New journal of chemistry

Supplementary materials

for

Synthesis and characterization of three pyrazolate inner diazonium salts: green, powerful and stable primary explosives

Yao Du[a], Jichuan Zhang[a], Panpan Peng[a], Hui Su[a], Shenghua Li*[a] and Siping Pang*[a]

a   School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, PR China

Crystal data

Table S1. Selected bond lengths (Å) and bond angles (°) in crystal for 3,5–dichloro–4–diazopyrazole zwitterion (**1**), 4–diazo–3,5–dinitropyrazole zwitterion (**2**)(**2′**[a]**),** and 4–diazo–5–nitro–pyrazol–3–one zwitterion (**3**)

Bonds	1 (Å)	Bonds	2 (Å)	2′(Å)	Bonds	3 (Å)
N1–C1	1.304(2)	N1–C1	1.3115(16)	1.3114(15)	C3–N2	1.367(2)
N1–N2	1.407(2)	N1–N2	1.3736(15)	1.3807(15)	N1–N2	1.3663(18)
N2–C3	1.3072(19)	N2–C3	1.3096(15)	1.3131(15)	N1–C1	1.2947(19)
N3–N4	1.106(2)	N3–N4	1.0986(14)	1.1007(14)	N3–N4	1.1060(19)
N3–C2	1.3325(19)	N3–C2	1.3523(15)	1.3527(14)	N3–C2	1.329(2)
C1–C2	1.416(2)	C1–C2	1.4023(15)	1.3953(17)	C3–C2	1.441(2)
C2–C3	1.414(2)	C2–C3	1.4046(16)	1.3975(16)	C1–C2	1.410(2)
Cl1–C1	1.7081(16)	N5–C1	1.4459(16)	1.4427(15)	O3–C3	1.2271(19)
Cl2–C3	1.7035(15)	N6–C3	1.4470(15)	1.4456(16)	N5–C1	1.439(2)
		N6–O4	1.2194(14)	1.2215(14)	O2–N5	1.2168(19)
		N6–O3	1.2252(14)	1.2224(15)	O1–N5	1.2235(17)
		N5–O2	1.2175(15)	1.2209(14)		
		N5–O1	1.2255(15)	1.2224(14)		

Bond angles	1 (°)	Bond angles	2 (°)	2′ (°)	Bond angles	3 (°)
C1–N1–N2	108.13(13)	C1–N1–N2	107.76(10)	107.63(10)	N1–N2–C3	115.12(12)
C3–N2–N1	108.19(13)	C3–N2–N1	108.16(10)	107.59(10)	C1–N1–N2	104.81(12)
N4–N3–C2	178.72(18)	N4–N3–C2	177.95(12)	179.22(13)	N4–N3–C2	176.14(17)
N1–C1–C2	110.19(14)	N1–C1–C2	111.14(11)	111.3(1)	N2–C3–C2	101.72(13)
N3–C2–C3	128.85(14)	N3–C2–C3	130.27(10)	128.90(11)	N3–C2–C1	130.66(14)
N3–C2–C1	127.66(14)	N3–C2–C1	127.70(11)	128.73(11)	N3–C2–C3	123.18(15)
C3–C2–C1	103.39(13)	C1–C2–C3	102.02(10)	102.28(10)	C1–C2–C3	106.05(13)
N2–C3–C2	110.08(13)	N2–C3–C2	110.91(10)	111.16(11)	N1–C1–C2	112.28(13)
N1–C1–Cl1	123.97(12)	N1–C1–N5	122.52(11)	122.39(11)	O3–C2–N2	127.37(14)
C2–C1–Cl1	125.83(12)	C2–C1–N5	126.25(11)	126.09(11)	O3–C3–C2	130.90(15)
N2–C3–Cl2	123.60(12)	N2–C3–N6	121.81(11)	122.60(11)	N1–C1–N5	121.13(14)
C2–C3–Cl2	126.31(12)	C2–C3–N6	127.27(11)	125.95(11)	C2–C1–N5	126.45(14)
		O4–N6–O3	125.91(11)	126.44(12)	O2–N5–O1	125.29(14)
		O4–N6–C3	117.99(11)	117.74(11)	O2–N5–C1	118.72(14)
		O3–N6–C3	116.1(1)	115.79(11)	O1–N5–C1	115.97(14)
		O2–N5–O1	125.89(12)	125.67(11)		
		O2–N5–C1	118.41(12)	118.02(10)		
		O1–N5–C1	115.69(11)	116.27(10)		

[a] For compound 2, and there are two different molecular structures in crystal, of which the crystal data are slightly distinct.

Table S2. Crystallographic data for **1**, **2**, and **3**.

	1	2	3
Empirical formula	$C_3Cl_2N_4$	$C_3N_6O_4$	$C_3HN_5O_3$
CCDC number	1018388	1018387	1018389
Temperature/K	153(2)	153(2)	293(2)
Formula weight/(g/mol)	162.97	184.09	155.09
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	Pbca	P2$_1$/n	P2$_1$/n
a /Å	8.814(3)	11.382(3)	5.536(4)
b /Å	9.208(3)	10.234(2)	9.134(7)
c /Å	14.261(4)	12.054(3)	11.526(8)
α /°	90	90	90
β /°	90	109.625(3)	91.852(6)
γ /°	90	90	90
V /Å³	1157.41(63)	1322.5(5)	582.47(7)
Z	8	8	4
ρ /(g·cm⁻³)	1.894	1.849	1.769
μ /mm⁻¹	1.016	0.171	0.158
F(000)	656.0	736.0	312.0
Crystal size/mm	0.48 × 0.46 × 0.31	0.50 × 0.42 × 0.28	0.24 × 0.22 × 0.22
θ /°	3.50~31.48	2.68~29.13	4.43~25.58
Limiting indices	−11 ≤ h ≤ 12 −13 ≤ k ≤ 13 −20 ≤ l ≤ 20	−15 ≤ h ≤ 14 −13 ≤ k ≤ 14 −16 ≤ l ≤ 13	−6 ≤ h ≤ 7 −12 ≤ k ≤ 9 −15 ≤ l ≤ 15
Reflections Collected	10549	13874	5344
Independent reflections	1914	3539	1468
Rint	0.0319	0.0338	0.0297
Final R indices [I > 2σ (I)]	R1 = 0.0370, wR$_2$ = 0.0997	R1 = 0.0368, wR$_2$ = 0.0949	R1 = 0.0456, wR$_2$ = 0.0985
Final R indices (all data)	R1 = 0.396, wR$_2$ = 0.1023	R1 = 0.0463, wR$_2$ = 0.1018	R1 = 0.0749, wR$_2$ = 0.1135

Heat of formation

Isodesmic reaction, in which numbers of electron pairs and chemical bond types are conserved, has been employed very successfully to give heat of formation[1]. Based on the optimized structures, the total energy (E_0) and thermodynamic parameters, including zero point energy (ZPE) and thermal correction to enthalpy (HT), were obtained at the B3LYP/6−311G++(d,p) level. For the isodesmic reaction (Scheme S1), gas−phase heat of reaction (ΔH_{298K}) can be calculated from the following Equation (1):

$$\Delta H_{298K} = \sum \Delta H_{f,P}(gas, 298K) - \sum \Delta H_{f,R}(gas, 298K) \tag{1}$$

where $H_{f,R}$ and $H_{f,P}$ are the gas−phase heats of formation for reactants and products at 298 K, respectively.

