groups in 3-amino-4-methylfyrazan followed by nitration/nitrosation with an excess of dinitrogen pentoxide in the presence of solid sodium fluoride would also lead to the formation of DNTF in an efficient way [85].



**Scheme 2.** One-pot synthesis of bifuroxanyl structures.



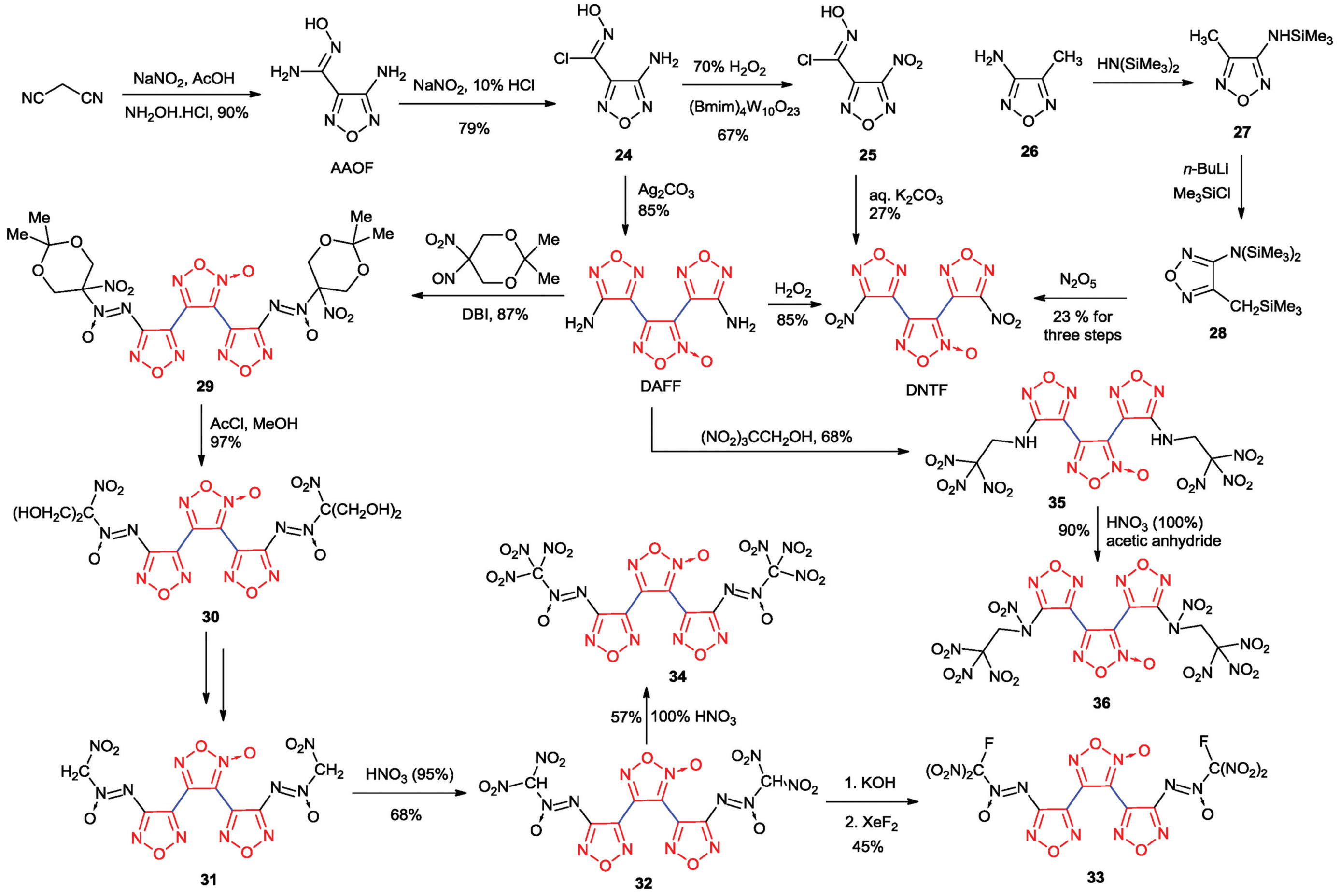
**Scheme 3.** Synthetic study towards energetic bifuroxanyl structures derivatives.

Nitro group has long been in a dominant position as the most important and widely used explosophore [44–48], which is unable to meet the rapid growing requirements of enhancing energy-density levels. In recent years, development of new explosophores to promote the energy-density properties of energetic compounds have been intensively investigated [86–88]. Poly nitroalkyl-ONN groups, designed and constructed *via* the combination of nitro with azo groups, are applied in the synthesis of several new energetic materials and exhibit great abilities in promoting energy-density levels [89,90]. Based on the scaffold structure of DAFF, two promising high energy substances bis(fluoronitromethyl-ONN-azoxyfurazanyl)furoxan and bis(trinitromethyl-ONN-azoxyfurazanyl)furoxan are obtained *via* a sequence of transformations

**Table 2**
Physiochemical properties and detonation parameters of energetic furazan-furoxan derivatives **22** and **23**.

| | **22** | **23** | RDX | HMX |
|---|---|---|---|---|
| d [g/ cm$^3$] | 1.751 | 1.806 | 1.800 | 1.905 |
| D [m/s] | 8836 | 9351 | 8795 | 9144 |
| P [GPa] | 33.9 | 38.3 | 34.9 | 39.2 |
| $\Delta H_f$ [kJ/mol] | 454.8 | 772.6 | 70.3 | 74.8 |
| $T_{Dec.}$ [°C] | 154 | 152 | 204 | 275 |
| IS [J] | 10 | 6 | 7.5 | 7.4 |
| FS [N] | 160 | 120 | 120 | 120 |
| $I_{sp}$ [s][a] | 273 | 285 | 267 | 266 |

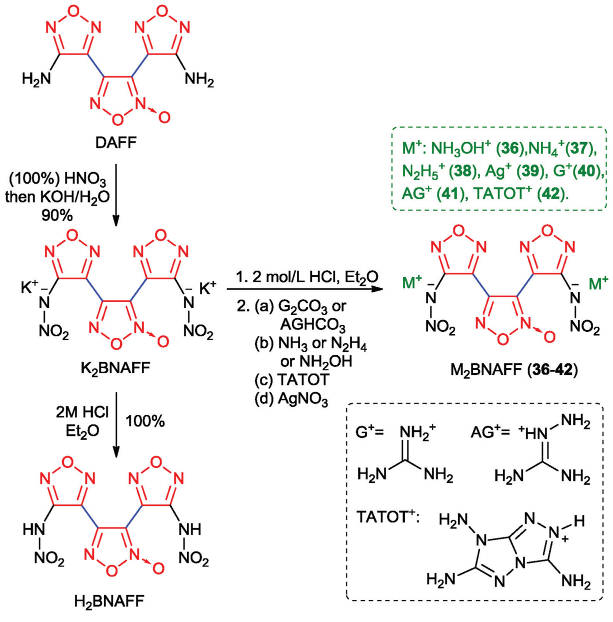
[a] $I_{sp}$: specific impulse.



**Scheme 4.** Synthetic studies towards DNTF and similar energetic structures.

including oxidative coupling, hydrolysis, bromination, reduction, nitration, salification and fluorination (Scheme 4) [91]. Calculation studies show that the detonation properties of DNTF are improved by replacing nitro groups with trinitromethyl-ONN-azoxy and fluoronitromethyl-ONN-azoxy groups, indicating the alternation of more powerful explosophoresis a highly effective approach for promoting the detonation performances of energetic materials. Polynitroalkylamino furazan compounds are also regarded as highly dense and energetic structures. Bis(trinitroethylamino) trifurazanoxide, a novel polynitroalkylamino furazan structure is achieved through Mannich condensation reaction between DAFF with trinitroethanol [92–94] and the N—H moieties can be further nitrated to *N*-nitrated trinitroethylamino derivative [84,95,96].

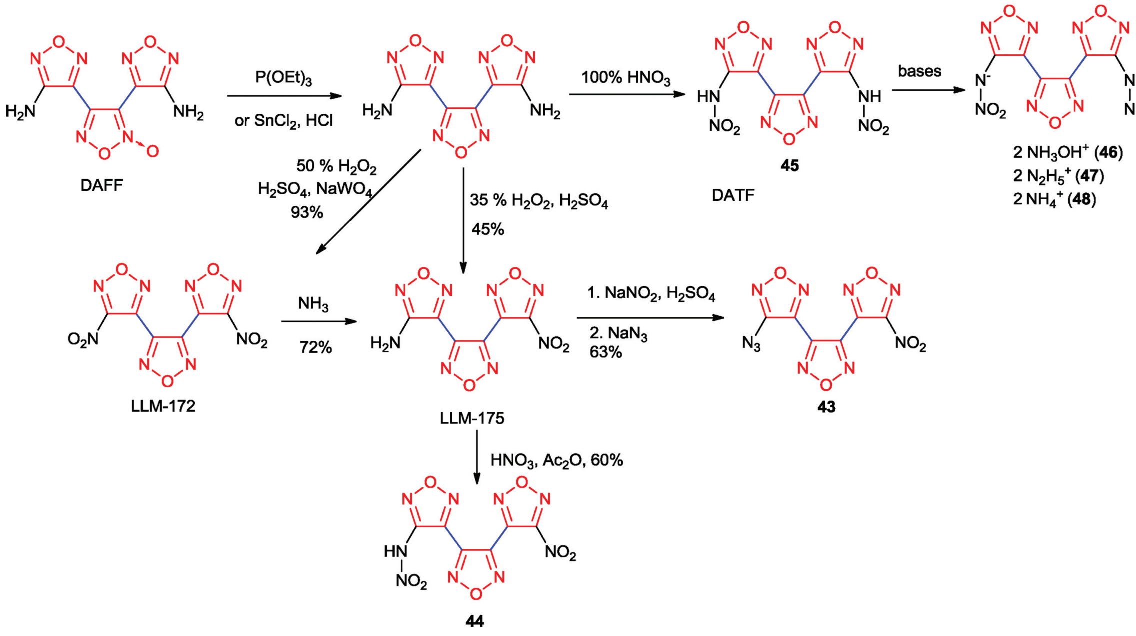
As shown in Scheme 5, nitration of DAFF by 100% $HNO_3$ followed by the treatment with KOH will lead to the formation of a corresponding energetic dipotassium salt of 3,4-bis(4-nitramino-furazan-3-yl)-1,2,5-furoxan ($K_2$BNAFF). The neutral nitramino-furoxan ($H_2$BNAFF), as well as its nitrogen-rich salts (ammonium, guanidinium, aminoguanidinium, hydrazinium and hydroxylammonium salts), are available from $K_2$BNAFF. $H_2$BNAFF is only stable at room temperature with 0.5 equiv. ether as a solvate while the stability of the BNAFF$^{2-}$ anion is greatly improved after forming alkali metal salts or by reacting it with nitrogen-rich bases, leading to the increase of the thermal stability up to 245 °C (Scheme 5). The densities of $H_2$BNAFF and its salts range from 1.53 g/cm$^3$ to 2.07 g/cm$^3$, meanwhile, highly positive heat of formations from 689 kJ/kg to 2239 kJ/kg are achieved, which exceed the value for the heat of formation of RDX (387 kJ/kg). Calculation study shows good detonation parameters, in which the ammonium salt shows the highest calculated detonation velocity (8579 m/s) and detonation pressure (30.5 GPa), whereas the guanidinium salt exhibits the lowest values (8099 m/s and 25.3 GPa) (Table 3) [96,97].



**Scheme 5.** Synthetic study towards $H_2$BNAFF and its salts.

**Table 3**
Physiochemical properties and detonation parameters of $H_2$BNAFF and its salts.

| | $K_2$BNAFF | **36** | **37** | **38** | **40** | **41** |
|---|---|---|---|---|---|---|
| Formula | $C_6K_2N_{10}O_8$ | | $C_6H_8N_{12}O_8$ | $C_6H_{10}N_{14}O_8$ | $C_8H_{12}N_{16}O_8$ | $C_8H_{14}N_{18}O_8$ |
| IS [J] | 3 | 12 | 7 | 8 | 15 | 8 |
| FS [N] | >72 | 180 | 216 | 216 | 360 | 360 |
| $OB_{(CO_2)}$ [%] | −19.12 | 0 | −34.02 | −35.45 | −48.66 | −48.95 |
| $T_{dec}$ [°C] | 245 | 171 | 161 | 170 | 189 | 156 |
| d [g/ $cm^3$] | 2.07 | 1.83 | 1.73 | 1.53 | 1.69 | 1.70 |
| $\Delta H_f$ [kJ/mol] | 689 | 801 | 1635 | 2239 | 1275 | 1650 |
| P [GPa] | 29 | 36 | 30 | 25 | 25 | 26 |
| D [m/s] | 8263 | 9046 | 8579 | 8105 | 8099 | 8364 |



**Scheme 6.** Synthesis of LLM-172, LLM-175 and corresponding salts.

Due to the excellent performances of DNTF, its analogues have been studied comprehensively [98,99]. The structure of DNTF consists both furazan and furoxan moieties. Compared with furazan moiety, the zwitterionic nature of *N*-oxide bond in furoxan moiety tends to increase the crystal densities, oxygen balance as well as the sensitivities [100,101].

