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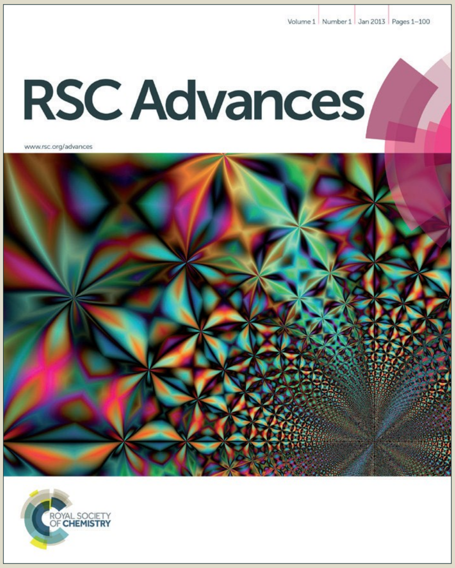

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Synthesis, Characterization and Properties of Heat-resistant Explosive Materials: Polynitroaromatic Substituted Difurazano[3,4-*b*:3’4’-*e*]pyrazines

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The synthesis of three heat-resistant explosive materials: 4,8-di(2,4,6-trinitrophenyl)difurazano[3,4-*b*:3’,4’-*e*]pyrazine (**1**), 4,8-di(2,4-dinitrophenyl)difurazano[3,4-*b*:3’,4’-*e*]pyrazine (**2**), 4-amino-8-(2,4,6-trinitrophenyl)difurazano[3,4-*b*:3’,4’-*e*]pyrazine (**3**),were reported and characterized by ^{1}H NMR,^{13}C NMR, IR as well as elemental analysis. An X-ray crystallographic analysis confirmed the structure of **2**, as well as displayed intermolecular hydrogen bonding. The thermal behaviors of these compounds were studied with differential scanning calorimetry (DSC) and thermal gravity-differential thermal gravity analysis (TG-DTG) methods. All compounds showed good thermal stability with exothermic decomposition peaks in the range of 283°C to 415°C, on DSC. Sensitivities and calculated explosive performances were also reported for these energetic materials. All results showed that polynitroaromatic substituted difurazano[3,4-*b*:3’4’-*e*]pyrazines have the potential to be useful heat-resistant explosive materials.

Introduction

The synthesis and development of new heat-resistant explosive materials with improved thermal stability and performance are of interest in modern military and civilian usage, such as in space industry or deep oil-well drilling.[1] Benzene compounds which are polysubstituted with nitro and amino groups have played an important role in the area of high-temperature resistant explosive.[2] The representative compound of such explosive is 1,3,5-triamino-2,4,6-trinitrobenzene (TATB),[3] which exhibits a density of 1.94 g cm^{-3} with decomposition temperature of 360°C.[4] It is often used as the benchmark for comparison of thermal stable and insensitive explosives. The aminonitro heterocyclic compounds are also proved to be useful as thermally stable energetic materials.[5] Pagoria *et al.* reported the synthesis of 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105), having a density of 1.92 g cm^{-3} and decomposition temperature of 354°C.[6] Other thermally stable explosives include 2,2’,4,4’,6,6’-hexanitrostilbene (HNS), tetranitrodibenzotetraazapentalene (TACOT) and 3,5-dinitro-2,6-bispicrylamino pyridine (PYX) (Fig.1).[7-9] However, new heat-resistant explosives with enhanced thermal stability and explosive performance, as well as lower sensitivity, are still in high demand.

The introduction of certain group to aromatic nitro compounds is one of the simplest approaches to impart thermal stability to explosive molecules. For instance, Agrawal *et al.* reported the synthesis of two thermally stable explosives, 1,3-bis(1,2,4-triazol-3-amino)-2,4,6-trinitrobenzene (BTATNB) and 4,4’-bis(1,2,4-triazol-3-ylamino)-2,2’,3,3’,5,5’,6,6’-octanitroazobenzene (BTDAONAB), by condensing triazole ring with aromatic nitro compounds.[10,11] Furazanopyrazine derivatives have been demonstrated their ability to form energetic materials as a result of their high nitrogen contents, high energy density and good oxygen balance.[12] On the other hand, furazanopyrazines have scarcely been studied as heat-resistant energetic materials for the low thermal stability. 4*H*,8*H*-Difurazano[3,4-*b*:3’,4’-*e*]pyrazine (DFP), reported by Sheremetev *et al.* and Starchenkov *et al.* respectively,[13] exhibit moderate thermal stability with decomposition temperature of 279°C.[14] In our idea, by incorporating polynitro aromatic or amino group to DFP, new generation heat-resistant materials can be derived. 4,8-Di(2,4,6-trinitrophenyl)difurazano[3,4-*b*:3’,4’-*e*]pyrazine (**1**) first reported by Tselinskii *et al.*, who have published its synthesis and some analytical data (IR spectroscopy and element analysis).[15] Nevertheless, no data about thermal performance, sensitivity and explosive properties of **1** has been published in the literature.

