

## Supporting Information (SI)

# Energetic Bi-diazole 'Transformers' toward High Energy Thermostable Energetic Compounds

*Jingwei Meng<sup>a</sup>, Teng Fei<sup>a\*</sup>, Jinxiong Cai<sup>a</sup>, Qi Lai<sup>a</sup>, Jinya Zhang<sup>a</sup>, Siping Pang<sup>a\*</sup> and Chunlin He<sup>a,b,c\*</sup>*

<sup>a</sup> Experimental Center of Advanced Materials, School of Materials Science & Engineering, Beijing Institute of Technology, Beijing, 10081 (China).

<sup>b</sup> State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing, 10081 (China).

<sup>c</sup> Chongqing Innovation Center, Beijing Institute of Technology, Chongqing 401120, China.

\*Email: [feiteng@bit.edu.cn](mailto:feiteng@bit.edu.cn) (T. Fei); [pangsp@bit.edu.cn](mailto:pangsp@bit.edu.cn) (S. Pang); [chunlinhe@bit.edu.cn](mailto:chunlinhe@bit.edu.cn) (C. He).

## **Table of Contents**

1.	Experimental section .....	S1
2.	X-ray crystallography details .....	S3
3.	Heat of formation .....	S6
4.	Stability and theoretical analysis .....	S7
5.	Spectrum Analysis and DSC plots .....	S9
6.	90 neutral energetic compounds with a $T_d > 300^\circ\text{C}$ were collected and summarized.....	S13
7.	Reference.....	S23

## 1. Experimental section

### 1.1 General methods

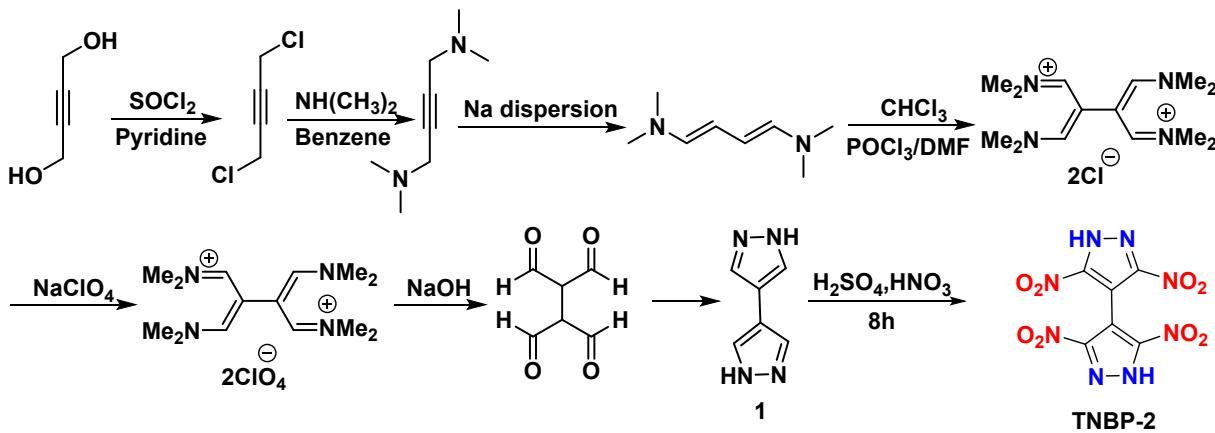
All reagents were purchased from Energy Chemical of analytical grade and used without further purification. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker 400 MHz spectrometers at 25 °C. Chemical shifts were reported relative to Me<sub>4</sub>Si as external standards. Infrared spectra (IR) were recorded on a Perkin Elmer Spectrum BX FT-IR instrument. Elemental analyses (C, H, N) were carried out on a Vario EL III Analyzer. Melting and decomposition (onset) points were recorded on a differential scanning calorimeter (TA Discovery DSC25) at a scan rate of 10 °C min<sup>-1</sup>. The sensitivities to impact (IS) and friction (FS) were determined according to BAM standards.

### 1.2 Safety precautions

Although none of the energetic materials described herein have exploded or detonated in the course of this research, they are potentially explosive energetic materials that may be sensitive to impact and friction. Appropriate safety precautions should be taken at all times when handling these materials.

### 1.3 Preparation of 4,4'-bipyrazole (**1**), **TNBP-2**, and **DATNBP-2**

Synthetic route of 4,4'-bipyrazole (**1**) [1] and **TNBP-2** according to the reported method (Scheme 1) are provided in this section.



