

## Supporting Information

# Assembly of thermostable fused compound with oxidizer for laser-ignited energetic materials

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**Table S1. Crystal data and structure refinement for compound 1.** Single crystal X-ray diffraction data was collected on an Oxford Xcalibur diffractometer with Mo-K $\alpha$  monochromated radiation ( $\lambda=0.71073$  Å). The crystal structures were solved by direct methods. The structures were refined on F2 by full-matrix least-squares methods using the SHELXTL script package. All non-hydrogen atoms were refined anisotropically.

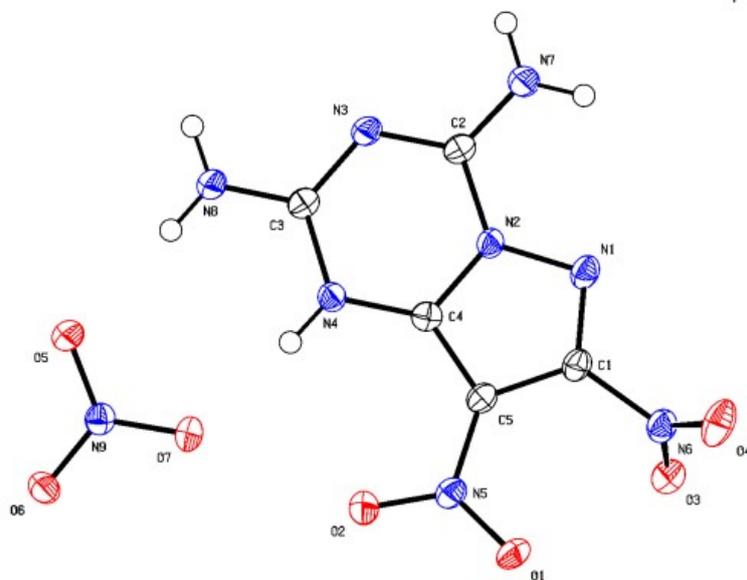
CCDC number	2322400
Empirical formula	C <sub>5</sub> H <sub>5</sub> N <sub>9</sub> O <sub>7</sub>
Formula weight	303.18
Temperature [K]	298.15
Crystal system	orthorhombic
Space group (number)	<i>Pbca</i> (61)
<i>a</i> [Å]	9.7501(6)
<i>b</i> [Å]	8.8976(5)
<i>c</i> [Å]	24.5696(16)
$\alpha$ [°]	90
$\beta$ [°]	90
$\gamma$ [°]	90
Volume [Å <sup>3</sup> ]	2131.5(2)
<i>Z</i>	8
$\rho_{\text{calc}}$ [gcm <sup>-3</sup> ]	1.890
$\mu$ [mm <sup>-1</sup> ]	0.174
<i>F</i> (000)	1232
2 $\theta$ range [°]	5.33 to 61.50 (0.69 Å)
Index ranges	-13 ≤ <i>h</i> ≤ 12 -12 ≤ <i>k</i> ≤ 9 -29 ≤ <i>l</i> ≤ 34
Reflections collected	13334
Independent reflections	2806
	$R_{\text{int}} = 0.0526$
	$R_{\text{sigma}} = 0.0484$
Data / Restraints / Parameters	2806/0/194
Goodness-of-fit on $F^2$	1.046
Final <i>R</i> indexes	$R_1 = 0.0429$
[ $I \geq 2\sigma(I)$ ]	$wR_2 = 0.0991$
Final <i>R</i> indexes	$R_1 = 0.0703$
[all data]	$wR_2 = 0.1107$
Largest peak/hole [eÅ <sup>-3</sup> ]	0.25/-0.37