Meanwhile, $\Delta H_{298 K}$ can also be calculated using the following Equation (2):

$$\Delta H_{298 K} = \Delta E_{298 K} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta HT + \Delta(nRT) \tag{2}$$

Where ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is

the difference between the zero−point energies of the products and the reactants; ΔHT is thermal correction from 0 K to 298.15 K. Since there is no change in number of total molecules, Δ(PV) = Δ(nRT) =0. Therefore, the heat of formation in gas−phase can be figured out according to $\Delta H_{298\,K}$ and gas−phase heats of formation of other reactants and products. Fortunately, these data can be acquired from the literature and handbook facilely.
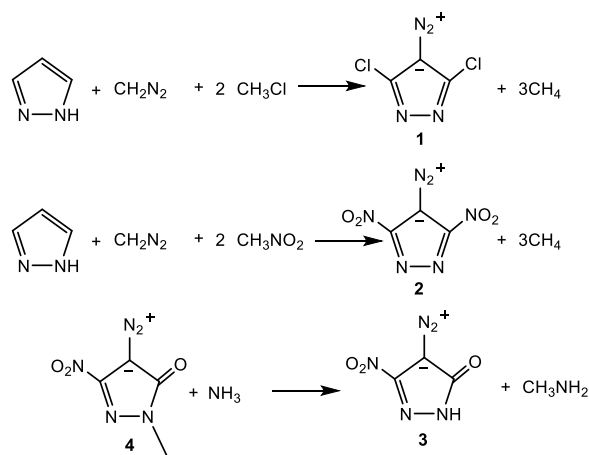
Scheme S1. Isodesmic reactions

Table S3. Calculated total energy (E_0), zero−point energy (ZPE), thermal correction (HT), and enthalpy of formation (HOF_{Gas}) of compounds **1−3** and reference compounds.

Compd.	E_0/a.u.	ZPE (kJ/mol)	HT (kJ/mol)	HOF_{Gas} (kJ/mol)
1H−pyrazole[2]	−226.265995	186.35	12.32	177.4
Methylamine[3]	−95.893889	167.46	11.52	−23.5
Nitromethane[4]	−245.091646	130.18	14.04	−81
Methane[5]	−40.533958	116.97	10.01	−74.6
Diazomethane[6]	−148.785743	83.10	11.91	206
Chloromethane	−500.151876	98.87	10.42	−81.9
Ammonia[7]	−56.582722	89.96	10.02	−40.90
1	−1253.746877	97.17	22.54	449.46
2	−743.608663	158.44	29.85	496.60
3	−614.343899	167.34	25.63	169.77
4[8]	−652.0221153	240.99	30.67	177.0

For assessment of the potential performance of the energetic material of interest, however, the desired quantity is usually the condensed phase ΔH_f. Condensed phase heats of formation can be determined using the gas−phase heats of formation and heat of phase transition (either sublimation or vaporization) according to Hess' law of constant heat summation. For compounds discussed in this paper, they are all solid at room temperature and their solid heat of formation can be calculated by Equation (3). The calculation of ΔH(Sublimation) can use the method proposed by Politzer and coworkers[9] shown as Equation (4).

$$\Delta H(\text{Solid}) = \Delta H(\text{Gas}) - \Delta H(\text{Sublimation}) \tag{3}$$

$$\Delta H(\text{Sublimation}) = a(\text{SA})^2 + b\sqrt{\sigma_{tot}^2 \nu} + c \tag{4}$$

where SA is the surface area of the 0.001 electron/bohr3 isosurface of the electron density of the molecule, σ_{tot}^2 is a measure of the variability of electronic potential on the surface, and ν is the

degree of balance between the positive and negative charges on the isosurface. The above three parameters can be calculated by Multiwfn(version 3.3.8).[10, 11] a, b, and c are constants and their value are 0.000267, 1.650087, and 2.966078, respectively.[12]

Table S4. Calculated solid heat of formation of **1−3**

Compounds	SA/Å^2	σ^2_{tot} /(kcal·mol)^2	ν	ΔH(Sublimation) /kJ·mol^{-1}	HOF$_{Gas}$ /kJ·mol^{-1}	ΔH(Solid)/ kJ·mol^{-1}
1	164.34	233.39	0.2400	94.30	449.46	355.16
2	178.60	206.42	0.1688	88.84	496.60	407.76
3	162.01	189.79	0.2028	84.60	169.77	85.17

Thermal stability

The DSC and TG spectra of compounds **1−3** are shown in Figure S1, and the thermal decomposition temperatures of some other aromatic diazonium salts and heterocyclic diazo compounds are listed in Table S5. As shown in the table, the decomposition temperatures for common diazonium salts mostly are not more than 100 °C, while the inner diazonium salts show decomposition temperatures more than 120 °C.

Figure S1. DSC and TG spectra of **1(a)**, **2(b)** and **3(c)**.

(a)

(b)

(c)
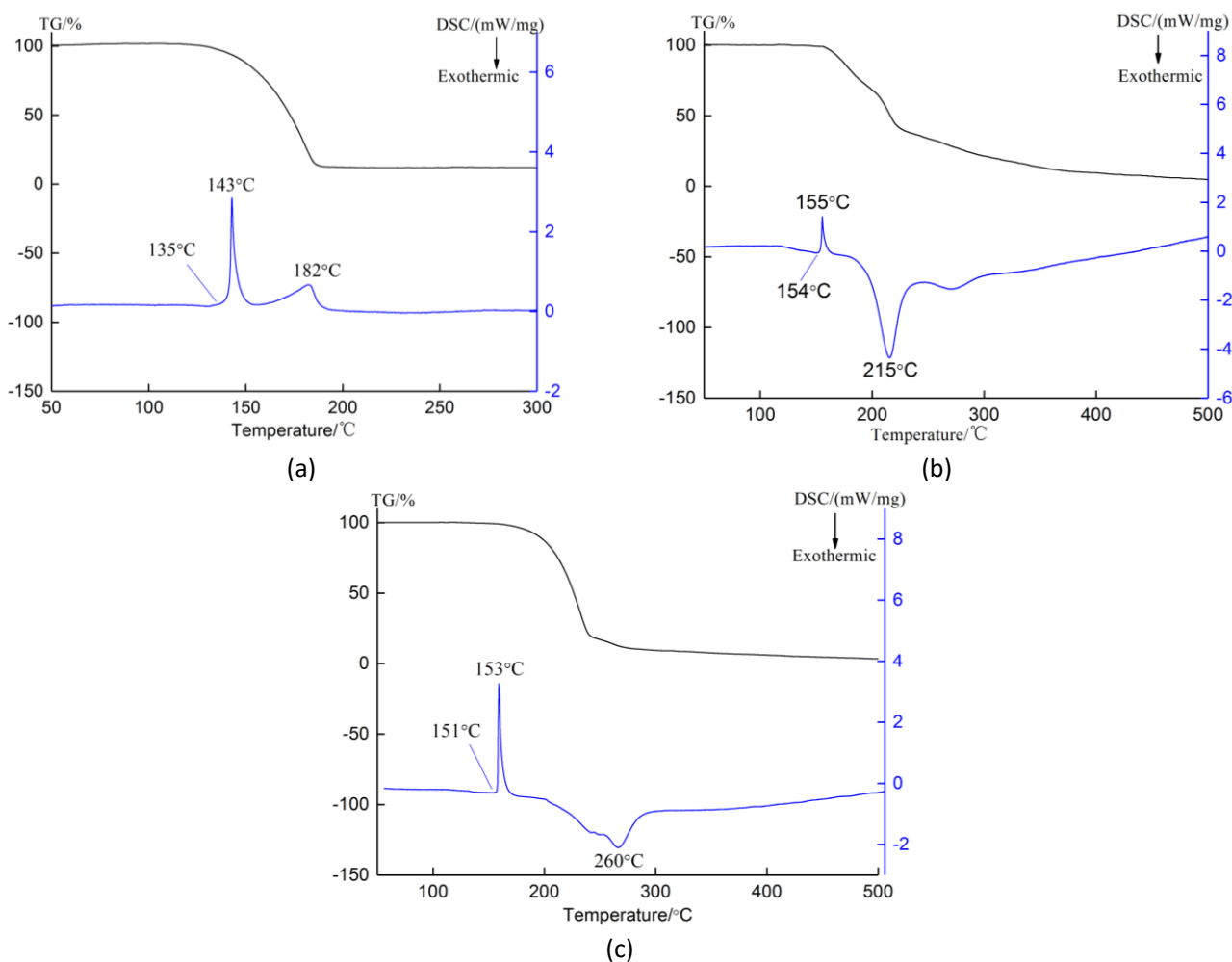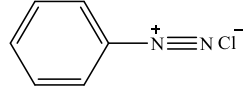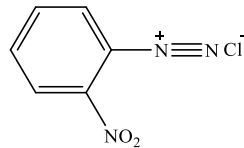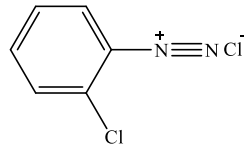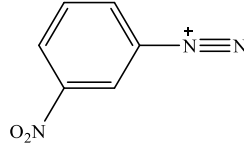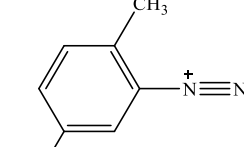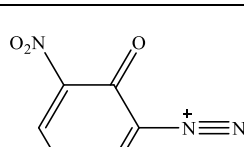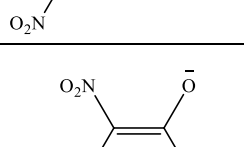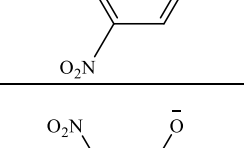
Table S5. Decomposition temperatures for aromatic diazonium salts and heterocyclic diazo compounds