**Synthesis of 4,4'-bipyrazole (**1**):** The precursor compound 4,4'-bipyrazole was synthesized according to the reported method<sup>1</sup>. The 1,4-bis(dimethylamino)butene was prepared from 1,4-dichloro-2-butyne using SOCl<sub>2</sub> as a reagent, and its rearrangement into the conjugated cis-trans-butadiene over Na metal dispersion and the subsequent Vilsmeier-Haack-Arnold formylation providing symmetric perchlorate salt. The latter was hydrolyzed to bis-dialdehyde and then

converted into the 4,4'-bipyrazole (1).  $^1\text{H}$  NMR(d<sub>6</sub>-DMSO): δ7.79, 12.76 (s,2H) ppm;  $^{13}\text{C}$  NMR(d<sub>6</sub>-DMSO): δ113.10, 130.76 ppm. Elemental analysis of C<sub>6</sub>H<sub>6</sub>N<sub>4</sub> (134.14): calcd: C,53.72; H,4.51; N,41.77%; found: C52.93 H4.76, N42.31%.

**Synthesis of 3,3',5,5'-tetranitro-4,4'-bipyrazole (TNBP-2):** Fuming HNO<sub>3</sub> (2.33 mL, 98%) was added to a warm solution of 1 (0.31 g, 2.3 mmol) in 98% H<sub>2</sub>SO<sub>4</sub> (14 mL). The mixture was placed into a pre-heated oil bath and the clear solution formed was stirred at 100°C (bath temperature) for 8 h. After cooling, the mixture containing a colorless solid reaction product was poured into crushed ice and left overnight at 5-10 °C. The crystalline deposit was filtered (0.706 g, 91%), washed with 40 mL of ice water and dried.  $T_d$ (onset): 298 °C.  $^1\text{H}$  NMR(d<sub>6</sub>-DMSO): δ9.46(s,2H) ppm;  $^{13}\text{C}$  NMR(d<sub>6</sub>-DMSO): δ101.04, 149.86 ppm. IR(KBr): 3740, 3208, 2967, 1567, 1519, 1482, 1416, 1348, 1320, 1274, 1207, 1018, 994, 842, 758, 744, 712, 675, 635, 580, 518 $\tilde{\nu}$ cm<sup>-1</sup>. Elemental analysis of C<sub>6</sub>H<sub>2</sub>N<sub>8</sub>O<sub>8</sub> (314): calcd: C22.94, H0.64, N35.67%; found: C23.06, H0.79, N35.72%.

**Synthesis of 1,1'-diamine-3,3',5,5'-tetranitro-4,4'-bipyrazole (DATNBP-2):** A mixture of TNBP-2(0.34 g, 1.08 mmol) and 1,8-diazabicycloundec-7-ene (DBU) (0.33 g, 2.16 mmol) in anhydrous acetonitrile (15 mL) was stirred at the ambient temperature for 0.5 h. And then fresh O-p-tolylsulfonylhydroxylamine (2.3 equiv, 9.2 mmol) in anhydrous dichloromethane solution (30 mL) was added with portions in 5 min. The mixture was stirred for 2.5 h, and the solvent was removed under vacuum. The DATNBP-2 was obtained by flash chromatography as a yellow solid (0.32 g, 86 %).  $T_d$ (onset): 305 °C.  $^1\text{H}$  NMR(d<sub>6</sub>-DMSO): δ8.03(s,2H), 7.43(s,2H) ppm;  $^{13}\text{C}$  NMR(d<sub>6</sub>-DMSO): δ100.50, 140.07, 145.53 ppm. IR(KBr): 3338.29, 3273.72, 1549.05, 1488.96, 1428.07, 1377.52, 1324.73, 1132.00, 1103.58, 1011.12, 868.47, 831.58, 730.06, 627.53, 612.90  $\tilde{\nu}$ cm<sup>-1</sup>. Elemental analysis of C<sub>6</sub>H<sub>4</sub>N<sub>10</sub>O<sub>8</sub> (344.02): calcd: C20.94, H1.17, N40.70%; found: C20.65, H2.23, N39.03%.

## 2. X-ray crystallography details

### 2.1 Single crystal preparation and crystallographic data

The crystal of **DATNBP-2** suitable for single-crystal XRD was obtained from slow evaporation of its petroleum ether and ethyl acetate solution at room temperature. Crystallographic data of compounds in this study are provided in this section.

