Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2023

Electronic Supplementary Information (ESI)

Concise Synthesis of A Fused Energetic Pyrazolotriazine with Good Performances

Haichuan Shi[a], Yuqing Wang[a], Xinyu Wang[a], Xiaotian Zhang[a], Ming Huang[b], Haijun Yang*[a], and Zhenghang Luo*[a]

a.School of Materials and Chemistry, Southwest University of Science and Technology, Mianyang, 621010, China.

b.Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang, 621999, China.

*E-mail address of Corresponding author: yanghaijun@swust.edu.cn

Table of Content

Experimental section

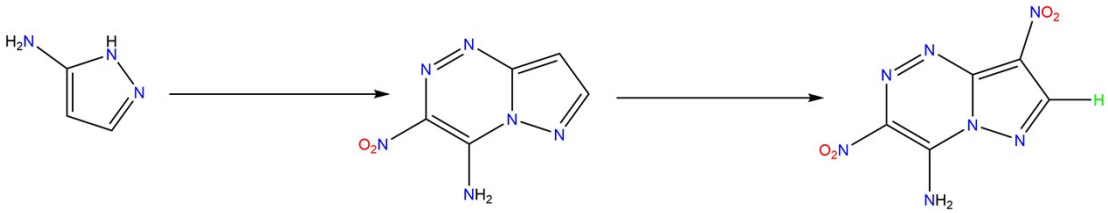
Caution!

As energetic materials have explosive risks, all operations should be carried out with helmets and behind safety shields. Mechanical actions such as friction and impact, as well as static electricity should be avoided.

General Methods:

Materials: 95% fuming nitric acid with an analytical purity was obtained from Chengdu Kelong Chemical Co., Ltd.; Other chemicals were purchased from Aladdin Reagent Company (Shanghai, China) and were used as supplied.

Product characterization: NMR spectra were recorded on Bruker Avance 600 nuclear magnetic resonance spectrometer; IR spectra were determined on Spectrum 100 Fourier transform infrared spectrometer by KBr pellet technique in the range of 400-4000 cm^{-1}; High-resolution mass spectra were performed on a Waters SYNAPT G2-Si mass spectrometer using electrospray ionization (ESI); TG/DSC tests were carried out on Jupiter STA449C comprehensive thermal analyzer; Impact and friction sensitivity measurements were made using a standard BAM Fallhammer and a BAM friction tester. The mechanical sensitivities of **GD-1** were tested according to GJB772 A-97. In fallhammer experiments, the weight of the fallhammer was 10 ± 0.01 kg, and the mass of **GD-1** was 50 ± 1 mg for each shot. The intensity data sets of **GD-1** were collected on a Agilent Xcalibur, Eos, Gemini CCD diffractometer equipped with a graphite-monochromated Mo Ka radiation (l = 0.71073 Å) at 293 K. The data sets were reduced by the CrysAlisPro program. The exposure time is set as 150 s with a scan width of 1 degree.



Synthesis of 4-amino-3-nitropyrazolo[5,1-*c*][1,2,4]triazine (2)

To a 20% aqueous solution of H_2SO_4 (50-100 mL) cooled with an ice-water bath was added 5-aminopyrazole (1.00 g, 12.05 mmol). Then, $NaNO_2$ (1.20 g, 24.10 mmol) dissolved in 5 mL water was added dropwise at 0-5 ºC. The resulting mixture was stirred at room temperature for 2h, giving solution A. To 6 mL of ice water was added NaOH (1.00 g, 24.00 mmol) and Nitroacetonitrile (NAN) (2.10 g, 24.00 mmol) with stirring, giving solution B. Solution B was added dropwise to solution A cooled with an ice-water bath. The reaction solution was stirred in ice-water bath overnight. A yellow precipitate was filtered, washed with water and dried, giving

1.95 g of **2** with a yield of 90%. ^{1}H NMR (DMSO-d_6, 600MHz) δ = 7.31 (s, 1H), 8.56 (s, 1H), 9.53 (s, 1H), 9.99 (s, 1H) ppm. ^{13}C NMR (DMSO-d_6, 150MHz) δ = 100.51, 135.93, 139.46, 147.84, 149.71 ppm. FT-IR (KBr): v = 3446, 1647, 1552, 1489, 1460, 1422, 1329, 1236, 1225, 1192, 839, 804, 669, 588 cm^{-1}. MS (ESI): m/z = 181.04651 $[M+H]^+$.