**Table S2. Bond lengths and angles for compound 1**

Atom–Atom	Length [Å]	Atom–Atom–Atom	Angle [°]
O5–N9	1.2553(18)	C4–N4–C3	118.20(14)
O6–N9	1.2491(17)	C4–N4–H4	120.6(14)
O7–N9	1.2559(18)	C3–N4–H4	121.2(14)
O3–N6	1.2212(19)	N1–N2–C2	125.14(13)
O4–N6	1.2170(19)	C4–N2–N1	113.71(13)
N4–C4	1.350(2)	C4–N2–C2	121.02(14)
N4–C3	1.376(2)	C2–N3–C3	120.01(14)
N4–H4	0.86(2)	O5–N9–O7	120.50(13)
N2–N1	1.378(2)	O6–N9–O5	120.05(14)
N2–C2	1.392(2)	O6–N9–O7	119.43(14)
N2–C4	1.359(2)	C1–N1–N2	102.15(13)
N3–C2	1.318(2)	H8A–N8–H8B	120
N3–C3	1.342(2)	C3–N8–H8A	120
N1–C1	1.309(2)	C3–N8–H8B	120
N8–H8A	0.86	O3–N6–C1	116.53(14)
N8–H8B	0.86	O4–N6–O3	125.90(15)
N8–C3	1.305(2)	O4–N6–C1	117.56(14)
N6–C1	1.462(2)	H7A–N7–H7B	120
N7–H7A	0.86	C2–N7–H7A	120
N7–H7B	0.86	C2–N7–H7B	120
N7–C2	1.303(2)	N3–C2–N2	118.90(14)
C4–C5	1.380(2)	N7–C2–N2	118.79(15)
C5–C1	1.404(2)	N7–C2–N3	122.30(15)
C5–N5	1.413(2)	N4–C4–N2	119.19(14)
N5–O1	1.2311(19)	N4–C4–C5	135.40(15)
N5–O2	1.2307(18)	N2–C4–C5	105.40(14)
		N3–C3–N4	122.24(15)
		N8–C3–N4	118.39(15)
		N8–C3–N3	119.36(15)
		C4–C5–C1	104.43(14)
		C4–C5–N5	127.96(15)
		C1–C5–N5	127.28(15)
		N1–C1–N6	120.77(14)
		N1–C1–C5	114.31(15)
		C5–C1–N6	124.88(14)
		O1–N5–C5	117.28(14)
		O2–N5–C5	117.48(14)
		O2–N5–O1	125.19(14)

**Table S3. The specific parameters of hydrogen bonds of 1**

Donor	Acceptor	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N7-H7A	O6	0.86	2.127	2.951	160.5
N7-H7A	O7	0.86	2.604	3.35	145.8
N8-H8B	O5	0.86	2.062	2.92	175.6
N4-H4	O7	0.86	1.91	2.767	174.2
N8-H8A	O5	0.86	2.107	2.964	174.3
N8-H8A	O6	0.86	2.428	3.032	127.8



**Table S4. Crystal data and structure refinement for compound 2.** Single crystal X-ray diffraction data was collected on an Oxford Xcalibur diffractometer with Mo-K $\alpha$  monochromated radiation ( $\lambda=0.71073$  Å). The crystal structures were solved by direct methods. The structures were refined on F2 by full-matrix least-squares methods using the SHELXTL script package. All non-hydrogen atoms were refined anisotropically.

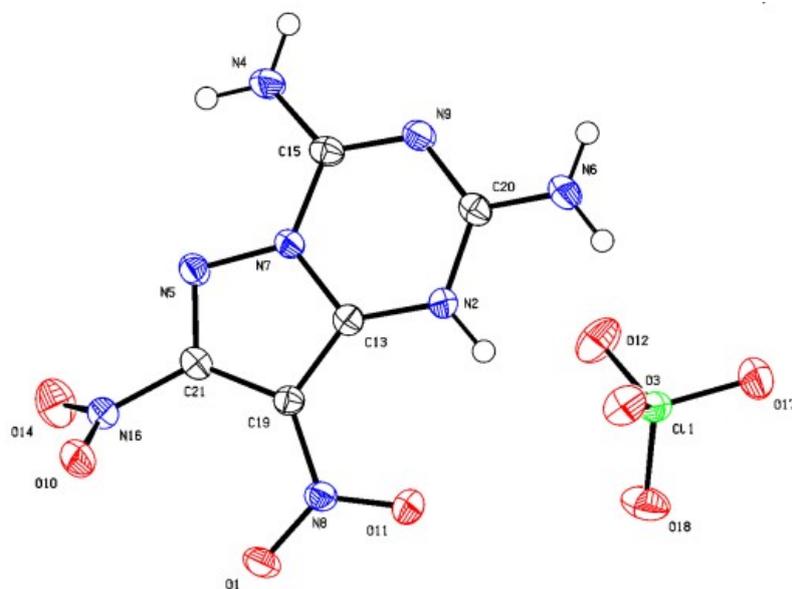
CCDC number	2322401
Empirical formula	C <sub>5</sub> H <sub>5</sub> ClN <sub>8</sub> O <sub>8</sub>
Formula weight	340.62
Temperature [K]	181.0
Crystal system	monoclinic
Space group (number)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (14)
<i>a</i> [Å]	7.2532(4)
<i>b</i> [Å]	12.1486(8)
<i>c</i> [Å]	13.3337(8)
$\alpha$ [°]	90
$\beta$ [°]	104.280(2)
$\gamma$ [°]	90
Volume [Å <sup>3</sup> ]	1138.61(12)
<i>Z</i>	4
$\rho_{\text{calc}}$ [gcm <sup>-3</sup> ]	1.987
$\mu$ [mm <sup>-1</sup> ]	0.406
<i>F</i> (000)	688
2 $\theta$ range [°]	4.60 to 55.06 (0.77 Å)
Index ranges	-9 ≤ <i>h</i> ≤ 8 -12 ≤ <i>k</i> ≤ 15 -17 ≤ <i>l</i> ≤ 17
Reflections collected	10654
Independent reflections	2577 <i>R</i> <sub>int</sub> = 0.0490 <i>R</i> <sub>sigma</sub> = 0.0433
Data / Restraints / Parameters	2577/0/199
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.040
Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0365 <i>wR</i> <sub>2</sub> = 0.0887
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0476 <i>wR</i> <sub>2</sub> = 0.0982
Largest peak/hole [eÅ <sup>-3</sup> ]	0.31/-0.46

