

## Supporting Information

# **An advanced primary explosive and secondary explosive based on zwitterionic pyrazole-triazole derivative**

Jie Tang,<sup>a†</sup> Hualin Xiong,<sup>a†</sup> Guojie Zhang,<sup>a</sup> Yongxing Tang,<sup>a</sup> Hongwei Yang,<sup>a\*</sup>  
Guangbin Cheng<sup>A\*</sup>

a. School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Xiaolingwei 200, Nanjing 210094, P. R. China. E-mail:  
gcheng@mail.njust.edu.cn; hyang@mail.njust.edu.cn

†. These authors contributed equally.

\* Corresponding authors.

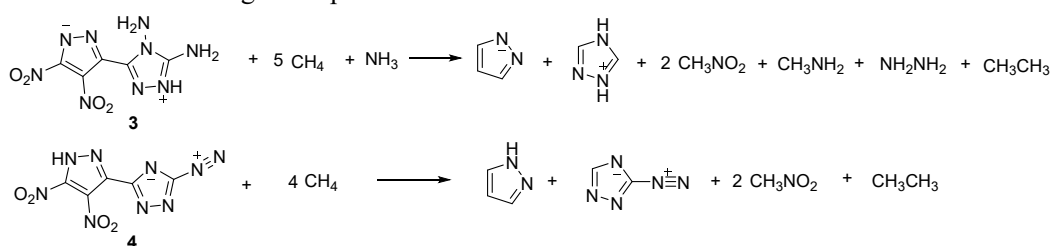
## Table of Contents

1. Computational details.....	3
2. Experimental Methods .....	4
3. Crystallographic datas .....	6
4. <sup>1</sup> H NMR and <sup>13</sup> C NMR of target compounds .....	8
5. Mass Spectra of Compounds.....	10
7. The DSC plots of synthesized compounds 3 and 4 .....	12
8. Reference .....	12

## 1. Computational details

Computations were performed by using the Gaussian09 suite of programs.<sup>1</sup> The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP)<sup>2</sup> functional with the 6-311+G\*\* basis set.<sup>3</sup> All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies.<sup>4</sup> The lattice energy of the trinitroethyl derivatives were predicted by using the formula suggested by Jenkins et al.

The predictions of heats of formation (HOF) used the hybrid DFTB3LYP methods with the 6-311+G\*\* basis set through designed isodesmic reactions. The isodesmic reaction processes, that is, the number of each kind of formal bond is conserved, were used with the application of the bond separation reaction (BSR) rules. The molecule was broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF of target compounds are shown in Scheme S1.



**Scheme S1.** The isodesmic reactions for calculating heat of formation for synthesized compounds.

The change of enthalpy for the reactions at 298K can be expressed by Equation (1):

$$\Delta H_{298} = \Sigma \Delta_f H_P - \Sigma \Delta_f H_R \quad (1)$$


Where  $\Sigma \Delta_f H_P$  and  $\Sigma \Delta_f H_R$  are the HOF of the reactants and products at 298 K, respectively, and  $\Delta H_{298}$  can be calculated from the following expression in Equation (2):

$$\Delta H_{298} = \Delta E_{298} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (2)$$

where  $\Delta E_0$  is the change in total energy between the products and the reactants at 0 K;  $\Delta ZPE$  is the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K;  $\Delta H_T$  is the thermal correction from 0 to 298 K. The  $\Delta(PV)$  value in Equation(2) is the  $PV$  work term. It equals  $\Delta nRT$  for the reactions of an ideal gas. For the isodesmic reactions  $\Delta n = 0$ , so  $\Delta(PV) = 0$ . On the left side of Equation (2), apart from target compound all the others are called reference compounds. The HOF of reference compounds are available either from experiments or from the high level computing such as G2.

**Table S1** Total energy and heat of formation for the title compounds at B3LYP/6-311+G\*\* level

Compound	$E_0^a$ /a.u.	ZPE <sup>b</sup> /kJ mol <sup>-1</sup>	$H_T^c$ / kJ mol <sup>-1</sup>	HOF <sup>d</sup> / kJ mol <sup>-1</sup>
CH <sub>4</sub>	-40.5339263	112.26	10.04	-74.6 <sup>e</sup>
NH <sub>3</sub>	-56.5826356	86.27	10.05	-45.9 <sup>e</sup>
CH <sub>3</sub> CH <sub>3</sub>	-79.8565413	187.31	11.79	-84 <sup>e</sup>
CH <sub>3</sub> NH <sub>2</sub>	-95.8938402	160.78	11.64	-22.5 <sup>e</sup>
NH <sub>2</sub> NO <sub>2</sub>	-261.124816	98.79	12.39	-3.9 <sup>e</sup>
CH <sub>3</sub> NO <sub>2</sub>	-245.091555	124.93	11.6	-80.8 <sup>e</sup>
CH <sub>3</sub> NNCH <sub>3</sub>	-189.333735	211.85	16.32	147.85
NHNO <sub>2</sub> <sup>-</sup>	-250.573074	65.76	11.37	-120.22 <sup>f</sup>

NH <sub>2</sub> NH <sub>2</sub>	-	134.28	11.16	95.4
Pyrazole anion	111.9105763	141.88	12.21	163.53
Pyrazole	-225.669742	179.2	12.57	177.4
triazole	-226.260331	150.39	12.06	192.7
	-242.320387	184.02	12.27	831.72

## 2. Experimental Methods

**General:** Although we have not encountered any difficulties in preparing the new energetic material, manipulations must be carried out by using standard safety precautions. Leather coat, ear protection, latex gloves, and face shield are strongly recommended for the experimental operation. All compounds should be handled with extreme care.

