

Supplementary Material for

A Promising Insensitive Energetic Material Based on Fluorodinitromethyl Explosophore Group and 1,2,3,4-Tetrahydro-1,3,5-Triazine: Synthesis, Crystal Structure and Performance

Huan Huo^{a,b}, Junlin Zhang^{a,b}, Jun Dong^a, Lian-jie Zhai^{a,b}, Tao Guo^a, Zi-jun Wang^a, Fu-qiang Bi^{a,b*}, Bo-zhou Wang^{a,b*}

a. Xi'an Modern Chemistry Research Institute, Xi'an 710065, China;

b. State Key Laboratory of Fluorine & Nitrogen Chemical, Xi'an 710065, China

Corresponding author e-mail: *bifuqiang@gmail.com, wbz600@163.com*

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1. Experimental Section

General methods: Hexahydro-3-tert-butyl-2,2-dinitromethylene-1,3,5-triazine (3) as a starting material was prepared according to the literature [1]. All reagents and solvents were purchased from Aladdin Bio-Chem Technology CO., Ltd (Shanghai, China) and were used without further purification unless otherwise indicated. Infrared spectra were measured by an EQUINOX 55 Fourier transform Infrared spectrometer (Bruker, Germany) in the range of 4000~400 cm^{-1} . ^{13}C NMR and ^1H NMR spectra were measured with AV 500 NMR spectrometer (Bruker, Switzerland). Elemental analyses were performed with the vario EL cube elemental analyzer (Elementar, Germany). The thermal analysis experiment and the glass transition temperature (T_g) were performed with a model TG-DSC STA 499 F3 instrument (NETZSCH, Germany). Single crystal X-ray experiment was carried out on a Bruker Apex II CCD diffractometer equipped with graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$) using ω and ϕ scan mode. Structures were solved by the direct method using SHELXTL and refined by means of full-matrix least-squares procedures on F^2 with the programs SHELXL-97. All nonhydrogen atoms were refined with anisotropic displacement parameters. The sensitivity towards impact (IS) and friction (FS) were determined according to BAM standards[2].

6-(Chlorodinitromethyl)-3-nitro-1,2,3,4-tetrahydro-1,3,5-triazine(**2**): Fuming HNO_3 ($d=1.5 \text{ g/cm}^3$, 90 mL) was added in a 250 mL round-bottom flask immersed in an ice bath, **1** (15.0 g, 61.2 mmol) was added slowly to the solution at the temperature of $0\sim 5^\circ\text{C}$. After the addition was complete, NH_4Cl (2.2 g, 41.1 mmol) was added over 1 h at the same temperature. The reaction mixture was stirred for 4 h and warmed to room temperature, and then poured into ice water with stirring for 1 h, the obtained precipitate was filtered off, washed with ice water, and air-dried to obtain 12.0 g solid (yield:73.2%).

Compound **2**: White solid; ^1H NMR ($\text{DMSO}-d_6$, 500 MHz), δ : 8.897 (s, 1H, NH), 5.512(s, 2H, CH), 5.266 (s, 2H, CH); ^{13}C NMR ($\text{DMSO}-d_6$, 125 MHz), δ : 146.903, 120.263, 63.574, 56.705; IR(KBr), $\nu(\text{cm}^{-1})$: 3423, 3256,3050, 2988, 1651, 1614, 1596, 1559, 1506, 1469, 1435, 1390, 1294, 1156, 1096, 1032, 968, 947,923, 839, 823, 784, 765, 691, 644, 620, 522, 437; Elemental analysis (%) calcd for $\text{C}_4\text{H}_5\text{ClN}_6\text{O}_6$: C, 17.89; H, 1.88; N, 31.29; found: C, 17.99; H, 2.05; N, 31.59.

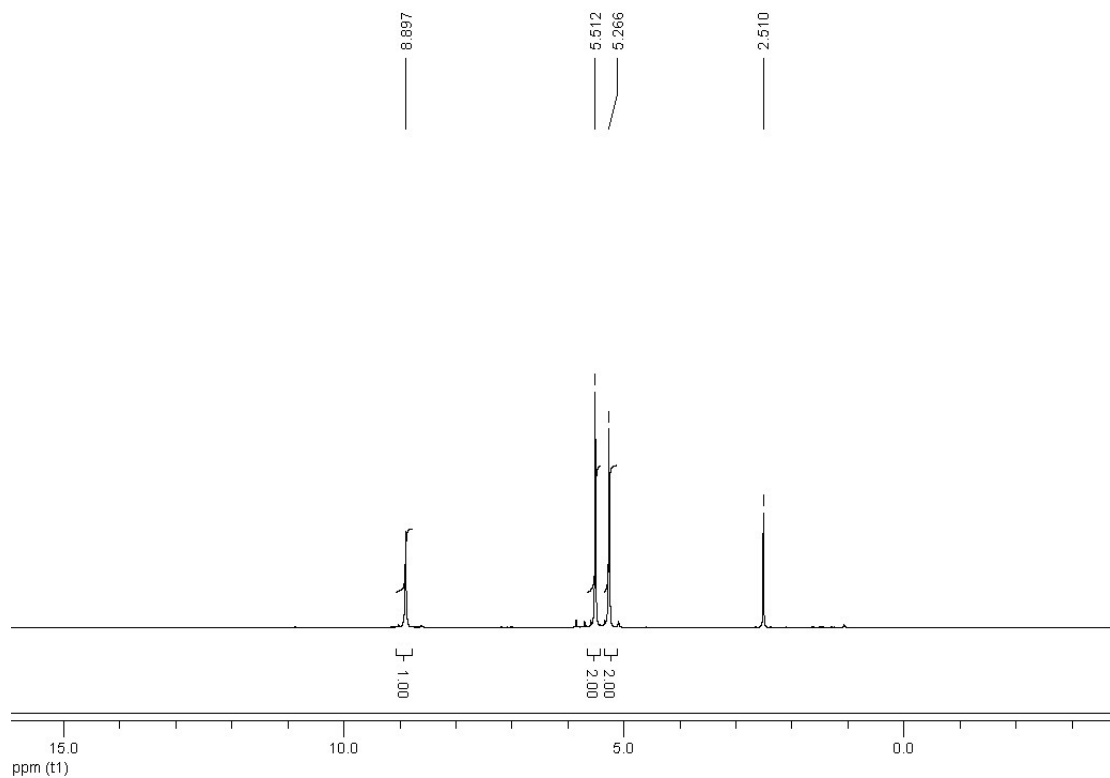


Fig. S1. ^1H NMR spectrum (500 MHz) of compound **2** in $\text{DMSO-}d_6$ at 25°C .