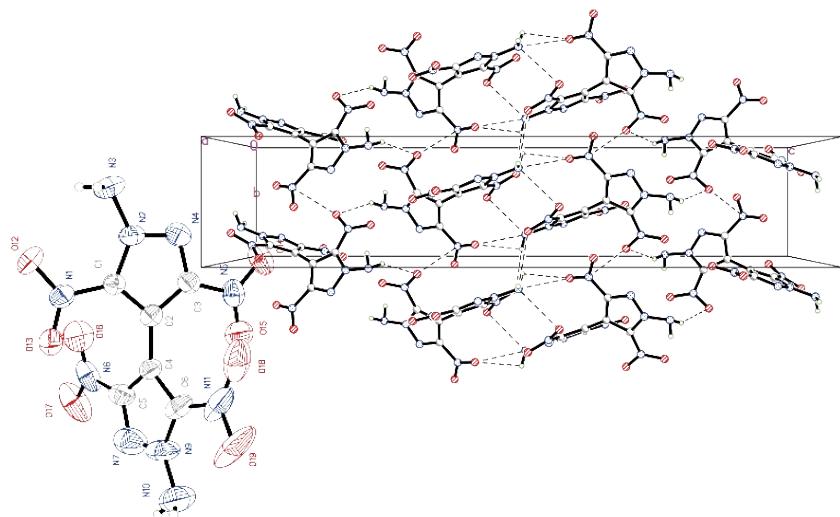
### 2.2 Hydrogen bond interaction

The strengths of the relevant intra-/intermolecular interaction were evaluated by the integrated value of the crystal orbital Hamilton population (COHP) below the Fermi energy, using a recently developed High Accuracy Atomistic Simulation for Energetic Materials (HASEM) package [2,3]. The generalized gradient approximation (GGA) is used for the exchange-correlation function in the Perdew-Burke-Ernzerhof (PBE) form.

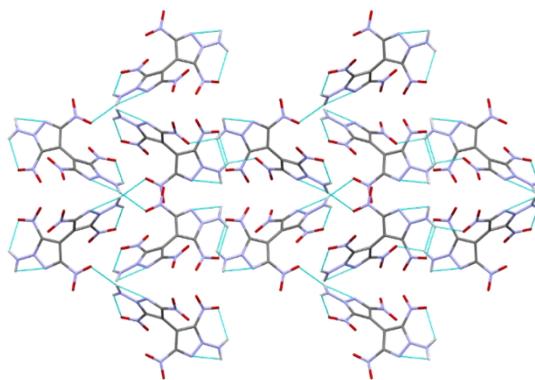
**Table S1** Crystallographic data for **DATNBP-2**.

Compound	<b>DATNBP-2</b>	<b>DATNBP-2</b>
CCDC No.	2268272	2206102
Formula	C <sub>6</sub> H <sub>4</sub> N <sub>10</sub> O <sub>8</sub>	C <sub>6</sub> H <sub>4</sub> N <sub>10</sub> O <sub>8</sub>
M <sub>w</sub>	344.19	344.19
Crystal system	orthorhombic	orthorhombic
Space group	Pbca	Pbca
a[Å]	12.899(6)	12.8197(17)
b[Å]	6.244(2)	6.1427(7)
c[Å]	30.293(10)	30.168(4)
α[°]	90	90
β[°]	90	90
γ[°]	90	90
V[Å <sup>3</sup> ]	2440.0(16)	2375.7(5)
Z	8	8
T[K]	298K	170K
λ[Å]	0.71073	0.71073
P <sub>calcd</sub> [g·cm <sup>-3</sup> ]	1.874	1.925
μ[mm <sup>-1</sup> ]	0.173	0.178
F(000)	1392.0	1392.0
Crystal size/mm <sup>3</sup>	0.12 × 0.06 × 0.05	0.09×0.04×0.03
θ range[°]	4.148-52.826	4.166-52.91

	-12≤h≤16	-14≤h≤14
Index ranges	-7≤k≤7	-6≤k≤7
	-37≤l≤37	-36≤l≤3
Data/restraints/ parameters	2441/16/229	2424/24/226
GOF on F2	1.021	1.053
R[F <sup>2</sup> >2σ(F <sup>2</sup> )]	0.0803	0.0839
wR(F <sup>2</sup> )	0.1862	0.1863



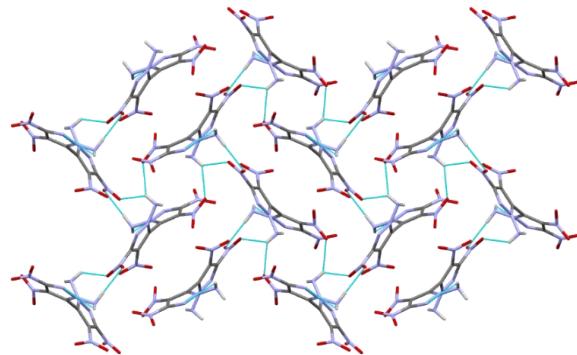
**Figure S1** Single-crystal X-ray structures and packing diagram of **DATNBP-2** at 170K



**Figure S2** Hydrogen bonds for **DATNBP-2**.

**Table S2** Hydrogen bonds for **DATNBP-2**.

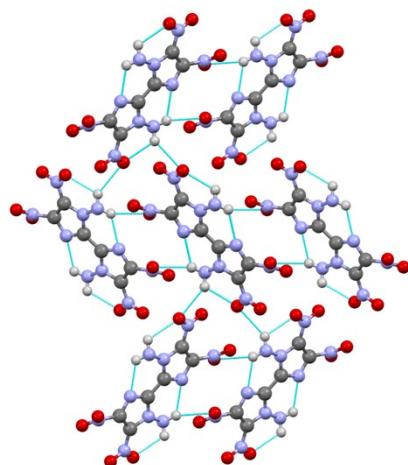
D-H...A	D-H/Å	H...A/Å	D...A/Å	D-H...A/°	Energy/kcal mol <sup>-1</sup>
N3-H3B...O7	0.88	2.56	2.931(7)	106	1.345580175
Intra N3-H3B...O2	0.88	2.24	2.777(6)	119	4.50832775
Intra N10-H10A...N9	0.88	1.58	1.97(2)	102	6.56486332
Intra N10-H10A...O6	0.88	2.43	2.918(13)	116	2.24655391
N10-H10A...O3	0.88	2.14	2.909(10)	146	5.114588295