**General methods:** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometers operating at 500 and 125 MHz, respectively, by using either DMSO-*d*<sub>6</sub> or acetone-*d*<sub>6</sub> as the solvent and locking solvent unless otherwise stated. Chemical shifts in <sup>1</sup>H and <sup>13</sup>C NMR spectra are reported relative to DMSO. DSC was performed at a heating rate of 5 °C min<sup>-1</sup> in closed Al containers with a nitrogen flow of 30 mL min<sup>-1</sup> on an STD-Q600 instrument. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR equipped with an ATR unit at 25 °C. Impact sensitivity, friction sensitivity and electrostatic discharge sensitivity of samples are measured by using the standard BAM methods.

**X-ray crystallography:** The data were collected with a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. A Kryo-Flex low-temperature device was used to keep the crystals at a constant 100 K during the data collection. The data collection and the initial unit cell refinement were performed by using APEX2 (v2010.3-0). Data reduction was performed by using SAINT (v7.68A) and XPREP (v2008/2). Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS (v2008/1). The structure was solved and refined with the aid of the programs in the SHELXTL-plus (v2008/4) system of programs. The full-matrix least-squares refinement on F<sup>2</sup> included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included in a riding model. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The nonhydrogen atoms were refined anisotropically. The hydrogen atoms were located and refined.

**Synthesis of 3-(4,5-diamino-4H-1,2,4-triazol-1-ium-3-yl)-4,5-dinitropyrazol-1-ide (3):** Phosphorus pentoxide (20.00 g, 0.15 mol) was added to aqueous phosphoric acid (85 wt%, 70.00 g, 0.60 mol) with portions, and then it was heated to 80 °C under stirring. A mixture of 4,5-dinitro-1H-pyrazole-3-carboxylic acid (10.10 g, 0.05 mol) and diaminoguanidine monohydrochloride (8.30

g, 0.33 mol) was added to the above solution with portions. Subsequently, the mixture was heated to 120 °C and reacted for another 8 h. Then it was cooled to the room temperature and ice water (200 mL) was added. The clear solution was basified until the pH became 8 using conc. sodium hydroxide. Then the precipitate was filtered, recrystallized with water and dried in a vacuum oven to give the pure product **3** as pale yellow solid. Yield: 9.24 g, 72.4%. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): δ=8.26 (s, 2H), 6.05 (s, 2H) ppm. <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>) δ=151.5, 150.7, 143.7, 132.6, 125.8 ppm. IR (KBr):3615.78, 1697.67, 1635.54, 1514.70, 1497.12, 1366.47, 1338.21, 1265.20, 1140.86, 1099.81, 1063.99, 968.44, 920.87, 845.82, 816.77, 794.66, 760.17, 728.02, 701.63, 674.98. Elemental analysis calcd (%) for C<sub>5</sub>H<sub>5</sub>N<sub>9</sub>O<sub>4</sub>(255.15): C 23.54, H 1.98, N 49.41, found: C 23.51, H 1.94, N 49.40. MS (ESI-) m/z: 254.12 [M-H]<sup>-</sup>.

**Synthesis of 3-(4,5-dinitro-1H-pyrazol-3-yl)-5-diazonium-1H-1,2,4-triazole (4):** To a mixture of 100% nitric acid (5.0 mL) and 98% H<sub>2</sub>SO<sub>4</sub> (5.0 mL) was added 3-(4,5-diamino-4H-1,2,4-triazol-1-ium-3-yl)-4,5-dinitropyrazol-1-ide (0.51 g, 2.00 mmol) in small portions at -10 °C. The mixture was held at 0 °C for 2 h. Then the mixture was poured on 50 g of ice and extracted with ether (10 mL×4), drying the organic phase with magnesium sulfate and evaporating the solvent to obtain 0.38 g of **4** as yellowish solid in a yield of 75.7%. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): δ: 6.01 (s, 1H) <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>) δ: 149.6, 147.9, 145.8, 130.9, 126.2 ppm. IR (KBr): 2146.07, 1451.83, 1425.37, 1329.93, 1245.31, 1225.69, 1104.97, 1050.71, 991.43, 759.27, 718.63. Elemental analysis calcd (%) for C<sub>5</sub>HN<sub>9</sub>O<sub>4</sub> (251.12): C 23.91, H 0.40 N 50.20, found: C 23.89, H 0.42, N 50.21. MS (ESI-) m/z: 250.12 [M-H]<sup>-</sup>.

### 3. Crystallographic datas

The crystal of **3** and **4** were performed on a Bruker Smart Apex II diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å), respectively. Integration and scaling of intensity data were accomplished using the SAINT program<sup>2</sup>. The structures were solved by intrinsic using SHELXT2014 and refinement was carried out by a full-matrix least-squares technique using SHELXT2014. The hydrogen atoms were refined isotropically, and the heavy atoms were refined anisotropically. N-H and O-H hydrogens were located from different electron density maps, and C-H hydrogens were placed in calculated positions and refined with a riding model. Data were corrected for the effects of absorption using SADABS4 Relevant crystal data and refinement results are summarized in Table S2.