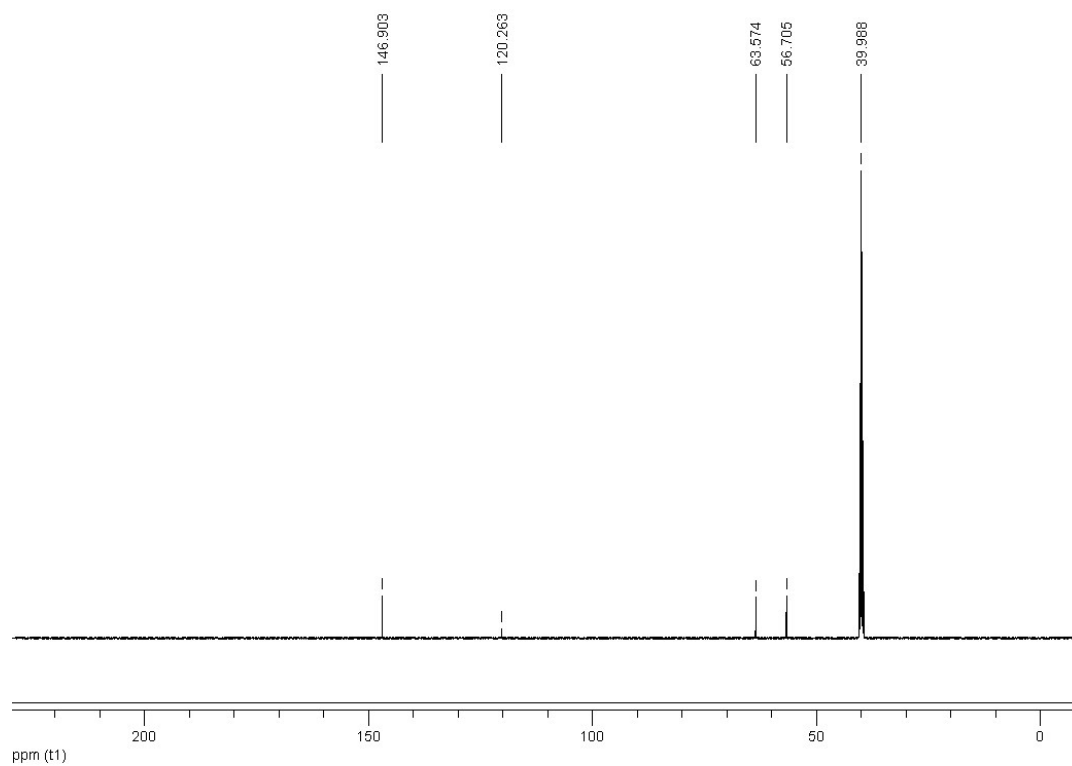


Fig. S2. ^{13}C NMR spectrum (125 MHz) of compound **2** in $\text{DMSO-}d_6$ at 25°C .

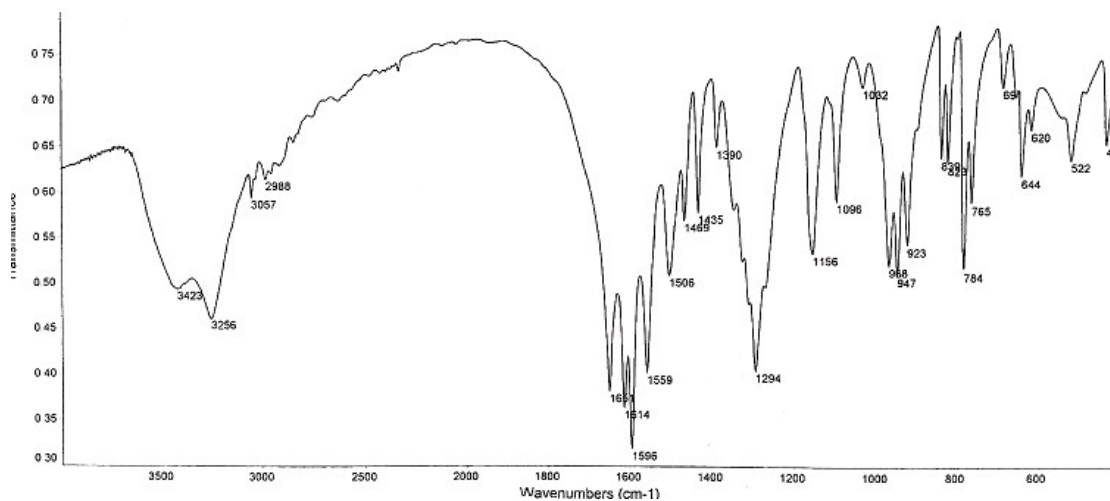


Fig. S3. Infrared spectrum of compound 2.