**Table S5. Bond lengths and angles for compound 2**

Atom–Atom	Length [Å]	Atom–Atom–Atom	Angle [°]
C11–O3	1.4470(14)	O12–C11–O3	110.09(9)
C11–O12	1.4243(15)	O12–C11–O17	108.76(10)
C11–O17	1.4394(15)	O12–C11–O18	111.08(10)
C11–O18	1.4358(14)	O17–C11–O3	108.84(9)
O1–N8	1.226(2)	O18–C11–O3	109.23(9)
N2–C13	1.345(2)	O18–C11–O17	108.79(10)
N2–C20	1.371(2)	C13–N2–C20	118.45(16)
N4–C15	1.308(2)	C21–N5–N7	102.37(15)
N5–N7	1.375(2)	N5–N7–C15	124.89(15)
N5–C21	1.307(2)	C13–N7–N5	113.64(14)
N6–C20	1.312(2)	C13–N7–C15	121.23(15)
N7–C13	1.355(2)	O1–N8–O11	124.72(16)
N7–C15	1.388(2)	O1–N8–C19	118.82(15)
N8–O11	1.235(2)	O11–N8–C19	116.46(15)
N8–C19	1.415(2)	C15–N9–C20	119.57(16)
N9–C15	1.317(2)	N2–C13–N7	118.64(15)
N9–C20	1.334(2)	N2–C13–C19	135.57(17)
O10–N16	1.222(2)	N7–C13–C19	105.78(15)
C13–C19	1.381(2)	N4–C15–N7	117.35(16)
O14–N16	1.213(2)	N4–C15–N9	123.68(17)
N16–C21	1.457(2)	N9–C15–N7	118.96(17)
C19–C21	1.410(3)	O10–N16–C21	116.43(16)
		O14–N16–O10	125.81(16)
		O14–N16–C21	117.69(16)
		C13–C19–N8	124.77(16)
		C13–C19–C21	103.94(15)
		C21–C19–N8	131.28(16)
		N6–C20–N2	118.17(17)
		N6–C20–N9	119.42(16)
		N9–C20–N2	122.41(16)
		N5–C21–N16	116.42(16)
		N5–C21–C19	114.25(15)
		C19–C21–N16	129.20(16)

**Table S6.** The specific parameters of hydrogen bonds of compound 2

Donor	Acceptor	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N6-H6A	O18	0.88	2.172	3.029	164.5
N2-H2	Cl1	0.88	2.928	3.538	128
N2-H2	O3	0.88	2.082	2.864	147.6
N6-H6B	O3	0.88	2.404	3.092	135.3
N4-H4A	Cl1	0.88	2.86	3.732	171.5
N4-H4A	O12	0.88	2.612	3.371	144.9
N4-H4A	O17	0.88	2.163	2.996	157.6
N4-H4B	O11	0.88	2.498	3.088	125
N6-H6B	O14	0.88	2.633	3.274	130.6
N4-H4B	O10	0.88	2.322	3.121	150.9



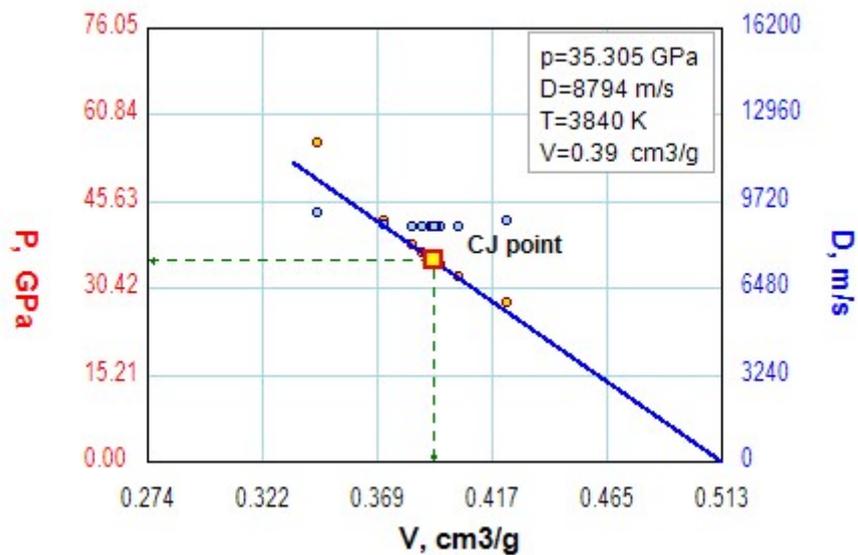


Fig.S1 The detonation performances figure of compound 1.