**Table S2** Crystallographic datas for compounds **3** and **4**

Compound	<b>3</b>	<b>4</b>
Empirical formula	2C <sub>5</sub> H <sub>5</sub> N <sub>9</sub> O <sub>4</sub> ·3H <sub>2</sub> O	C <sub>5</sub> HN <sub>9</sub> O <sub>4</sub>
Formula weight	564.41	291.15
Temperature/K	100.0	100
Crystal system	monoclinic	monoclinic
Space group	C2/c	P2 <sub>1</sub> /c
a/Å	18.7708(11)	9.324(3)
b/Å	7.4519(4)	11.795(4)
c/Å	16.5460(10)	9.195(3)
$\alpha$ /°	90	90
$\beta$ /°	110.017(2)	115.308(9)
$\gamma$ /°	90	90
Volume/Å <sup>3</sup>	2174.6(2)	914.3(5)
Z	4	4
$\rho$ (calc) mg/mm <sup>3</sup>	1.724	1.825
Absorption coefficient m/mm <sup>-1</sup>	0.154	0.159
F(000)	1160.0	504.0
Crystal size/mm <sup>3</sup>	0.08×0.07 × 0.07	0.12×0.08 × 0.02
2 $\theta$ range for data collection	4.62 to 52.392	4.832 to 51.664
Index ranges	-23 ≤ h ≤ 23, -8 ≤ k ≤ 9, -20 ≤ l ≤ 20	-9 ≤ h ≤ 11, -14 ≤ k ≤ 13, -11 ≤ l ≤ 11
Reflections collected	11710	5469
Independent reflections	2189[R <sub>int</sub> = 0.0657, R <sub>sigma</sub> = 0.0480]	1729[R <sub>int</sub> = 0.067, R <sub>sigma</sub> = 0.0835]
Data/restraints/parameters	2189/2/194	1729/0/163

Goodness-of-fit on F <sup>2</sup>	1.019	1.030
Final R indexes [I>2σ (I)]	0.0444, 0.1028	0.0686, 0.1460
Final R indexes [all data]	0.0679, 0.1168	0.1267, 0.1756
CCDC	1918907	1918909

**Table S3** Hydrogen bonds for [Å and °] for compound **3**

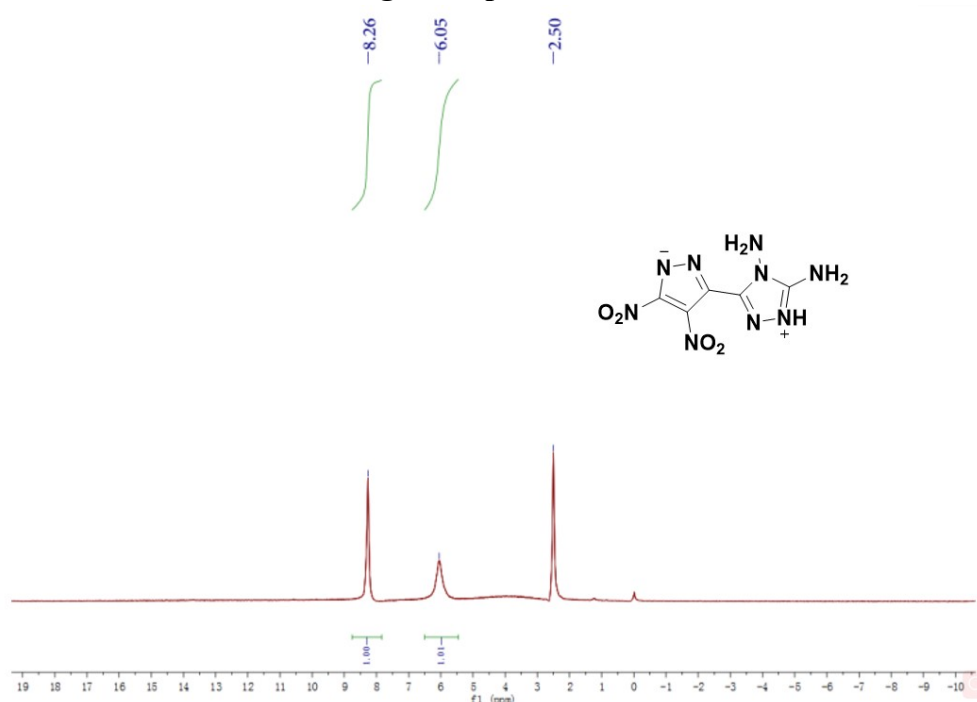
D—H...A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °
N5-H5 ...N2	0.87(3)	2.03(3)	2.891(3)	173(3) <sup>i</sup>
O5-H5A...O6	0.87(3)	1.95(3)	2.783(3)	160(4) <sup>ii</sup>
O6-H6A...N3	0.88(4)	1.88(4)	2.747(3)	168(3)
O6-H6B...O1	0.91(4)	2.15(4)	2.951(3)	148(3) <sup>iii</sup>
N7-H7A...O5	0.8800	1.9800	2.854(3)	168.00
N7-H7B...N4	0.8800	2.2800	3.035(3)	143.00 <sup>iv</sup>
N7-H7B...O1	0.8800	2.3400	3.030(3)	135.00 <sup>iii</sup>
N8-H8A...O6	0.8800	1.8900	2.764(3)	170.00 <sup>i</sup>
N8-H8B...N7	0.8800	2.5100	2.803(3)	100.00
N8-H8B...O2	0.8800	2.3600	3.128(3)	146.00 <sup>v</sup>
N8-H8B...O3	0.8800	2.5800	2.990(3)	109.00 <sup>v</sup>

