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# Design and Synthesis of Polycyclic DFP-based Low-sensitivity Energetic Materials with Excellent Thermal Stability

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**Abstract:** The development of new energetic materials with high energy, low sensitivity, and high thermal stability is always desirable. In this study, a series of tetrazole-linked 4,8-dihydrodifurazano[3,4-b,e]pyrazine (DFP) based energetic salts have been synthesized and fully characterized. The as-synthesized energetic salts exhibited excellent comprehensive performances in terms of high decomposition temperature ( $T_d > 260$  °C), low mechanical sensitivity ( $IS \geq 20$  J and  $FS \geq 360$  N), and high detonation velocity ( $D > 8800$  m·s<sup>-1</sup>). Notably, the thermal decomposition temperature of di(aminoguanidinium)-4,8-di(1*H*-tetrazol-5-yl)-difurazano[3,4-b,e]pyrazine (compound **4e**) is up to 314 °C, while its detonation velocity and impact sensitivity are highly desirable with the values of 9005 m·s<sup>-1</sup> and 25 J, respectively. Overall, these novel energetic compounds have shown their great-potential as insensitive high-energy-density materials.

**Key words:** high-energy-density materials; 4,8-dihydrodifurazano[3,4-b,e]pyrazine; tetrazole; detonation performance; sensitivity

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## 1 Introduction

Since the discovery of black powder in China and its wide application in coal and mining industry in Europe, the design and synthesis of new high-energy density materials (HEDMs) has gained increasing interest due to the importance in both fields of civil engineering and military applications<sup>[1]</sup>. Over the past two centuries, the energy level of energetic materials have been significantly im-

proved, from benzene skeleton-based 2,4,6-trinitrotoluene (TNT)<sup>[2]</sup>, to cycloaliphatic nitroamines of cyclo-1,3,5-trimethylene-2,4,6-trinitamine (RDX) and 1,3,5,7-tetranitrotetraazacyclooctane (HMX)<sup>[3]</sup>, to caged nitroamines of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) and octanitrocubane (ONC)<sup>[4]</sup>. Despite high energy of modern energetic materials, their safety issues decreased along with increased sensitivities to external stimuli. In the design of modern energetic materials, parallel to the pursuit of high energy, low sensitivities towards external stimuli have become more and more important due to the safety requirements in some large combat platform (such as aircraft carrier and submarine). Against this background, the development of new energetic materials with high detonation performances and low sensitivities is still important but challenging task in energetic materials<sup>[5-6]</sup>. In recent years, the design and synthesis of new energetic materials continue to focus on nitrogen-rich heterocyclic energetic salts due to their tailored ener-

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gy and sensitivity properties through rational combination of energetic anions and cations<sup>[7]</sup>. Accordingly, numerous nitrogen-rich energetic salts have been reported, where dihydroxylammonium 5, 5'-bistetrazole-1, 1'-diolate (TKX-50) is a typical example due to its excellent detonation performances and low mechanical sensitivities<sup>[8]</sup>. However, the thermal stability of TKX-50 is relatively poor with the value of thermal decomposition temperature at 221 °C. In fact, present developed energetic salts always show such a drawback and most decomposition temperatures are lower than 250 °C. It is well-known that the energy, safety, and thermal stability are three important parameters of energetic materials. Therefore, the development of novel high detonation-performing energetic salts with low sensitivity and high thermal stability is very desirable.

The inherent nature of energetic salts depends on the combination between energetic anions and cations. Hence, the development of new energetic salts is strongly driven by the structural innovation of energetic anions (e.g., azolate anions) and energetic cations including metal cations, and nitrogen-rich cations (e.g., ammonium, hydrazonium, guanidine, and azole cations)<sup>[9]</sup>, in which energetic anions play an important role in the detonation properties of energetic salts. Although multiple factors would determine the energy level, safety, and thermal stability of energetic materials, most molecular-level and crystal-level factors have previously been addressed<sup>[10]</sup>. In general, those energetic materials with high thermal stability and low sensitivities often possess several common features, e.g.,  $\pi$ -conjugated molecular structures, extensive hydrogen bonds, and strong  $\pi$ - $\pi$  stacking in crystals<sup>[11]</sup>. In addition, high density and positive enthalpy of formation contribute to the high detonation performances (Fig. 1a). Since the density of energetic materials is linearly related with its oxygen balance, high density always implies high oxygen balance and consequently causes the undesired high mechanical sensitivities of energetic materials.