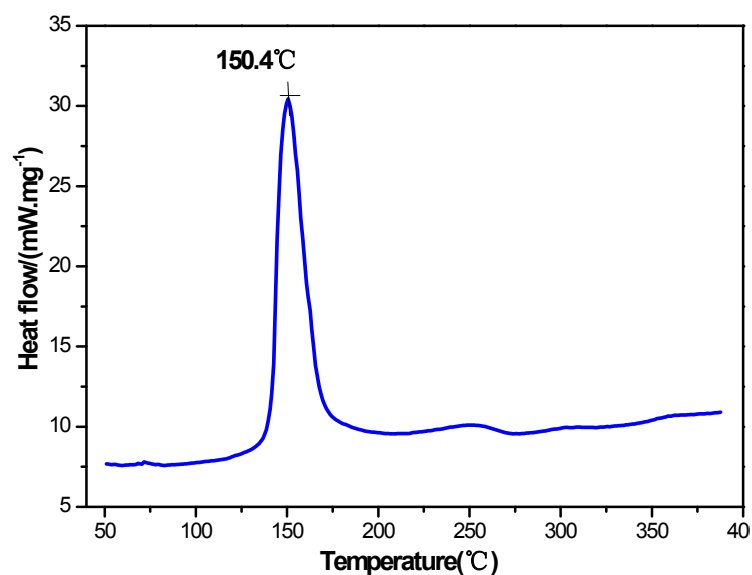


Fig. S4. DSC Curve of 2

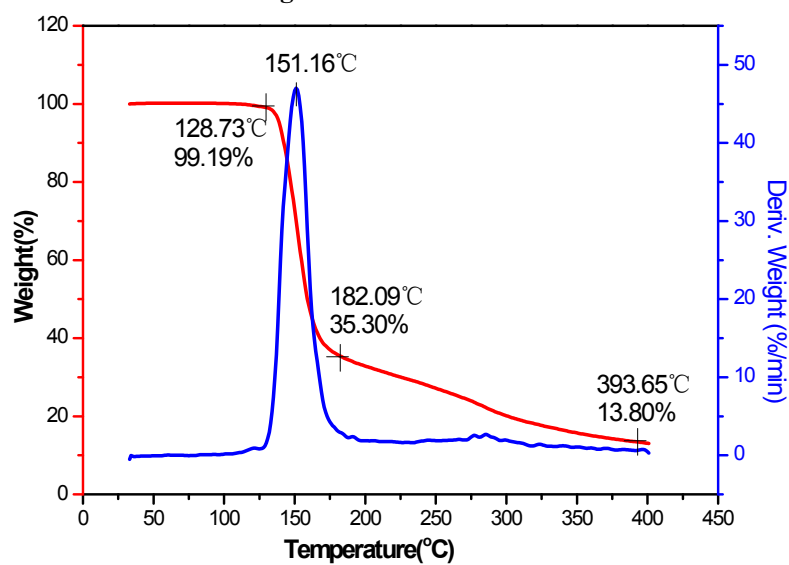


Fig. S5. TG Curve of 2

Potassium salt of 6-dinitromethyl- 3-nitro-1,2,3,4-tetrahydro-1,3,5- triazine (**3**) : A solution of KI(5.6 g, 33.7 mmol) in methanol(45 mL) was stirred at room temperature and treated by dropwise addition of **2** (4.5 g, 16.8mmol) solution in 45 mL methanol. The reaction mixture was stirred at the same temperature for 1 h. The obtained precipitate was filtered off, washed washed with methanol and anhydrous ether, and air-dried to obtain 3.6 g solid (yield: 78.8%).

Compound **3**: Yellow solid; $^1\text{H NMR}$ ($\text{DMSO-}d_6$, 500 MHz), δ : 7.684 (s, 1H, NH), 5.532(s, 2H, CH), 5.208(s, 2H, CH); $^{13}\text{C NMR}$ ($\text{DMSO-}d_6$, 125 MHz), δ : 149.656, 131.548, 60.392, 56.762; IR(KBr), $\nu(\text{cm}^{-1})$: 3594, 3335, 3223, 2918, 2879, 2741, 2477, 1670, 1538, 1510, 1480, 1405, 1384, 1354, 1322, 1246, 1126, 1060, 1014, 951, 813, 756, 705, 665; Elemental analysis (%) calcd for $\text{C}_4\text{H}_6\text{N}_6\text{O}_6$: C, 17.65; H, 1.85; N, 30.87; found: C, 17.32; H, 2.01; N, 30.72.

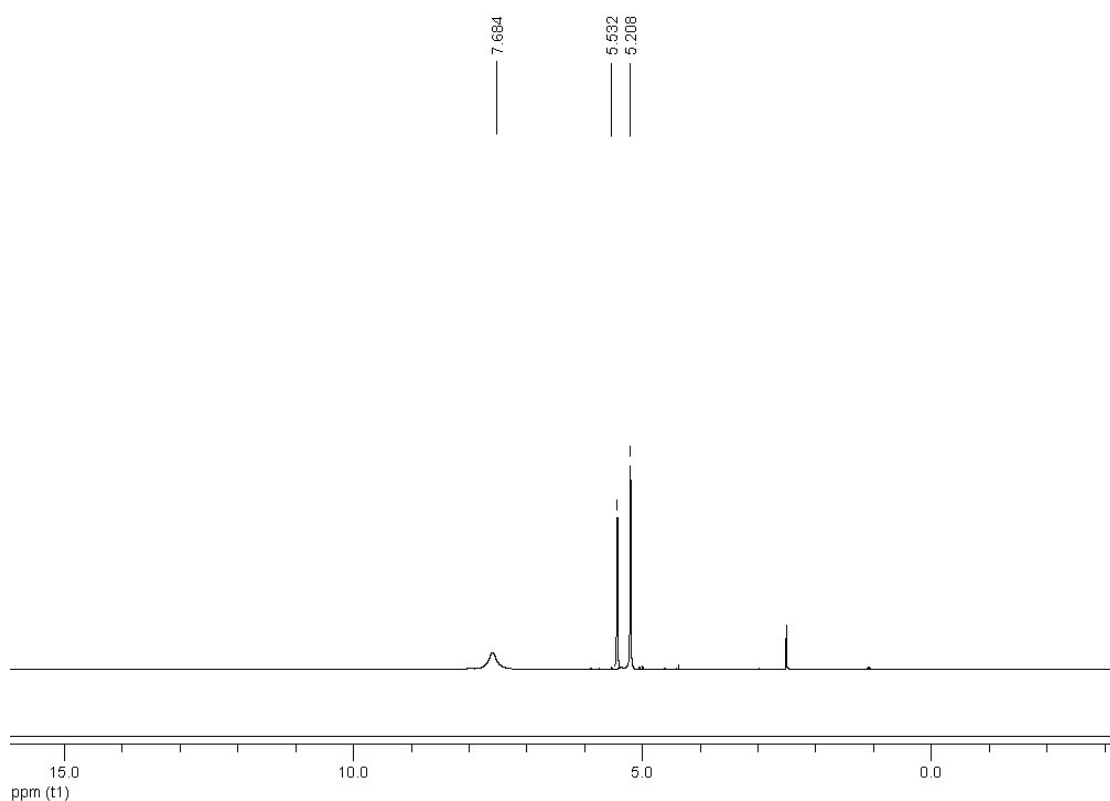


Fig. S6. $^1\text{H NMR}$ spectrum (500 MHz) of compound **3** in $\text{DMSO-}d_6$ at 25°C .