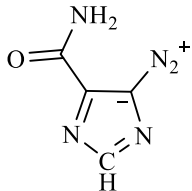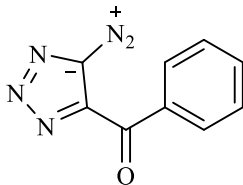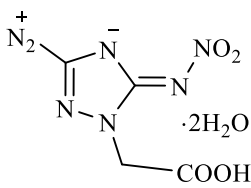| Compound name	Structure formula	Decomposition temperature/ ℃	Reference
Benzenediazonium chloride		40 (10K/min)	*R. Ullrich, T. Grewer, Thermochimica Acta 1993, 225, 201−211*
2-nitrobenzenediazonium chloride		60 (10K/min)	*R. Ullrich, T. Grewer, Thermochimica Acta 1993, 225, 201-211*
3-chlorobenzenediazonium chloride		120 (10K/min)	*R. Ullrich, T. Grewer, Thermochimica Acta 1993, 225, 201-211*
3-nitrobenzenediazonium chloride		90 (20K/min)	*R. Ullrich, T. Grewer, Thermochimica Acta 1993, 225, 201-211*
2-methyl-5-nitro benzenediazonium chloride		80 (20K/min)	*R. Ullrich, T. Grewer, Thermochimica Acta 1993, 225, 201-211*
2-diazo-4,6-dinitrophenol		142(5K/min)	*Kaiser M, Ticmanis U. Thermochimica acta, 1995, 250(1): 137-149*
3-Amino-6-diazo-2,4-dinitrophenol		170(5K/min)	*Izsák D, Klapötke T M, Preimesser A, et al. Zeitschrift für anorganische und allgemeine Chemie, 2016, 642(1): 48-55.*
2-Diazo-5-chloro-3,6-dinitrophenol		165(5K/min)	*Izsák D, Klapötke T M, Preimesser A, et al. Zeitschrift für anorganische und allgemeine Chemie, 2016, 642(1): 48-55.*
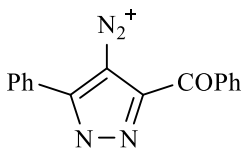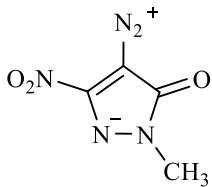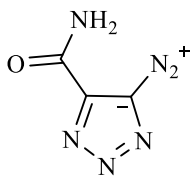
|			
3-benzoyl-4-diazo-5-phenylpyrazole		190	*Farnum D G, Vates P. Journal of the American Chemical Society, 1962, 84(8): 1399-1406.*
N-Methyl-3-nitro-4-diazo-5-oxide pyrazole		190	*He C, Zhang J, Parrish D A, et al. Journal of Materials Chemistry A, 2013, 1(8): 2863-2868.*
4-diazonium-1,2,3-triazolate-5-carboxamide		175	*Shealy Y F, STRUCK R F, HOLUM L E E B, et al. The Journal of Organic Chemistry, 1961, 26(7): 2396-2401*
5-Diazoimidazole-4-carboxamide		210	*Shealy Y F, STRUCK R F, HOLUM L E E B, et al. The Journal of Organic Chemistry, 1961, 26(7): 2396-2401*
4-diazonium-1,2,3-triazolate-5-(phenyl)methanone		134	*STADLER D, ANSCHUETZ W, REGITZ M, et al. Chemischer Informationsdienst, 1976, 7(9).*
1-Carboxymethyl-3-diazonio-5-nitrimino-1,2,4-triazole dihydrate		142	*Thomas M. Klapöke, Nordheider A, Jörg Stierstorfer. New Journal of Chemistry, 2012, 36(36):1463-1468.*
$1,10\text{-}B_{10}H_8(N_2)_2$	$1,10\text{-}B_{10}H_8(N_2)_2$	125	*Knoth W H. Journal of the American Chemical Society, 1966, 88(5): 935-939.*
$1,10\text{-}B_{10}Cl_8(N_2)_2$	$1,10\text{-}B_{10}Cl_8(N_2)_2$	180	*Knoth W H. Journal of the American Chemical Society, 1966, 88(5): 935-939.*
$1,10\text{-}B_{10}I_8(N_2)_2$	$1,10\text{-}B_{10}I_8(N_2)_2$	160	*Knoth W H. Journal of the American Chemical Society, 1966, 88(5): 935-939.*