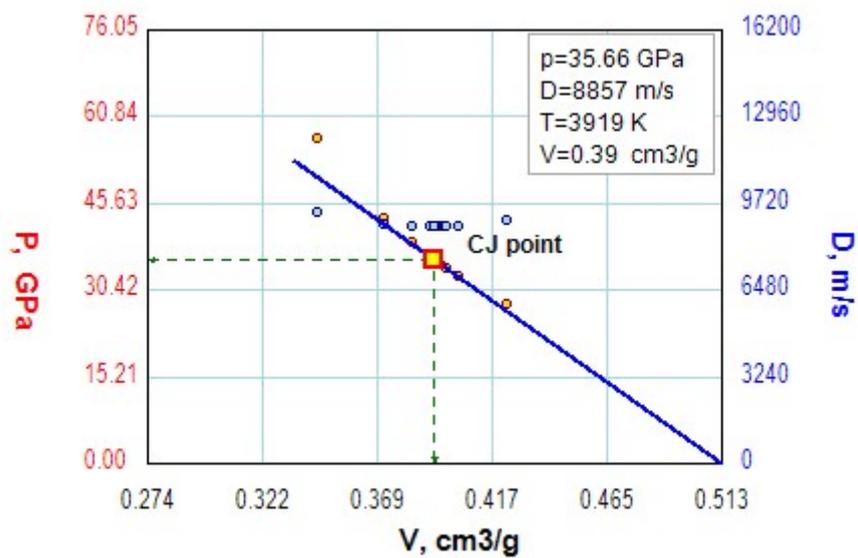
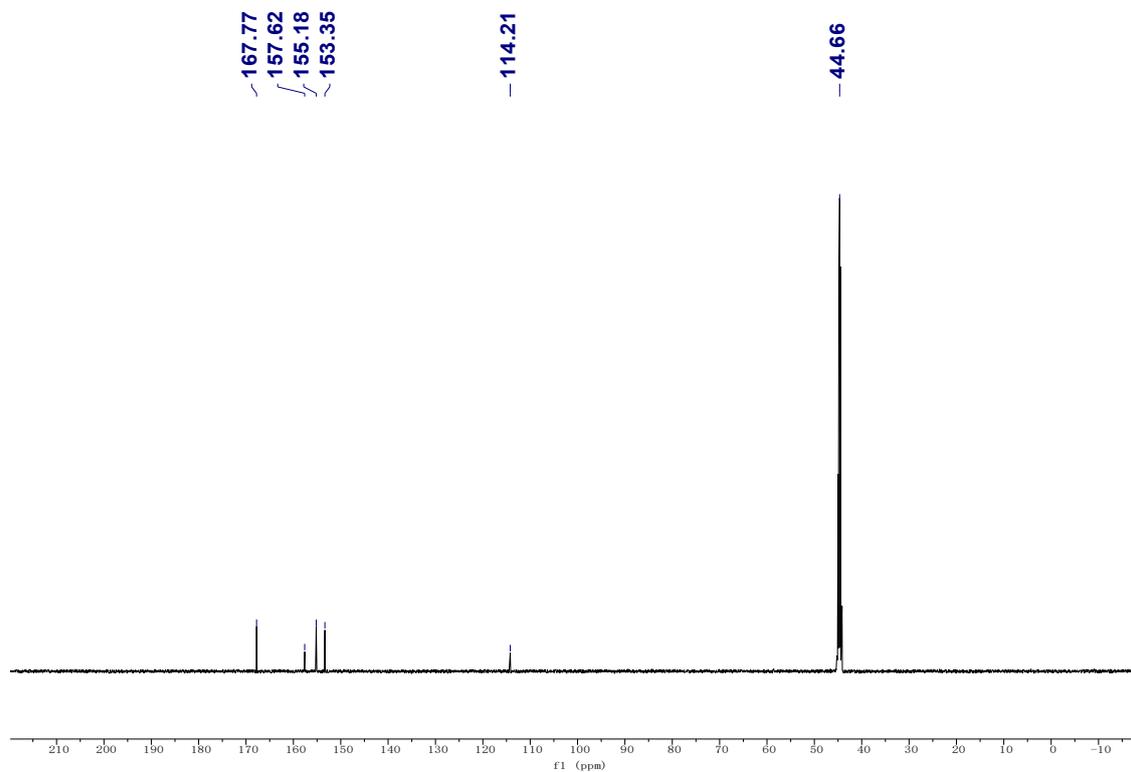