**Figure S3** Hydrogen bonds for **DATNBP-1**.

**Table S3.** Hydrogen bonds for **DATNBP-1**.

D-H...A	D-H/Å	H...A/Å	D...A/Å	D-H...A/°	Energy/kcal mol <sup>-1</sup>
N5-H5B...O2	0.87	2.24	2.944	120	2.046158
N5-H5B...O6	0.87	2.37	3.023	133	1.14726
N6-H6B...O1	0.90	2.27	3.132	160	1.396774



**Figure S4** Hydrogen bonds for **DATNBP-1**.

**Table S4** Hydrogen bonds for **DATNBP-1**.

D-H...A	D-H/Å	H...A/Å	D...A/Å	D-H...A/°	Energy/kcal mol <sup>-1</sup>
Intra N3-H3B...O1	0.86	2.24	2.759	119	4.30832775

N3-H3B...O1	0.86	2.53	3.244	141	1.64121657
N3-H3A...O4	0.86	2.42	3.166	145	1.92341630
Intra N3-H3B...O1	0.86	2.26	2.830	124	4.02853527

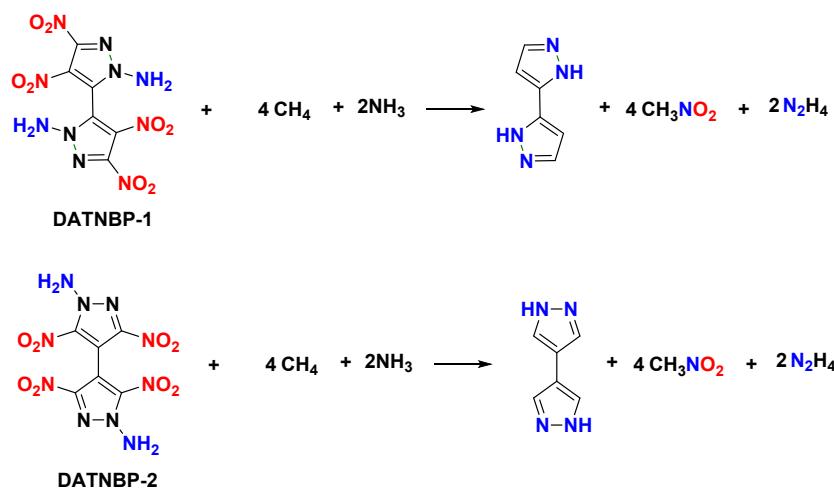
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### 3. Heat of formation

Theoretical calculations were performed by using the Gaussian09 program and Multiwfn software [4,5]. Gas phase heats of formation of the title compounds were computed based on an isodesmic reaction (Scheme S2). The geometric optimization and frequency analyses of the structures employed B3LYP/6-31++G\*\* level, Zero-point energies (ZPE), and total energy( $E_0$ ) were calculated at the M062X/6-311++(d,p) level.

The heat of formation was obtained by using the isodesmic reaction approach. Atomization energies were obtained by employing the G2 ab initio method. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. The heats of formation in the solid state were further obtained by employing Trouton's rule according to equation 1[6].

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



**Scheme S2** Isodesmic reactions for **DATNBP-1**, **DATNBP-2**.

Table S5 The zero point energy (ZPE), temperature correction coefficient ( $H_T$ ), total energy ( $E_0$ ), heat of formation (HOF) of **DATNBP-2**

Compound	ZPE (a.u)	$H_T$ (a.u)	$E_0$ (a.u)	HOF (kJ mol <sup>-1</sup> )
<b>DATNBP-1</b>	0.165464	0.18725900	-1376.857830	457.5
<b>DATNBP-2</b>	0.165038	0.18662000	-1376.913937	477.3
CH <sub>4</sub>	0.044558	0.00381000	-40.4966719	-74.6
NH <sub>3</sub>	0.034252	0.00366528	-56.5405858	-45.9
bipyrazole	0.069995	0.00850752	-448.8305749	286.8
CH <sub>3</sub> NO <sub>2</sub>	0.049628	0.00531000	-244.9716281	-81.0
N <sub>2</sub> H <sub>4</sub>	0.053276	0.057481	-111.8435902	110.6

## 4. Stability and theoretical analysis

### 4.1 Lattice parameter

Lattice parameter of two **DATNBP-1** were analyzing by using VASP (Vienna Ab initio Simulation Package) [7]. The calculations were performed using projected augmented wave (PAW) formalism of the Kohn–Sham density functional theory. Geometry optimization was done using GGA, including van der Waals interaction using DFT-D3.