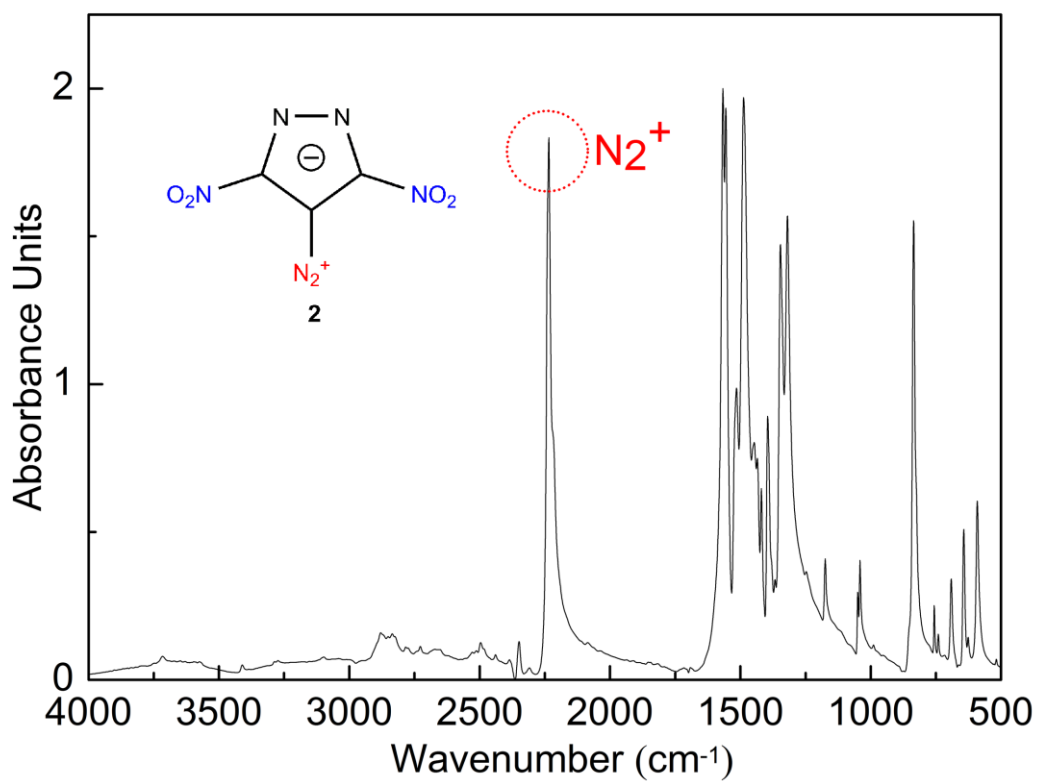**Figure S2**. IR spectrum of **1**
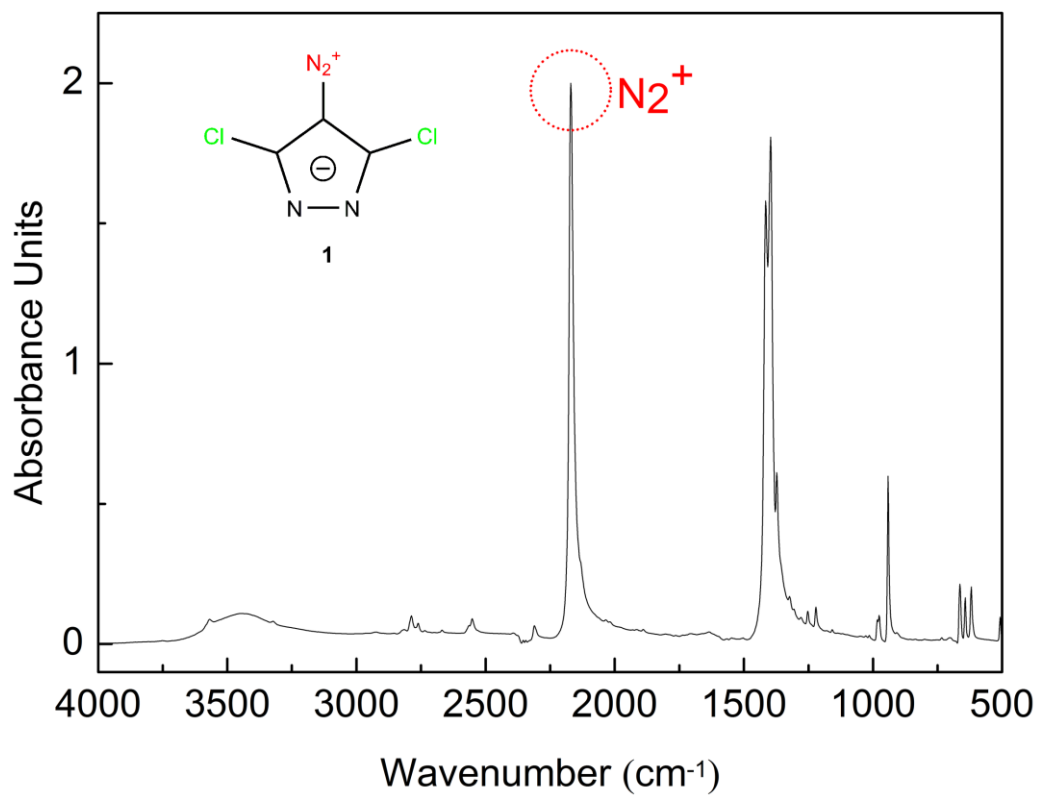
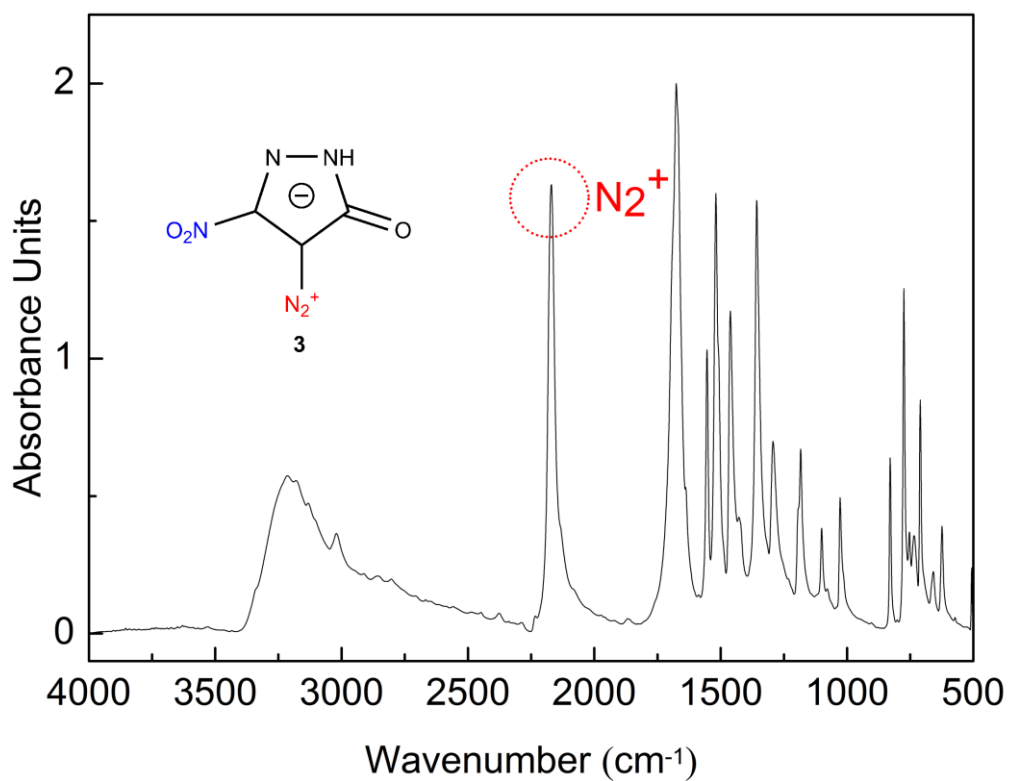**Figure S3**. IR spectrum of **2**