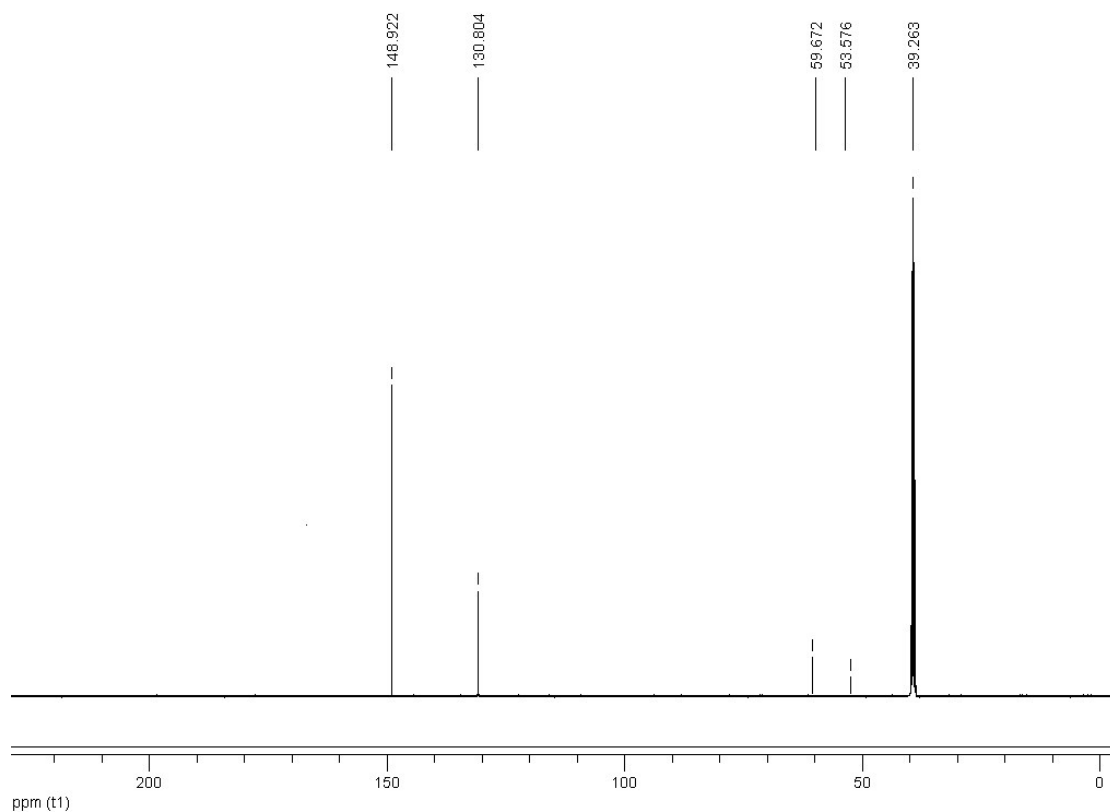


Fig. S7. ^{13}C NMR spectrum (125 MHz) of compound **3** in $\text{DMSO-}d_6$ at 25°C .

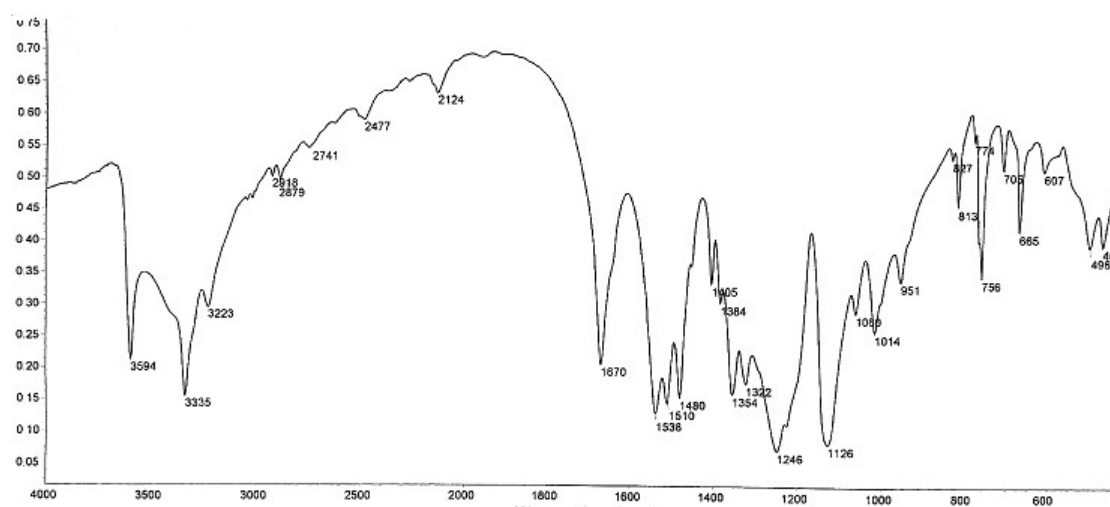


Fig. S8. Infrared spectrum of compound **3**.

6-(Fluorodinitromethyl)-3- nitro-1,2,3,4- tetrahydro- 1,3,5-triazine(**FMTNT**): A solution of **3** (3.0 g, 12.8 mmol) in anhydrous acetonitrile(30 mL) was stirred at 20°C and treated by addition of XeF_2 (4.35 g, 25.65 mmol). The reaction mixture was stirred at the same temperature for 48 h. The solvent was removed by evaporation at reduced pressure and the residue was washed to give a colorless solid. The residue was adequately dissolved with anhydrous ether. The solvent was filtered and the filtrate was concentrated in vacuum to obtain 1.35 g title compound (yield: 41.8%).