Herein, we synthesize **1** and two new derivatives 4,8-di(2,4-dinitrophenyl)difurazano[3,4-*b*:3’,4’-*e*]pyrazine (**2**) and 4-amino-8-(2,4,6-trinitrophenyl)difurazano[3,4-*b*:3’,4’-*e*]pyrazine (**3**), characterize the structures and compare the properties of these materials. These substances display outstanding thermal stability and high energy performance comparable with common heat-resistant explosives.

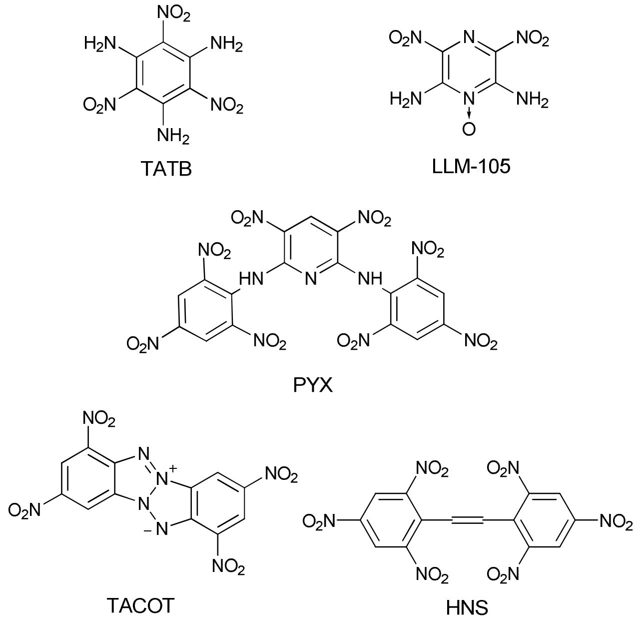
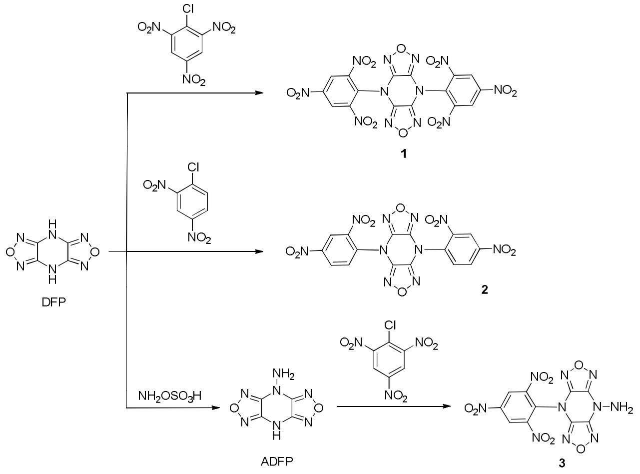


Fig.1 Structures of common heat-resistant explosives.

Results and discussion

Synthesis Aspects

As illustrated in Scheme 1, the targeted three compounds were obtained by the reactions of the respective nitrobenzene derivatives with DFP or 4-amino-difurazano[3,4-*b*:3',4'-*e*]pyrazine (ADFP) in acetonitrile. The synthetic route was according to the previously reported procedure by Tselinskii *et al.*.[15] It was observed that the reactivity of DFP and 1-chloro-2,4-dinitrobenzene was lower than that of 2-chloro-1,3,5-trinitrobenzene. A supposed reason is that the eletrophilicity of 2-chloro-1,3,5-trinitrobenzeneis is stronger than 1-chloro-2,4-dinitrobenzene. ADFP can also be used as an appropriate nucleophile to give the corresponding product in high yield. However, **3** was not able to separate from acetonitrile, the pure compound was obtained by column chromatography.



Scheme 1 Synthesis of compounds **1**, **2** and **3**.