Symmetry Code: i: x,1-y,-1/2+z ii: 1-x,y,3/2-z iii: 1/2-x,1/2-y,1-z iv: 1/2-x,1/2+y,3/2-z v: 1/2+x,3/2-y,1/2+z

**Table S4** Hydrogen bonds for [Å and °] compound **4**

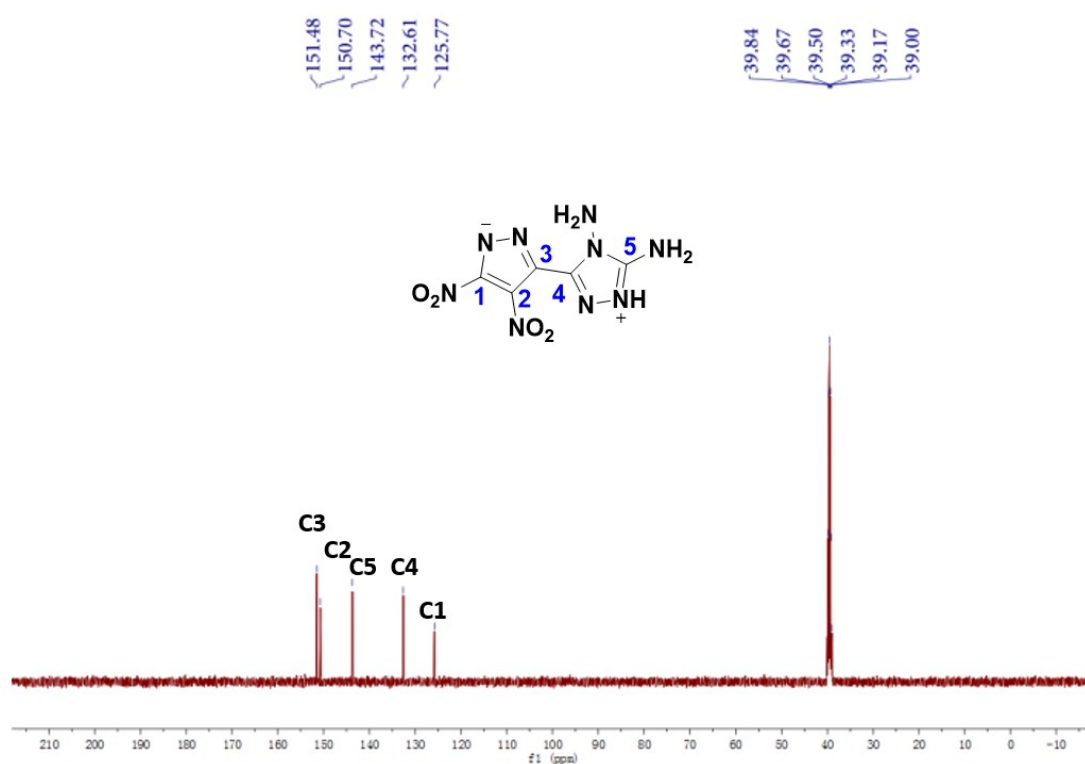
D—H...A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °
N4-H4...N6	0.8800	1.9700	2.790(5)	155.00

#### 4. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR of target compounds



**Figure S1.**  $^1\text{H}$  NMR spectra in  $\text{DMSO}-d_6$  for compound **3**

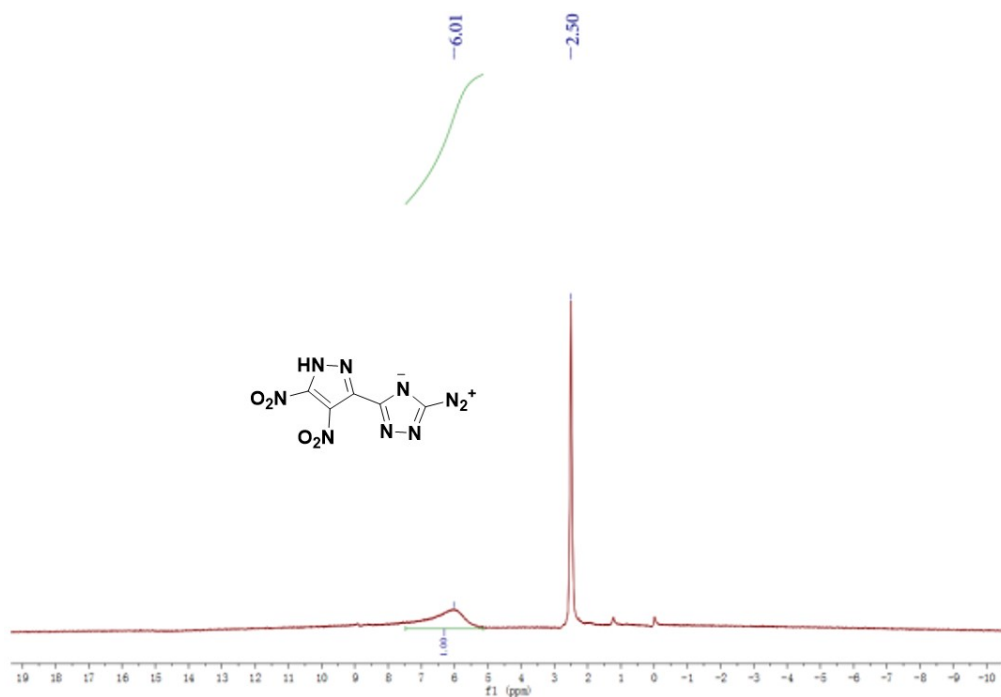
In the  $^1\text{H}$  NMR spectrum of **3**, the signal for the C-NH<sub>2</sub> was observed at 8.26 ppm. The signal for the N-NH<sub>2</sub> was observed at 6.05 ppm. The signal for the NH<sup>+</sup> was not observed.