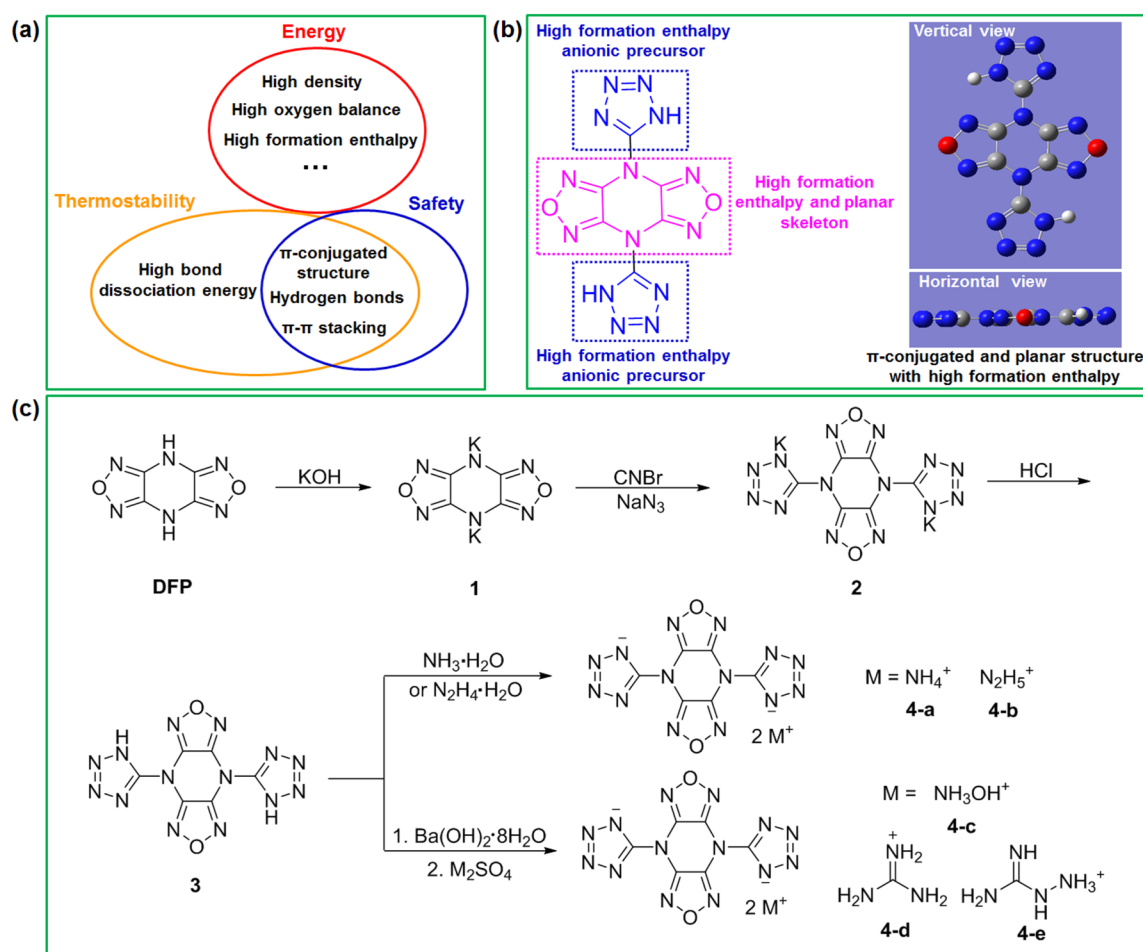
## 2 Design Principle

Nowadays, one of the popular strategies for solving this problem is to increase the material's enthalpy of formation with the aim of achieving high detonation performance, while the oxygen balance of energetic materials still fall in a reasonable range<sup>[12]</sup>. So our general design principle is to develop a big  $\pi$ -conjugated molecular system with high enthalpy of formation and moderate oxygen balance. Among common single-ring azole compounds, tetrazole possesses the highest formation enthalpy. Hence, the tetrazole skeleton was selected as a basic structural unit of energetic anions. On the other hand, 4, 8-dihydrodifurazano [3, 4-b, e] pyrazine (DFP) is a promising skeleton compound with two fused two-furazans by a pyrazine ring. The presence of multiple C—N, N—O and C=N bonds can contribute to its high enthalpy of formation (93.0 kJ·mol<sup>-1</sup>). Notably, DFP is a symmetric planar molecule with relatively high N / O content (70%), and has a surprisingly high crystal density of 2.01 g·cm<sup>-3</sup><sup>[13]</sup>. Thus, we chose the DFP as a linker to connect the two tetrazole rings and form a novel nitrogen-rich energetic compound **3**. Theoretical structural optimizations have confirmed that compound **3** has a big  $\pi$ -conjugated structure and a planar molecular configuration (Fig. 1b), with high gas-phase enthalpy of formation of 1309.4 kJ·mol<sup>-1</sup>. Such a big  $\pi$ -conjugated and planar molecular structure enables compound **3** with elevated thermal stability and low sensitivity. The high enthalpy of formation for compound **3** is also helpful for its desired detonation properties.