Compound **FMTNT**: White solid; ^1H NMR($\text{DMSO-}d_6$, 500 MHz), δ : 9.174(1H,

NH), 5.499(2H,CH₂), 5.320(2H,CH₂). ¹³C NMR (DMSO-*d*₆, 125 MHz), δ : 143.896, 118.894, 63.488, 58.202; ¹⁹F NMR (DMSO-*d*₆, 470.5 MHz): δ : -101.872; IR(KBr), ν (cm⁻¹): 3386, 3052, 2966, 2914, 1669, 1614, 1600, 1564, 1540, 1510, 1461, 1440, 1386, 1353, 1303, 1267, 1223, 1152, 1104, 1020, 947, 844, 828, 799, 763; Elemental analysis (%) calcd for C₄H₅FN₆O₆: C, 19.06, H, 2.00, N, 33.33; found: C, 19.03, H, 2.34, N, 32.92. BAM drophammer:20 J; friction tester: 240 N.

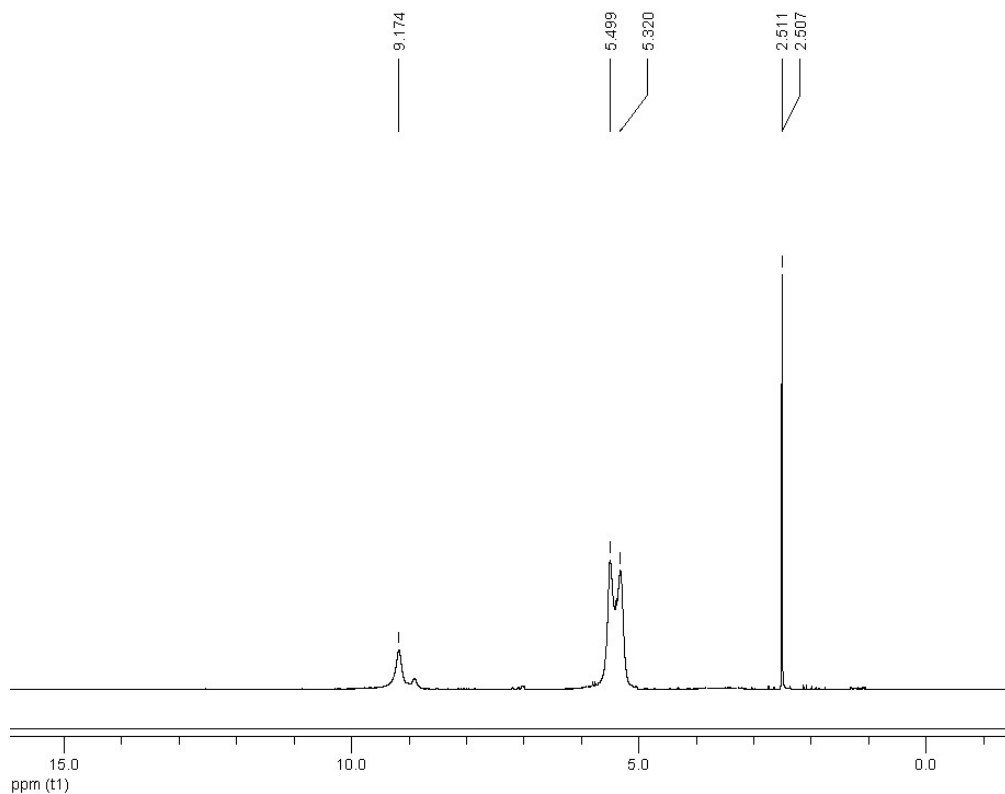


Fig. S9. ¹H NMR spectrum (500 MHz) of FMTNT in DMSO-*d*₆ at 25 °C.

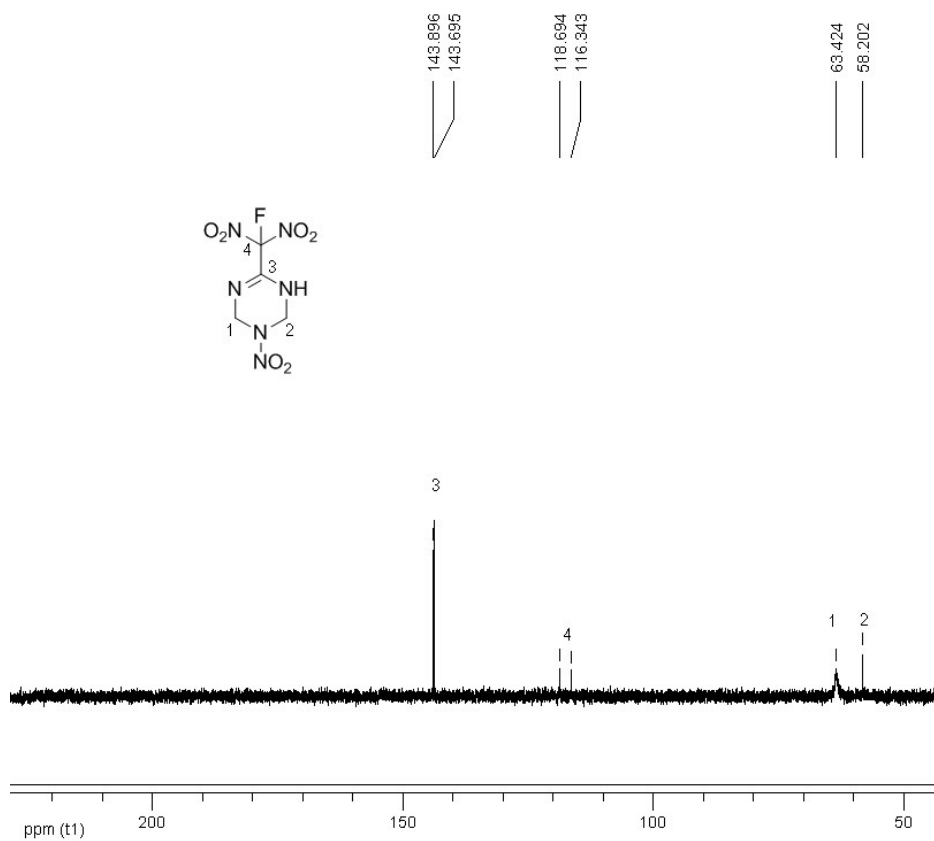


Fig. S10. ¹³C NMR spectrum (125 MHz) of FMTNT in DMSO-*d*₆ at 25 °C.