**Table S5** Correlation energy of crystal of **DATNBP-1** and **DATNBP-2**

Name	Total Energy	Energy of Molecule	Lattice Energy(ev)	Lattice Energy (kJ mol <sup>-1</sup> )
DATNBI	-388.407881	-192.58147975	-1.622460965	-156.5436329
DATNBP-1	-772.6030224	-191.4780852	-1.672670425	-161.3881078
DATNBP-2	-1659.130717	-205.4989431	-1.892396546	-182.5884485

### 4.2 The bond properties of selected bonds in **DATNBP-2**, **DATNBP-1**, and **DATNBI**

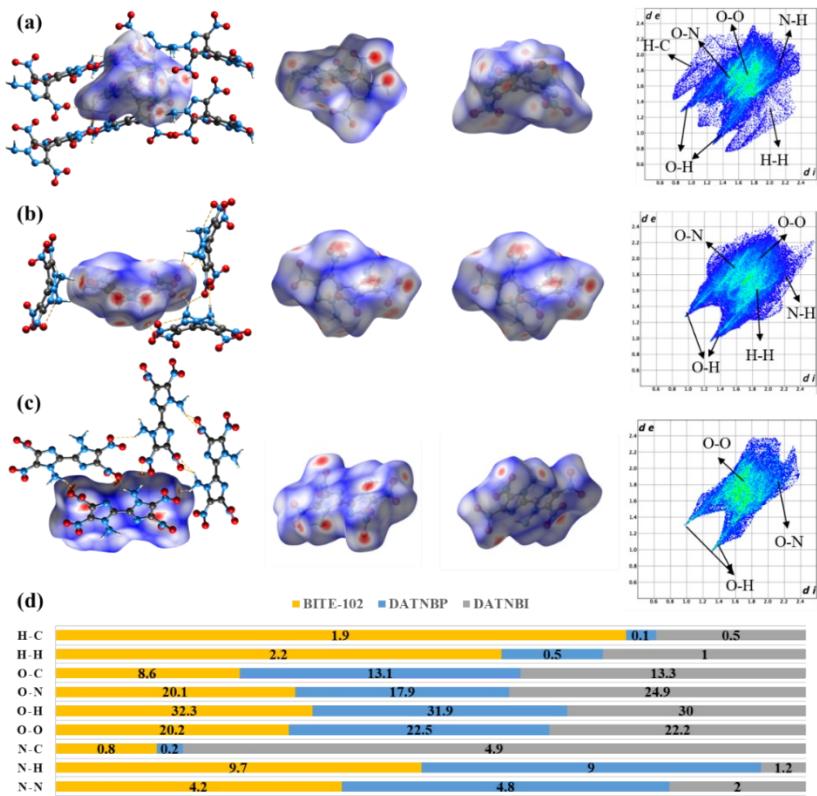
The Mayer bond orders, the bond dissociation energy (BDE), and the bond length for C-NO<sub>2</sub> bonds in **DATNBP-2**, **DATNBP-1**, and **DATNBI** are calculated by the Gaussian 09 software and Multiwfn software.

**Table S6** The bond properties of selected bonds in **DATNBP-1** and **DATNBP-2**

	Label	BDE (kcal mol <sup>-1</sup> )	Mayer Order	Bond length (Å)
DATNBP-2	C13-N4	64.09	0.89240660	1.44877
	C17-N8	65.85	0.89771746	1.42808
	C20-N16	64.09	0.89238630	1.44877
	C22-N12	65.85	0.89771741	1.42808
DATNBP-1	C19-N15	57.58	0.77284767	1.45680
	C20-N16	64.20	0.82748265	1.42922
	C23-N17	64.20	0.82757670	1.42874
	C24-N18	57.58	0.77314367	1.45680
DATNBI	C10-N8	59.88	0.82393386	1.43285
	C11-N9	57.56	0.74622171	1.46854
	C24-N22	59.88	0.82391675	1.43286
	C25-N23	57.56	0.74622720	1.46853

### 4.3 The Hirschfeld Surfaces and The Two-dimensional(2D) Fingerprint

To better understand the relationship between structure and mechanical sensitivity, the Hirschfeld surfaces and the two-dimensional(2D) fingerprint are studied (Fig.S5) [8].



**Figure S5** 2D fingerprint plots in crystal stacking and Hirschfeld surfaces of **DATNBP-2(a)** and **DATNBP-2(b)**, and the individual atomic contact percentage contribution of two **DATNBP-1(c)**.

## 5. Spectrum Analysis and DSC plots

$^1\text{H}$ ,  $^{13}\text{C}$  NMR, and IR spectra of compounds in this study are provided in this section. The thermal stability of DATNBP-2 was tested using the differential scanning calorimeter (DSC) method and the DSC plots are shown in Fig. S13.