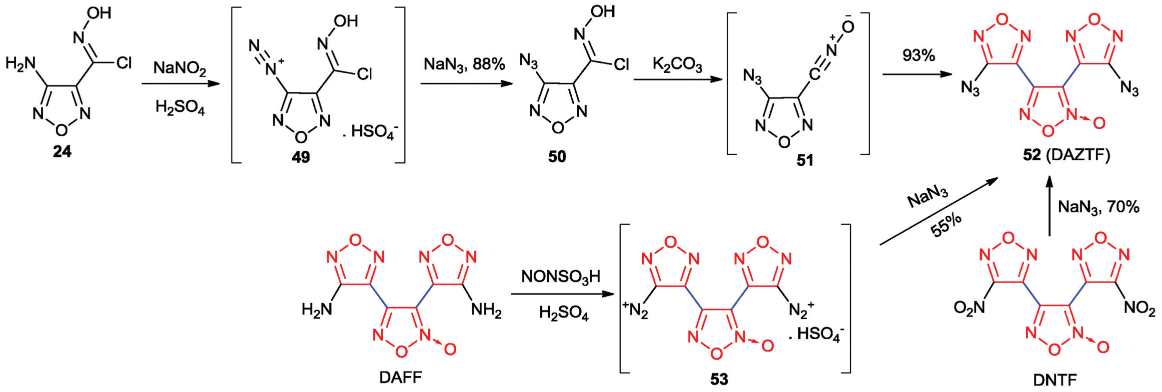
Ideal energetic materials must be insensitive and be capable of withstanding unwanted stimuli such as heat, friction, impact and shock. Despite the excellent detonation performances, the sensitivity of DNTF is unsatisfactory, especially when treated with shock waves [102]. To improve the stability of DNTF, modifications on both nitrofurazan and furoxan structures have been carried out, affording two derivatives of 3,4-bis(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole (LLM-172) [103] and 3-(4-nitro-1,2,5-oxadiazol-3-yl)-4-(4-amino-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole (LLM-175) [104,105].

With a density of 1.83 g/$cm^3$ and a melting point of 84 °C, LLM-172 showed good thermal stability and energetic performance similar to HMX, which is suitable for booster or main-charge energetic material. From structural point of view, the only difference existing between DNTF and LLM-172 is DNTF contains an *N*-oxide moiety, whereas LLM-172 does not. The absence *N*-oxide moiety makes the melting point of LLM-172 significantly lower than that of DNTF, thus shifting the former material further into the melt-castable range. The absence of *N*-oxide functionality not only makes the performance of LLM-172 lower than that of DNTF, but also reduces the sensitivity to ignition stimuli. The synthesis of LLM-172 is based on DAFF's reduction product (DATF) and following complete oxidation [106,107]. Treated LLM-172 with $NH_3$ can lead to the formation of LLM-175, another energetic structure similar with DNTF obtained through oxidation under weaker conditions (Scheme 6). LLM-175 has a density of 1.78 g/$cm^3$ and a melting point of 100 °C. Compared with LLM-172, both the energy-density level and sensitivity level of LLM-175 is lower; in other words, good stability is achieved by sacrificing detonation properties (Table 4) [108,109]. Direct nitration of DATF and treatment with bases will lead to the formation of high densities salts and the amino groups in LLM-175 are suitable for the synthesis of azido or nitramino group substituted DNTF analogs (Scheme 6) [104].

Organic azides are widely applied in the preparation of energetic plasticizers. The introduction of an azido group into an organic

**Table 4**
Physiochemical properties and detonation parameters of DNTF analogs.

| | LLM-172 | LLM-175 | **46** | **47** | **48** |
|---|---|---|---|---|---|
| d [g/ $cm^3$] | 1.83 | 1.78 | 1.79 | 1.76 | 1.65 |
| D [m/s] | 8750 | 8620 | 8979 | 8968 | 8287 |
| P [GPa] | 35 | 33 | 36 | 34 | 27 |
| $\Delta H_f$ [kJ/mol] | 175.3 | 160.2 | 810.2 | 1017.7 | 503.0 |
| $T_{dec}$ [°C] | 293 | 274 | 179 | 231 | 180 |
| IS [J][f] | >25 | – | 8 | 12 | 25 |
| FS [N][g] | 19.2 | 36 | 280 | 270 | 256 |

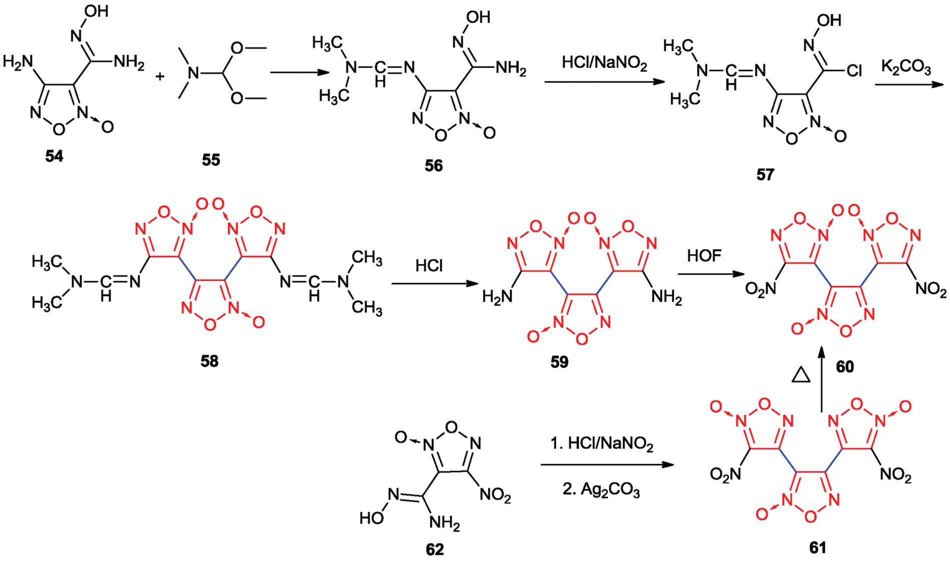


**Scheme 7.** Introduction of azido group into DAFF scaffold.

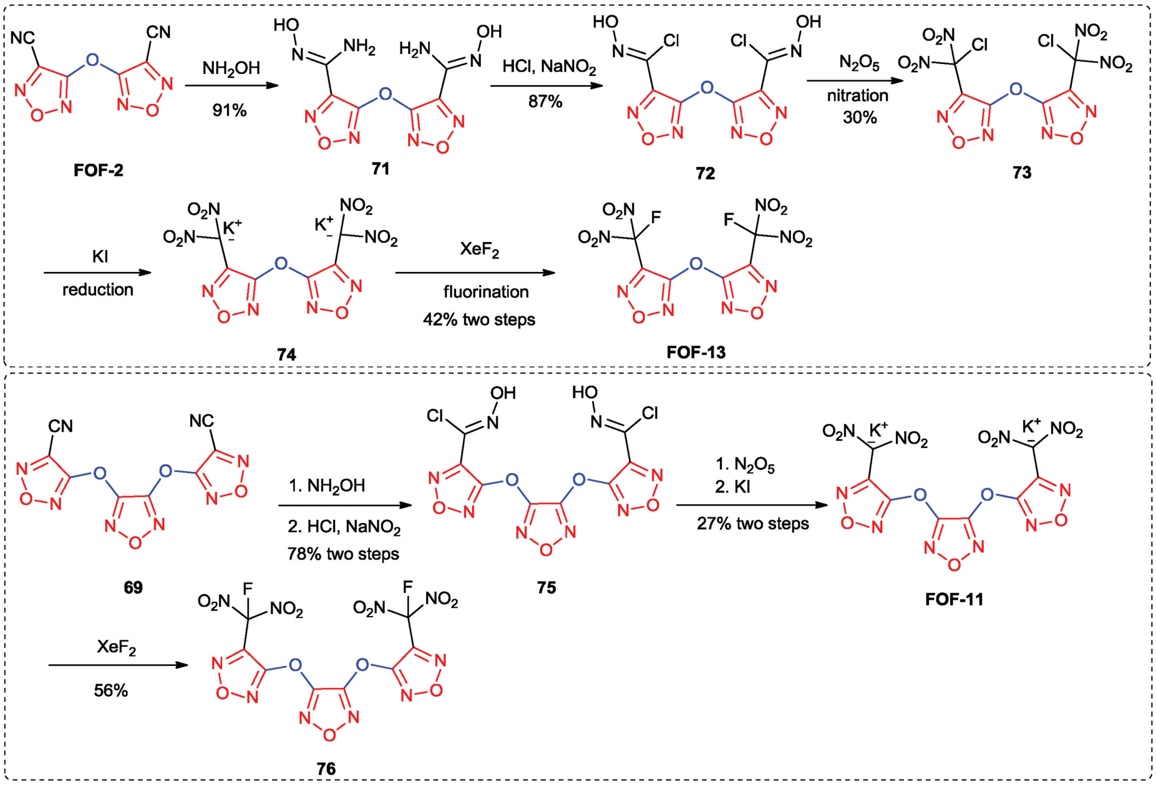
molecule will increase its energy by ~355 kJ/mol, therefore the presence of azido group in energetic compounds is clearly favorable on thermodynamic grounds [110]. Starting from DNTF, azido groups are introduced to replace the nitro groups *via* nucleophilic aromatic substitution, affording a new designed energetic structure of 3,4-bis(4-azidofurazan-3-yl)furoxan (DAZTF) [111]. Dimerization of 4-azidofurazan-3-carbonitrile oxide generated *in situ* from the oxime chloride compound (**50**) [112] or diazotization of the DAFF followed by azidation will also lead to the formation of DAZTF (Scheme 7) [113]. Compared to DNTF, DAZTF shows higher sensitivity to mechanical impact since azido group itself is more sensitive to various mechanical stimulus than nitro group, meanwhile, the replacement of nitro groups with azido groups also results in a dramatic decrease in the packing densities of the molecules and, consequently, a decrease in the density of the single crystal and the detonation velocity. Nevertheless, due to the low melting point (51–52 °C) and high thermal stability, DAZTF still attracts great interest for formulation of fusible explosives.

Calculation results show that density and detonation velocity will increase approximately 0.1 g/cm$^3$ and 700 m/s by replacing a furazan ring with a furoxan ring in LLM-172 [114]. Based on this, studies on replacing of all the furazan rings in LLM-172 by furoxan rings are carried out intensively to improve the detonation performances. Trifuroxan moieties connected with C—C bonds will lead to the formation of 3,4-bis(3-nitrofuroxan-4-yl)furoxan isomers and different *N*-oxide orientations of the furoxan moieties in the isomers result in great differences of their properties. When all the *N*-oxide towards to the outer sides, the trifuroxan system can achieve superior density level (1.98 g/cm$^3$), detonation velocity (9867 m/s) and detonation pressure (45 GPa) to those of a similar trifuroxan system with all the *N*-oxide towards to the inner sides (d = 1.91 g/cm$^3$, D = 9503 m/s and P = 41 GPa) [115]. Starting from 3-hydroximoyl-4-aminofuroxan, amino-protection [116] is needed first followed by the diazotization and base-catalyzed 1,3-dipolar cycloaddition to achieve the synthesis of trifuroxan system. Alternatively, diazotization-cycloaddition process from 3-nitro-4-aminoximidofuoxan will also afford the trifuroxan system. (Scheme 8).

Benzofuroxan structures are generally far more stable than furoxan structures and most synthetic methods towards benzofuroxan moieties involve a heating process of ortho-nitroarylazides [117–119]. Benzotrifuroxan (BTF) is a traditional famous explosive that does not contain any hydrogen and the synthesis of BTF is achieved by 1,3,5-trichloro-2,4,6-trinitrobenzene (or 1,3,5-trifluoro-2,4,6-trinitrobenzene) reacting with sodium azide [120]. Moreover, sulfur can be used as a low-cost and selective reducing agent for the reduction of benzofuroxan moiety in BTF to benzofurazan moiety (Scheme 9) [121].