Synthesis of 4-amino-3,8-dinitro-pyrazolo[5,1-*c*][1,2,4]triazine (GD-1)

To 95% fuming HNO_3 (10 mL) was added **2** (1.00 g, 5.60 mmol) with stirring at room temperature. The mixture was stirred at r.t. for 12 h, and then poured onto crushed ice. Filtration, washing with water and drying gave 1.01 g of bright yellow **GD-1** with a yield of 81%. ^{1}H NMR (DMSO-d_6, 600MHz) δ = 9.25 (s, 1H), 9.93 (s, 1H), 10.50 (s, 1H) ppm. ^{13}C NMR (DMSO-d_6, 150MHz) δ = 123.90, 139.07, 139.84, 143.55, 144.27 ppm. FT-IR (KBr): v = 3299, 3067, 2361, 1674, 1632, 1571, 1520, 1442, 1399, 1342, 1325, 1289, 1226, 1192, 1014, 955, 844, 818, 767, 689 cm^{-1}. MS (ESI): m/z = 226.03124 $[M+H]^+$.

NMR and MS Spectra

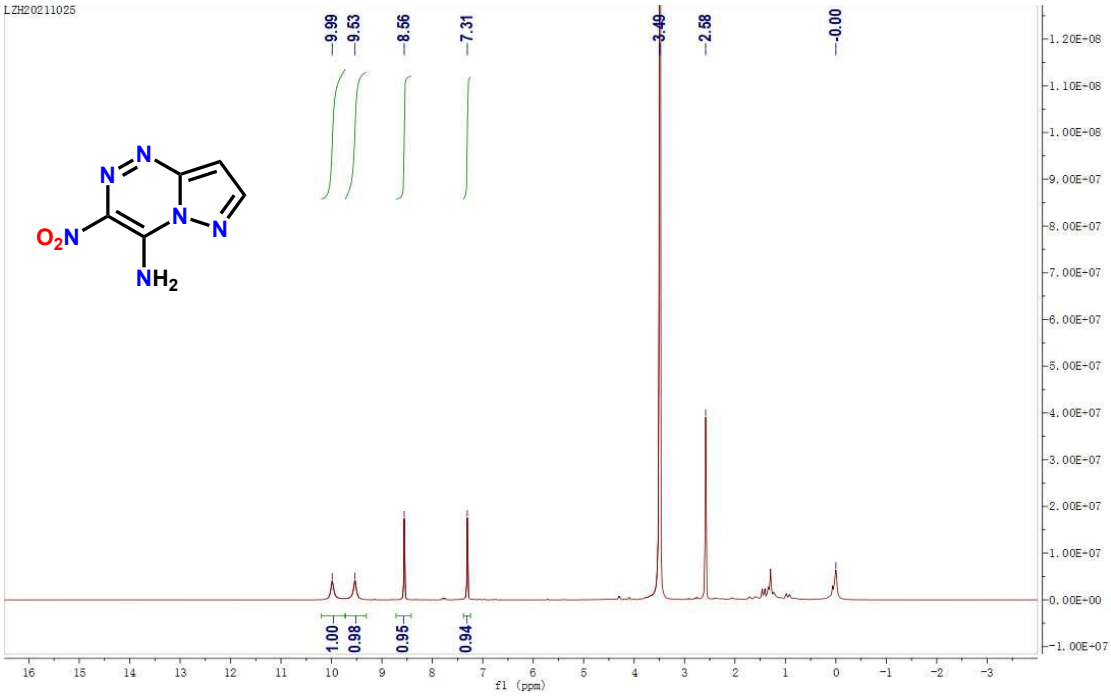