X-ray crystallographyof 2

The molecular structure of the crystalline **2** is shown in Fig.2. **2** crystallizes in the space group P2(1)/n with four formula units in the unit cell and a density of 1.734 g cm^{-3}.The analytical results indicate that the whole molecule presents mirror symmetry. The bond distances of C8−N3 [1.391(4) Å] and C8−N5 [1.290(3) Å] are close to typical C−N double bond, which are close to the value of DFP.[16] The torsion angle of C7−N3−C8−N5 is -179.22°, which indicates that furazanopyrazine ring is coplanar as a result of conjugation. However, the benzene ring are twisted out of the plane, which can be seen from the torsion angle of C7−N3−C6−C5 (-134.92°). Further investigation on hydrogen bonds within the packing arrangement of **2** reveals that the existence of substantial intermolecular interactions contribute to an increase in density (Fig.3). Relevant data and parameters of the X-ray measurement and refinement are given in Table 1.

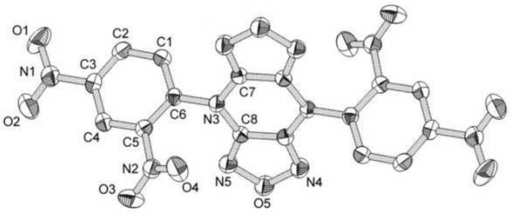


Fig.2 X-ray structure of **2** with thermal ellipsoids at 50% probability.

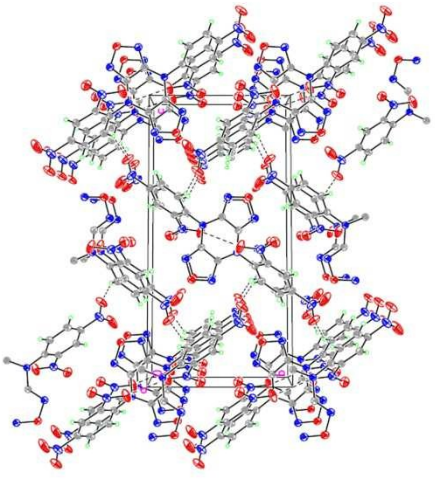


Fig.3 Packing diagram of **2** viewed down the a axis.

Table 1 Crystal data and structure refinement parameters of **2**.

Empirical formula	$C_8H_3N_5O_5$
Formula weight	249.15
T/K	296(2)
λ/Å	0.71073
Crystal system	Monoclinic
space group	P2(1)/n
Unit cell dimensions/Å,°	*a* = 5.8796(12), α = 90 *b* = 8.9227(18), *β* = 98.193 *c* = 18.378(4), *γ* = 90
V/$Å^3$	954.3(3)
Z	4
Dc/g·cm^{-3}	1.734
Absorption coefficient/mm^{-1}	0.149
F (000)	504

Goodness-of-fit on F^2	1.044
Final R indices (I>2σ(I))	R_1 = 0.0314, wR_2 = 0.0786
R indices (all data)	R_1 = 0.0347, wR_2 = 0.0810
Largest diff. peak and hole/e. Å^{-3}	0.199 and -0.220

Thermal Behavior

The typical DSC curves (Fig.4) indicated that all three compounds exhibit excellent thermal stability. It can be seen from the figure that exothermic decomposition for these nitro compounds occurred between 280 and 420°C. Among these materials, **1** has the highest thermal stability with exotherm peak at 415.4°C, which is far superior to those of common heat-resistant materials (TATB: 360°C; TACOT: 401°C; PYX: 385°C). For each compound, no melting event was observed prior to decomposition.

The TG–DTG curves of these compounds are shown in Figs. 5 to 7, respectively. For **1** and **2**, the total weight loss are 95.41% and 85.10% over one decomposition phase. For **3**, there are three continuous decomposition processes with the DTG peaks from 297.7 to 376.2°C, and the total weight loss is 88.57%. In this decomposition temperature range there are three exothermic processes suggested by DSC curve. In contrast to DFP,[14] the structures of the employed polynitro aromatic group displayed significant effects upon the thermal stability.

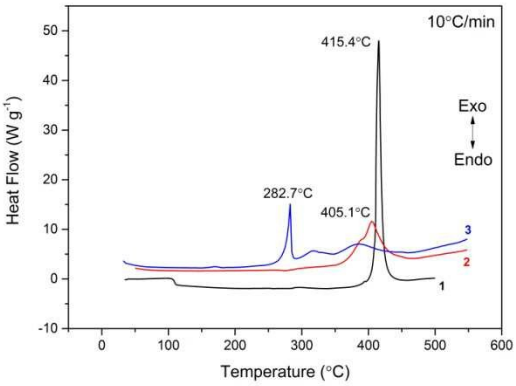


Fig.4 The DSC curves of **1**, **2** and **3**.