Figure S4. IR spectrum of **3**
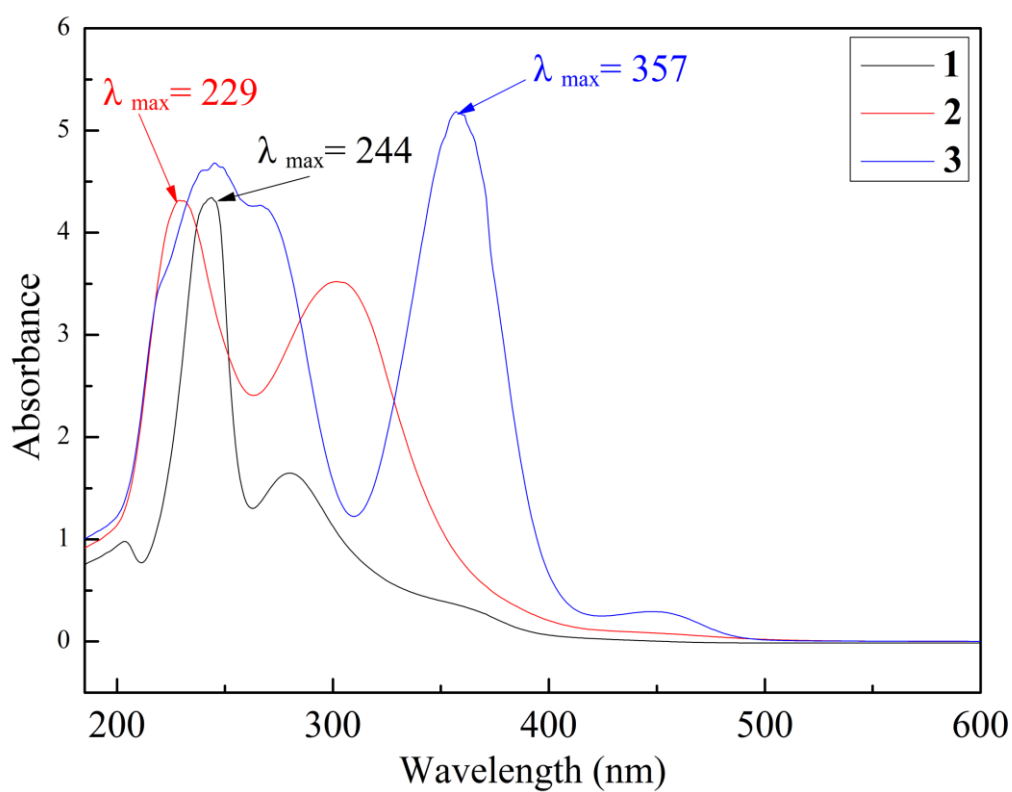

Figure S5. UV/Vis spectra for three compounds

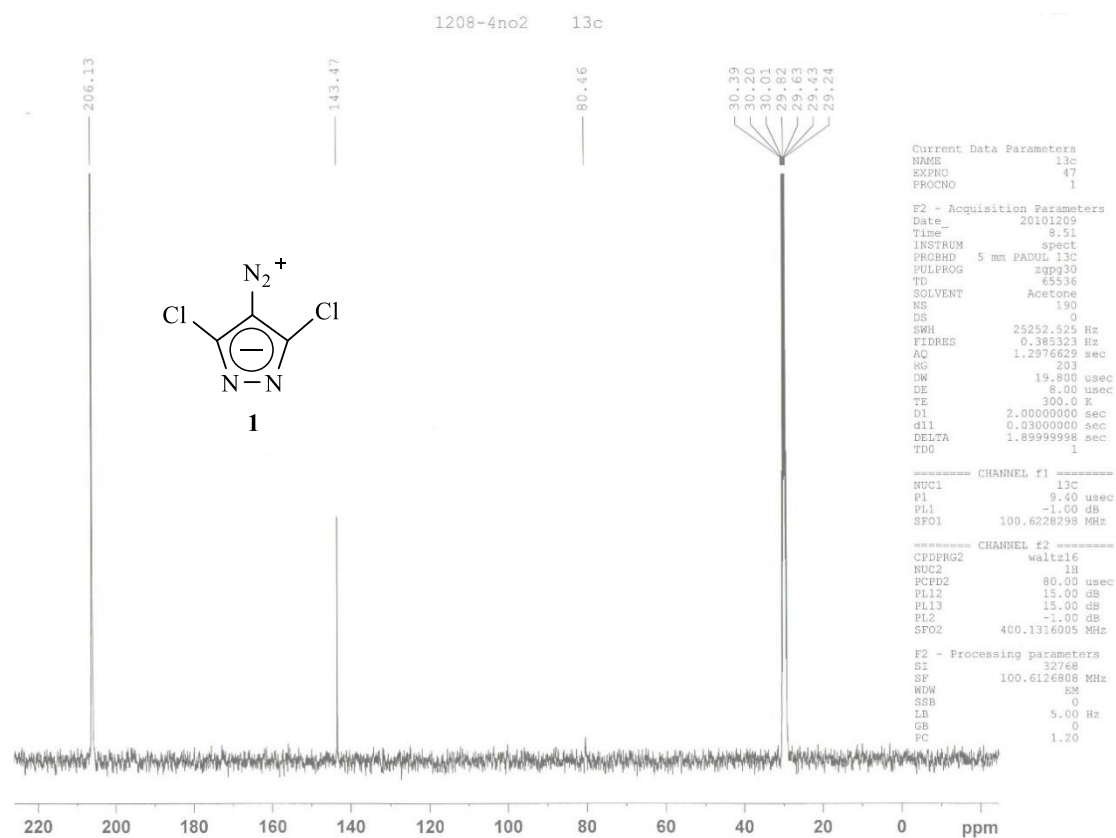**Figure S6**. ^{13}C NMR spectrum (100 MHz) of **1** in Acetone-d_6 at 25 °C.
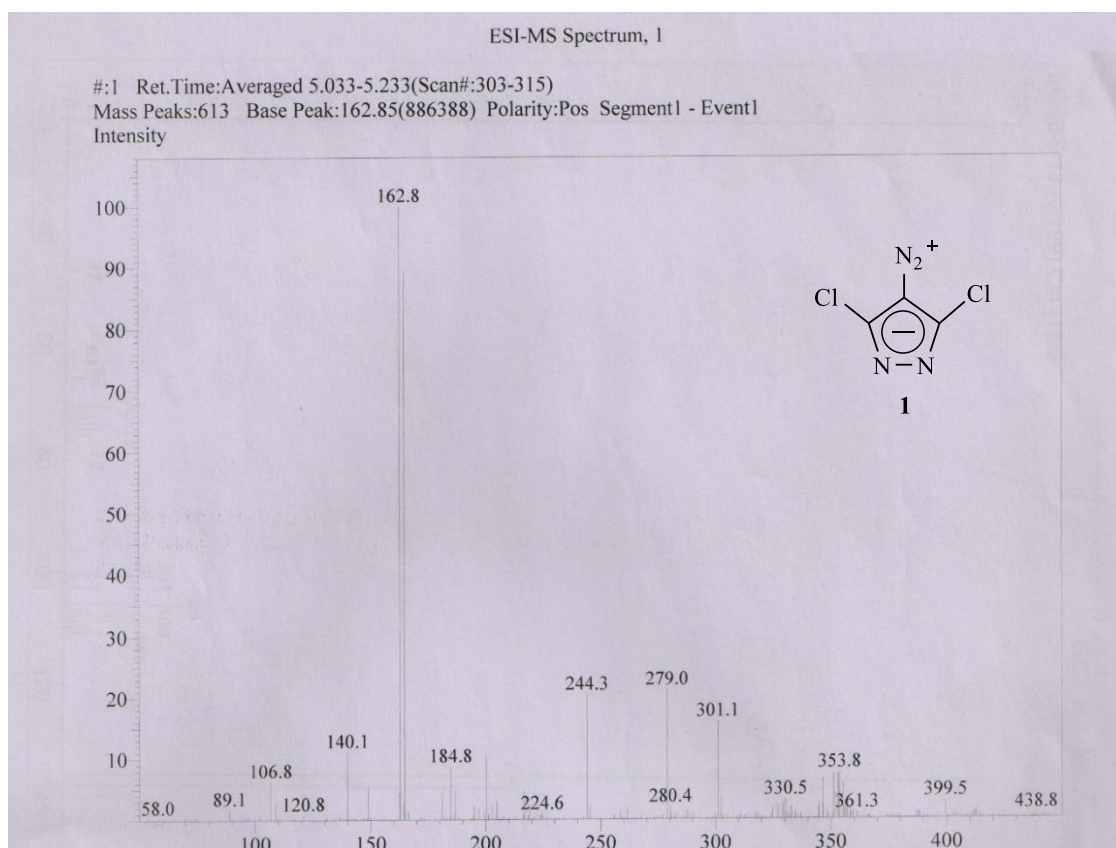

Figure S7. ESI-MS spectrum of **1**.