Figure S1 ^{1}H NMR spectrum of **2**

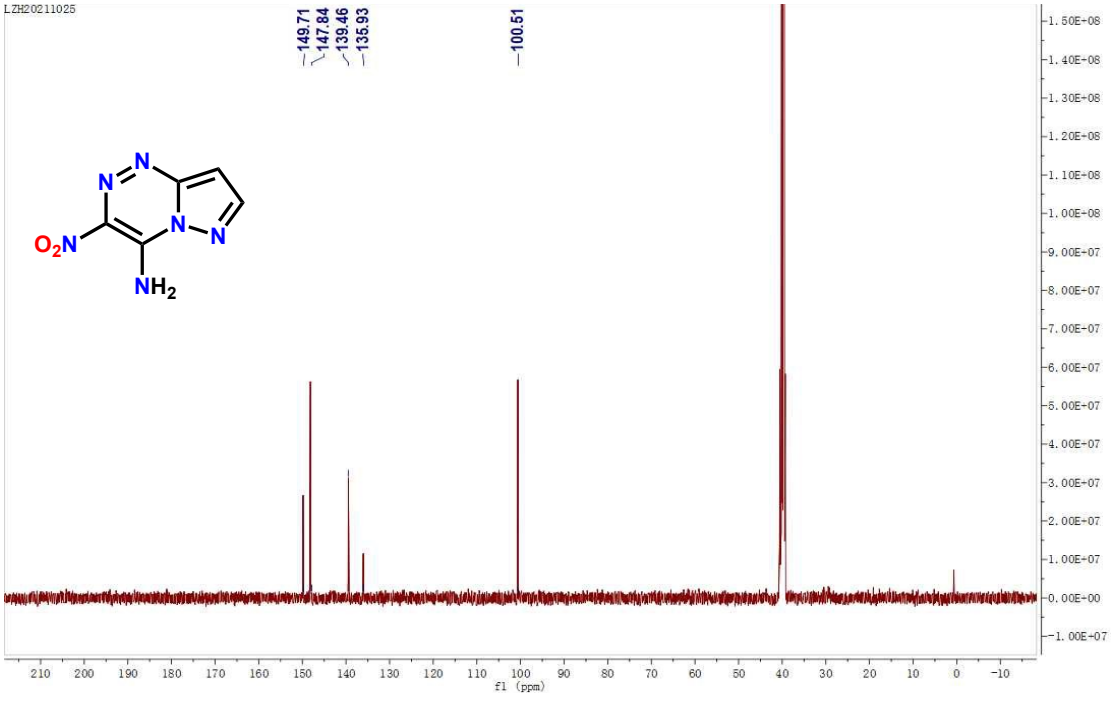


Figure S2 ^{13}C NMR spectrum of **2**

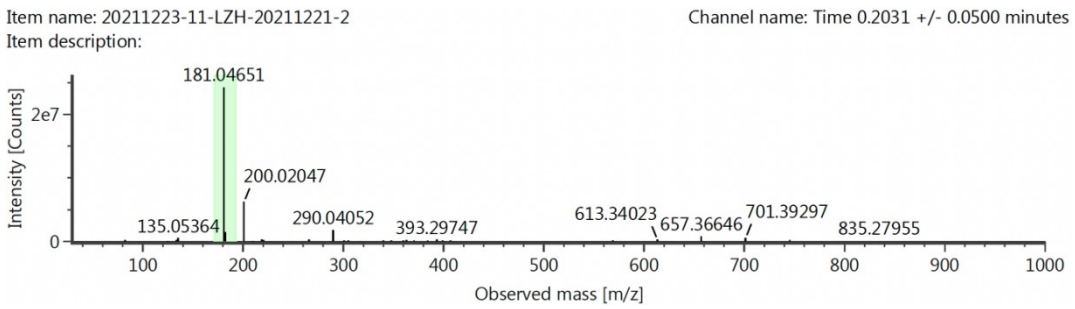


Figure S3 MS spectrum of **2**

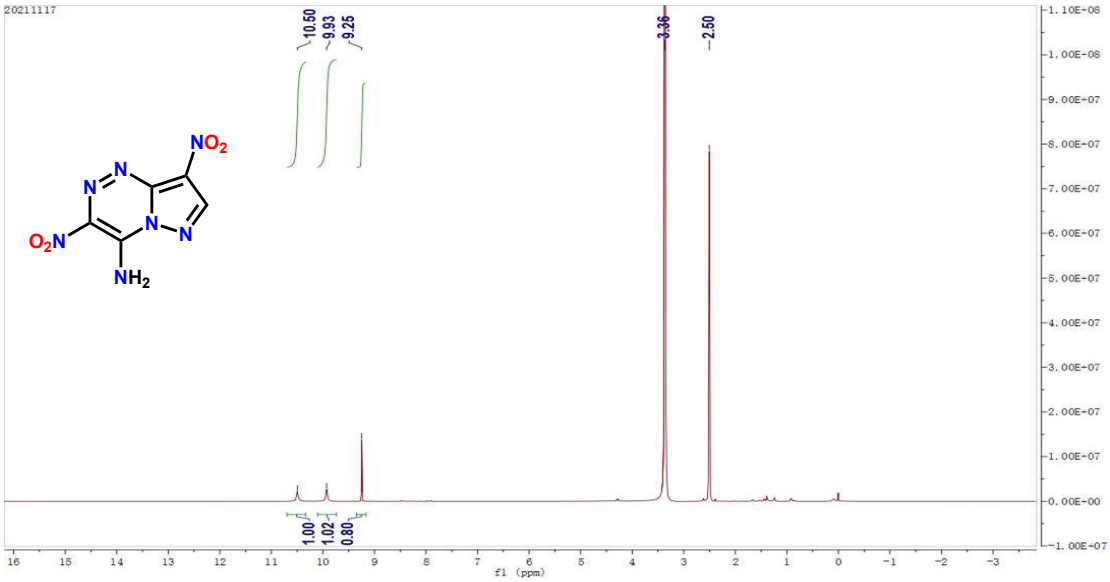


Figure S4 ^{1}H NMR spectrum of **GD-1**

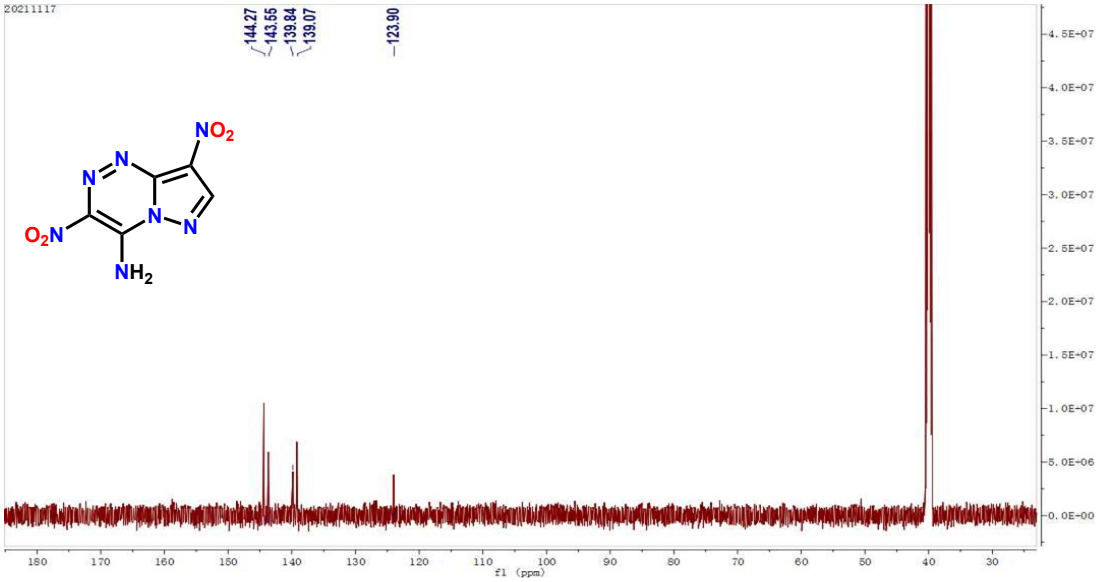


Figure S5 ^{13}C NMR spectrum of **GD-1**

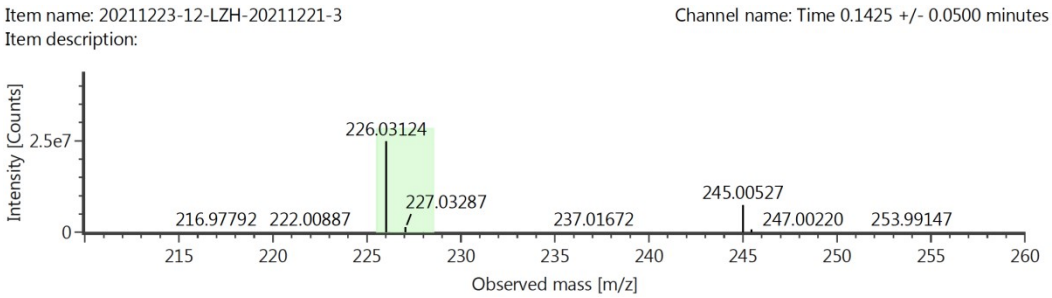


Figure S6 MS spectrum of **GD-1**

Crystallographic data

(1) **GD-1·2H$_2$O**

The crystal structure of **GD-1·2H$_2$O** is based on extremely weak data (CCDC2239586).

Table S1 Crystal data and structure refinement for GD-1·2H$_2$O

CCDC	2239586
Empirical formula	$C_5H_7N_7O_6$
Formula weight	261.18
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/m$