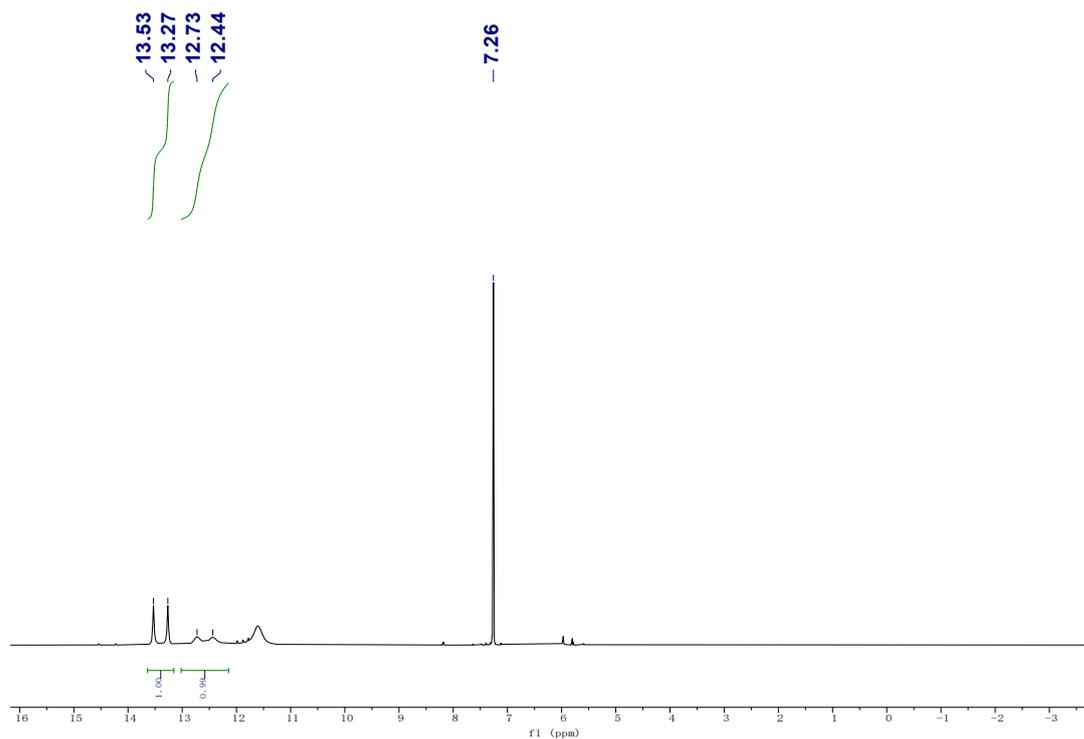