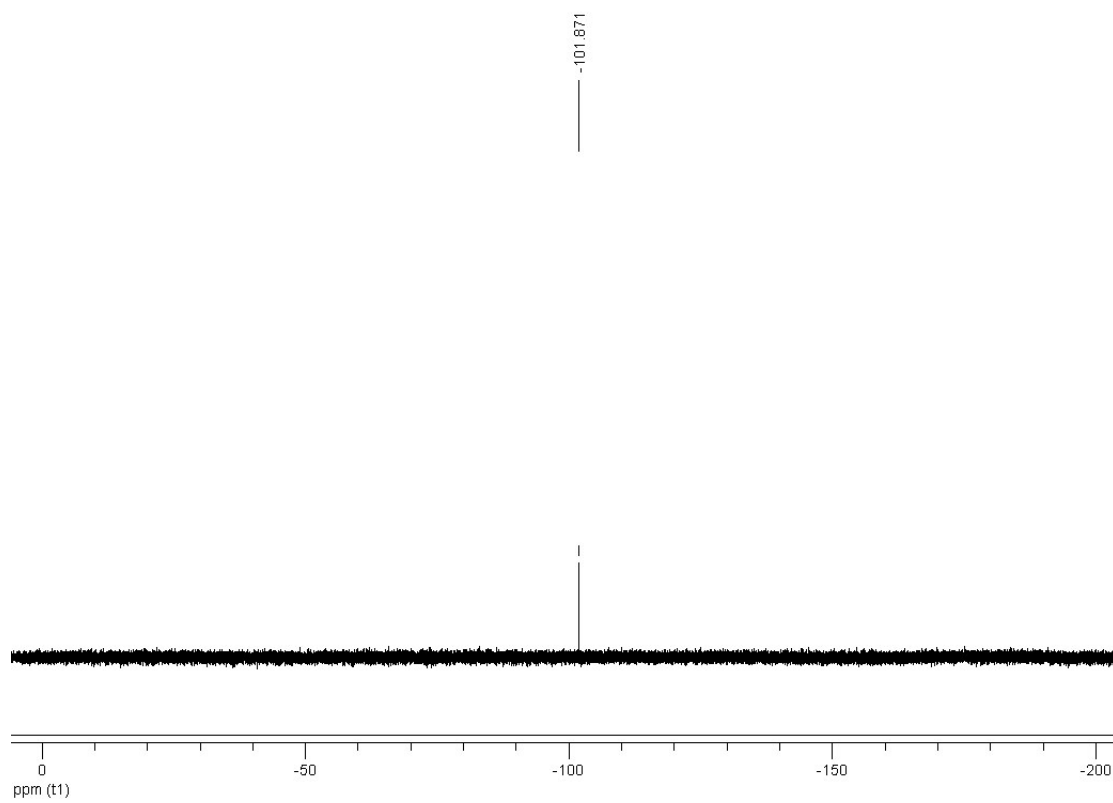


Fig. S11. ¹⁹F NMR spectrum (470.5 MHz) of FMTNT in DMSO-*d*₆ at 25 °C.

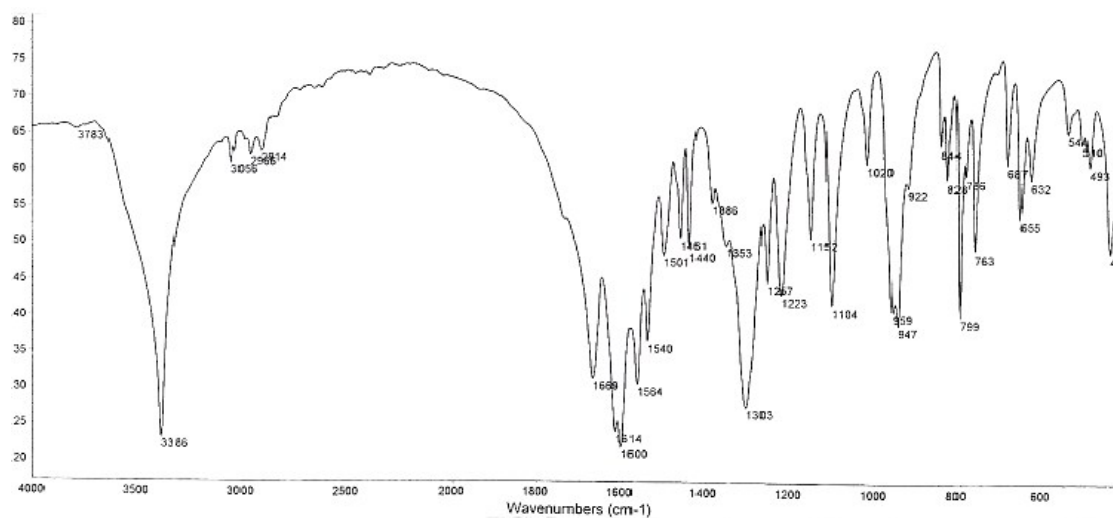


Fig. S12. Infrared spectrum of FMTNT.