**Scheme 8.** Synthetic approach towards trifuroxan system.



**Scheme 9.** Synthesis of BTF and the reduction of benzofuroxans.

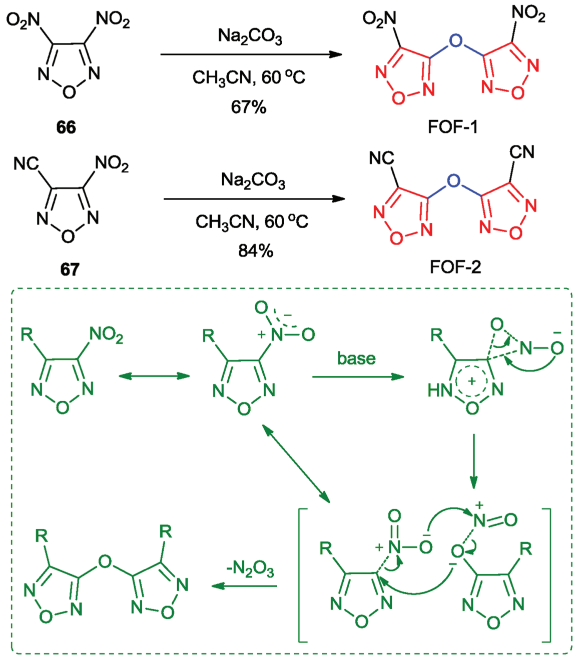
## 3. Poly furazan and furoxan structures linked by oxygen and nitrogen atoms

### *3.1. Structures linked by oxygen atoms*

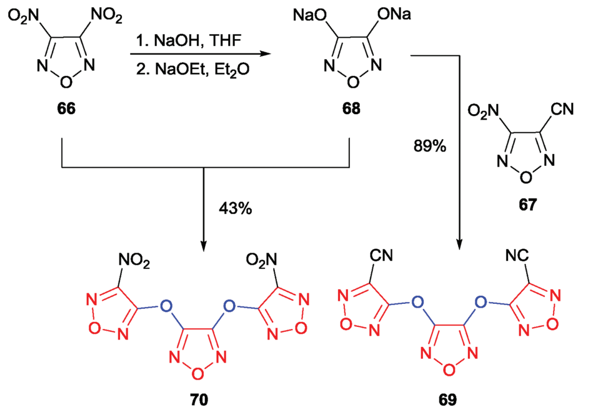
Poly furazan and furoxan structures linked through oxygen, also called furazanyl ethers, are popular building blocks for the preparation of high-energy materials owing to their high standard enthalpy of formation, high energy density, good thermal stability and low melting point [122,123]. Symmetrical difurazanyl ethers, such as 3,3'-dinitrodifurazan ether (FOF-1) and 3,3'-dicyanodifurazan ether (FOF-2), are achieved from nitrofurazans and the ready availability of the starting nitrofurazans make this straightforward approach highly practical [124–128]. Possible mechanism of these transformations is through an intermediate nitrite ester *via* base-promoted intramolecular nitro-nitrite rearrangement. Although cyano group is not ideal explosophore due to the low energetic properties, its derivative explosophore like fluorodinitromethyl group, exhibits excellent energetic performances (Scheme 10) [129].

Starting from dinitrofurazan, symmetrical dinitro-trifurazanyl diether is synthesized through hydrolysis, neutralization and substitution reactions. Different with the symmetrical difurazanyl ether, sodium salt of 3,4-diol-furazan needs to be prepared first followed by the addition of nitrofurazan to form the oxygen-bridges in corresponding symmetrical trifurazanyl diethers. A similar transformation is developed by mixing the sodium salt of 3,4-diol-furazan and 3-cyano-4-nitrofurazan, leading to symmetrical dicyano-trifurazanyl diether (Scheme 11) [130].

As a newly developed explosophore, fluorodinitromethyl group has been widely applied for the design of new energetic materials [131–133]. 3,3-Bis(fluorodinitromethyl)difurazanyl ether (**FOF-13**) is an energetic structure achieved based on the structure of **FOF-2** and its synthetic route involves nitration of 3,3'-bis(chlorohydroxyminomethyl)difurazanyl ether, reduction of 3,3-bis(chlorodinitromethyl)difurazanyl ether and fluorination of potassium salt of 3,3'-bis(dinitromethyl)difurazanyl ether [129,134]. Impressively, **FOF-13** exhibits excellent physicochemical and detonation properties, including high density (1.97 g/cm$^3$), good thermal stability ($T_{dec}$ > 270 °C), reasonable mechanical sensitivity (IS = 14 J) and high detonation velocity (8497 m/s).



**Scheme 10.** Synthesis of symmetrical difurazanyl ethers.



**Scheme 11.** Synthesis of symmetrical trifurazanyl ether.

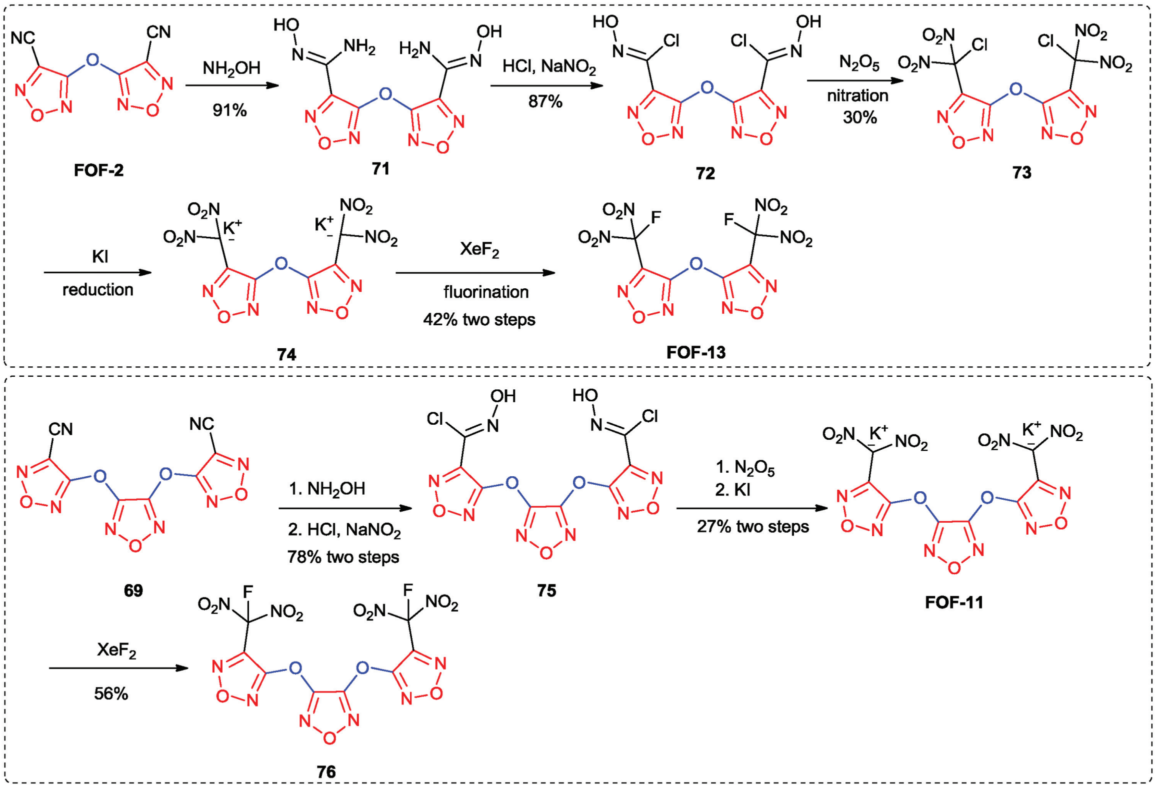
Another furazanyl ether with fluorodinitromethyl groups, 3,4-bis(fluorodinitromethylfurazan-4-oxy)furazan (**FOF-11**), is prepared through similar transformations, leading to good energetic properties (d = 1.88 g/cm$^3$, D = 8318 m/s, P = 32 GPa and IS = 11 J) [135]. These outstanding properties make both **FOF-13** and **FOF-11** promising high-energy plasticizers for solid propellants in rockets (Scheme 12).

Besides fluorodinitromethyl group, other intensively investigated explosophores such as fluoronitromethyl-ONN-azoxy and nitro-NNO-azoxy, are also introduced into the difurazanyl ether scaffolds. Starting from 3-amino-4-nitrofurazan and applying similar procedures in the synthesis of fluoronitromethyl-ONN-azoxy group in DNTF derivatives, 3-(fluorodinitromethyl-ONN-azoxy)-4-nitrofurazan is achieved and further treatment with weak bases in anhydrous media will lead to the formation of corresponding difurazanyl ether derivative [136]. In contrast, bis-3,3'-(nitro-NNO-azoxy)-difurazanyl ether is obtained through $N_2O_5$ oxidation of 3-amino-4-(*tert*-butyl-NNO-azoxy)-furazan followed by etherification and nitrolysis (Scheme 13) [137].

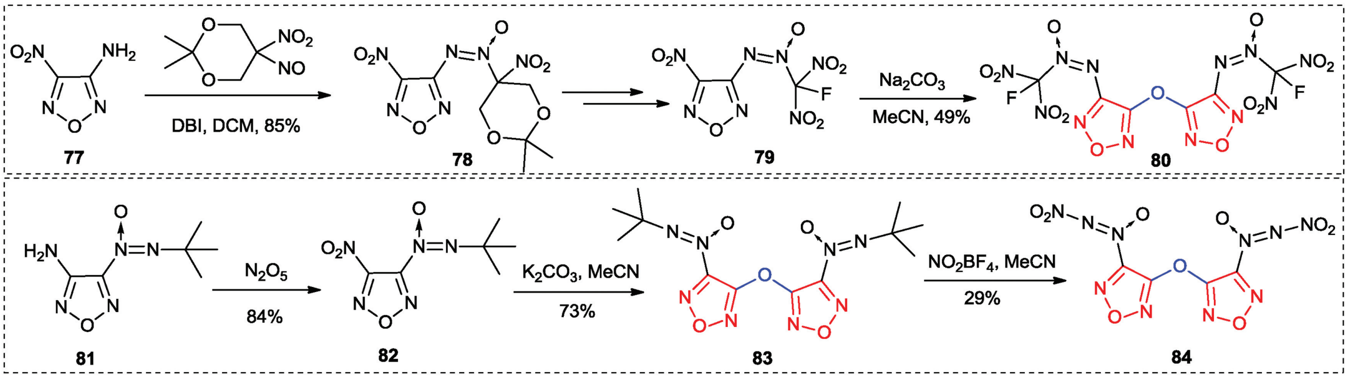
### *3.2. Structures linked by nitrogen atoms*

4,8-Dinitraminodifurazano[3,4-b,e]pyrazine, a nitrogen linked cyclic difurazan structure with good detonation performances (D = 9320 m/s, P = 40.4 GPa) can be synthesized from 4,8-dihydrodifurazano[3,4-b,e]pyrazine (DFP) through ammoniation and nitration process [138,139]. The compound has also been converted to its potassium-based energetic metal-organic framework (E-MOF) by treating with KOH [140,141]. The E-MOF structure exhibits high crystal density (2.114 g/cm$^3$), high thermal stability ($T_{dec}$ = 292 °C), high detonation velocity (9660 m/s), high impact and friction sensitivities (2 J and 1 N, respectively), making it a potential high-performing primary explosive (Table 5). *N*-Nitration of DFP is carried out with $HNO_3/P_2O_5$ nitration, leading to the formation of a mixture product of 4-nitro-8-nitroso-4*H*,8*H*-bis[1,2,5]oxadiazolo[3,4-b:3′,4′-]pyrazine and 4,8-dinitro-4*H*,8*H*-bis[1,2,5]oxadiazolo[3,4-b:3′,4′-e]pyrazine (Scheme 14) [138].

A novel energetic liquid, 5-(4-nitro-1,2,5-oxadiazol-3-yl)-5*H*-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazolium inner salt (NOTO), which contains 50% by mass of nitrogen, was obtained through a five-step synthetic route starting from azidation of 4,4′-diamino-3,3'-azoxyfurazan (DAAF). Heating the diazide in acetonitrile induces cyclization to the triazole, followed by reduction and oxidation of the remaining azide group. NOTO is also available through a cyclization reaction in the presence of diacetoxyliodobenzene followed by the oxidation with Caro's acid (Scheme 15) [142, 143].



**Scheme 12.** Synthesis of difurazanyl ethers with fluorodinitromethyl groups.



**Scheme 13.** Synthesis of difurazanyl ethers with fluoronitromethyl-ONN-azoxy and nitro-NNO-azoxy groups.

**Table 5**
Physiochemical properties and detonation parameters of 4,8-dinitraminodifurazano[3,4-b,e]pyrazine and related energetic salts.