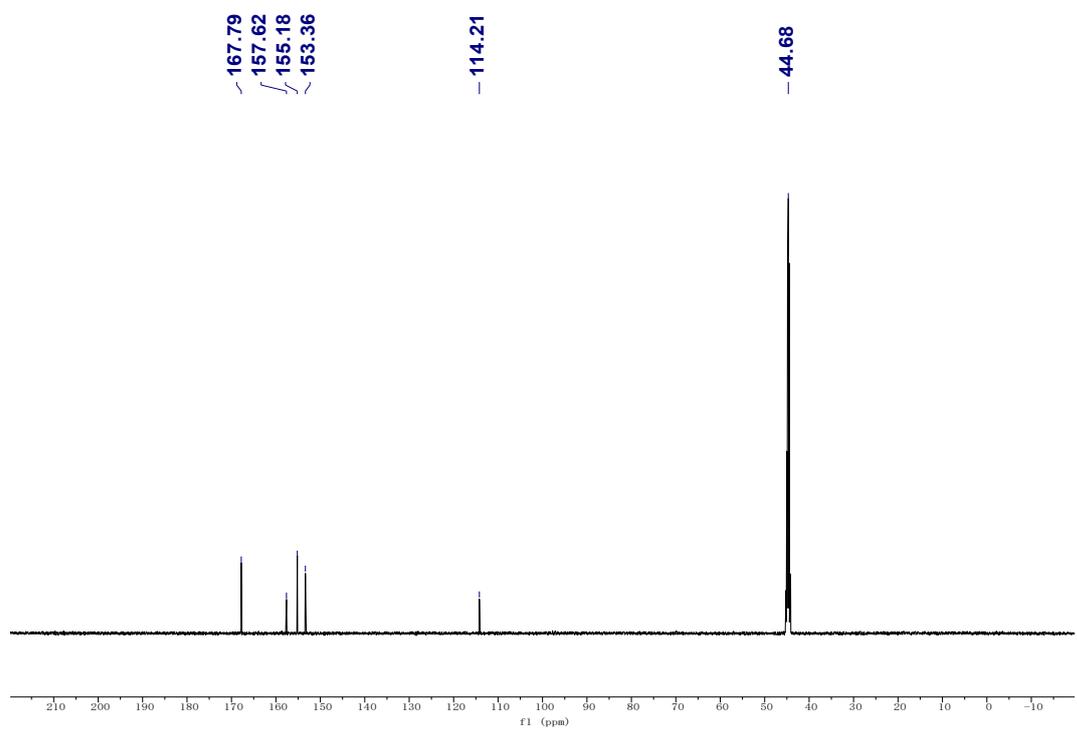
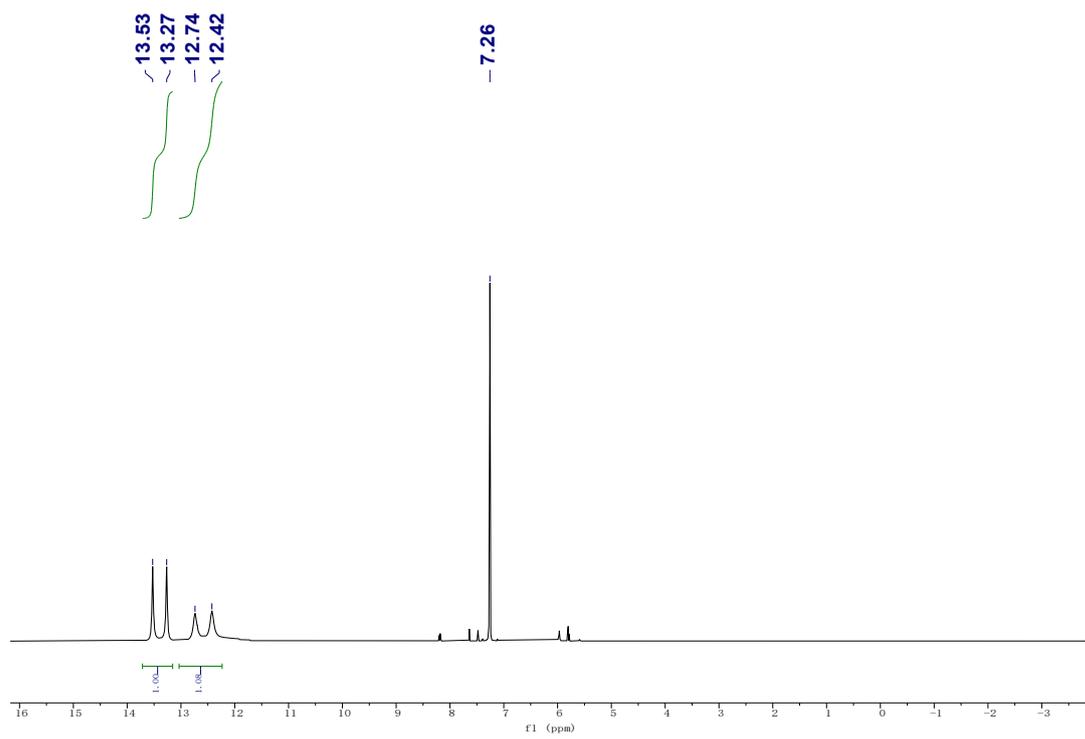