a/Å	9.2737(13)
b/Å	6.2094(8)
c/Å	9.4529(12)
α/°	90
β/°	114.864(16)
γ/°	90
Volume/Å^3	493.88(13)
Z	2
ρcalcg/cm^3	1.756
μ/mm^{-1}	0.160
F(000)	270.0
Crystal size/mm^3	0.22 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	8.086 to 58.292
Index ranges	-12 ≤ h ≤ 12, -8 ≤ k ≤ 8, -12 ≤ l ≤ 12
Reflections collected	6317
Independent reflections	1318 [R_{int} = 0.0383, R_{sigma} = 0.0966]
Data/restraints/parameters	1318/0/109
Goodness-of-fit on F^2	0.947
Final R indexes [I>=2σ (I)]	R_1 = 0.0837, wR_2 = 0.1914
Final R indexes [all data]	R_1 = 0.1584, wR_2 = 0.2129
Largest diff. peak/hole / e Å^{-3}	0.71/-0.22

(2) **GD-1·CH_3OH**

Table 1 Crystal data and structure refinement for GD-1·CH_3OH

CCDC	2239587
Empirical formula	$C_6H_7N_7O_5$
Formula weight	257.19
Temperature/K	298.15
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	8.5784(8)
b/Å	26.550(2)
c/Å	4.5184(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1029.09(17)
Z	4
ρ_{calc}g/cm^3	1.660
μ/mm^{-1}	0.814
F(000)	528.0
Crystal size/mm^3	0.22 × 0.2 × 0.18
Radiation	GaKα (λ = 1.34138)
2Θ range for data collection/°	10.682 to 114.222
Index ranges	$-10 \le h \le 10$, $-32 \le k \le 33$, $-5 \le l \le 3$
Reflections collected	8708
Independent reflections	1830 [R_{int} = 0.0501, R_{sigma} = 0.0389]
Data/restraints/parameters	1830/1/165
Goodness-of-fit on F^2	1.111
Final R indexes [I>=2σ (I)]	R_1 = 0.0371, wR_2 = 0.0852
Final R indexes [all data]	R_1 = 0.0492, wR_2 = 0.0932
Largest diff. peak/hole / e Å^{-3}	0.14/-0.20
Flack parameter	0.0(6)