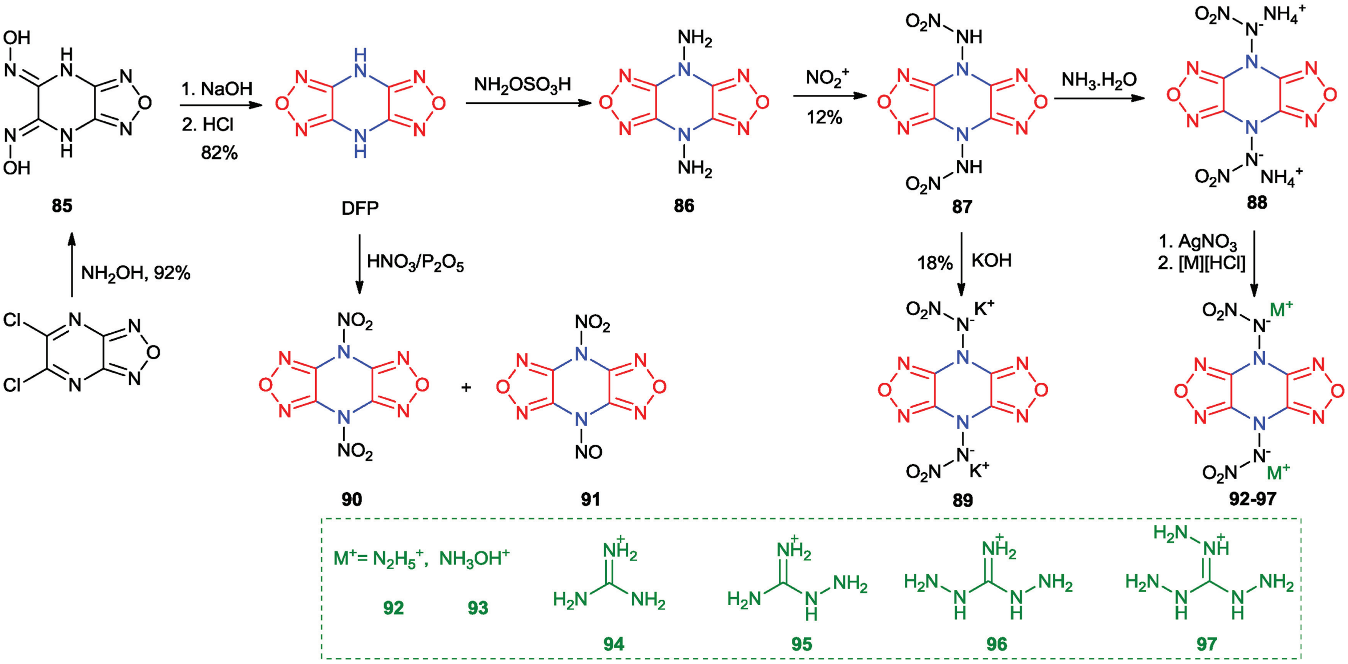
| | 88 | 92 | 93 | 94 | 95 | 96 | 97 |
|---|---|---|---|---|---|---|---|
| d [g/cm$^3$] | 1.75 | 1.78 | 1.79 | 1.61 | 1.63 | 1.71 | 1.70 |
| D [m/s] | 8921 | 9378 | 9156 | 8135 | 8509 | 9166 | 9413 |
| P [GPa] | 32 | 36 | 36 | 24 | 26 | 31 | 33 |
| $\Delta H_f$ [kJ/mol] | 558.6 | 882.8 | 680.0 | 607.0 | 828.0 | 1045.5 | 1380.5 |
| $T_{dec}$ [°C] | 208 | 189 | 155 | 232 | 190 | 187 | 207 |
| IS [J] | 2 | 1 | 1 | 8 | 10 | 8 | 3 |
| FS [N] | 42 | 24 | 28 | 120 | 112 | 108 | 54 |

## 4. Poly furazan and furoxan structures linked by azo and azoxy bridges

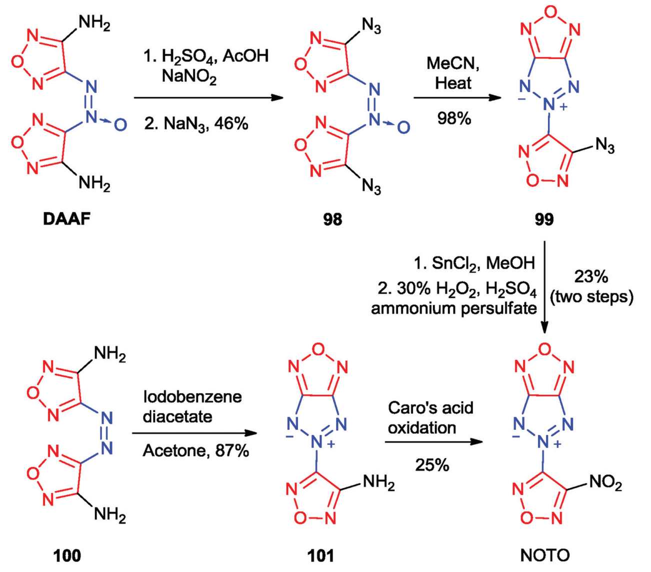
### 4.1. Azo/azoxy bridges constructed through chemical reagents

Azo and azoxy groups are ideal linkers that can give rise to additional energetic properties due to their high nitrogen and oxygen content. With introduction of azo and azoxy moieties, the energy-density level will be greatly improved [144]. During the past decades, azo and azoxy groups are widely applied as linkers in the design of poly furazan and furoxan structures and have played an important role in achieving superior energetic performance [145].

Most azo and azoxy groups in energetic structures are constructed under oxidation conditions and the selection of oxidants often play vital role in the transformations [146–148]. The amino groups in diamino furazan can easily be converted to azo and azoxy groups by treating with different oxidants like $KMnO_4$ and oxone, leading to 4,4'-bis(nitramino)azofurazan (DAAzF) and 4,4'-bis(nitramino) azoxyfurazan (DAAF), respectively [149–152]. When the mixture of 30% aqueous hydrogen peroxide, sodium tungstate and ammonium persulfate in concentrated sulfuric acid is applied as oxidant, DAAzF will be partially oxidized to 4-amino-4'-nitro-3,3'-azofurazan [153]. In contrast, under stronger oxidants such as hydrogen peroxide solutions, deep oxidation of both amino groups, even the azo group, can be achieved to afford 4,4'-dinitro-3,3'-azofurazan and 4,4'-dinitro-3,3'-azoxyfurazan [154,155]. Alternatively, 4,4'-dinitro-3,3'-azofurazan is also synthesized through the oxidative coupling of 3-amino-4-nitrofurazan [156,157]. The *N*-nitration of the amino groups in DAAF and DAAzF with fuming $HNO_3$ will lead to the



**Scheme 14.** Synthesis of 4,8-dinitraminodifurazano[3,4-b,e]pyrazine and related energetic salts.



**Scheme 15.** Synthesis of poly furazan structure linked by all nitrogen-inner salt bridge.

formation of 4,4'-bis(nitramino)azofurazan and 4,4'-bis(nitramino)azoxyfurazan, which can be further converted to their corresponding energetic salts [151,152,158]. 4,4'-Bis(nitramino) azofurazan, 4,4'-bis(nitramino)azoxyfurazan as well as their salts showed good energetic performance, remarkably, the crystal density of 3,3'-dinitroamino-4,4'-azoxyfurazan (2.02 g/cm$^3$) calculated at 173 K is a highest value recorded to date for the crystal density of *N*-oxide energetic compounds (Table 6 and Scheme 16) [152].

Compared with furazan, furoxan generally achieves superior energetic properties. From the point of structure design, replacement of furazan by furoxan in 4,4'-dinitro-3,3'-azofuroxan, similar energetic structure of 4,4'-dinitro-3,3'-diazenofuroxan (DDF) is obtained, however, its synthesis has proved to be much more complicated [159].

DDF is synthesized through oxidative coupling of 4-amino-3-(azidocarbonyl)furoxan, followed by Curtius rearrangement and oxidation of the resulting amino groups to nitro groups. Experimental studies show detonation velocity of DDF reaches an outstanding 10000 m/s at a crystal density of 2.02 g/cm$^3$, making it a powerful high explosive with performance comparable to that of other famous high explosives such as octanitrocubane (ONC) and hexanitrohexaazaisowurtzitane (CL-20). The high density of DDF is possible due to the highly efficient crystal packing (Scheme 17) [160].

The symmetry of azo group successfully avoids potential isomers when serving as the linkers; in contrast, isomers are often observed when azoxy groups are applied to connect furazan moieties. Dinitro trifurazans with azo bridge have been prepared through $KMnO_4$/HCl oxidation, a traditional oxidation condition for the synthesis of azo group, and the azo bridge can further be oxidized to azoxy bridge by treating with ammonium persulfate in oleum, affording three isomeric di-*N,N'*-oxides (Scheme 18) [130].

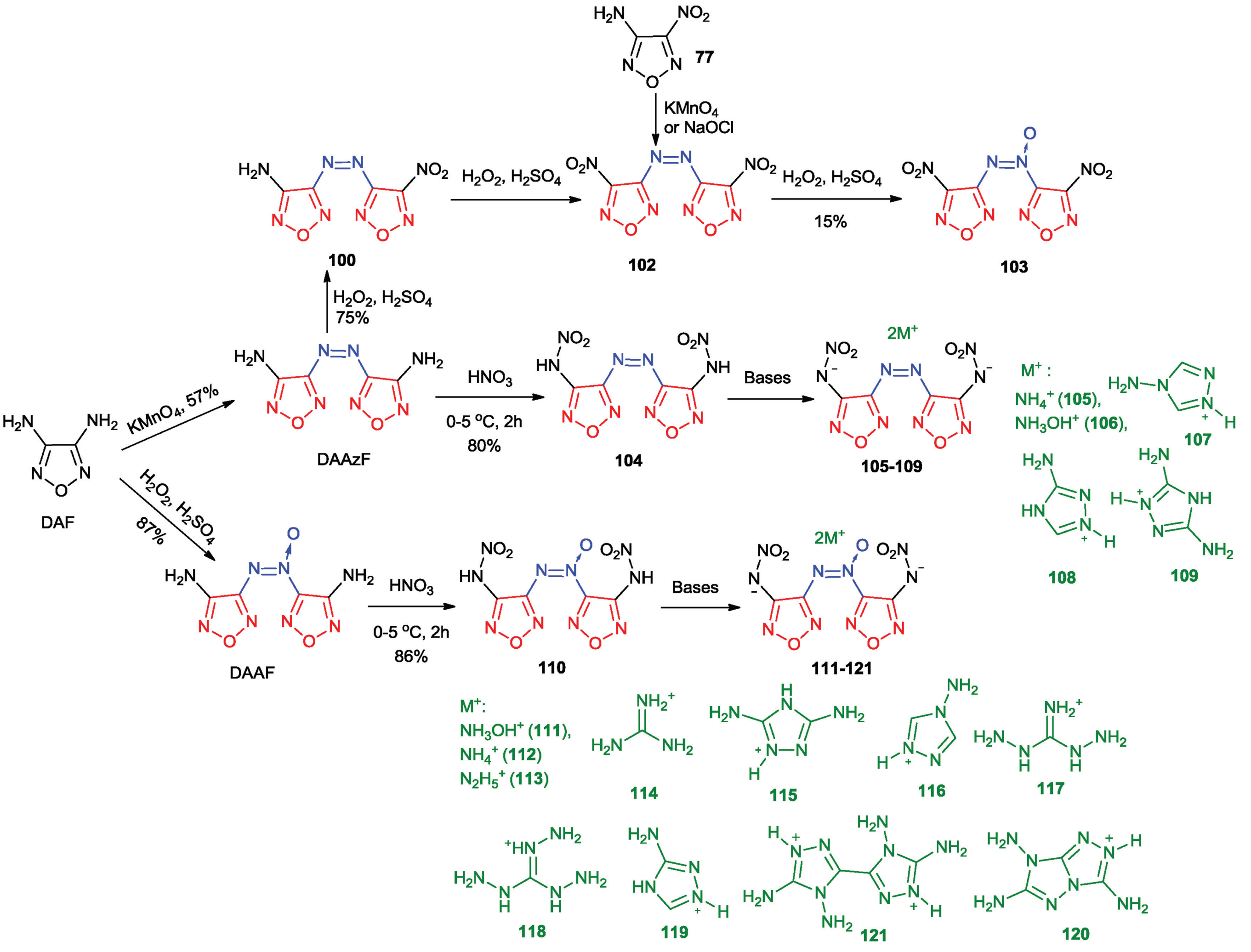
Bis(4-aminofurazanyl-3-azoxy)azofurazan (ADAAF) is achieved from DAAF through potassium bromate ($KBrO_3$) oxidation. Based on the structure of ADAAF, bis(4-nitraminofurazanyl-3-azoxy)azofurazan can be obtained through N-nitration process with 100% $HNO_3$. Corresponding energetic salts of bis(4-nitraminofurazanyl-3-azoxy)azofurazan have further been prepared by reacting with various nitrogen-rich bases. The tetrafurazan molecule shows even better energetic performance than its salts. The densities of bis(4-nitraminofurazanyl-3-azoxy) azofurazan and its salts are in the range of 1.71~1.88 g/cm$^3$ while the detonation velocities and pressures of these energetic compounds range from 8584 m/s to 9541 m/s and 29–40 GPa (Scheme 19, Table 7) [161].