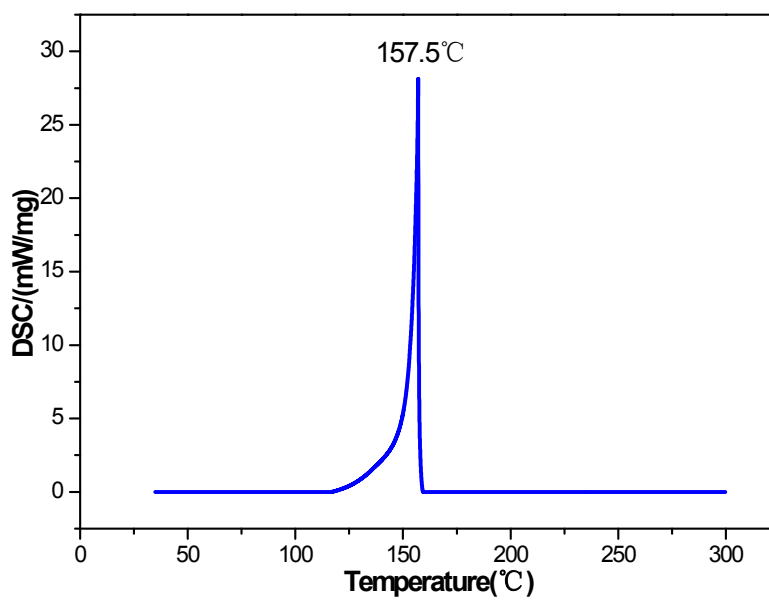


Fig. S13. DSC Curve of FMTNT

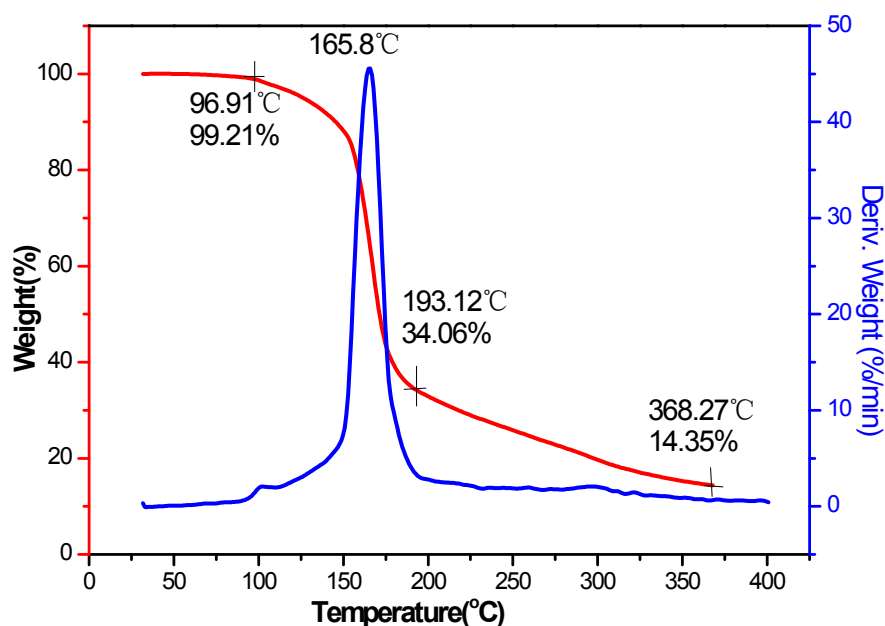


Fig. S14. TG Curve of FMTNT

2. X-ray Diffraction

For FMTNT, a Bruker SMART Apex II X-ray diffractometer with a CCD area detector was employed for data collection at 296 K using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXL-97 programs[3]. Relevant data are given in Table S1.

Table S1. Crystallographic details of FMTNT

<i>Compd</i>	FMTNT
Formula	C ₄ H ₅ FN ₆ O ₆
Formula weight	252.14
T (K)	296(2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
a (Å)	11.592(14)
b (Å)	8.138(10)
c (Å)	11.045(14)
Volume (Å ³)	951(2)
Z	4
Dc (g/cm ³)	1.761
F (000)	512
θ range/(°)	1.92 to 25.10
Reflections collected/unique	4464/1693 [$R_{(int)} = 0.1367$]
Refinement method	Full-matrix least-squares on F^2
GOF on F^2	0.949
Final R indexes ($I > 2\sigma(I)$)	$R_1 = 0.0751, wR_2 = 0.1752$

Final R indexes (all data)	$R_1 = 0.1924$, $wR_2 = 0.2415$
Largest diff peak and hole (e Å ⁻³)	0.328 and -0.349
GOF on F ₂	0.949
CCDC number	1908214

Table S2. Selected Bond Lengths (Å) and Bond Angles (°) for the Title Compound

Bond	Dist.	Bond	Dist.	Bond	Dist.
F(1)-C(1)	1.400(7)	N(3)-C(3)	1.449(7)	N(6)-O(6)	1.233(7)
N(1)-O(2)	1.195(7)	N(3)-H(3)	0.8600	C(1)-C(2)	1.515(9)
N(1)-O(1)	1.223(7)	N(4)-C(2)	1.271(7)	C(3)-H(3A)	0.9700
N(1)-C(1)	1.539(8)	N(4)-C(4)	1.465(7)	C(3)-H(3B)	0.9700
N(2)-O(4)	1.203(7)	N(5)-N(6)	1.394(7)	C(4)-H(4A)	0.9700
N(2)-O(3)	1.205(7)	N(5)-C(4)	1.451(8)	C(4)-H(4B)	0.9700
N(2)-C(1)	1.527(8)	N(5)-C(3)	1.453(7)		
N(3)-C(2)	1.346(7)	N(6)-O(5)	1.223(7)		
Angle	(°)	Angle	(°)	Angle	(°)
O(2)-N(1)-O(1)	127.1(6)	O(5)-N(6)-O(6)	123.3(7)	N(3)-C(3)-H(3A)	109.8
O(2)-N(1)-C(1)	116.6(6)	O(5)-N(6)-N(5)	117.7(7)	N(5)-C(3)-H(3A)	109.8
O(1)-N(1)-C(1)	116.3(6)	O(6)-N(6)-N(5)	118.9(6)	N(3)-C(3)-H(3B)	109.8
O(4)-N(2)-O(3)	127.8(7)	F(1)-C(1)-C(2)	113.5(5)	N(5)-C(3)-H(3B)	109.8
O(4)-N(2)-C(1)	114.7(7)	F(1)-C(1)-N(2)	107.6(5)	H(3A)-C(3)-H(3B)	108.2
O(3)-N(2)-C(1)	117.5(6)	C(2)-C(1)-N(2)	109.1(5)	N(5)-C(4)-N(4)	112.9(5)
C(2)-N(3)-C(3)	116.2(5)	F(1)-C(1)-N(1)	107.6(5)	N(5)-C(4)-H(4A)	109.0
C(2)-N(3)-H(3)	121.9	C(2)-C(1)-N(1)	114.1(5)	N(4)-C(4)-H(4A)	109.0
C(3)-N(3)-H(3)	121.9	N(2)-C(1)-N(1)	104.4(5)	N(5)-C(4)-H(4B)	109.0
C(2)-N(4)-C(4)	116.2(5)	N(4)-C(2)-N(3)	129.0(6)	N(4)-C(4)-H(4B)	109.0
N(6)-N(5)-C(4)	116.0(6)	N(4)-C(2)-C(1)	116.2(6)	H(4A)-C(4)-H(4B)	107.8
N(6)-N(5)-C(3)	113.5(6)	N(3)-C(2)-C(1)	114.8(5)		
C(4)-N(5)-C(3)	111.7(5)	N(3)-C(3)-N(5)	109.5(5)		