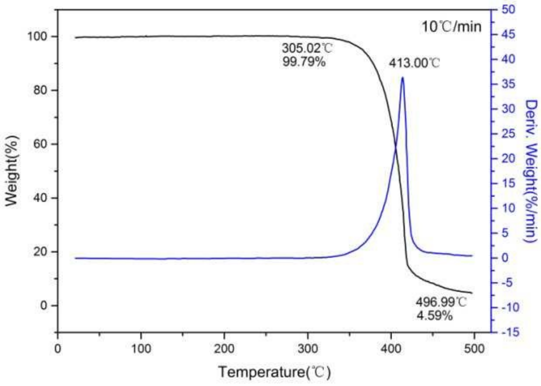


Fig.5 The TG–DTG curves of **1**.

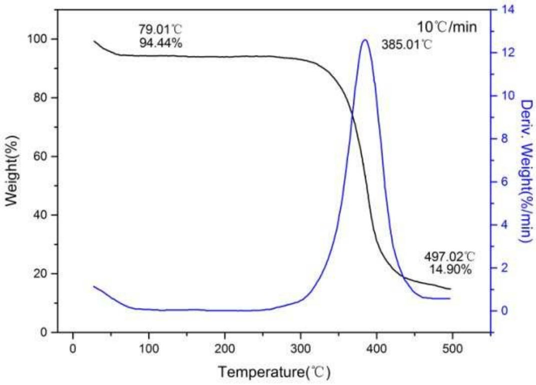


Fig.6 The TG–DTG curves of **2**.

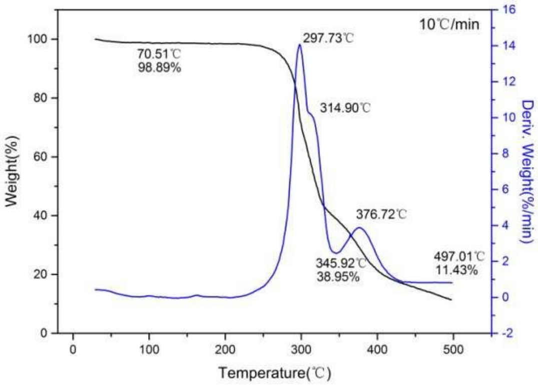


Fig.7 The TG–DTG curves of **3**.

Energetic Characterization

As shown in Table 2, the furazanopyrazine derivatives exhibit energetic properties. The densities of all the compounds were measured by a gas pycnometer, falling in the range of 1.72-1.82 cm^{-3}, which equals or exceeds that of common heat-resistant explosives. In addition, **1** possesses the highest density (1.82 g cm^{-3}) in these compounds. This result proves that the increase of nitro group has a positive effect on the molecular density. The sensitivities of all explosives were determined experimentally according to standard BAM methods.[17] All of the compounds, with impact sensitivities range from 10 J to 20 J, are less sensitive than HNS (5 J) and PYX (9 J). The friction sensitivity is 240 N for compound **1** and drops to >360 N for compound **3**. Thus, according to the range of sensitivities from UN recommendations,[18] **1** and **2** are to be classified as sensitive towards impact and friction, whereas **3** is sensitive towards impact and insensitive towards friction.

The heats of formation of furazanopyrazine compounds wer calculated using the Gaussian 09 quantum chemistry package by designing appropriate isodesmic reactions (see ESI†). All compounds exhibit high positive heats of formation (782.6 mol^{-1} to 894.1 kJ mol^{-1}), which are even far more than that of common heat-resistant explosives. Detonation parameters were calculated by the Kamlet-Jacobs equation by using the calculate values for the heats of formation and the experimental values fo the densities.[19] The calculated detonation pressures and velociti lie in the range of 23.0-28.2 GPa and 7200-7874 m s^{-1}, respectively. In terms of detonation velocity, **1** is superior to those of thermally stable explosives. The calculated properties coupled with the rather high thermal stabilities suggest that these furazanopyrazine compounds may be attractive candidates for heat-resistant energetic applications.

Table 2 Energetic properties of of heat-resistant explosives.