Figure S8. ^{13}C NMR spectrum (100 MHz) of **2** in Acetone-d$_6$ at 25 °C.
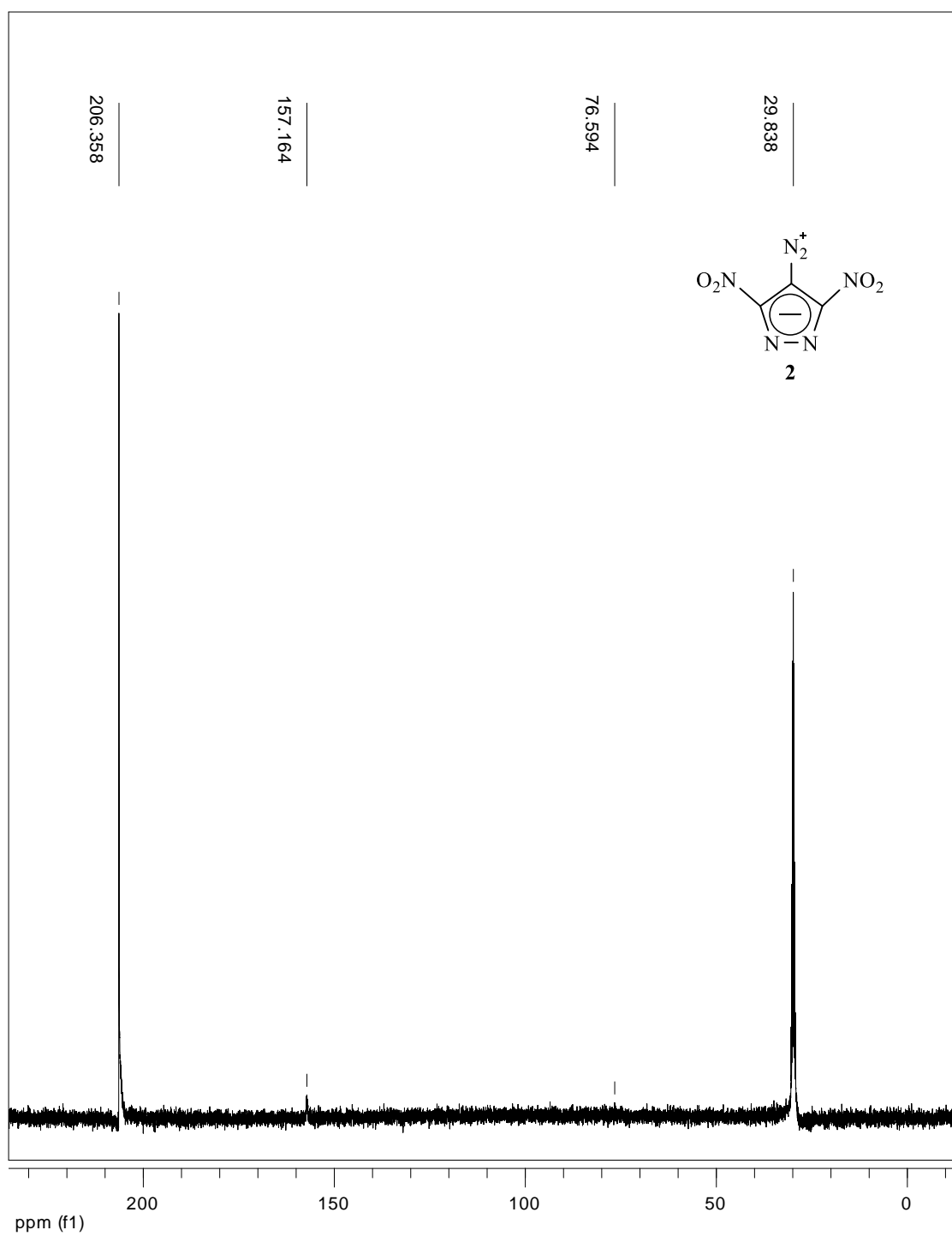
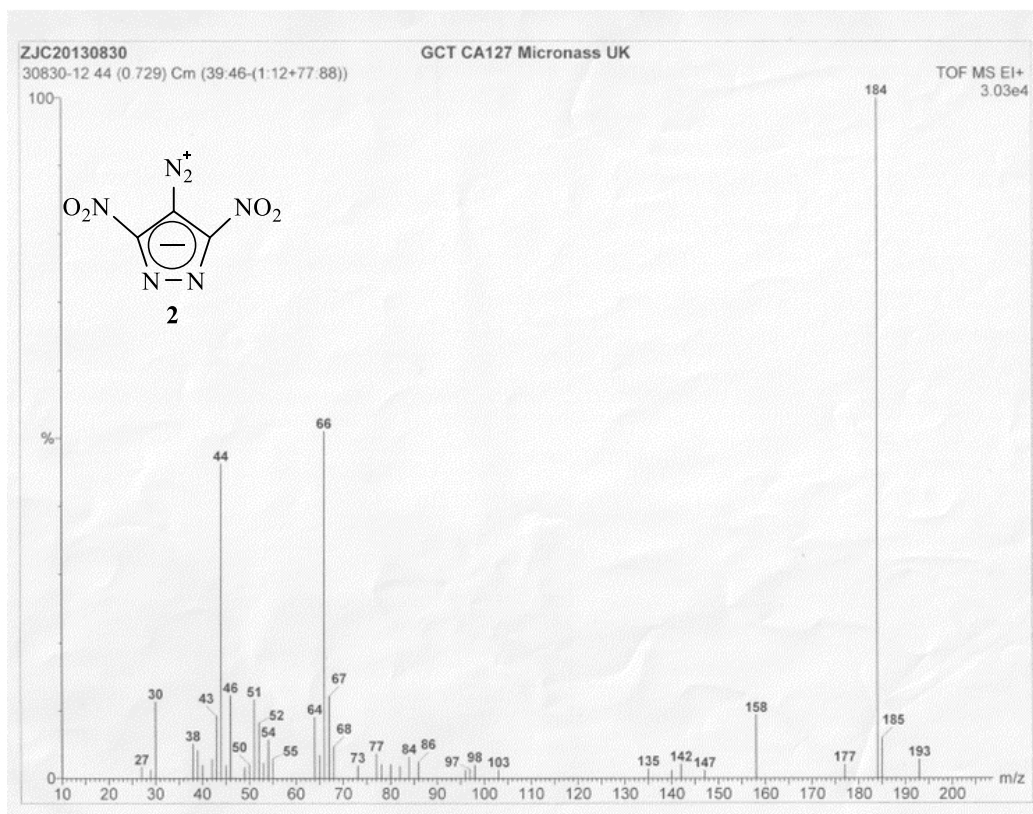**Figure S9**. EI-MS spectrum of **2**.

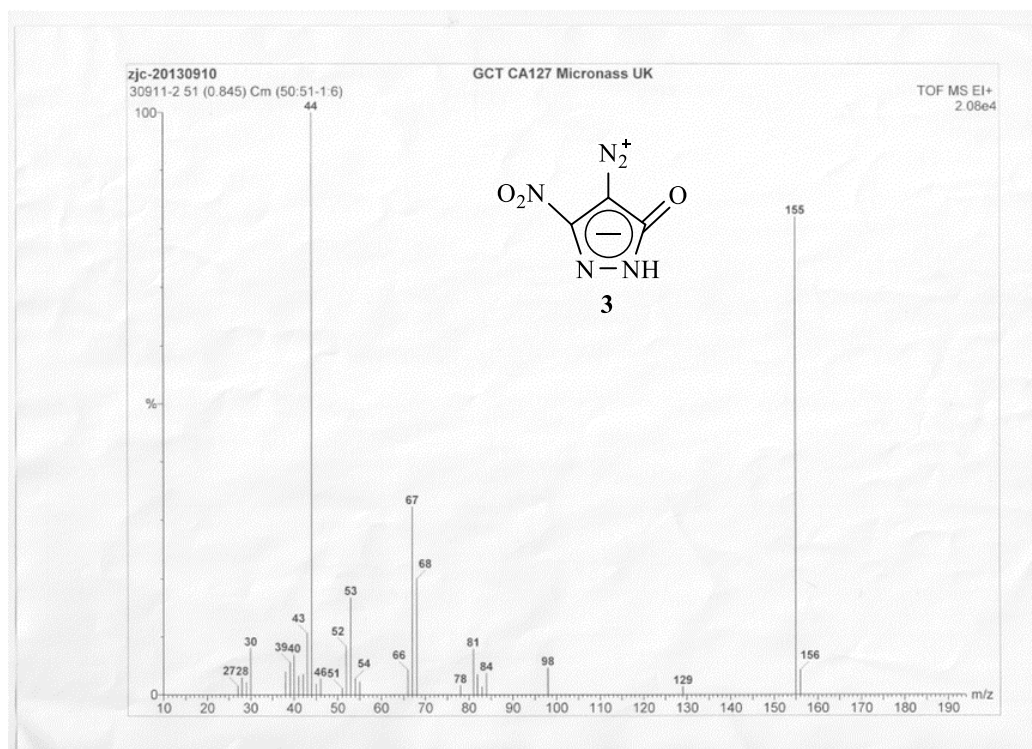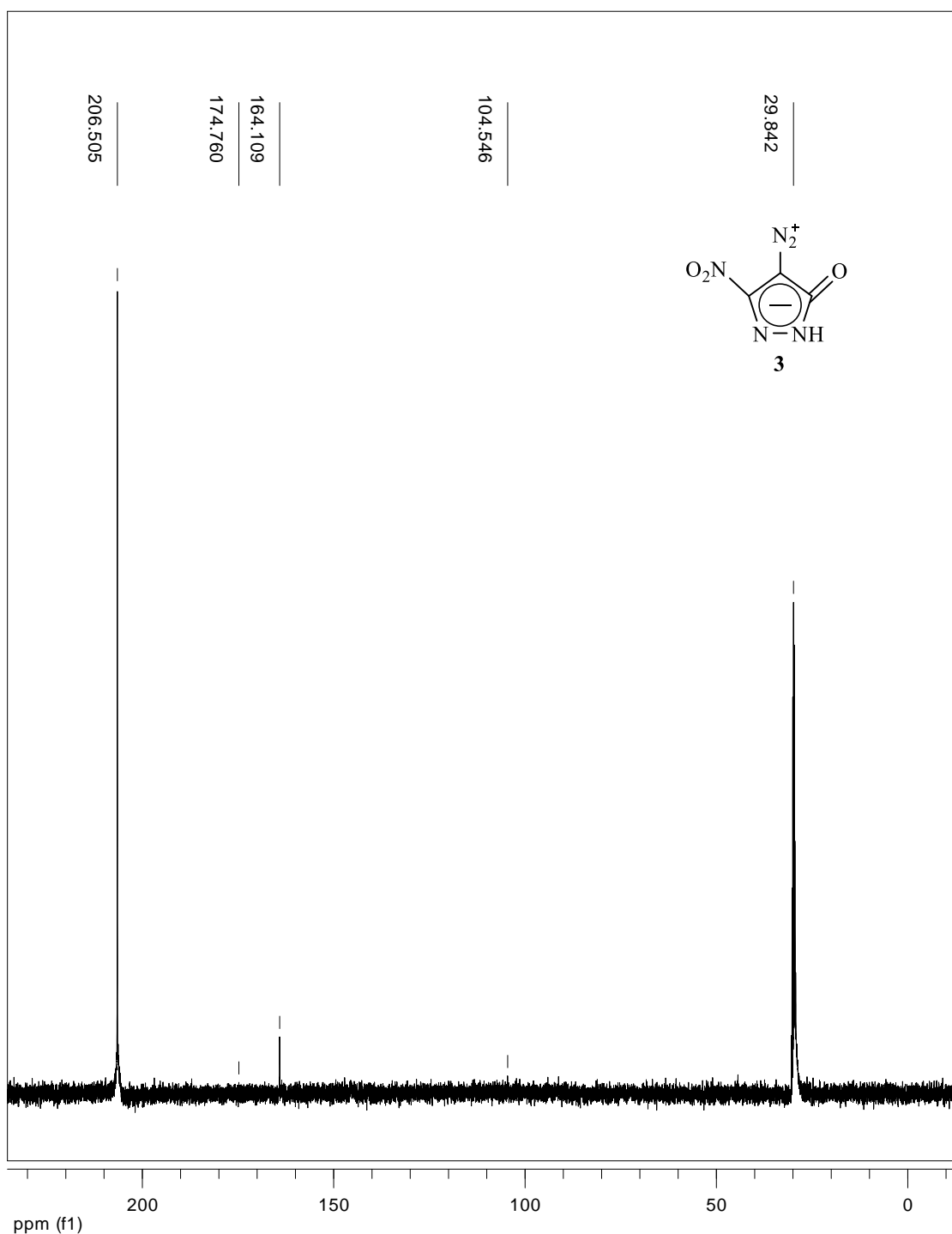**Figure S10**. EI-MS spectrum of **3**