Table S3. Selected Torsion Angles (°)

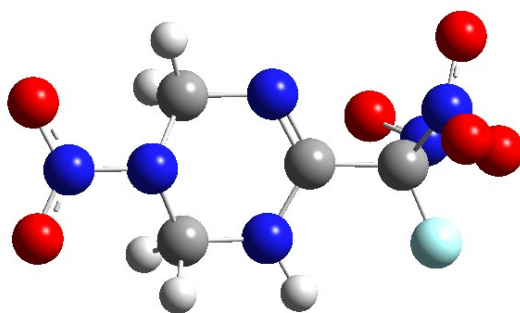
Angle	(°)	Angle	(°)	Angle	(°)
C(4)-N(5)-N(6)-O(5)	29.6(8)	O(1)-N(1)-C(1)-F(1)	-140.0(5)	N(1)-C(1)-C(2)-N(4)	93.0(7)
C(3)-N(5)-N(6)-O(5)	161.0(5)	O(2)-N(1)-C(1)-C(2)	166.3(6)	F(1)-C(1)-C(2)-N(3)	38.5(7)
C(4)-N(5)-N(6)-O(6)	-153.9(5)	O(1)-N(1)-C(1)-C(2)	-13.1(8)	N(2)-C(1)-C(2)-N(3)	158.4(5)
C(3)-N(5)-N(6)-O(6)	-22.6(8)	O(2)-N(1)-C(1)-N(2)	-74.7(7)	N(1)-C(1)-C(2)-N(3)	-85.3(6)
O(4)-N(2)-C(1)-F(1)	40.6(8)	O(1)-N(1)-C(1)-N(2)	105.8(6)	C(2)-N(3)-C(3)-N(5)	-32.8(7)
O(3)-N(2)-C(1)-F(1)	-142.2(6)	C(4)-N(4)-C(2)-N(3)	2.9(9)	N(6)-N(5)-C(3)-N(3)	-78.0(6)
O(4)-N(2)-C(1)-C(2)	-83.0(7)	C(4)-N(4)-C(2)-C(1)	-175.1(5)	C(4)-N(5)-C(3)-N(3)	55.4(7)
O(3)-N(2)-C(1)-C(2)	94.2(7)	C(3)-N(3)-C(2)-N(4)	3.8(9)	N(6)-N(5)-C(4)-N(4)	82.0(7)

O(4)-N(2)-C(1)-N(1)	154.7(6)	C(3)-N(3)-C(2)-C(1)	-178.2(5)	C(3)-N(5)-C(4)-N(4)	-50.2(7)
O(3)-N(2)-C(1)-N(1)	-28.1(8)	F(1)-C(1)-C(2)-N(4)	-143.3(5)	C(2)-N(4)-C(4)-N(5)	20.7(8)
O(2)-N(1)-C(1)-F(1)	39.4(7)	N(2)-C(1)-C(2)-N(4)	-23.3(8)		

3. Computation details

All of the ab initio calculations involved in this work were carried out using the Gaussian 09 suite of programs[4] and visualized by GaussView 5.08[5]. The enthalpies (H°) and free energies (G°) were calculated using the complete basis set method (CBS-4M) based on X-ray diffraction data, in order to obtain accurate[6,7]. The enthalpies of the gas-phase species were estimated according to the atomization energy method[8].

Cartesian Coordinates of Optimized geometries



C	1.632093	-0.466788	-1.825606
N	0.211052	-0.200801	-1.842064
C	-0.066478	0.844483	-0.874827
N	0.460804	0.584913	0.476694
C	1.586636	-0.047643	0.583323
C	2.180682	-0.321631	1.960366
F	3.130472	-1.315659	1.926970
N	1.125481	-0.763537	2.913814
O	0.857644	-1.978395	2.929072
O	0.547640	0.079054	3.620180
N	2.876516	0.861602	2.540753
O	2.824767	1.945014	1.934943
O	3.544963	0.683705	3.574392
N	-0.307748	-0.000958	-3.091485
O	0.248947	-0.599125	-4.015885
O	-1.292294	0.734129	-3.180823
H	3.045858	-1.158683	-0.426616
H	1.829573	-1.439369	-2.294346
H	2.172471	0.281582	-2.422064
H	-1.150642	0.953599	-0.746260

H	0.313222	1.820219	-1.208513
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The solid state enthalpy of formation for neutral compounds can be estimated by subtracting the heats of sublimation from gas phase heats of formation. On the basis of the literatures[9], the heat of sublimation can be estimated with Trouton's rule according to eq 1, where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition:

$$\Delta H_{\text{sub}} = 188/\text{J mol}^{-1} \text{ K}^{-1} \times T \quad (1)$$

4. References

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