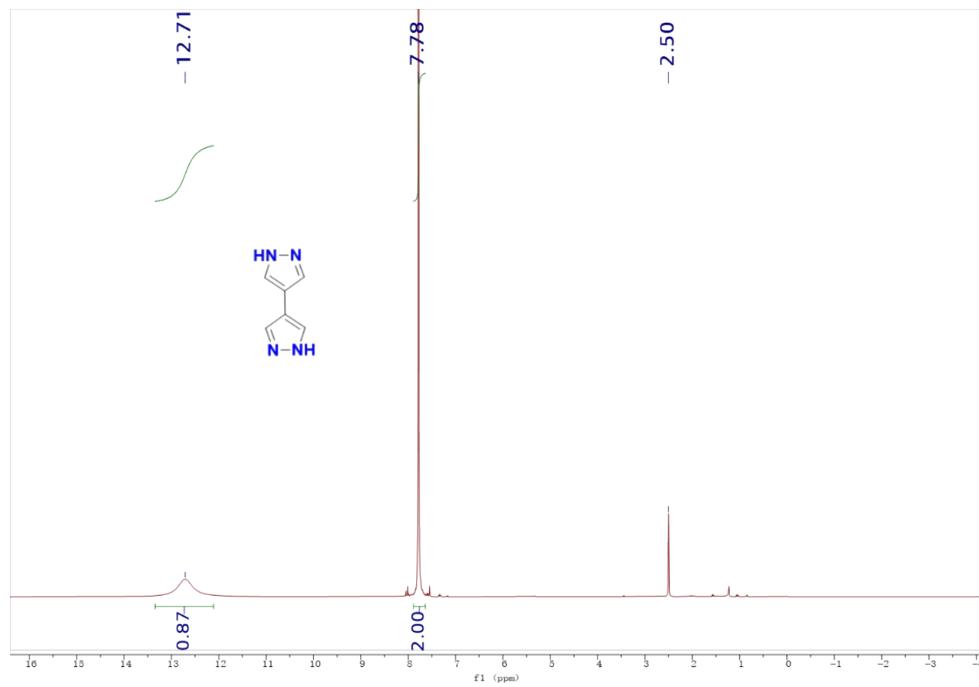


Figure S6  $^1\text{H}$  NMR spectrum of **1** in  $\text{d}_6\text{-DMSO}$ .