## 3 Results and Discussion

### 3.1 Synthesis

In our continuing efforts to seek new high-performance energetic materials<sup>[14]</sup>, here we present our attempts at developing new *N*-heterocyclic energetic salts with high performances in terms of high energy, low sensitivity, and excellent thermal stabil-



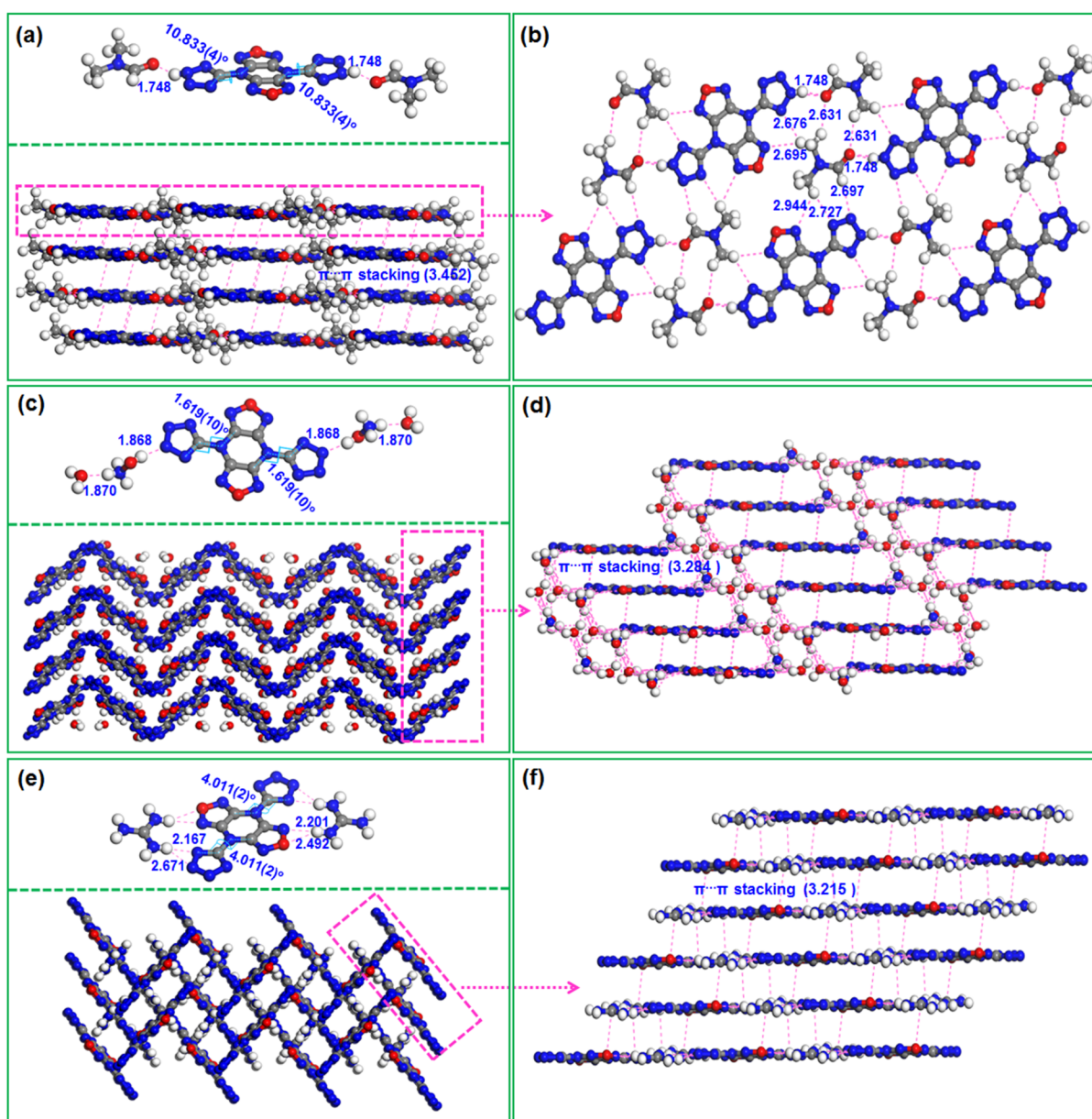
**Fig.1** (a) Some characteristic affecting factors on the three important basic properties (energy, safety, and thermal stability) of energetic materials (b) Molecular structural analysis of candidate energetic anionic compound of compound **3** and its planar molecular configuration (c) Synthetic route of compound **3** and its energetic salts **4a–4e**

ity. A series of new high-performance energetic salts were designed and prepared by combining tetrazole-linked 4, 8-dihydrodifurazano [3, 4-b, e] pyrazine (DFP) based parent molecules with nitrogen-rich cations. The synthetic route of compound **3** and its energetic salts **4a–4e** are shown in Fig. 1c. The synthetic details are provided in the Experimental Section. Compound **1** was prepared according to reported procedures<sup>[15]</sup>. Next, compound **1** was treated with CNN<sub>3</sub>, obtained by reaction of CNBr and NaN<sub>3</sub><sup>[16]</sup>, to form potassium 4, 8-di(1H-tetrazol-5-yl)-difurazano [3, 4-b, e] pyrazine (**2**). The acidification of compound **2** with dilute hydrochloric acid resulted in the target compound **3**. The ammonium (**4a**) and hydrazinium (**4b**) salts were obtained by dissolving **3** in MeOH followed by reac-

tion with excess ammonia or hydrazine hydrate. Salts **4c–4e** were prepared by one-pot reaction of **3** with Ba(OH)<sub>2</sub>·8H<sub>2</sub>O and corresponding sulfate. The structures of **3**, **4c**, and **4d** were further investigated by single crystal X-ray diffraction analysis, and the corresponding CCDC numbers of the crystals were determined as 1836550, 1836551, and 1836552.