Fig.S2 The detonation performances figure of compound 2.



**Fig.S3** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for compound 1



**Fig.S4** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for compound 2

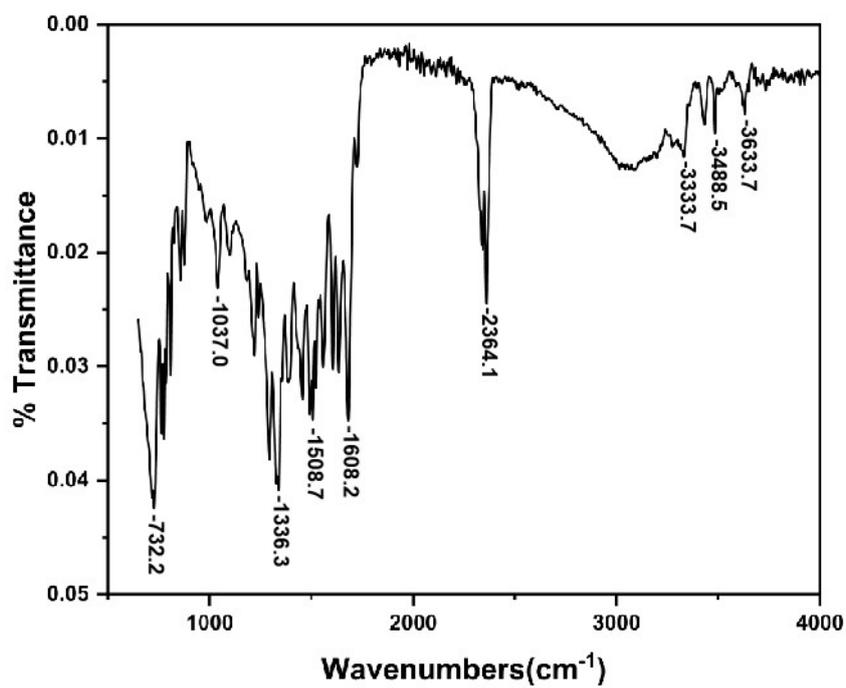


Fig.S5 IR spectra for compound 1

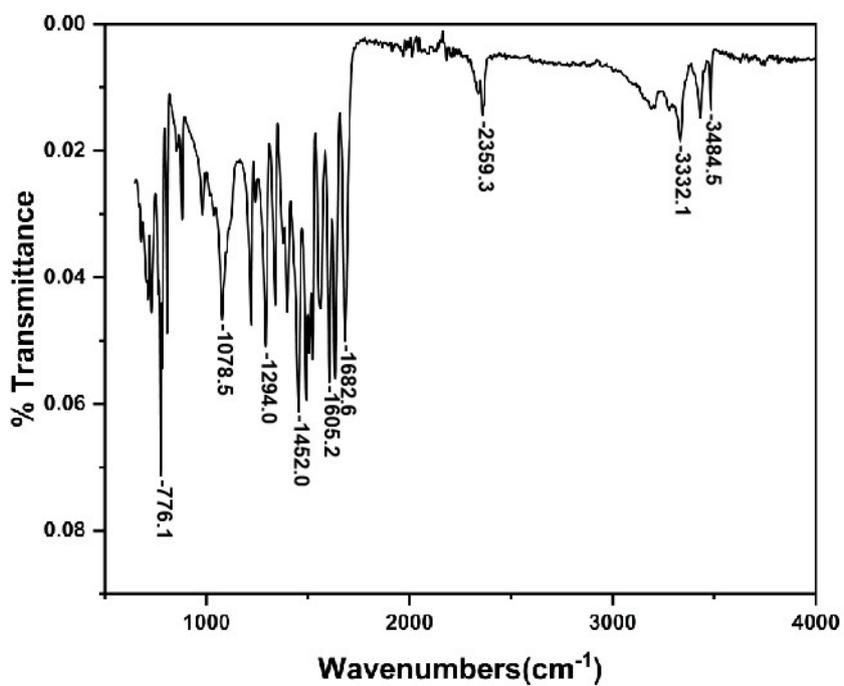


Fig.S6 IR spectra for compound 2

### Preparation of 4-nitro-1H-pyrazole-3,5-diamine hydrochloride

4-nitro-1H-pyrazole-3,5-diamine was prepared according to a previously reported route [24]. Concentrated hydrochloric acid (3 mL) was added to the suspension of 4-nitro-1H-pyrazole-3,5-diamine (3 mmol, 0.429g) in MeOH (5 mL). After stirring for 10 minutes, light yellow solid was filtered and washed using EtOAc to afford 4-nitro-1H-pyrazole-3,5-diamine hydrochloride (yield of 80%).

### Preparation of 8-nitropyrazolo[1,5-a][1,3,5]triazine-2,4,7-triamine

This intermediate was prepared according to a previously reported route with slight changes [25]. First, 4-nitro-1H-pyrazole-3,5-diamine hydrochloride (3 mmol, 0.54g) was suspended in EtOH (11 mL). Then, dicyandiamide (4mmol, 0.33g) was added in the suspension. The mixture was refluxed at 80 °C for 6 hours. During the refluxing, orange solid gradually appeared in the solution. The orange solid was filtered and recrystallized using water at 80 °C to give a yellow solid (8-nitropyrazolo[1,5-a][1,3,5]triazine-2,4,7-triamine; yield of 60%).