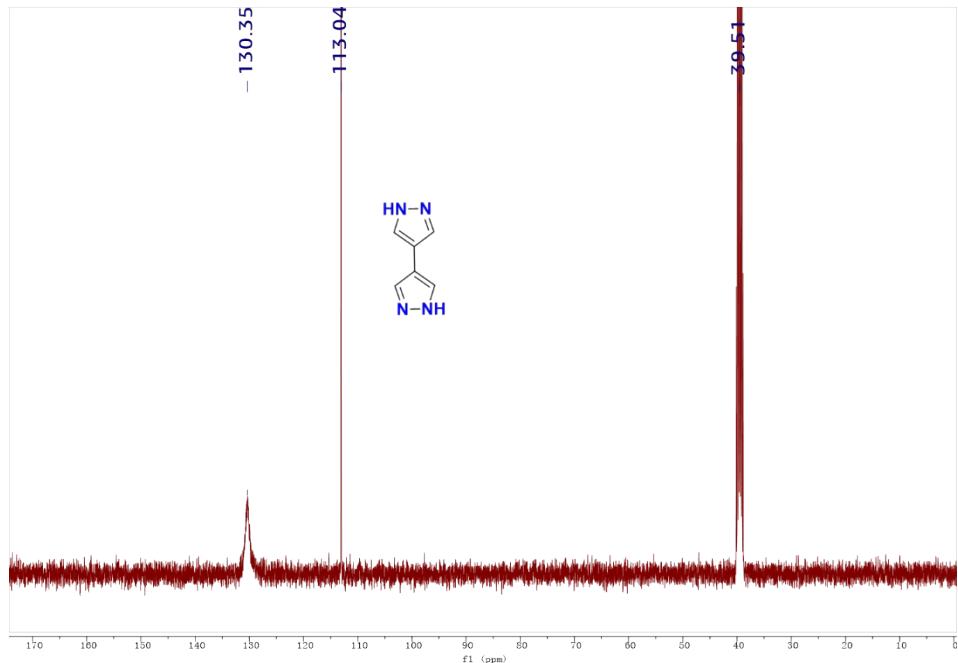
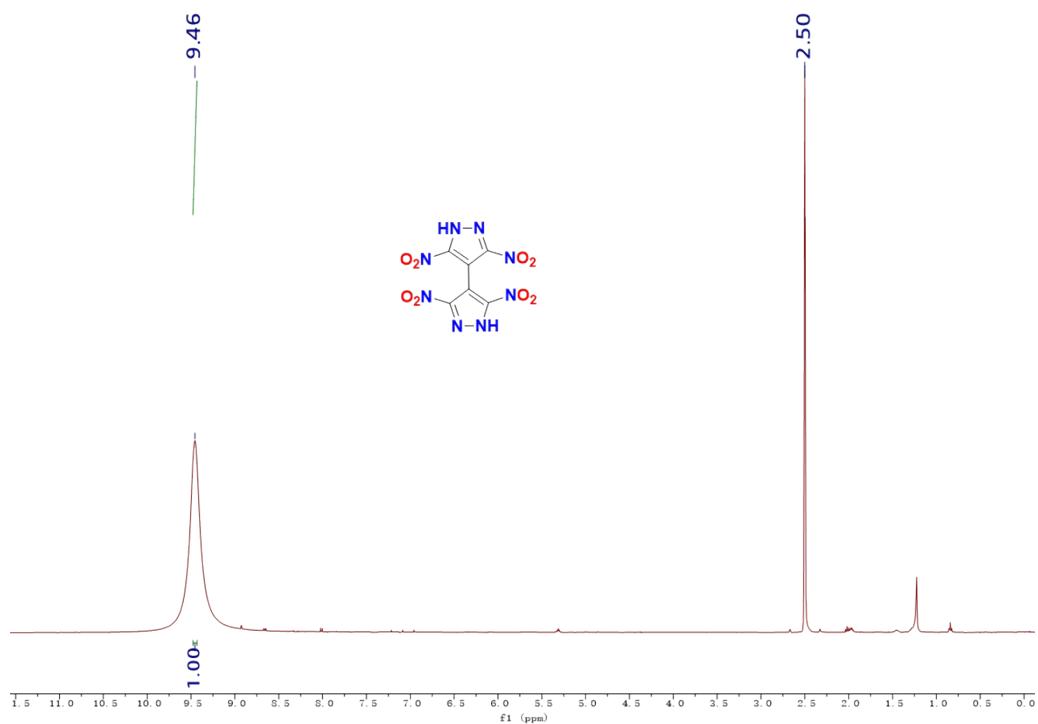
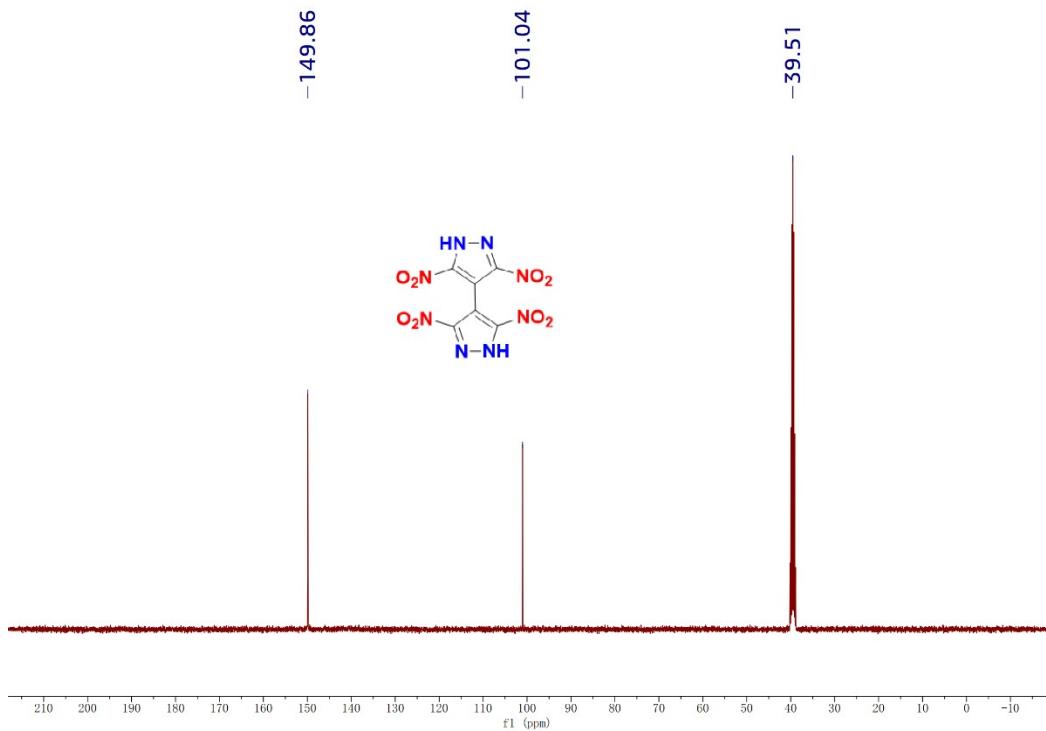