Figure S11. ^{13}C NMR spectrum (100 MHz) of **3** in Acetone-d$_6$ at 25 °C.


Compatibility for compounds 1, 2, and 3

Energetic materials are rarely used alone, and the incompatibility between energetic materials and other components may change the thermal stability for the energetic material itself and then accelerate aging. Therefore, the compatibility of new explosive should be investigated before practical application. Differential scanning calorimetry (DSC) has been widely used in compatibility tests for energetic materials.[13, 14] The compatibilities of three target compounds with RDX and CL-20 were studied using DSC, and the DSC curves of the single and mixture systems measured at

the heating rate of 5°C min^{-1} are shown in Figure S12. The evaluation standards of compatibility for explosives and contacted materials are listed in Table S6.[15]

Table S6. Evaluation standards of the compatibility for explosives and contacted materials

| Criteria ΔT_p (°C)	Rating	Note
≤2	A. Compatible or good compatibility	Safe for use in any explosive design
3–5	B. Slightly sensitized or fair compatibility	Safe for use in testing when the device will be used in a very short period of time; not to be used as abinder material or when long–term storage is desired
6–15	C. Sensitized or poor compatibility	Not recommended for use with explosive items
>15	D. Hazardous or poor compatibility	Hazardous. Do not use under any conditions
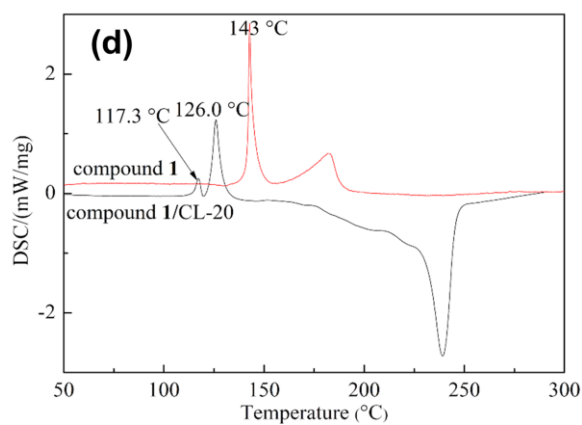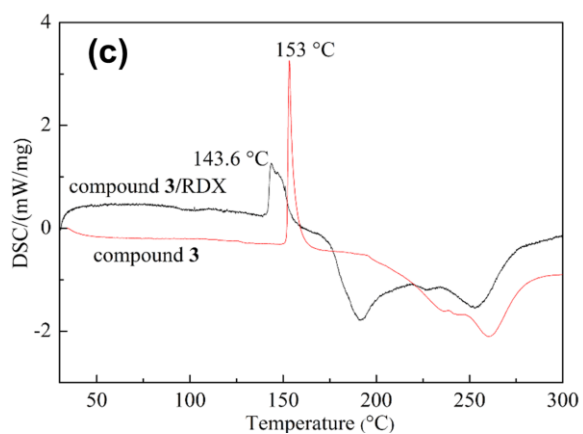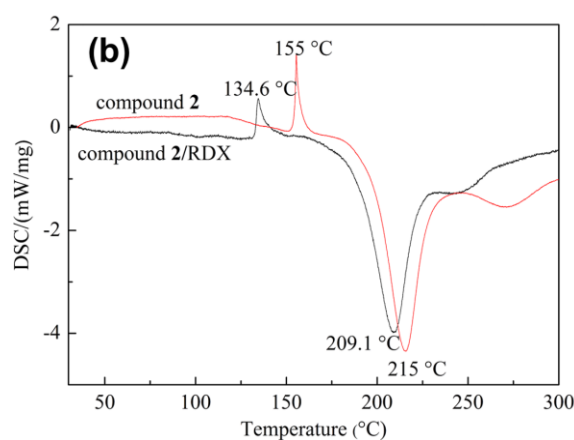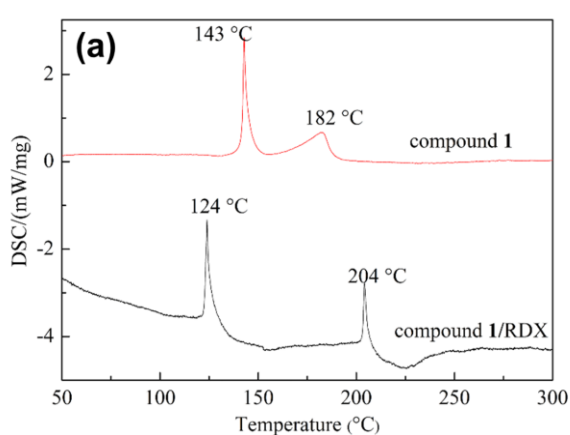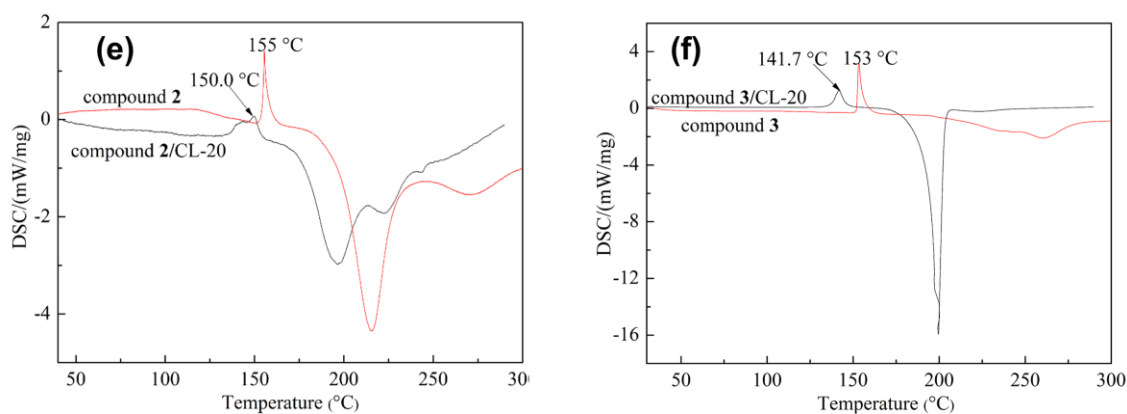
Figure S12. DSC curves of single and mixture systems

The first peak temperatures and the calculated difference between the single system and the mixture system are shown in Table S7. According to Table S7, the rating for the binary systems RDX/**1**, RDX/**2**, and RDX/**3** are C or D, which shows that they have poor compatibility. The results also indicate that compounds 1 and 3 both have poor compatibilities with CL-20, while compound 2 show fair compatibility with CL-20.