Similar with furazanyl ethers, some newly developed explosophores as nitro-NNO-azoxy, bis(trinitromethyl-ONN-azoxy) azoxy and fluoronitromethyl-ONN-azoxy have also been introduced into the azo- and azoxy- based polyfurazan scaffolds. The intermediate for the synthesis of bis-3,3'-(nitro-NNO-azoxy)-difurazanyl ether can be applied in the preparation of bis-3,3'-(nitro-NNO-azoxy)-4,4'-azofurazan through the destructive *N*-nitration of *t*-Bu-NNO-azoxy with a density of 1.87 g/cm$^3$, detonation velocity of 9466 m/s and detonation pressure of 44 GPa [162]. Using 3,3'-diamino-4,4'-azoxyfurazan (DAAF) as starting materials, energetic compound 3,3'-bis(fluoronitromethyl-ONN-azoxy)azoxyfurazan (FDNAF) and bis(trinitromethyl-ONN-azoxy)azoxyfurazan are designed and synthesized through the transformations of oxidation coupling, hydrolysis, bromization, reduction, nitration, salification and fluorination. Among them, FDNAF shows an impressive high energy-density level (d = 2.02 g/cm$^3$, $T_{dec}$ = 233.4 °C, $OB_{<CO_2>}$ = 6.72 %, D = 9735 m/s and P = 44 GPa) (Scheme 20, Table 8) [163–165].

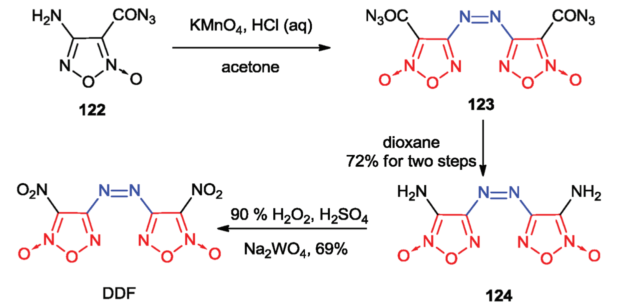
There are numerous applications of polynitro groups for functionalization of energetic materials due to its positive oxygen balance values and high densities. Energetic structures containing trinitroethyl moieties generally exhibit high densities and good detonation performances. Moreover, they are easily accessible by adding trinitroethanol (or trinitromethane and formaldehyde) to an amine. Condensation between azoxyfurazan with trinitroethanol will results the secondary amine and can be subjected to nitration to give *N,N'*-bis(2,2,2-trinitroethyl)-3,3'-dinitramino-4,4'-azoxyfurazan with an ideal oxygen balance of near zero (+2.5%), density (1.92 g/cm$^3$) and excellent detonation property (detonation pressure of 41.2 GPa, detonation velocity of 9458 m/s) [166]. Esterification of furazan based acids with polynitro alcohols is also an efficient approach for the synthesis of polynitrofunctionalized furazan structures and highly concentrated $H_2SO_4$ or acid sulfates of polynitro alcohols are needed due to the low nucleophilicity of the *O*-atom of the hydroxyl group in *β*-polynitro alcohols (Scheme 21).

**Table 6**
Physiochemical properties and detonation parameters of difurazanyl structures with azo and azoxy groups.

| | **104** | **105** | **106** | **107** | **108** | **109** | **115** | **116** | **119** |
|---|---|---|---|---|---|---|---|---|---|
| $T_{dec}$ [°C] | 100 | 194 | 177 | 180 | 198 | 197 | 188 | 193 | 169 |
| d [g/cm$^3$] | 1.89 | 1.77 | 1.85 | 1.74 | 1.78 | 1.73 | 1.75 | 1.75 | 1.79 |
| $\Delta H_f$ [kJ/mol] | 820.2 | 579.9 | 693.8 | 1372.9 | 1099.4 | 1058.5 | 1014.3 | 1322.6 | 1051.7 |
| D [m/s] | 9517 | 8937 | 9328 | 8670 | 8664 | 8458 | 8557 | 8883 | 8843 |
| P [GPa] | 41 | 33 | 39 | 30 | 30 | 27 | 29 | 33 | 32 |
| IS [J] | 2 | 17 | 12 | 24 | 16 | 28 | 35 | 20 | 29 |
| FS [N] | 10 | 160 | 120 | 160 | 160 | 240 | 160 | 160 | 160 |

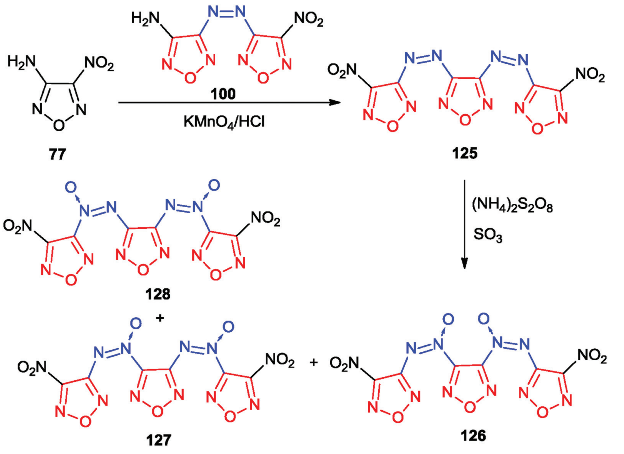


**Scheme 16.** Synthesis of difurazanyl structures with azo and azoxy groups.

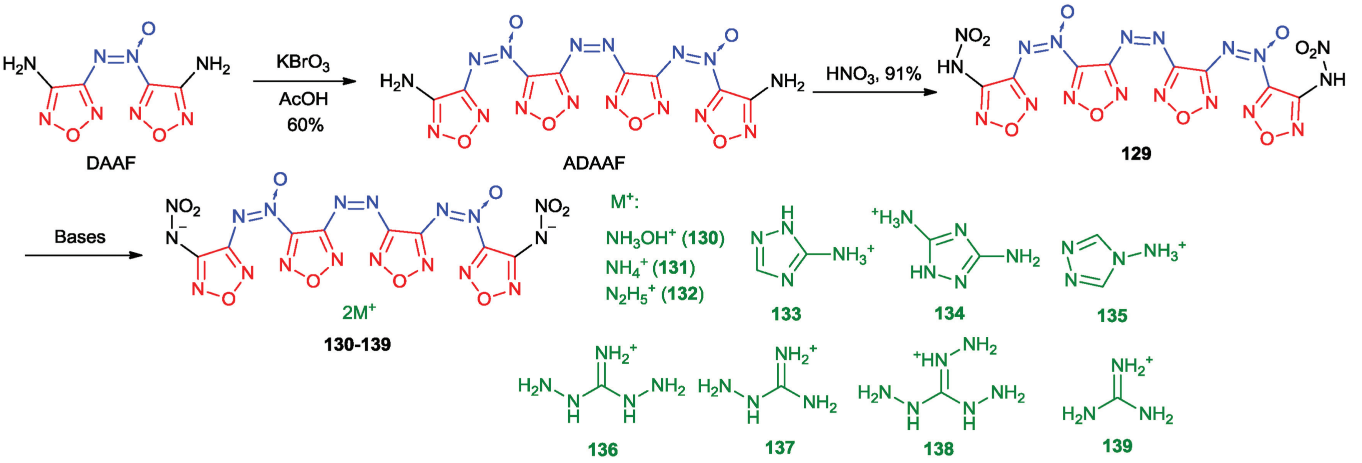


**Scheme 17.** Synthesis of difurazanyl structures with azo and azoxy groups.

Macrocyclic structures are a consistently useful source in the development of energetic materials, especially for the design and synthesis of poly furazan and furoxan structures. A most convenient and useful synthetic method for macrocyclic energetic structure is through the formation of azo or azoxy linkages. Macrocycle poly furazan structure linked with azoxy moieties can be achieved by oxidative coupling of 3-amine-4-nitroso-furazan with *N,N*-dibromoacetamide [167]. Oxidation coupling reaction of diaminofurazan through AcOBr or Pb(OAc)$_4$ will afford a novel azo-linked tetramer compound TATF (3,4:7,8:11,12:15,16-tetrafurazan-1,5,9,13-tetrazocyclohexadecane), in which the azo linker can be further oxidized, affording an azoxy bridges linked macrocyclic energetic structure (TOATF). Moreover, Caro's acid can oxidize diaminofurazan to DAAF which can be further converted to azo and



**Scheme 18.** Synthesis of azo and azoxy based trifurazan system through oxidative coupling reaction.



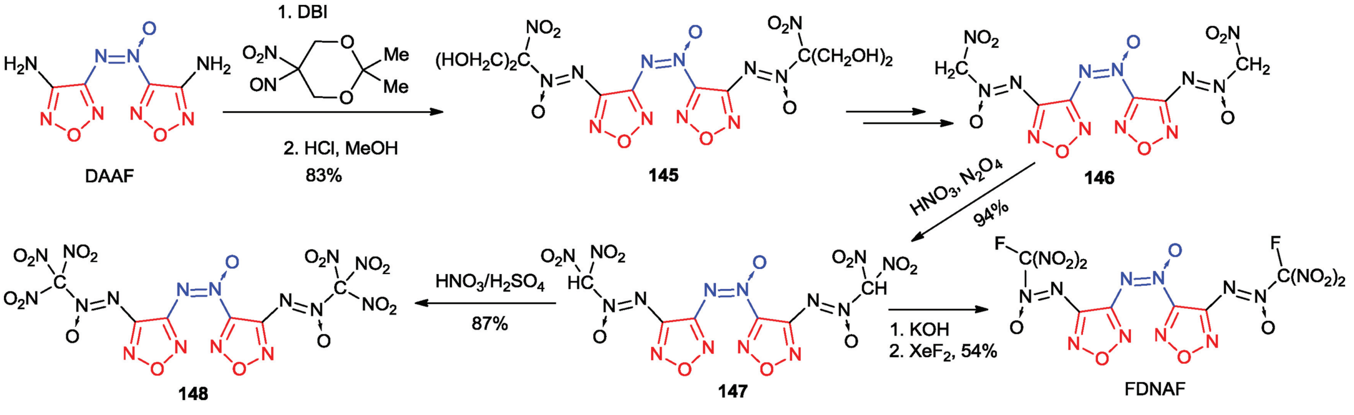
**Scheme 19.** Synthesis of bis(4-nitraminofurazanyl-3-azoxy)azofurazan and its energetic salts.

**Table 7**
Physiochemical properties and detonation parameters of bis(4-nitraminofurazanyl-3-azoxy)azofurazan and its energetic salts.

| | 129 | 130 | 131 | 132 | 133 | 134 | 135 | 136 | 137 | 138 | 139 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $T_{dec}$ [°C] | 120 | 154 | 175 | 124 | 151 | 181 | 189 | 209 | 195 | 203 | 209 |
| d [g/cm$^3$] | 1.88 | 1.75 | 1.78 | 1.83 | 1.78 | 1.72 | 1.80 | 1.75 | 1.71 | 1.73 | 1.79 |
| $\Delta H_f$ [kJ/mol] | 1623.4 | 1507.7 | 1791.2 | 1600.2 | 1949.1 | 2242.5 | 1913.7 | 1464.5 | 1688.3 | 1904.3 | 2217.8 |
| D [m/s] | 9541 | 8893 | 9065 | 9256 | 8768 | 8649 | 8890 | 8716 | 8584 | 8803 | 9015 |
| P [GPa] | 40 | 33 | 35 | 38 | 31 | 30 | 32 | 31 | 29 | 30 | 32 |
| IS [J] | 2 | 15 | 14 | 15 | 21 | 17 | 25 | 26 | 22 | 19 | 15 |
| FS [N] | 10 | 120 | 120 | 120 | 160 | 120 | 240 | 240 | 240 | 160 | 120 |

azoxy bridge-linked macrocyclic energetic molecule (DOATF) through $Pb(OAc)_4$ oxidation reaction (Scheme 22) [168–170].

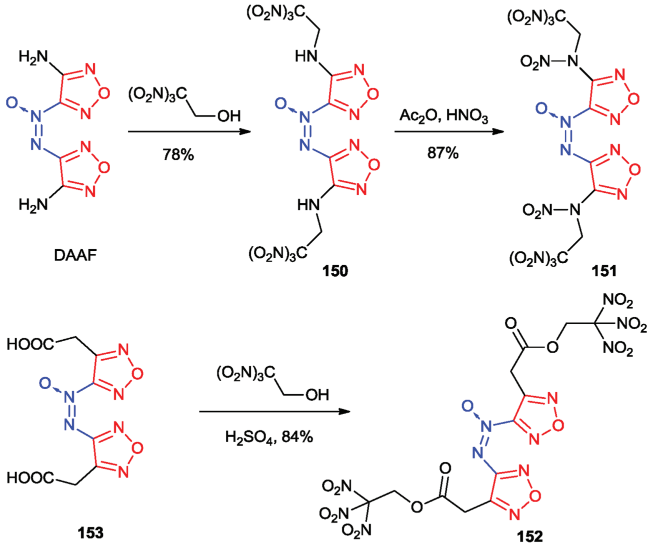
4,4'-Dicyano-3,3'-azofurazan can be achieved smoothly through oxidation of 3-amino-4-cyanofurazan and further converted to 4,4'-bischlorohydroximoyl-3,3'-azofurazan by treating with 50% aqueous hydroxylamine in ethanol, followed by diazotization in dilute hydrochloric acid [171]. The nitration of 4,4'-bischlorohydroximoyl-3,3'-azofurazan with a mixture of 100% nitric acid and trifluoroacetic acid anhydride (TFAA), followed by treatment with KI will afford potassium 4,4'-bis(dinitromethyl)-3,3'-azofurazanate ($K_2$DNMAF) [172,173], which exhibits good thermal stability with an onset decomposition temperature of 229.8 °C. The impact and friction sensitivities of $K_2$DNMAF are 2 J and 20 N, while the calculated heat of formation, the measured density, the detonation velocity and pressure are 110.1 kJ/mol, 2.039 g/cm$^3$, 8138 m/s and 30.1 GPa, respectively. $K_2$DNMAF can also be converted to of 4,4'-bis(fluorodinitromethyl)-3,3'-azofurazan (FDNMAF) through fluorination with selectfluor and 4,4'-Bis (dinitromethyl)-3,3'-azofurazan (DNMAF) can be obtained by acidifying $K_2$DNMAF with concentrated hydrochloric acid. Further treatment of DNMAF with either ammonia or hydrazine monohydrate will result in the formation of its corresponding salts. The bishydroxylammonium salt is not available by reacting DNMAF with hydroxylamine directly, but it can be prepared through the metathesis reaction of bisilver 4,4'-bis (dinitromethyl)-3,3'-azofurazanate ($Ag_2$DNMAF) with hydroxylammonium hydrochloride. FDNMAF and DNMAF melt at 155 and 108 °C while decompose at 166 and 140 °C, in contrast, the ammonia, hydrazine and hydroxylammonium salts of DNMAF decompose at 202, 189 and 127 °C, respectively, indicating that the salt formation effect greatly influences the thermal stabilities of DNMAF derivatives.