### 3.2 Crystal structure

Colorless crystals of compounds **3**, **4c** and **4d** were obtained by slow evaporation of corresponding DMF solution at room temperature. Single-crystal X-ray diffraction revealed that compound **3** co-crystallized with two DMF molecules in triclinic P-1 space group to yield a density of 1.573 g·cm<sup>-3</sup> at 173 K. Two DMF molecules were strongly bonded to molecule **3** with a very short hydrogen bond



**Fig. 2** (a) Molecular configuration of **3** and 3D graphitic-like layered packing of **3**·2DMF (b) Intra-layer packing of **3**·2DMF (c) Molecular configuration, intermolecular hydrogen bonds and 3D wave-like layered packing of **4c**·2H<sub>2</sub>O (d) An enlarged view of the layer-by-layer  $\pi$ - $\pi$  stacking of **4c**·2H<sub>2</sub>O (e) Molecular configuration, intermolecular hydrogen bonds and 3D cross-like layered packing **4d** (f) An enlarged view of the layer-by-layer  $\pi$ - $\pi$  stacking of **4d**

(N—H $\cdots$ O) distance of 1.748 Å. The molecular configuration of **3** was little twisted with a dihedral angle between DFP and tetrazole rings of 10.833(4) $^\circ$  (Fig. 2a), indicating a big  $\pi$ -conjugated structure. The 3D structure of **3**·2DMF was graphitic-like structure with an interlamellar spacing of 3.452 Å, in which molecule **3** firstly formed isolated layer-by-layer stacking structure by  $\pi$ - $\pi$  interactions then extended through DMF molecules as linkers (Fig. 2a, bottom).

The enlarged view of intra-layer packing of **3**·2DMF showed that two DMF molecules formed a dimer with two C—H $\cdots$ O hydrogen bonds (2.631 Å). These further interacted with molecule **3** by hydrogen bonding (including C—H $\cdots$ N and N—H $\cdots$ O) to yield a 2D supramolecular sheet (Fig. 2b).

Similar to neutral molecule **3**, the energetic salt **4c** also co-crystallized with two solvated water molecules, where energetic anion, hydroxylamine cat-

ions and water molecules all successively connected by hydrogen bonding with distances of 1.868 Å and 1.870 Å, respectively. The molecular configuration of the energetic anion can be thought as complete plane due to the small dihedral angle ( $1.619(10)^\circ$ ) between DFP and tetrazole rings (Fig.2c, top). The same phenomenon was also observed in energetic salt **4d**. The energetic anion in salt **4d** showed better molecular planarity with dihedral angle of  $4.011(2)^\circ$  when compared to molecule **3** with dihedral angle of  $10.833(4)^\circ$  (Fig.2a and 2e). The 3D structure of salt **4c** was wave-like (Fig.2c, bottom), and the further enlarged view showed that the energetic anion in **4c** also formed isolated layer-by-layer stacking structure by  $\pi$ - $\pi$  interactions and extended through hydroxylamine cation and water molecule as linkers (Fig.2d). The corresponding  $\pi$ - $\pi$  interactions were obviously stronger than that of neutral crystal **3**·2DMF (3.284 Å vs 3.452 Å) (Fig.2a and 2d).

For energetic salt **4d**, its crystal did not contain any crystal solvent molecules. Two guanidine cations interacted with the energetic anion by N—H···N and N—H···O at distances ranging 2.167 Å to 2.671 Å (Fig.2e top). The 3D structure of 4-d was cross-like (Fig. 2e, bottom), and the further amplified view confirmed the same stacking mode as with **3**·2DMF and **4c**·2H<sub>2</sub>O. Furthermore, the energetic anions in

salt **4d** firstly formed isolated layer-by-layer stacking structures through  $\pi$ - $\pi$  interactions, which then were extended with guanidine cations as linkers (Fig.2a, 2d and 2f). Owing to lack of disturbance from solvent molecules, the  $\pi$ - $\pi$  interactions in salt **4d** were the strongest in the three crystals with the value of 3.215 Å (Fig.2f). Based on above discussions, the main driven force of crystal packing in compound **3** and its corresponding salts was based on the  $\pi$ - $\pi$  interactions originated from the big  $\pi$ -conjugated molecule **3** and its anion. The other components like water molecules and small cations played the role of linkers to extend these  $\pi$ - $\pi$  interactions.