Thermal Analysis of GD-1

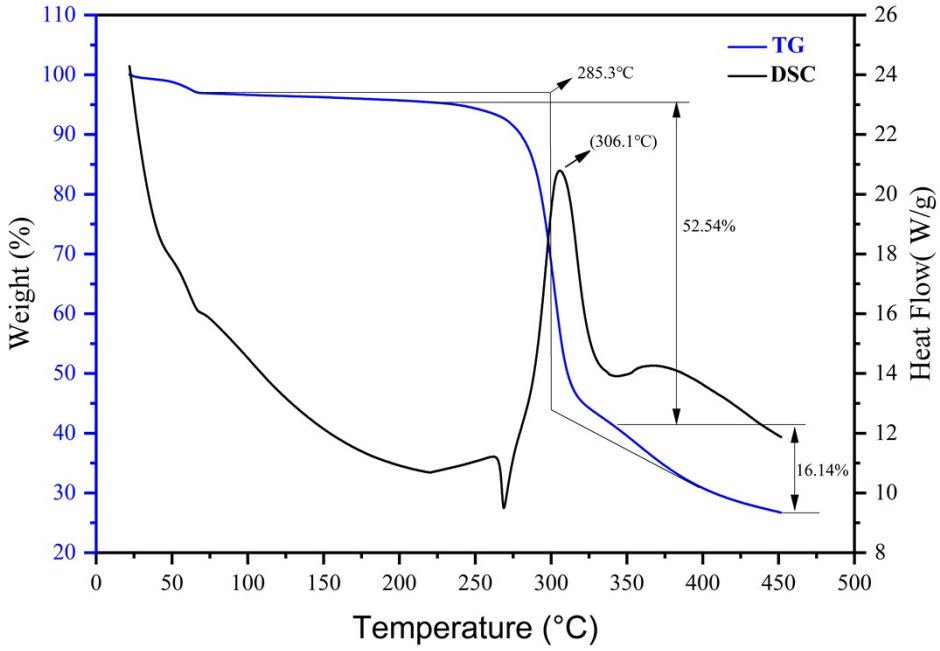


Figure S7 DSC-TG curves of **GD-1** (10 ℃/min)

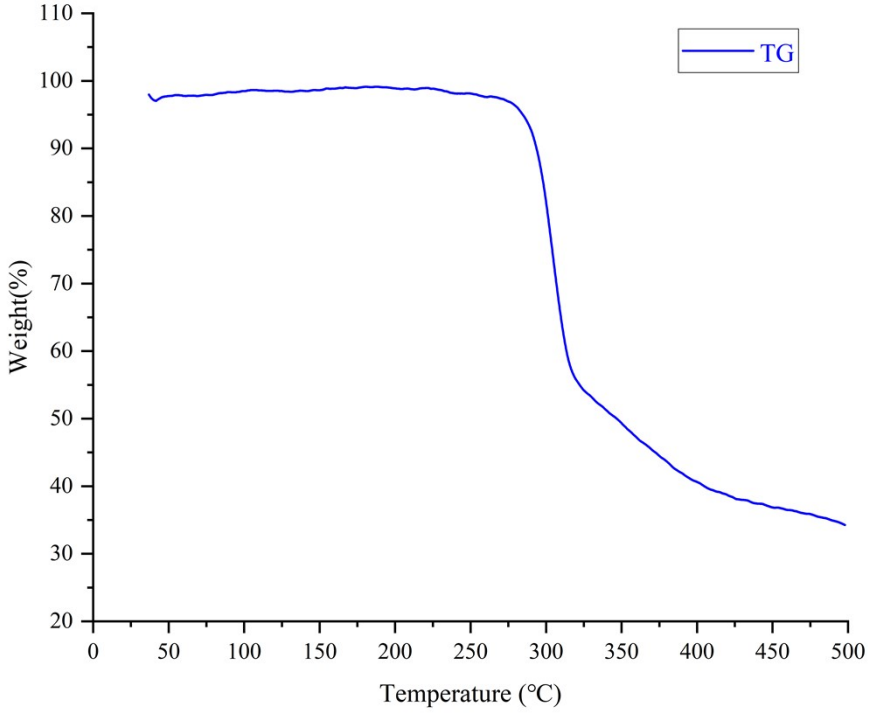


Figure S8 TG curve of previously dried **GD-1** (10 ℃/min)

GD-1 sample for TG analysis was obtained via drying in vacuum at 100 ºC for 6 h and then stored in air at room temperature for more than 24 h.