**Scheme 20.** Synthesis of azo- and azoxy-based polyfurazan with nitro-NNO-azoxy, bis(trinitromethyl-ONN-azoxy)azoxy and fluoronitromethyl-ONN-azoxy groups.

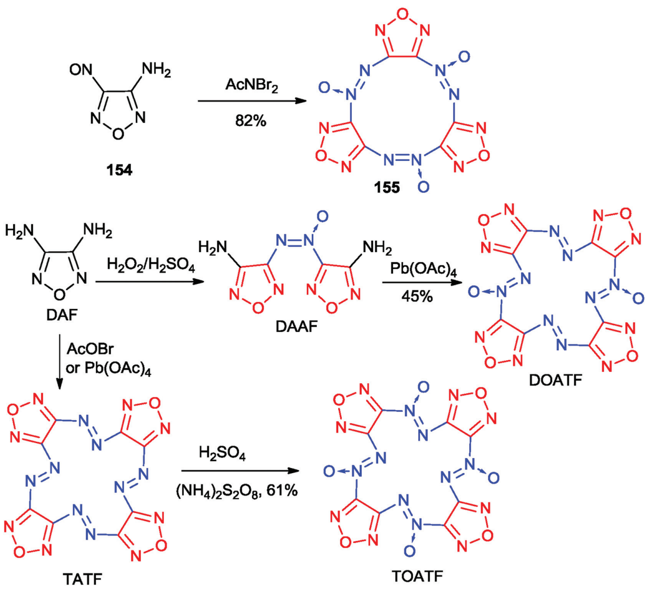
**Table 8**
Physiochemical properties and detonation parameters of azo- and azoxy-based polyfurazan with nitro-NNO-azoxy, bis(trinitromethyl-ONN-azoxy)azoxy and fluoronitromethyl-ONN-azoxy groups.

| | **146** | **147** | **148** | FDNAF | **144** |
|---|---|---|---|---|---|
| $T_{dec}$ [°C] | 116 | 149 | – | 233 | 132 |
| d [g/cm$^3$] | 1.84 | 1.94 | 2.00 | 2.02 | 1.87 |
| $\Delta H_f$ [kJ/mol] | 727 | 660 | 614 | 500 | 1169 |
| D[m/s] | 8793 | 9333 | 8943 | 9735 | 9466 |
| P [GPa] | 35 | 41 | 38 | 44 | 44 |



**Scheme 21.** Synthesis of polynitrofunctionalized structures.

Using $K_2DNMAF$ in a self-assembly strategy, high-energy metal–organic frameworks (HE-MOFs), $\{Ag_2(DNMAF)(H_2O)_2\}_n$ and $\{Ag_2(DNMAF)\}_n$ are obtained. $\{Ag_2(DNMAF)(H_2O)_2\}_n$ exhibits a 3D HE-MOF structure with coordinated water molecules while $\{Ag_2(DNMAF)\}_n$ exhibits compact solvent-free 3D HE-MOFs. Both compounds show good thermostability (decomposition temperature of 211 and 218 °C) and superior detonation velocities of 9673 m/s and 10242 m/s, detonation pressures of 50 and 58 GPa, respectively, which are even higher than those of RDX and HMX (Scheme 23, Table 9) [174,175].



**Scheme 22.** Oxidative coupling of furazan and furoxan structures.

Both the structures of 3,3'-dinitrile-4,4'-azofuroxan and 3,3'-dicarboxamide-4,4'-azofuroxan have been achieved through oxidative coupling reactions of 4-amino-3-cyanofuroxan and 4-amino-3-carboxamidefuroxan. In the same time, heating 3,3'-dicarbamoyl-4,4'-azofuroxan and 3,3'-dicarboxamide-4,4'-azoxyfuroxan with TFAA/pyridine can lead to dehydration of the amido groups to form their corresponding dinitriles [176,177]. Although the energetic properties of cyano group itself are very limited, it is the essential synthetic precursor of other excellent explosophores like dinitromethyl group, fluorodinitromethyl group and their corresponding salts. Diazido derivative of the azo-linked dinitrofuroxan system is synthesized by the reaction of 3,3'-dinitro-4,4'-azofuroxan with sodium azide through nucleophilic displacement of the nitro groups by the azido groups. Based on a similar azo-linked difuroxan scaffold, nitration with fuming nitric acid in acetic anhydride will afford the corresponding bis(nitroxymethyl) derivative (Scheme 24) [178].

### 4.2. Azo/azoxy bridges constructed through electrochemical method

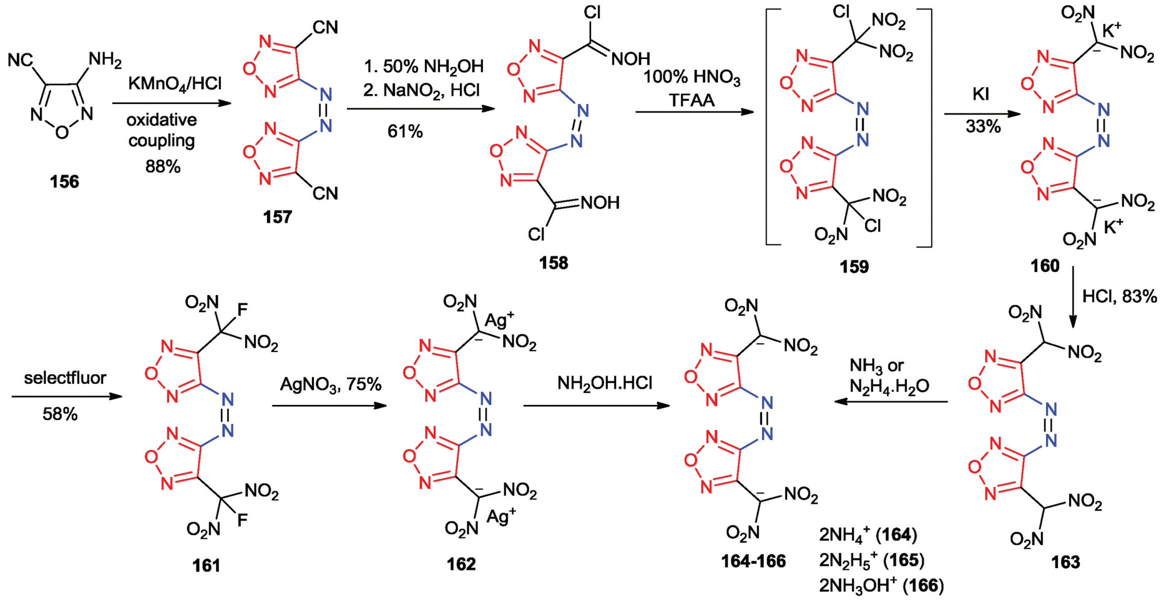
Organic electrooxidation has been proved to be a green and efficient way for oxidation process. It has been widely applied for the construction of carbon–carbon, carbon–nitrogen, and carbon–oxygen bonds in recent years [179–181]. Experiment studies show nickel oxyhydroxide (NiOOH) anode is an effective tool for the oxidation of aminofurazans to azofurazans in *ca.* 1% aqueous alkali at room temperature. Highly sensitive 4,4'-diazido-3,3'-azofurazan structure is successfully afforded through this practical anodic oxidation of aminofurazans to azofurazans [182]. Meanwhile, electrochemical reaction is obvious a simpler and more convenient approach, eliminating the use of expensive and toxic organic or inorganic oxidants. Viewed from mechanism, this green economic preparation of azo moieties is clean since produce only $H_2$ as a result of cathodic reduction (Scheme 25).

## 5. Poly furazan and furoxan structures linked by the combination of different linkers

### 5.1. Linked by azo/azoxy and heteroatoms linkers

Based on carefully designed coupling strategies, various poly furazan and furoxan structures connected *via* the combination of different linkers, including carbon-carbon bonds, oxygen/nitrogen atoms as well as azo/azoxy bridges, have been developed and found wide applications in the research field of energetic materials.

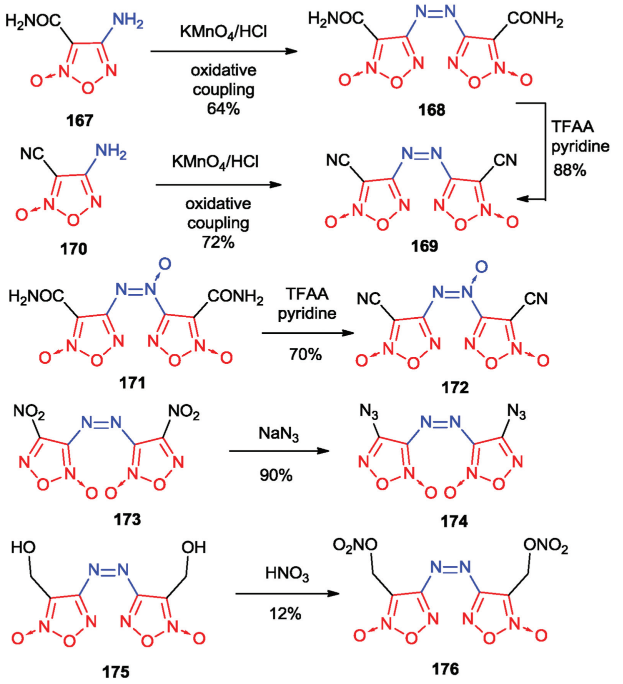
Dinitro-trifurazan structures connected *via* the combination of oxygen atom and azo/azoxy bridges are achieved from dinitroazofurazan through aromatic substitution reaction. 4-Hydroxy-4'-nitroazofurazan (**179**) was prepared by treatment with NaOH in the mixture of hydrogen peroxide and acetonitrile of the 4,4'-dinitro-3,3'-azofurazan, and its sodium salt (**180**) is given by treatment with sodium ethoxide and additional oxygen bridge is introduced by nucleophilic displacement of the nitro group in nitroazofurazan with the sodium salt. Earlier research found that the deep oxidation of the azo group to azoxy group are not possible through some well-established synthetic approaches for azoxy groups, even under strong conditions like peracides acid, trifluoroperacetic acid and performic acid oxidations. However, successful oxidation of the azo bridge in compound **181** is finally achieved by utilizing ammonium persulfate in oleum, affording a mixture with desired azoxy bridges (Scheme 26) [130].