### 3.3 Physicochemical and energetic properties

As shown in Table 1, the physicochemical and energetic properties of all as-prepared energetic compounds were determined by both calculations and measurements. Most of these energetic compounds (except compound **2**) had high nitrogen contents ranging from 60.9% (**4c**) to 68.8% (**4b**), exceeding that of RDX. The CO-based oxygen balances of these compounds varied from -20.7 to -46.2 due to existence of only two oxygen atoms in energetic ionic parent structure. The thermal stabilities of neutral compound **3** and its energetic salts were investigated by differential scanning calorimetry (DSC) at heating rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ . Except for energetic salt **4c**

**Table 1** Physicochemical and energetic properties of compounds **2**, **3**, and **4a-4e** compared to RDX

| compound  | <b>2</b>   | <b>3</b>   | <b>4a</b>  | <b>4b</b>   | <b>4c</b>  | <b>4d</b>   | <b>4e</b>   | RDX <sup>[17]</sup>   |
|---|--|--|--|---|--|---|---|---|
| formula <sup>[a]</sup>                                    | C <sub>6</sub> K <sub>2</sub> N <sub>14</sub> O <sub>2</sub> | C <sub>6</sub> H <sub>2</sub> N <sub>14</sub> O <sub>2</sub> | C <sub>6</sub> H <sub>8</sub> N <sub>16</sub> O <sub>2</sub> | C <sub>6</sub> H <sub>10</sub> N <sub>18</sub> O <sub>2</sub> | C <sub>6</sub> H <sub>8</sub> N <sub>16</sub> O <sub>4</sub> | C <sub>8</sub> H <sub>12</sub> N <sub>20</sub> O <sub>2</sub> | C <sub>8</sub> H <sub>14</sub> N <sub>22</sub> O <sub>2</sub> | C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub> |
| <i>M<sub>w</sub></i> / g·mol <sup>-1</sup> <sup>[b]</sup> | 378.0  | 302.1  | 336.1  | 366.1   | 368.1  | 420.4   | 450.2   | 222.0   |
| <i>N</i> / % <sup>[c]</sup>                               | 51.8   | 64.9   | 66.7   | 68.8  | 60.9   | 66.7  | 68.4  | 37.8  |
| $\Omega$ / % <sup>[d]</sup>                               | -21.2  | -26.5  | -38.1  | -39.3   | -26.1  | -45.7   | -46.2   | 0   |
| <i>T<sub>d</sub></i> / °C <sup>[e]</sup>                  | 279  | 278  | 271  | 264   | 229  | 260   | 314   | 204   |
| $\Delta_f H$ / kJ·mol <sup>-1</sup> <sup>[f]</sup>        | 783.8  | 1205.7   | 1046.1   | 1351.0  | 1146.7   | 1011.2  | 1246.1  | 70.3  |
| $\Delta_f H$ / kJ·g <sup>-1</sup> <sup>[f]</sup>          | 2.07   | 3.99   | 3.11   | 3.69  | 3.12   | 2.41  | 2.77  | 0.32  |
| <i>D<sub>c</sub></i> / g·cm <sup>-3</sup> <sup>[g]</sup>  | 1.86   | 1.84   | 1.61   | 1.69  | 1.71   | 1.73  | 1.71  | 1.80  |
| <i>D</i> / m·s <sup>-1</sup> <sup>[h]</sup>               | 7653   | 8884   | 8200   | 9035  | 8820   | 8808  | 9005  | 8795  |
| <i>p</i> / GPa <sup>[i]</sup>                             | 20.3   | 31.4   | 23.7   | 29.7  | 28.4   | 27.4  | 28.0  | 34.9  |
| <i>IS</i> / J <sup>[j]</sup>                              | 35   | 20   | >50  | 38  | >50  | 35  | 25  | 7.4   |
| <i>FS</i> / N <sup>[k]</sup>                              | 360  | 360  | >360   | 360   | >360   | 360   | 360   | 120   |

Note: [a] molecular formula. [b] molecular weight. [c] nitrogen content. [d] OB for C<sub>a</sub>H<sub>b</sub>O<sub>c</sub>N<sub>d</sub>,  $1600(c-a-b/2)/MW$  (based on CO). [e] decomposition temperature (onset temperature at a heating rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ ). [f] heat of formation. [g] density measured using a gas pycnometer at room temperature. [h] detonation velocity [i] detonation pressure [j] impact sensitivity. [k] friction sensitivity.



(229 °C), compound **3** and other salts all exhibited high thermostability values with decomposition temperatures above 260 °C. These values were obviously superior to those of common explosives RDX (204 °C), CL-20 (215 °C), and TKX-50 (221 °C). Especially, the decomposition temperature of salt **4e** reached as high as 314 °C, indicating its great potential as heat-resistant explosive.