### Preparation of 7,8-dinitropyrazolo[1,5-a][1,3,5]triazine-2,4-diamine (ICM-104)

In the ice-water bath, 8-nitropyrazolo[1,5-a][1,3,5] triazine-2,4,7-triamine (3 mmol, 0.63g) was added to concentrated sulfuric acid (6 mL) in portion. Then, 30% hydrogen peroxide (2.5 mL) was added dropwise to the solution. After stirring under room temperature for 3 hours, the reaction was quenched using crashed ice and the solution was extracted using EtOAc. Then, EtOAc was removed using rotary evaporation. Light yellow solid was collected as the target compound (7,8-dinitropyrazolo[1,5-a][1,3,5]triazine-2,4-diamine (ICM-104, yield of 42%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz) δ: 8.81 (s, 1H, NH<sub>2</sub>), 8.56 (s, 1H, NH<sub>2</sub>), 8.04 (s, 1H, NH<sub>2</sub>), 7.77 (s, 1H, NH<sub>2</sub>) ppm; <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz) δ: 162.41, 153.61, 150.44, 147.42, 109.47 ppm (See Figure S12). ESI-HRMS: m/z calculated for [M-H]<sup>-</sup>: 239.0283, found: 239.0282(1). IR (KBr, cm<sup>-1</sup>): 3483.42, 3431.90, 3333.44, 3205.61, 1684.94, 1633.17, 1605.24, 1565.96, 1523.60, 1491.91, 1453.41, 1396.89, 1340.13, 1291.72, 1242.11, 1220.57, 1091.12, 983.45, 881.85, 851.93, 807.86, 784.96, 775.28, 728.80, 714.26, 600.36, 550.32. Elemental analysis (%) calcd: C 25.01, H 1.68, N 46.66; found: C 24.67, H 1.82, N 46.40.

## The theoretical calculations on the solid-state heat of formation of Compound 1 and Compound 2

The enthalpy ( $H$ ) for compound at standard condition (298K, 1atm) were directly calculated by G4(MP2)-6x or G4(MP2)-XK method with Gaussian09 (Revision D.01) suite of program. G4(MP2)-6x method (*J. Chem. Theory Comput.*, 2011, 7, 112-120) is a composite procedure with a lower cost but performance approaching that of G4. In this method, geometries were optimized with the BMK functional using the 6-31+G(2df, p) basis set. Zero-point vibrational energies (ZPVEs) and thermal corrections to enthalpy ( $\Delta H$ ) at 298K, derived from scaled BMK/6-31+G(2df, p) frequencies, were incorporated into the total energies. Single-point energies were obtained at the HF/GFHF3, HF/GFHF4, MP2(FrzG4)/GTMP2LargeXP, and CCSD(T, FrzG4)/GTBas1 levels with composite procedures. However, since Pople basis set is not applicable to iodine element, for Iodine-containing compound G4(MP2)-XK method is adopted. G4(MP2)-XK method (*J. Chem. Theory Comput.*, 2019, 15, 4478–4484) is variant of the G4(MP2)-6X method with expanded applicability for main-group elements up to Radon.

After acquiring the enthalpy of compound or ions, their gas phase enthalpy of formation can be calculated by atomization method as following equation (1):

$$\begin{aligned} \Delta H_f(g) = & H(C_1H_mO_nN_iCl_j(g)) - 1H(C(g)) - 0.5(m-j)H(H_2(g)) \\ & - 0.5nH(O_2(g)) - 0.5iH(N_2(g)) - 0.5jH(HCl(g)) + 1H_{\text{vap}}(\text{graphite}) \quad (1) \end{aligned}$$

For neutral compounds with calculated gas state heat of formation, the solid state heat of formation was calculated by the following equation (2). The heat of sublimation  $\Delta H_{SUB}$  was estimated by the following equation (3). T is the melting point or decomposition point temperature in Kelvin.

$$\Delta H_f(s) = \Delta H_f(g) - \Delta H_{SUB} \quad (2)$$

$$\Delta H_{SUB}(g) = 0.188 * T \quad (3)$$

For ionic compound, solid state heat of formation was calculated by equation (4). In the equation, enthalpy of lattice  $\Delta H_L$  was estimated by equation (5) and (6). In equation 5 and 6, p, q are charge number for cation and anion;  $n_M$ ,  $n_X$ ,  $\gamma$  and  $\delta$  are constant decided by structure of ion;  $\rho_m$  and  $M_m$  are density and molecular weight.

More details about the parameters for equation 7 and 8 can be found in *Inorg. Chem.* 2002, 41, 2364–2367.

$$\Delta H_f(\text{ion,s}) = m\Delta H_f(\text{cation,g}) + n\Delta H_f(\text{anion,g}) - \Delta H_L \quad (4)$$

$$\Delta H_L = U_{\text{pot}} + [p(0.5n_M - 2) + q(0.5n_X - 2)]RT \quad (5)$$

$$U_{\text{pot}} = \gamma(\rho m/Mm)^{1/3} + \delta \quad (6)$$