**Scheme 23.** Synthesis of DNMAF derivatives.

**Table 9**
Physiochemical properties and detonation parameters of DNMAF derivatives.

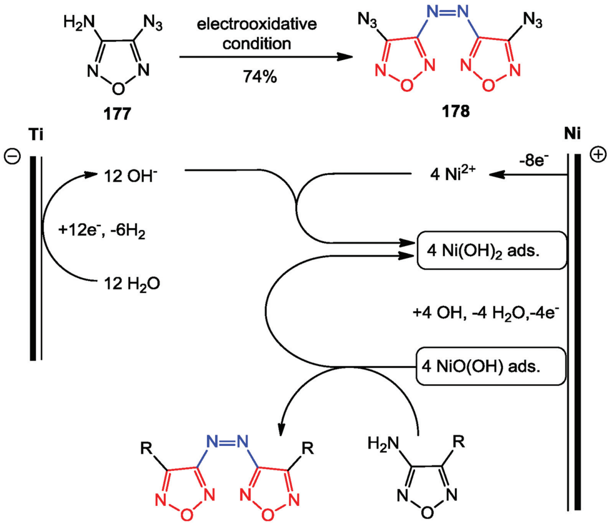
| | 161 | 163 | 164 | 165 | 166 |
|---|---|---|---|---|---|
| $T_{dec}$ [°C] | 166 | 140 | 202 | 189 | 127 |
| d [g/cm] | 1.86 | 1.81 | 1.73 | 1.79 | 1.77 |
| $\Delta H_f$ [kJ/mol] | 175.8 | 526.2 | 193.1 | 637.5 | 444.0 |
| D [m/s] | 8492 | 8936 | 8507 | 8916 | 8815 |
| P [GPa] | 30 | 34 | 31 | 35 | 35 |
| IS [J] | 5 | 2 | 12 | 4 | 3 |
| FS [N] | 120 | 40 | 240 | 120 | 120 |



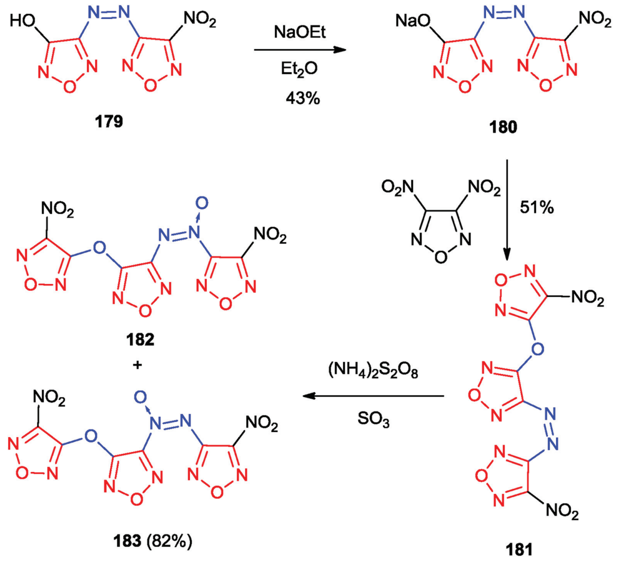
**Scheme 24.** Oxidative coupling of furazan and furoxan structures.

### 5.2. Linked by azo/azoxy and carbon-carbon bonds

Oxidative coupling of DAFF can be carried out in an intermolecular way, affording a macrocyclic structure with a density of 1.86 g/cm$^3$ and high thermal decomposition temperature of 215 °C, which are ideal for the preparation of heat-resistance explosives. Experiment results show the chlorine-based oxidizing reagents, such as trichloroisocyanuric acid (TCICA) and *tert*-butyl hypochlorite, are the most successful oxidants for the conversion of diamine structures to their macrocyclic products [183,184]. Like DAFF, the intermolecular oxidation of diamino trifurazan (DATF) by TCICA affords a similar macrocyclic structure with a density of 1.82 g/cm$^3$ and a thermal decomposition temperature of 176 °C. Obviously, thermal stability of the new macrocyclic structure is greatly reduced after the introduction of *N*-oxides moieties. Dibromoisocyanurate (DBI) has also been successfully applied in macrocyclization of diamine structures and the oxidative coupling of 4,4'-diamino-3,3'-difurazan by DBI



**Scheme 25.** Electrooxidation for oxidative coupling reaction.

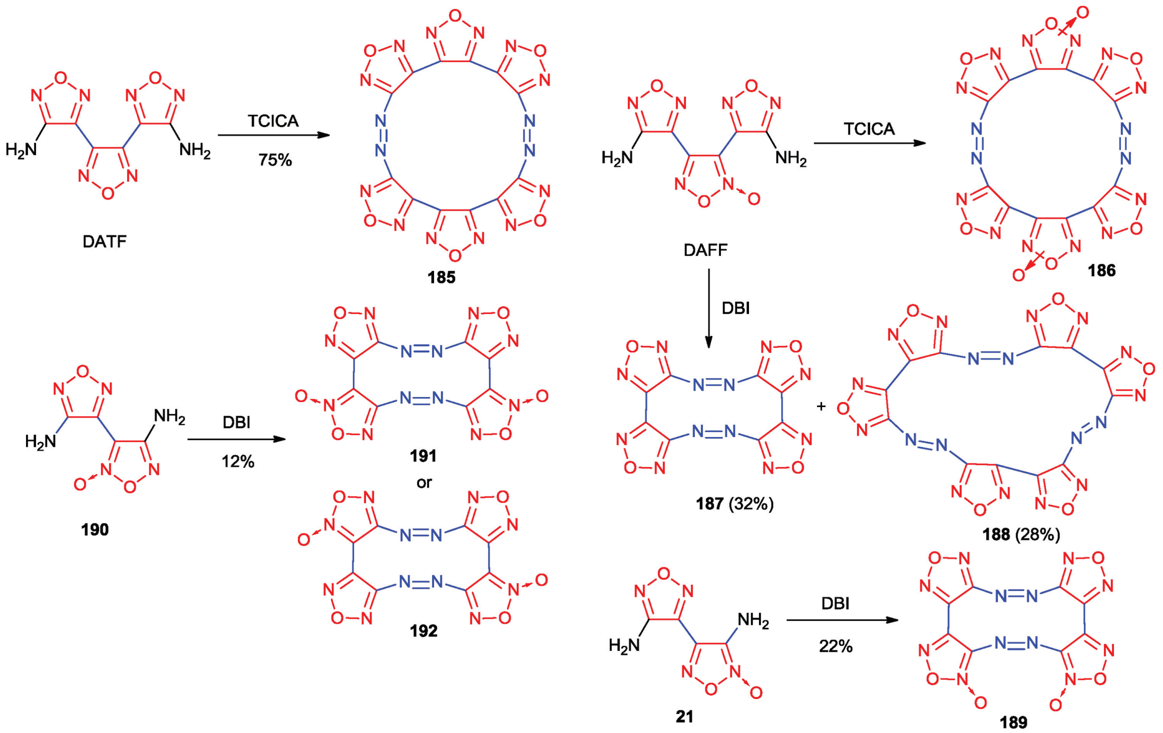


**Scheme 26.** Synthesis of trifurazan structures linked *via* oxygen and azo/azoxy bridges.

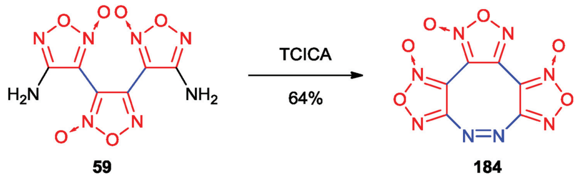
affords a mixture of macrocyclic products with two and three azobifurazanyl fragments, respectively [74]. In contrast, oxidative coupling of the diamine structures of 4,4'-diamino-[3,3'-bi(1,2,5-oxadiazole)]-5-oxide and 4,4'-diamino-[3,3'-bi(1,2,5-oxadiazole)]-2-oxide by DBI can lead to the formation of macrocyclic structures only containing two azobifurazanyl fragments, while the later products existing as isomers (Scheme 27). No intramolecular coupling products are observed during these oxidative conditions, which may due to high reaction barriers for the azacyclooctane scaffolds formation.

An intramolecular azo bridge is constructed by oxidative coupling of amino groups in the trifuroxan structure **59** with TCICA, affording a furoxan fused 1,2-diazocine macrocyclic product with a high density of 1.89 g/cm$^3$ and a thermal decomposition temperature of 161 °C. From structure standpoint, the construction of intramolecular azo-bridge will create a 1,2-diazocine scaffold with high strain energy. However, different from the oxidative coupling of DAFF, no intermolecular coupling products are observed during the coupling studies, exhibiting an impressive chemoselectivity [115] (Scheme 28). Along with a zero oxygen balance and superior detonation performances (D = 9417 m/s and P = 39.6 GPa) relative to RDX and HMX as well as reasonable sensitivities (IS = 19 J and FS = 80 N), it exhibits a promising potential as a cyclic high explosive.

Nitro groups binding with furazans are ideal leaving moieties for aromatic nucleophilic substitutions and can usually be displaced smoothly by nucleophiles with oxygen or nitrogen atom. Some studies show the etherification of poly furazan and furoxan structures will increase their flexibilities and reduce their melting points [185,186], based on that, two furazan-ether structures, trifurazanooxacycloheptatriene (TFO) [187] and bifurazano[3,4-b:3',4'-f]furoxano[3",4"-d] oxacyclohetpatriene (BFFO) [188], are synthesized through intramolecular etherification of DNTF and LLM-172, with a density of 1.76 g/cm$^3$ and 1.86 g/cm$^3$ respectively. The melting point of BFFO and TFO are 94 °C and 78 °C, which are highly suitable for the melt-cast technologies. Although the absence of nitro groups lead to the detonation performance degradation, the insensitivities of BFFO and TFO to impact and friction stimuli are greatly improved when compared with DNTF and LLM-172. The low melting point and the good insensitivities make both TFO and BFFO promising candidates in advanced melt-cast explosives and solid propellants.



**Scheme 27.** Synthesis of macrocyclic energetic molecules.



**Scheme 28.** Oxidative coupling of trifuroxan system.

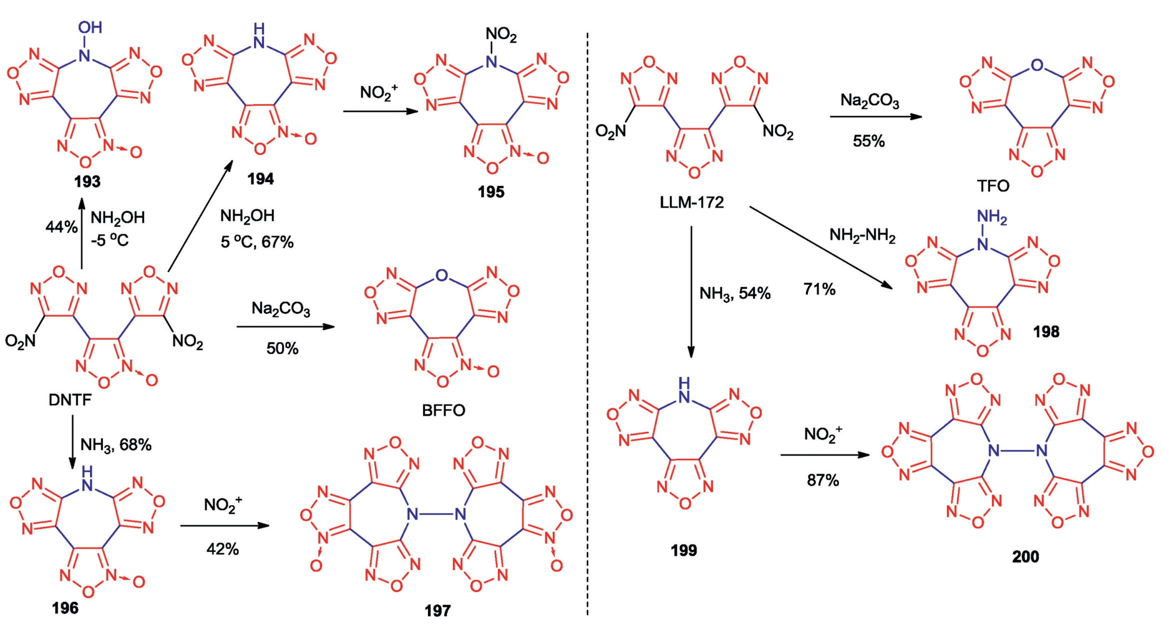
### 5.3. Linked by heteroatoms and carbon-carbon bonds

DNTF and LLM-172 can react readily with nucleophiles with nitrogen atom like primary amines and ammonia to produce azepine scaffolds. Reaction between DNTF and $NH_2OH$ at low temperature will afford 7-hydroxy-difurazano[3,4-b:3',4'-f]furoxano[3”,4”-d]azepine while 7*H*-difurazano[3,4-b:3',4'-f]furoxano[3”,4”-d]azepine is the major product when the reaction is carried out at higher temperatures [189]. In contrast, the azepine derivatives of DNTF and LLM-172 are obtained by treating with $NH_3$. *N*-Nitration studies of these azepine derivatives lead to unexpected results since most nitration conditions, such as $HNO_3/Ac_2O$, $HNO_3/H_2SO_4$, $HNO_3$/oleum and $HNO_3/(CF_3CO)_2O$, cannot give the expected N-nitration products. Instead, oxidative "dimerization" of the azepine derivatives are achieved in which new N(7)-N(7') bond between two substrate molecules are formed (Scheme 29) [190].