Table S7. Data of binary systems obtained by DSC

System		Peak temperature			
Mixture system[a]	Single system[b]	T_{p1} (°C)[c]	T_{p2} (°C)[d]	ΔT_p (°C)[e]	Rating
RDX/**1**	**1**	143	124.0	19.0	D
RDX/**2**	**2**	155	134.6	11.4	C
RDX/**3**	**3**	153	143.6	9.4	C
CL-20/**1**	**1**	143	117.3	25.7	C
CL-20/**2**	**2**	155	150.0	5.0	B
CL-20/**3**	**3**	153	141.7	11.3	C

[a] Mixture system; 50/50-target compounds/energetic component binary system.

[b] Single system; the component with an exothermic peak temperature lower than another one in a two-component system.

[c] T_{P1}, the maximum exothermic peak temperature of a single system.

[d] T_{P2}, the maximum exothermic peak temperature of the mixture system.

[e] $\Delta T_p = T_{p1} - T_{p2}$

Hydrolysis of three compounds

The hydrolysis of three compounds were studied in different solutions of various pH. They are all compatible with neutral water. Compounds **2** and **3** decompose in alkaline solutions with pH > 9, which is monitored by Thin layer chromatography (TLC); however, compounds **1** could stably exist

under condition with pH = 8, 9, and 10.

Prices of compounds 1, 2, and 3

The overall synthesis route to three target compounds is outlined in Scheme S2. 4-Chloropyrazole is an important chemical intermediates and can be bought from most Chemical Companies with low cost.(e.g. 1500 RMB/ 100 g, Pure chemistry Scientific Inc). Other chemical reagents in the reactions are also most commonly used and economically priced. Based on the chemical reagent prices, labor costs, and energy costs, the prices for three compounds are initially estimated to be 100 RMB/g.
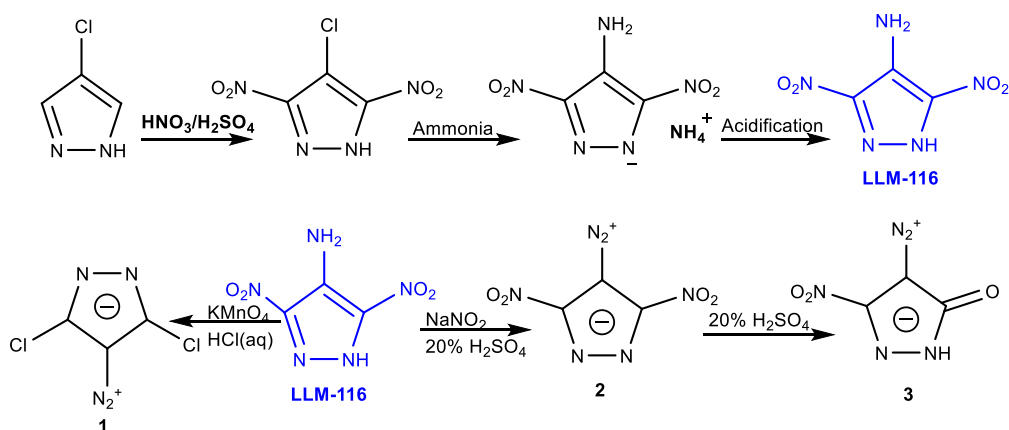
Scheme S2. Synthesis of compounds **1**, **2** and **3**

Crystal morphologies for compounds 1, 2, and 3

Crystal morphologies images for compounds **1** (a), **2** (b), and **3** (c) were carried out using an Olympus BX43 microscope and photographed using a digital camera Canon EOS 600D camera. As seen in Figure S13, micrograph for compound 1 shows that it is needle-shaped crystals, while those of compounds 2 and 3 indicate that they are bulk crystals.
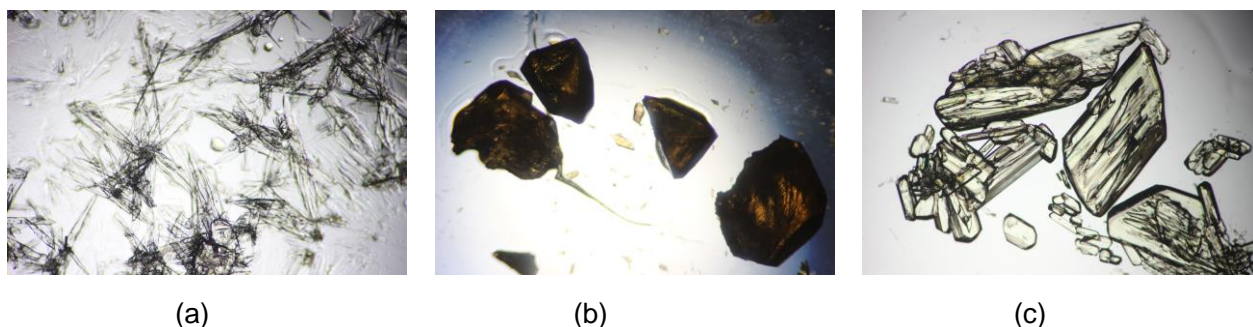

(a)   (b)   (c)

Figure S13. Crystal morphologies for compounds **1** (a), **2** (b), and **3** (c)

References

1. B. M. Rice, S. V. Pai and J. Hare, *Combust. Flame*, 1999, **118**, 445-458.
2. M. Zaheeruddin and Z. Lodhi, *Chem.(Peshawar)*, 1991, **10**, 111.
3. J. G. Aston, C. W. Siller and G. H. Messerly, *J. Am. Chem. Soc.*, 1937, **59**, 1743-1751.
4. Y. K. Knobel', E. Miroshnichenko and Y. A. Lebedev, *Russ. Chem. Bull.*, 1971, **20**, 425-428.
5. J. A. Manion, *J. Phys. Chem. Ref. Data*, 2002, **31**, 123-172.
6. G. S. Paulett and R. Ettinger, *The Journal of Chemical Physics*, 1963, **39**, 825-827.

7. M. W. Chase, *J. Phys. Chem. Ref. Data*, 1996, **25**, 551-603.

8. C. He, J. Zhang, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem. A.*, 2013, **1**, 2863-2868.

9. P. Politzer, J. S. Murray, M. E. Grice, M. Desalvo and E. Miller, *Mol. Phys.*, 1997, **91**, 923-928.

10. T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.

11. T. Lu and F. Chen, *J. Mol. Graphics Modell.*, 2012, **38**, 314-323.

12. E. F. Byrd and B. M. Rice, *The Journal of Physical Chemistry A*, 2006, **110**, 1005-1013.

13. H. Huang, Y. Shi, J. Yang and B. Li, *Journal of Energetic Materials*, 2015, **33**, 66-72.

14. Q.-L. Yan, L. Xiao-Jiang, Z. La-Ying, L. Ji-Zhen, L. Hong-Li and L. Zi-Ru, *J. Hazard. Mater.*, 2008, **160**, 529-534.

15. X. Li, B.-L. Wang, Q.-H. Lin and L.-P. Chen, *Journal of Energetic Materials*, 2016, **34**, 409-415.