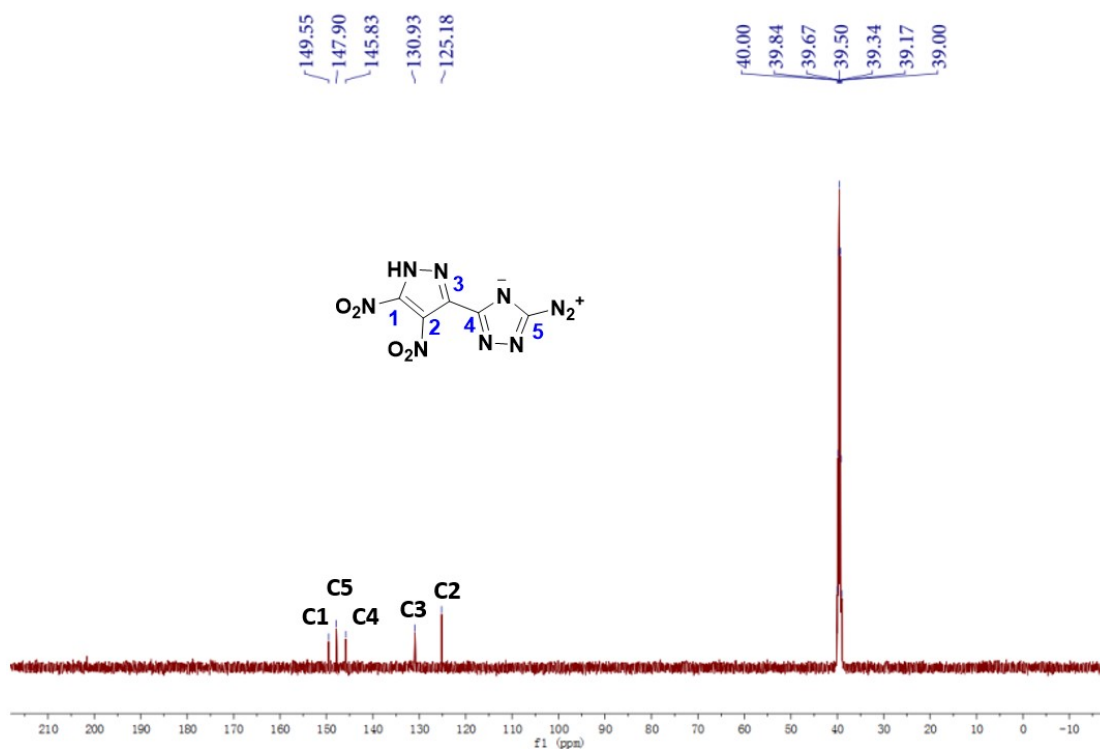
**Figure S2.**  $^{13}\text{C}$  NMR spectra in  $\text{DMSO}-d_6$  for compound **3**

In the  $^{13}\text{C}$  NMR spectrum of **3**, the signals for the C1-C5 were observed at 125.8, 150.7, 151.5, 132.6, 143.7 ppm, respectively.





**Figure S3.**  $^1\text{H}$  NMR spectra in  $\text{DMSO-}d_6$  for compound **4**  
 In the  $^1\text{H}$  NMR spectrum of **4**, the signal for the NH was observed at 6.01 ppm.



**Figure S4.**  $^{13}\text{C}$  NMR spectra in  $\text{DMSO-}d_6$  for compound **4**  
 In the  $^{13}\text{C}$  NMR spectrum of **4**, the signals for the C1-C5 were observed at 149.6, 125.2, 130.9, 145.8, 147.9 ppm, respectively.

## 5. Mass Spectra of Compounds

T: - c Q1MS [ 200.00-500.00]