The heat of formation and density are two important parameters determining the detonation velocity and detonation pressure of energetic materials. First, the solid heat of formation of compound **3** and its corresponding salts were calculated by Gaussian 09 program package<sup>[18]</sup>. As expected, the integration of furazan and tetrazole rings enabled compound **3** and its salts with high positive heats of formation with values ranging 783.8 kJ·mol<sup>-1</sup> (**2**) to 1351.0 kJ·mol<sup>-1</sup> (**4b**), and 2.07 kJ·g<sup>-1</sup> (**2**) to 3.99 kJ·g<sup>-1</sup> (**3**). These values were significantly superior to that of RDX (70.3 kJ·mol<sup>-1</sup>, 0.32 kJ·g<sup>-1</sup>). Next, the densities of compound **3** and its salts were obtained by gas pycnometer at room temperature and they ranged from 1.61 to 1.86 g·cm<sup>-3</sup>. Using the measured densities and calculated heats of formation, the detonation velocity ( $D$ ) and pressure ( $p$ ) values of compound **3** and its salts were evaluated by EXPLO5 (v6.02) program<sup>[19]</sup>. As shown in Table 1, except compound **2** ( $D$ : 7653 m·s<sup>-1</sup>) and salt **4a** ( $D$ : 8200 m·s<sup>-1</sup>), the detonation velocities of compound **3** and the other salts were all above 8800 m·s<sup>-1</sup>, hence higher than that of RDX ( $D$ : 8795 m·s<sup>-1</sup>). For salts **4b** and **4e**, their detonation velocities exceeded 9000 m·s<sup>-1</sup> with values of 9035 m·s<sup>-1</sup> and 9005 m·s<sup>-1</sup>, respectively. The detonation pressures of these energetic materials ranged from 20.3 GPa to 31.4 GPa. A standard BAM method was employed to evaluate the impact and friction sensitivities of these energetic materials. As expected, all materials showed low impact sensitivities ( $IS$ ) and friction sensitivities ( $FS$ ) with values of  $\geq 20$  J and  $\geq 360$  N, respectively, which were far superior to that of RDX ( $IS$ : 7.4 J,  $FS$ : 120 N). It is notable that the impact sensitivities of compounds **4a** and **4c**

were more than 50 J. Overall, these new developed tetrazole-DFP energetic materials depicted excellent comprehensive performances in terms of high decomposition temperatures ( $T_d > 260$  °C), high detonation velocities ( $D > 8800$  m·s<sup>-1</sup>), and low mechanical sensitivities ( $IS \geq 20$  J,  $FS \geq 360$  N). These features could be attributed to the substantial  $\pi$ -conjugated molecular structure and strong  $\pi$ - $\pi$  interactions in the crystals.

## 4 Conclusions

In summary, a series of novel tetrazole-linked 4, 8-dihydrodifurazano [3, 4-b, e] pyrazine (DFP) based energetic salts have been synthesized and characterized by NMR spectroscopy, IR spectroscopy, and elemental analysis. X-ray diffraction analysis of compounds **3**, **4c**, and **4d** demonstrated the main driven force of crystal packing in compound **3** and its corresponding salts was the  $\pi$ - $\pi$  interactions, which contributed to their inherent high thermal stabilities. The obtained energetic salts exhibited high detonation velocities ( $D > 8800$  m·s<sup>-1</sup>), low mechanical sensitivities ( $IS \geq 20$  J and  $FS \geq 360$  N), and high thermal decomposition temperatures ( $T_d > 260$  °C). In particular, the thermal decomposition temperature of energetic salt **4e** is up to 314 °C, while its detonation velocity and impact sensitivity were 9005 m·s<sup>-1</sup> and 25 J, respectively. Our studies have demonstrated that the as-synthesized tetrazole-linked DFP-based energetic salts are promising insensitive high-energy density materials.

## 5 Experimental Section

### 5.1 Caution!

Cyanogen azide is extremely toxic and dangerous. Therefore, it must always be dissolved in a solvent to give a dilute solution in the process of synthesizing compound **2**. Although all of these compounds are insensitive materials, these compounds must be handled by using eye protection and leather gloves. All of the energetic compounds must be synthesized only in small amounts, and mechanical ac-

tions involving scratching or scraping must be avoided in the synthesis process.

DFP and compound **1** were prepared according to the reference procedures and were identified by comparison of their spectral data with those reported in the literatures[15]. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. NMR spectra were obtained on a Bruker AV II-600 ( $^1\text{H}$  NMR at 600 MHz and  $^{13}\text{C}$  NMR at 150 MHz) spectrometer. The  $^1\text{H}$  NMR chemical shifts were measured relative to  $\text{DMSO-}d_6$  as the internal reference ( $\text{DMSO-}d_6$ )  $\delta$ : 2.50. The  $^{13}\text{C}$  NMR chemical shifts were given using  $\text{DMSO-}d_6$  as the internal standard ( $\text{DMSO-}d_6$ )  $\delta$ : 39.52. IR spectra were recorded on PerkinElmer Spectrum Two IR Spectrometers. Elemental analyses were performed on Vario Micro cube elemental analyzer. X-Ray single-crystal diffraction data were collected on an Oxford Xcalibur3 diffractometer with  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Thermal property measurements were made using a TGA/DSC Mettler Toledo calorimeter. Densities were obtained on a Micromeritics Accupyc II 1340 gas pycnometer. Impact and friction sensitivities were measured by employing a standard BAM fallhammer and a BAM friction tester.