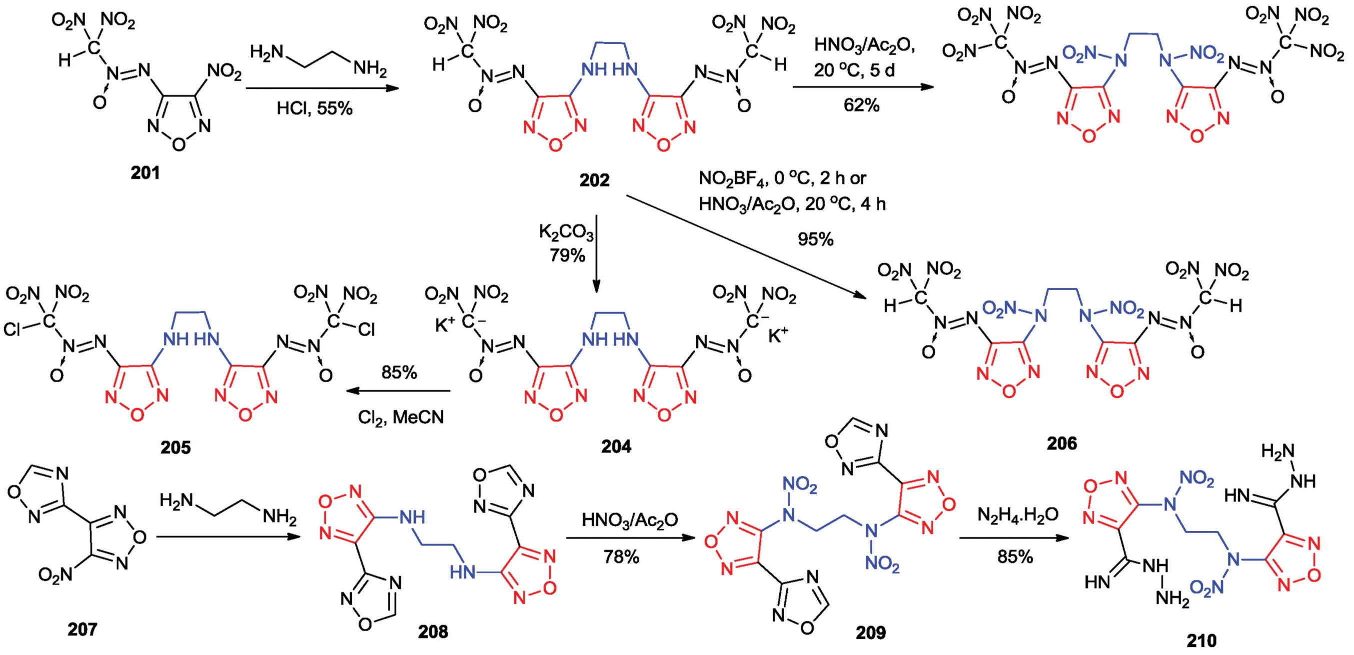
Nucleophilic displacements between primary amines and nitrofurazans provide efficient synthetic strategies for the coupling of furazan structures with poly nitro groups. Experiment results show the electronic effect of the nitroalkyl substituent at the ONN-azoxy group does not affect the nucleophilic substitution of nitro group binding with the heterocycle of furazan, therefore, ethylenediamine is applied as the nucleophile and reacted with 3-(dinitromethyl-ONN-azoxy)-4-nitro-furazan, affording a coupling product of *N,N*'-bis-[4-(dinitromethyl-ONN-azoxy)furazan-3-yl] ethylenediamine. In contrast, the nitration of compound **202** can affect two reaction centers. Treatment with nitronium tetrafluoroborate during 2 h at 0 °C or with $HNO_3/Ac_2O$ during 4 h at 20 °C will lead to N-nitration product, however, if nitrated with $HNO_3/Ac_2O$ during 5 days at 20 °C, the trinitromethyl-ONN-azoxy derivative will be achieved. The analogous 3-(fluorodinitromethyl-ONN-azoxy) derivative is prepared through fluorination of the potassium salts with $XeF_2$ [187]. Introduction of the ethylene linkage based on nucleophilic substitution of the nitro group in 3-nitro-4-(1,2,4-oxadiazol-3-yl)furazan with ethylene diamine will give the double nucleophilic substitution product 208. Designed bisnitramide structure of *N,N*'-dinitro-*N,N*'-bis[3-(1,2,4-oxadiazol) furazan-4-yl]ethylenediamine (**209**) is obtained by treating **208** with a mixture of acetic anhydride and 100% $HNO_3$. Because of the low degree of aromaticity of the 1,2,4-oxadiazole ring, it is easy to open the 1,2,4-oxadiazole ring with hydrazine hydrate, enabling an easy transformation of bisnitramide compound **209** to its corresponding high nitrogen-containing hydrazino(imino)methyl substituted furazan structure (**210**) (Scheme 30) [191,192].

Except ethylenediamine, methylenediamine moieties also have been applied in the synthesis of energetic materials, and Mannich reaction of amines and formaldehyde are still the most convenient synthetic method to afford the desired methylenediamine bridges. 4-Aminofuroxans can be involved into the condensation processes, meanwhile, structures derived from *N,N*-bis(furoxanyl)methylenedinitramines have been designed for the research of potential new energetic materials, in which the Mannich reactions are achieved through the formation of iminium cation and controls of the pH value are highly important for the transformations. Nitramine explosophores have also been obtained through *N*-nitration to further enhance its energetic properties [193]. Similarly, when substituted furazan-amine precursor, 4-(1,2,4-oxadiazol-3-yl)furazan-3-amine (**215**) is treated with 37% aqueous formaldehyde solution, the methylene linkage is introduced to yield the intermediate product **216**. *N*-Nitration process will afford bisnitramide product of *N,N*'-dinitro-*N,N*'-bis[3-(1,2,4-oxadiazol) furazan-4-yl]ethylenediamine (**217**) which is further converted to its hydrazino(imino)methyl substituted furazan derivate **218** (Scheme 31) [191,192].

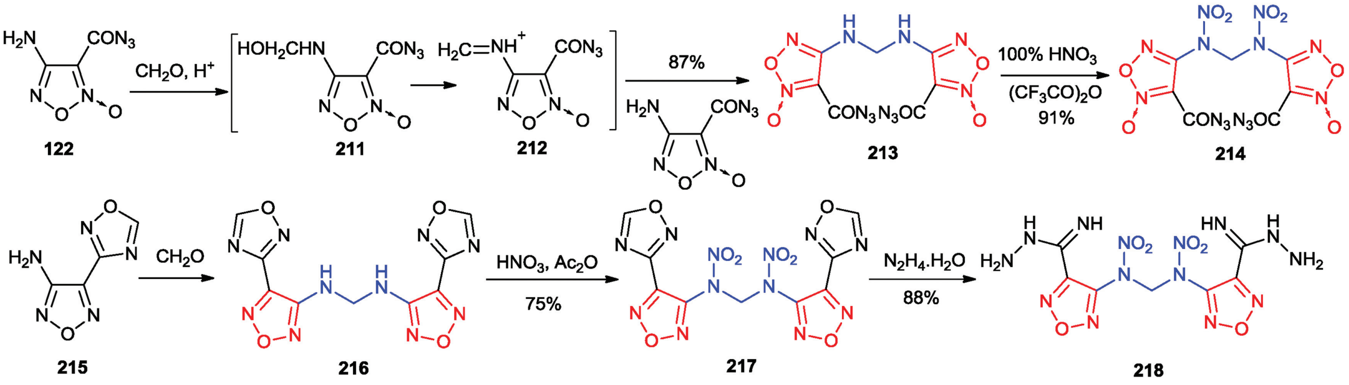
Although substitutions of nitrofurazans with nucleophilic amines usually afford aminofurazans smoothly through displacement of the nitro groups, the reaction between nitrofurazans and 4*H*,8*H*-bis([1,2,5]oxadiazolo)[3,4-b:3′,4′-e]pyrazine (DFP) is not



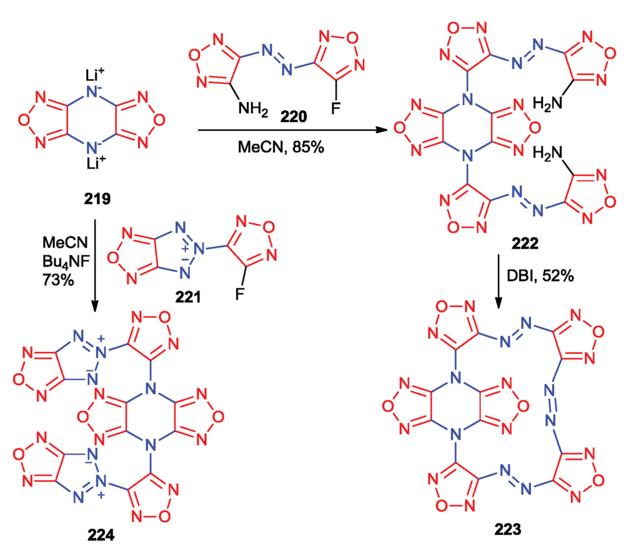
**Scheme 29.** Synthesis of oxepine and azepine derivatives from DNTF and LLM-172.



**Scheme 30.** Poly furazan structures linked through ethylnediamine.



**Scheme 31.** Synthesis of Poly furoxan structure linked by methylenedinitramine.



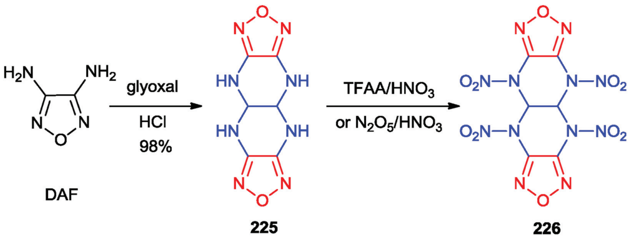
**Scheme 32.** Substitutions of fluorofurazans with DFP.

successful, even stronger nucleophilic lithium dianion salts are prepared first. Alternatively, fluorofurazans can undergo smooth fluorine displacement with anion **219** to give tertiary amine derivatives **222** and **224**. Moreover, intramolecular azo bridge is also formed in compound **222** through DBI oxidation to achieve a macrocyclic structure **223** (Scheme 32) [194].

Acyclic condensation structure is obtained from the reaction of difurazan (DAF) and glyoxal in warm HCl solution, in which two furazan heterocycles are connected through both nitrogen and carbon-carbon bridges. *N*-Nitration of the nitrogen atoms by either mixtures of trifluoroacetic anhydride (TFAA)-100% nitric acid or a solution of $N_2O_5$ in 100% nitric acid can lead to the formation of its nitramine derivative (**226**), an unstable structure undergoing slow decomposition even at room temperatures. However, the stability of compound **226** is greatly improved and can be stored at -20 °C for months (Scheme 33) [195].

## 6. Conclusions

Different from other heterocycles, furazan and furoxan themselves are perfect explosophoric units which are intensively



**Scheme 33.** Synthesis of Furazano[3,4-b]piperazines and its nitro derivatives.

exploited as precursors or building blocks in the synthesis of advanced energetic materials. Poly furazan and furoxan structures have aroused great interest during the past decades, which is not only because of the compact scaffolds and high positive heats of formation, but also because of the rich combination modes and variable synthetic methods present great possibilities of new substances with higher densities and energy levels. This review comprehensively covered literatures regarding the formation of poly furazan and furoxan structures with different linkers and different synthetic strategies. From synthetic point of view, flexibilities of the structures are increased when heteroatom like oxygen and nitrogen are applied as linkers, in contrast, C—C bonds or azo/azoxy bridges can render the poly structures with higher rigidity. In most cases, C—C bond linkers are formed during the construction of the molecular scaffolds while oxidative coupling and nucleophilic aromatic substitution reactions are the most commonly used strategies towards the synthesis of azo/azoxy and heteroatom linkers. Generally, macromolecular structures linked through C—C bonds, azo/azoxy bridges or combined linkers to form larger heterocycles will obviously expand the conjugated systems, therefore, additional stabilization effect will be achieved, leading to better stabilities, especially thermal stabilities. Typical examples include macrocyclic poly furazan structures which exhibit impressive thermal stabilities and would be highly valuable in the preparations of new heat resistant energetic materials. It is also noteworthy that the low melting points of tri-furazan/furoxan derivatives are highly suitable for melt-cast technologies. To improve the energetic levels, further modifications on the poly furazan and furoxan structures are often taken into consideration, such as replacement of furazan by furoxan, deep oxidation of azo to azoxy, adjustment of oxygen balances through the formations of salts and *N*-nitration of the nitrogen linkers. Meanwhile, introductions of some newly developed explosophores like nitro-NNO-azoxy, bis(trinitromethyl-ONN-azoxy)azoxy and fluoronitromethyl-ONN-azoxy are also efficient approaches to enhance the detonation performances.

Poly furazan and furoxan structures will certainly continue to trigger increasing research in the future with development of new linkers and synthetic strategies. With the booming of new poly furazan and furoxan structures, we believe more advanced energetic materials with excellent detonation performances, high thermal stabilities, good insensitivities to impact/friction and convenient synthesis approaches will be achieved. Working in this field will be even more satisfying if expertise from organic, inorganic, physical and theoretical chemistry as well as materials science, nanoscience, toxicology and engineering are combined.

## Caution

The information given in this review covers most of the research progress on poly furazan and furoxan structures. Most of the compounds collected in this review are energetic materials that are extremely dangerous and should only be prepared by research groups skilled in this area and licensed to do so, even then, in any case carefully planned safety protocols and proper protective equipment, such as Kevlar gloves, ear protection, safety shoes and plastics patulas, should be applied.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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