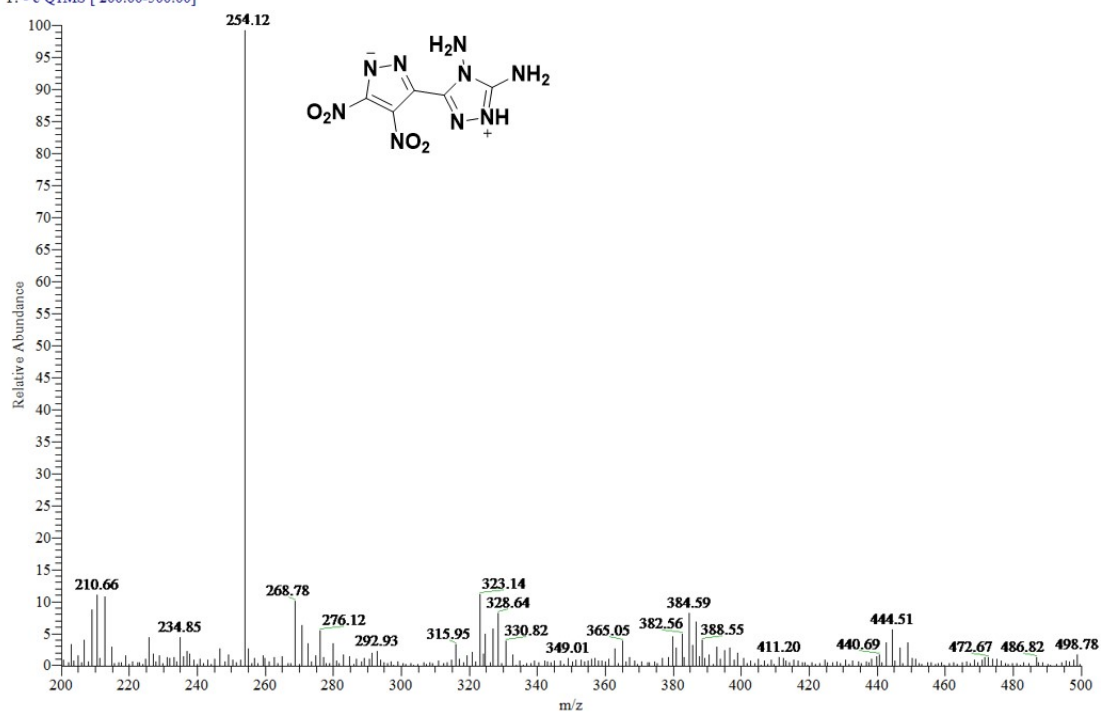


Figure S5. Mass spectra of compound 3

T: - c Q1MS [ 200.00-500.00]

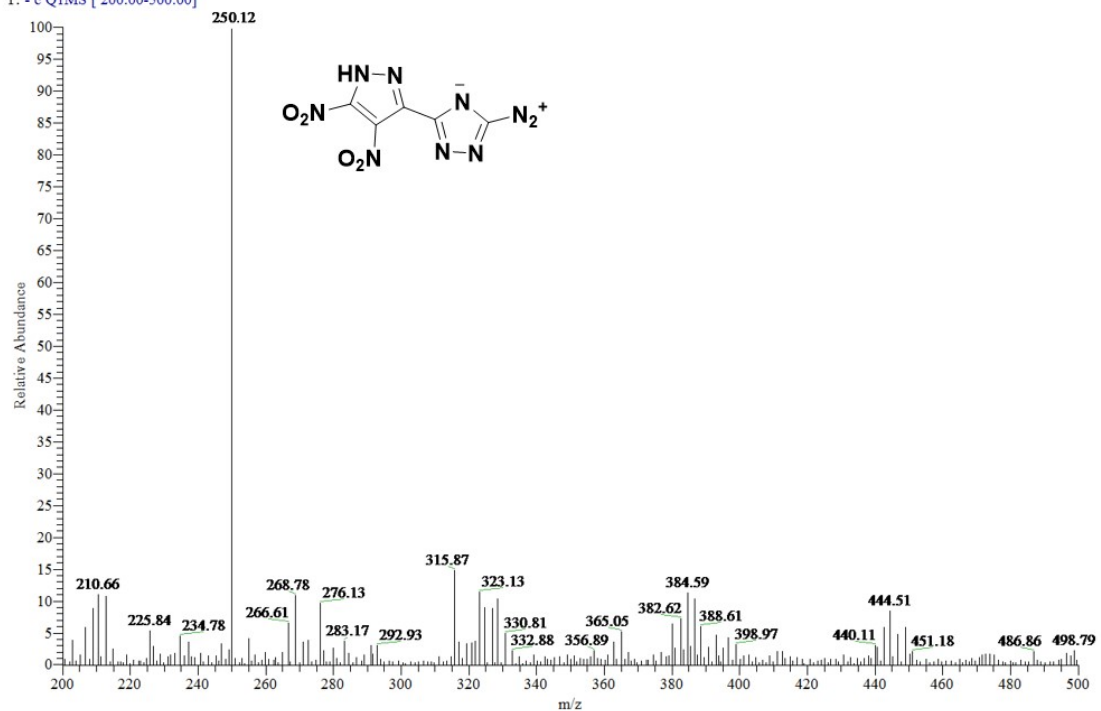
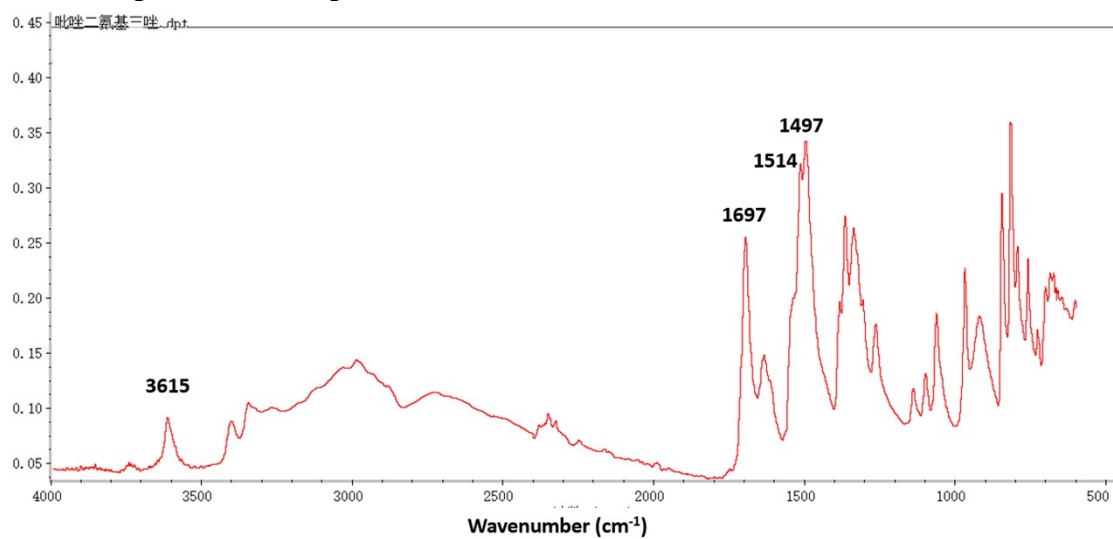