## 5.2 Synthesis and Characterization of Energetic Materials

### Potassium 4, 8-di(1*H*-tetrazol-5-yl)-difurazano [3, 4-b, e] pyrazine (2)

Cyanogen bromide (2.65 g, 25.0 mmol) was dissolved in anhydrous acetonitrile (100 mL) at 0 °C, and then sodium azide (6.50 g, 100 mmol) was added in batch to the above solution. The inorganic salt was filtered off after the mixture was stirred at 0–5 °C for 4 h. The cyanogen azide solution was added to the aqueous solution of compound **1** (1.21 g, 5.0 mmol, in 40 mL of water). After stirring overnight at ambient temperature, the solvent was removed in air. The product was purified by washing with acetonitrile and cold water, and after filtration and drying to give a slight yellow solid **2** (1.05 g, yield: 56%). IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3400,

2148, 1638, 1580, 1501, 1389, 1202, 1129, 1094, 1058, 1019, 944, 916, 858, 844, 736, 669, 552, 470.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 147.1, 155.3. Elemental analysis, Anal. calcd for  $\text{C}_6\text{K}_2\text{N}_{14}\text{O}_2$  (%): C 19.05, N 51.83; found: C 17.90, N 50.57.

### 4, 8-Di(1*H*-tetrazol-5-yl)-difurazano [3, 4-b, e] pyrazine (3)

Compound **2** (1.0 g, 2.65 mmol) was dissolved in hot water (50 mL), hydrochloric acid (2 N) was used to adjust the pH to 12. After filtration and drying to give a white solid **3** (0.78 g, yield: 97%). IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3164, 2976, 2850, 1721, 1643, 1604, 1587, 1544, 1493, 1407, 1373, 1224, 1158, 1097, 1057, 1037, 945, 936, 926, 877, 846, 768, 738, 674, 553.  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 10.45 (s, 2H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 146.0, 155.3. Elemental analysis, Anal. calcd for  $\text{C}_6\text{H}_2\text{N}_{14}\text{O}_2$  (%): C: 23.85, H: 0.67, N: 64.89; found: C 23.94, H 1.11, N 63.43.

### General procedure for synthesis of 4a to 4b

Compound **3** (604 mg, 2.0 mmol) was suspended in methanol (50 mL) and heated to 60 °C, and then excess ammonia or hydrazine hydrate was added. The solvent was removed after stirring 2 h at 60 °C. The product was purified by washing with methanol, and after filtration and drying to give **4a–4b**.

### Diammonium-4, 8-di(1*H*-tetrazol-5-yl)-difurazano [3, 4-b, e] pyrazine (4a)

White solid (520 mg, 77%), IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3186, 3050, 2918, 2137, 1846, 1709, 1631, 1576, 1509, 1413, 1385, 1249, 1204, 1133, 1093, 1054, 1026, 944, 920, 844, 793, 736, 666, 554, 498, 470.  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 7.28 (s, 8H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 147.1, 155.3. Elemental analysis, Anal. calcd for  $\text{C}_6\text{H}_8\text{N}_{16}\text{O}_2$  (%): C 21.43, H 2.40, N 66.65; found: C 22.16, H 2.82, N 65.22.

### Dihydrazinium-4, 8-di(1*H*-tetrazol-5-yl)-difurazano [3, 4-b, e] pyrazine (4b)

White solid (545 mg, 69%), IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3348, 3298, 3200, 2962, 2869, 2749, 2637, 2139, 1606, 1640, 1581, 1502, 1535, 1425,

1391, 1318, 1237, 1211, 1117, 1029, 1018, 970, 946, 920. 866, 844, 820, 735, 634, 553.  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ ):  $\delta$ =6.14 (s, 10H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ ):  $\delta$ =147.1, 155.4. Elemental analysis, calcd for  $\text{C}_6\text{H}_{10}\text{N}_{18}\text{O}_2$  (%): C 19.68, H 2.75, N 68.84; found: C 18.77, H 3.47, N 67.51.

#### General procedure for synthesis of 4c-4e

Compound **3** (302 mg, 1.0 mmol) was suspended in water (60 mL),  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  (316 mg, 1 mmol) was added after the temperature reaching to 60 °C, and continue to react for 2 hours. Then the corresponding sulphate (1 mmol) was added to the solution. White solid ( $\text{BaSO}_4$ ) was removed by filtering after the mixture stirring for 4 hours at 60 °C, and then the solvent of filtrate was removed by rotary evaporation. The residue was recrystallized from methanol and water to give **4c-4e**.