Compd.	T_d [a] (°C)	ρ[b] (g cm^{-3})	ΔH_f [c] (kJ mol^{-1})	P[d] (GPa)	D[e] (m s^{-1})	IS[f] (J)	FS[g] (N)	ESD[h] (J)
1	415	1.82	894.1	28.2	7874	10	240	1
2	405	1.74 (1.73)[i]	845.6	23.0	7200	16	300	1.5
3	283	1.72	782.6	25.7	7641	20	>360	3
TATB	360	1.94	-139.8	29.1	7867	50	>360	11
HNS	324	1.73	57.7	21.8	7170	5	240	5
TACOT	401	1.76	536.0	24.5	7200	28	>360	7
PYX	385	1.77	80.3	24.2	7448	9	280	1

[a] Decomposition temperature. [b] Density measured by gas pycnometer (25°C). [c] Heat of formation. [d] Detonation pressure (calculated with K-J equation). [e] Detonation velocity (calculated with K-J equation). [f] Impact sensitivity. [g] Friction sensitivity. [h] Electrostatic discharge sensitivity. [i] Crystal density at 298 K.

Conclusions

In summary, the syntheses and su bsequent characterizations of nitrophenyl derivatives of DFP were carried out. Single-crystal X-ray measurement was accomplished for **2** and deliver insight into structural characteristic. The thermodynamic analysis (DSC and TG-DTG analysis) results indicate these compounds have excellent thermal stability. Compound **3** was the most insensitive derivative, with an impact sensitivity 20 J and friction sensitivity >360 N. As a result of the experimental densities and calculated high positive heat of formations, the calculated detonation pressures and velocities fall in the range of 23.0-28.2 GPa and 7200-7874 m s^{-1}. Worth mentioning is compound **1**, which has a remarkably high decomposition temperature of 415°C and good performance value, make it an interesting candidate for applications in heat-resistant explosive.

Experimental Section

General Information.

All reagents and solvents were used as received. 4*H*,8*H*-Difurazano[3,4-*b*:3',4'-*e*]pyrazine (DFP) and 4-amino-difurazano[3,4-*b*:3',4'-*e*]pyrazine (ADFP) were prepared by the literature procedure.[13b,16] ^1H NMR and ^{13}C NMR were obtained on a Bruker AV500 NMR spectrometer. Infrared spectra were obtained from KBr pellets on a Nicolet NEXUS870 Infrared spectrometer in the range of 4000-400 cm^{-1}. Elemental analyses (C, H and N) were performed on a VARI-El-3 elemental analyzer. Differential scanning calorimetry (DSC) were carried out in a platinum sample containerusing a Shimadzu DSC-60 at a heating rate of 10 °C min^{-1}. The TG-DTG experiments were performed with a SDT-Q600 apparatus (TA, USA) operating at a heating rate of 10 °C min^{-1} in a flow of dry oxygen-free nitrogen at 10 mL min^{-1}. For all materials, the impact sensitivity were determined with a ZBL-B impact sensitivity instrument, the friction sensitivity were determined with a FSKM 10 friction sensitivity instrument, the electrostatic discharge sensitivity were determined with a ESD 2008A electric spark tester.

X-Ray crystallography of 2.

A thin plate of dimensions 0.38×0.31×0.24 mm^2 was mounted on a MiteGen MicroMesh using a small amount of Cargille Immersion Oil. Diffraction data were collected at 296(2) K on a Oxford diffraction Gemini S Ultra diffractometer using Mo-*Kα* radiation (λ = 0.71073 Å). The structure was solved by direct methods using SHELXS-97 program[20] and refined against *F*2 by full-matrix least-squares using SHELXL-97 program.[21]

Theoretical study—computational details.

Computations were performed with the Gaussian 09 (Revision B. 01) suite of programs.[22] The geometric optimization of the structures and frequency analyses were carried out using B3LYP functional with the 6-31+G** basis set, and single-point energies were calculated at the MP2(full)/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. According to the method of isodesmic reactions, the gas phase enthalpies of formation were computed and the enthalpy of reaction is obtained by combining the MP2/6-311++G**energy difference for the reactions, the scaled zero point energies, and other thermal factors. The detonation velocity (*D*) and detonation pressure (*P*) were evaluated by the empirical Kamlet–Jacobs (K–J) equations as shown in Equations (1), (2) and (3).

$$P = 1.558\,\rho^2\Phi \qquad (1)$$

$$D = 1.01\Phi^{1/2}(1.011+1.312\,\rho) \qquad (2)$$

$$\Phi = 0.4889N\,(MQ)^{\ 1/2} \qquad (3)$$

D is the predicted detonation velocity (m s^{-1}), *P* is the detonation pressure (GPa), and ρ is the compound density (g cm^{-3}). Φ, N, M and Q are characteristic parameters of an explosive; Q is the chemical energy of detonation (kJ g^{-1}). The densities and the calculated heats of formation were used to compute the *D* and *P* values.