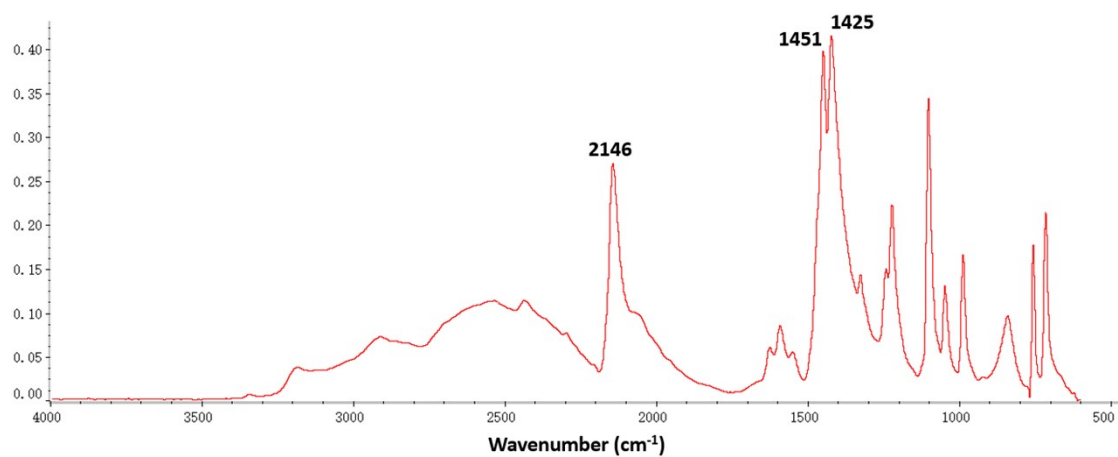
Figure S6. Mass spectra of compound 4

## 6. IR Spectra of Compounds 3 and 4



**Figure S7.** IR spectra of compound **3**

In the IR spectrum of **3**, the signals for the -NO<sub>2</sub> and -NH<sub>2</sub> were observed at 1514 and 3615 cm<sup>-1</sup>, respectively.



**Figure S8.** IR spectra of compound **4**

In the IR spectrum of **4**, the signals for the -N<sub>2</sub><sup>+</sup> and -NO<sub>2</sub> were observed at 2146 and 1425-1451 cm<sup>-1</sup>, respectively.