#### Dihydroxyammonium-4,8-di(1H-tetrazol-5-yl)-difurazano[3,4-b,e]pyrazine (4c)

White solid (280 mg, 76%), IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3319, 3227, 2678, 2032, 1637, 1583, 1528, 1501, 1392, 1323, 1222, 1135, 1097, 1031, 1006, 946, 922, 871, 847, 710, 693, 554.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$ : 10.23 (s, 8H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$ : 147.1, 155.3. Elemental analysis, Anal. calcd for  $\text{C}_6\text{H}_8\text{N}_{16}\text{O}_4$  (%): C 19.57, H 2.19, N 60.86; found, C: 17.98, H 2.38, N 61.24.

#### Diguanidinium-4,8-di(1H-tetrazol-5-yl)-difurazano[3,4-b,e]pyrazine (4d)

White solid (367 mg, 87%), IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3468, 3376, 3181, 2228, 1667, 1653, 1638, 1579, 1532, 1495, 1388, 1315, 1200, 1115, 1068, 944, 921, 841, 819, 732, 606, 551.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$ : 7.10 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$ : 146.9, 158.0. Elemental analysis, Anal. calcd (%) for  $\text{C}_8\text{H}_{12}\text{N}_{20}\text{O}_2$  (%): C 22.86, H 2.88, N 66.65; found: C 22.73, H 3.19, N 65.94.

#### Di(aminoguanidinium)-4,8-di(1H-tetrazol-5-yl)-difurazano[3,4-b,e]pyrazine (4e)

White solid (380 mg, 84%), IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3440, 3349, 3167, 3086, 2777, 1673, 1627, 1601, 1573, 1504, 1448, 1385, 1210, 1109, 991,

943, 916, 838, 737, 686, 574, 552, 519.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$ : 4.69 (s, 4H), 6.76 (s, 4H), 7.24 (s, 4H), 8.58 (s, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$ : 147.1, 155.2, 158.7. Elemental analysis, Anal. calcd for  $\text{C}_8\text{H}_{14}\text{N}_{22}\text{O}_2$  (%): C 21.34, H 3.13, N 68.43; found: C 20.53, H 3.59, N 67.86.

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## 高热稳定和低感度多环类含能材料的设计与合成

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**摘要:** 发展具有高能、低感、高热稳定性的新型含能材料是人们一直追求的目标。本研究设计、合成了一系列基于四唑连4,8-双呋喃并[3,4-b,e]吡嗪(DFP)的含能离子盐。含能离子盐具有优异的综合性能,如热分解温度较高( $T_d$ : >260 °C),感度较低( $IS \geq 20$  J,  $FS \geq 360$  N)和爆速较高等( $D > 8800$  m·s<sup>-1</sup>)。值得特别指出的是,化合物**4e**的热分解温度高达314 °C,并且其爆速及撞击感度分别为9005 m·s<sup>-1</sup>和25 J,是一种极具潜力的钝感高能量密度材料。

**关键词:** 高能量密度材料; 双呋喃并吡嗪; 四唑; 爆轰性能; 感度

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## 含能材料基因科学研究中心招聘启事

### 一、中心简介

含能材料基因科学研究中心位于四川绵阳,隶属于中国工程物理研究院化工材料研究所。中心现拥有计算含能材料科学团队、含能分子创制团队、含能材料晶体科学团队、纳米含能材料与器件团队、含能材料高效表征与分析团队五个科研团队,中心成员承担军科委项目、总装专项、国家自然科学基金、973项目等多个课题,在 *Chem. Rev.*, *Nat. Commun.*, *Angew.*, *Nano Energy*, *JACS* 等 SCI 期刊发表论文近 300 篇,获得国家发明奖、军队科技进步一等奖、邓稼先青年科技奖等多项奖励,现面向国内外招聘。

### 二、研究领域

含能材料分子设计与合成、结晶化学、微纳米含能材料、计算材料学、微观表征与分析

三、应聘条件: 研究生学历,中国国籍,遵纪守法。

四、工作地点: 四川省绵阳市

五、福利待遇: 1. 稳定有吸引力的薪酬待遇;提供职工公寓或周转房,职工食堂;

2. 购买五险、住房公积金,发放安家费、住房补贴;

3. 除法定节假日,还享受年休假、有薪事假、探亲假、保健假等;

### 六、研究生及博士后培养

1. 招收“材料科学与工程”、“兵器科学与技术”硕博研究生及凝聚态物理博士研究生。

2. 博士后研究方向: 钝感高能材料理论计算、设计合成、分析表征。

含能晶体制备与表征;纳米含能材料与器件。

应聘博士后需在博士毕业两年内申请,博士后在站期间薪酬优厚,出站就业经双方选择,可留所工作。

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