4,8-Di(2,4,6-trinitrophenyl)difurazano[3,4-*b*:3',4'-*e*]pyrazine (1).

To a solution of DFP (7 g, 42 mmol) in anhydrous acetonitrile (100 mL) was added NEt_3 (8.48 g, 84 mmol). After stirring for 20 min at room temperature, a solution of 2-chloro-1,3,5-trinitrobenzene (22.28 g, 90 mmol) in anhydrous acetonitrile (50 mL) was added. The reaction mixture was held for 5 h at room temperature and was left stand for 24 h. The solid was filtered and washed with acetonitrile, hot water and methanol to give 19.70 g (79.8%) of the desired product as yellow powder. ^1H NMR (DMSO-d_6, 500 MHz, ppm): δ = 9.47 (s, 4H, C_6H_2). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ = 149.08, 146.44, 145.89, 126.91, 123.44. IR (KBr, cm^{-1}): υ = 3100, 2887, 1613, 1584, 1549, 1478, 1409, 1386, 1341, 1191, 1083, 914, 846. Anal. Calcd for $C_{16}H_4N_{12}O_{14}$:C 32.67, H 0.69, N 28.57; Found C 32.49, H 0.47, N 28.56.

4,8-Di(2,4-dinitrophenyl)difurazano[3,4-*b*:3',4'-*e*]pyrazine (2). To a solution of DFP (1 g, 6 mmol) in anhydrous acetonitrile (15 mL) was added NEt_3 (1.21 g, 12 mmol). After stirring for 20 min at room temperature, a solution of 1-chloro-2,4-dinitrobenzene (2.43 g, 12 mmol) in anhydrous acetonitrile (5 mL) was added. The reaction mixture was refluxed for 8 h, cooled to room temperature, and was left stand for 24 h at -18°C. The solid was filtered and washed with acetonitrile, hot water and methanol to give 1.87 g (62.3%) of the desired product as red crystal. ^1H NMR (Acetone-d_6, 500 MHz, ppm): δ = 9.13 (d, 1H, C_6H_3), 8.90 (s, 1H, C_6H_3), 8.50 (d, 1H, C_6H_3). ^{13}C NMR (Acetone-d_6, 125 MHz, ppm): δ = 149.40, 147.94, 145.70, 133.61, 132.22, 131.98, 123.38. IR (KBr, cm^{-1}): υ = 3092, 1707, 1651, 1612, 1588, 1550, 1340, 1086, 1055, 922, 830. Calcd for $C_{16}H_6N_{10}O_{10}$: C 38.57, H 1.21, N 28.11; Found C 38.52, H 1.25, N 28.39.

4-Amino-8-(2,4,6-trinitrophenyl)difurazano[3,4-*b*:3',4'-*e*]pyrazine (3).

To a solution of ADFP (1.36 g, 7.5 mmol) in anhydrous acetonitrile (20 mL) was added NEt_3 (0.75 g, 7.5 mmol). After stirring for 10 min at room temperature, a solution of 2-chloro-1,3,5-trinitrobenzene (1.86 g, 7.5 mmol) in anhydrous acetonitrile (10 mL) was added. The reaction mixture was held for 4 h at room temperature. The solvent was evaporated under vacuum, and the residue was purified by column chromatography (silica gel, eluted using 20% CH_3COOEt-petroleum ether) to give 2.48 g (84.4%) of the desired product as brown powder. ^1H NMR (DMSO-d_6, 500 MHz, ppm): δ = 9.38 (s, 2H, C_6H_2), 6.03 (s, 2H, NH_2). ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ = 149.67, 148.66, 146.46, 145.82, 126.50, 124.49. IR (KBr, cm^{-1}): υ = 3367, 3095, 1613, 1547, 1551, 1406, 1386, 1342, 1085, 941, 827. Calcd for $C_{10}H_4N_{10}O_8$: C 30.62, H 1.03, N 35.71; Found C 30.57, H 1.08, N 35.91.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [X-ray crystallography, theoretical study, ^1H and ^{13}C NMR spectra of compounds **1**-**3**]. See DOI: 10.1039/b000000x/

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Three heat-resistant explosive materials were synthesized and their thermal behaviors, sensitivities and calculated explosive performances were also reported.