## 7. The DSC plots of synthesized compounds 3 and 4

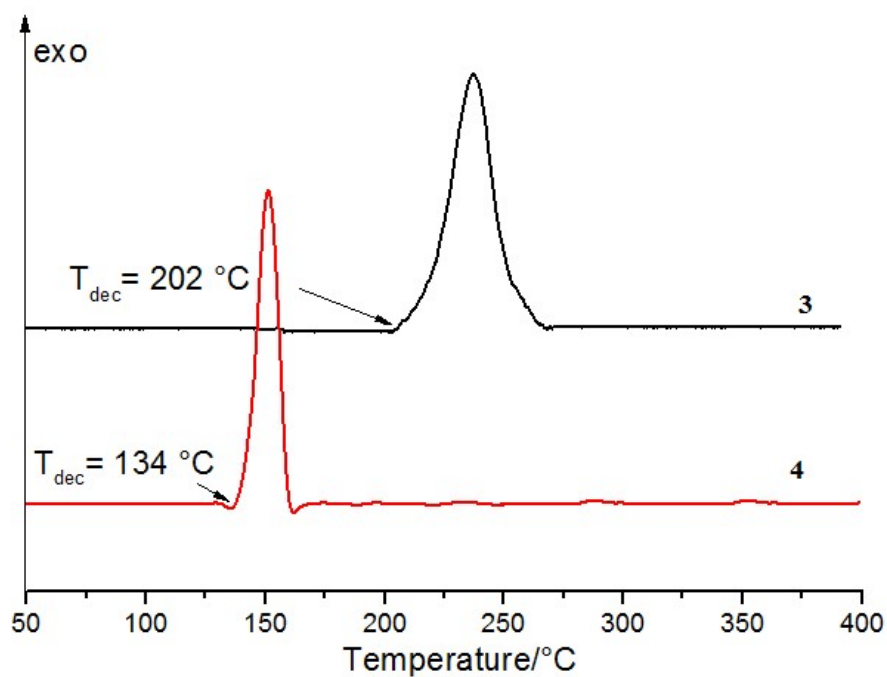


Figure S9. The DSC plots of compounds 3 and 4

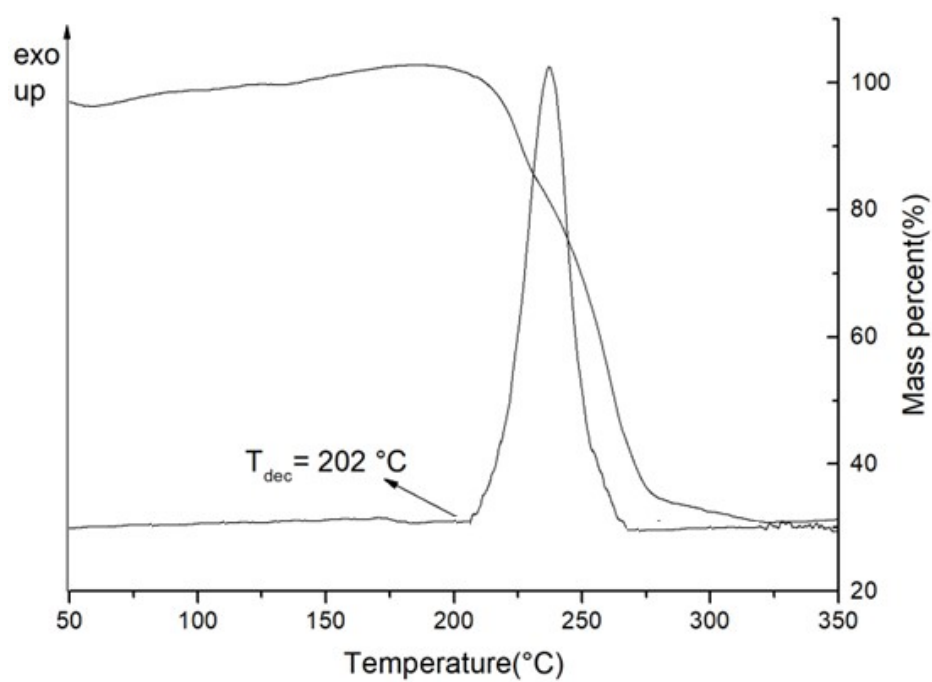
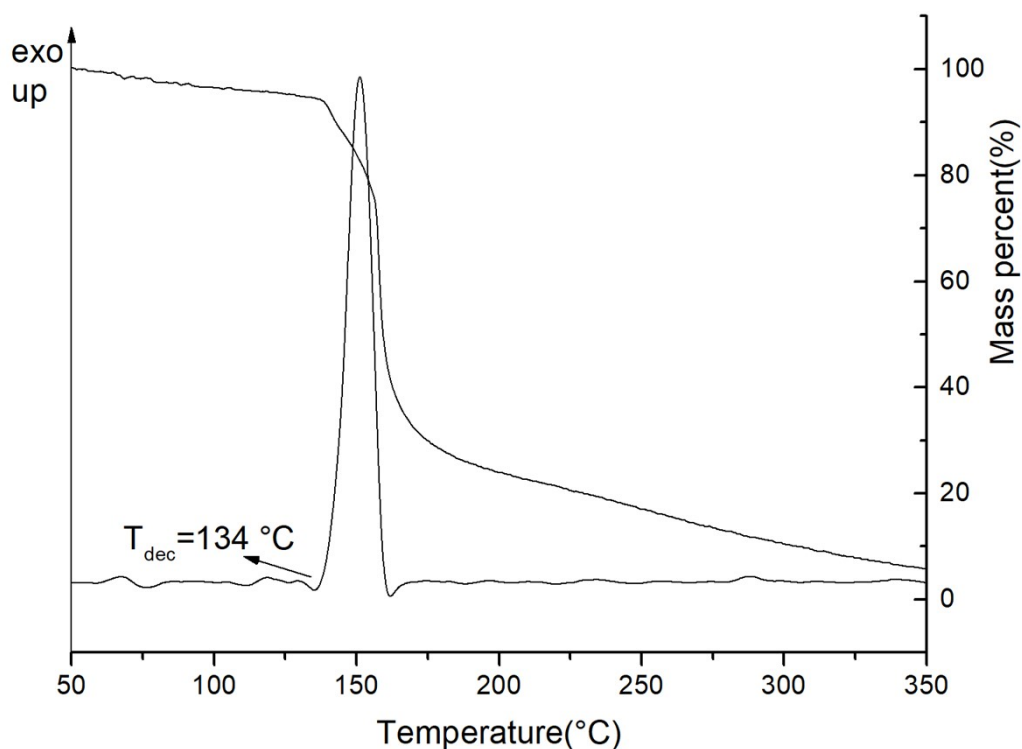


Figure S10. The TG-DSC plots of compound 3



**Figure S11.** The TG-DSC plots of compound 4

Herein, differential scanning calorimetry (DSC) was carried out to determine the thermal stabilities of all synthesized compounds with a linear heating rate of  $5\text{ }^{\circ}\text{C min}^{-1}$  under a nitrogen atmosphere.

## 8. Reference

- [1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D. 01, Gaussian, Inc. Wallingford CT, **2009**.
- [2] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta.* **1973**, 28, 213-222.
- [3] Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A. A complete basis set model chemistry. V. Extensions to six or more heavy atoms. *J. Chem. Phys.* **1996**, 104 (7), 2598-2619.
- [4] Jenkins, H. D. B.; Tudeal, D.; Glasser, L. Lattice Potential Energy Estimation for Complex Ionic Salts from Density Measurements. *Inorg. Chem.*, **2002**, 41 (9), 2364-2367.