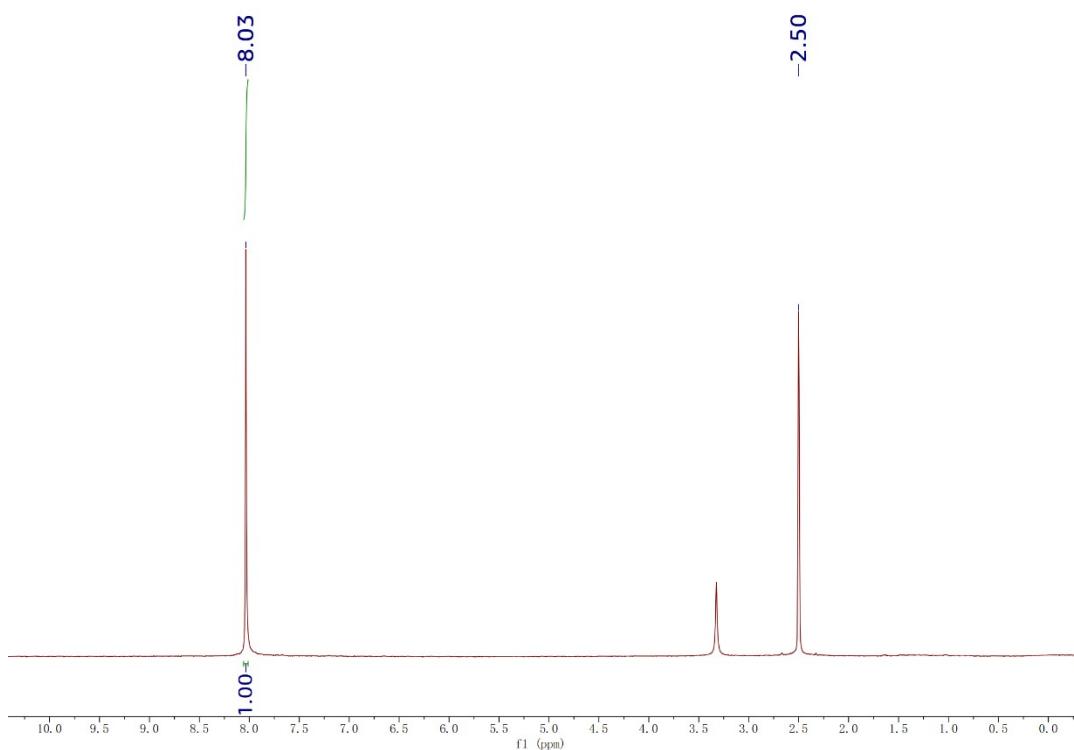
Figure S7  $^{13}\text{C}$  NMR spectrum of **1** in  $\text{d}_6\text{-DMSO}$ .



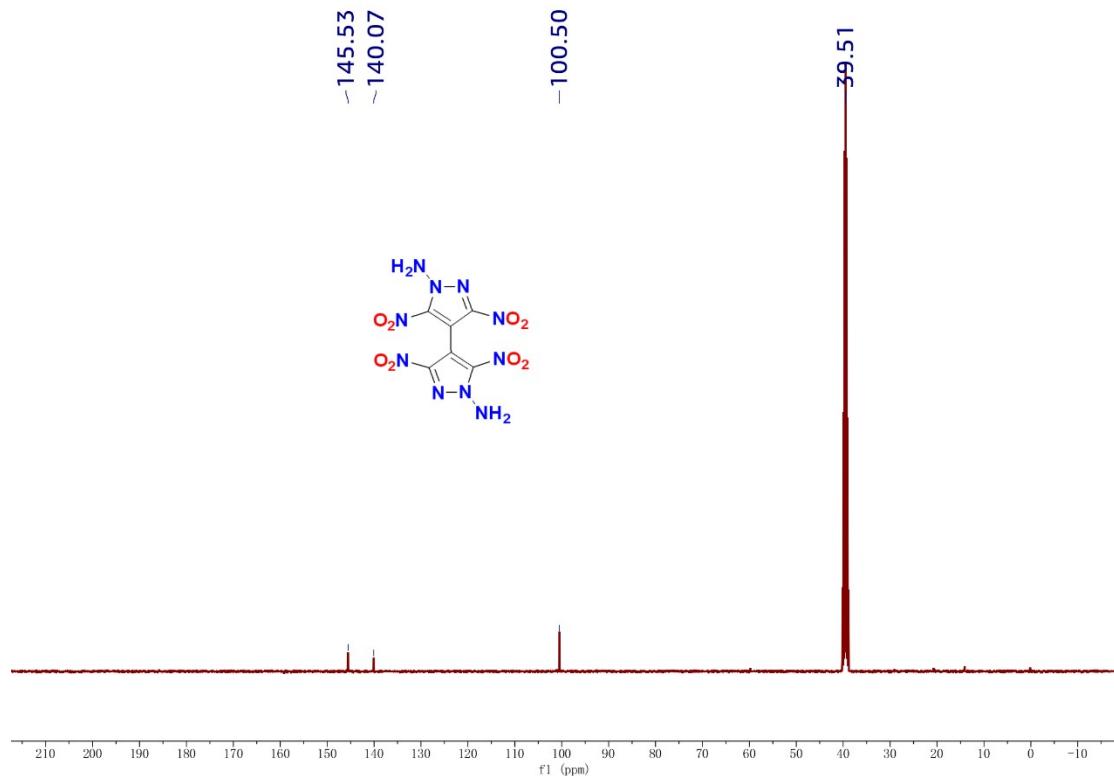
**Figure S8**  $^1\text{H}$  NMR spectrum of TNBP-2 in d6-DMSO.



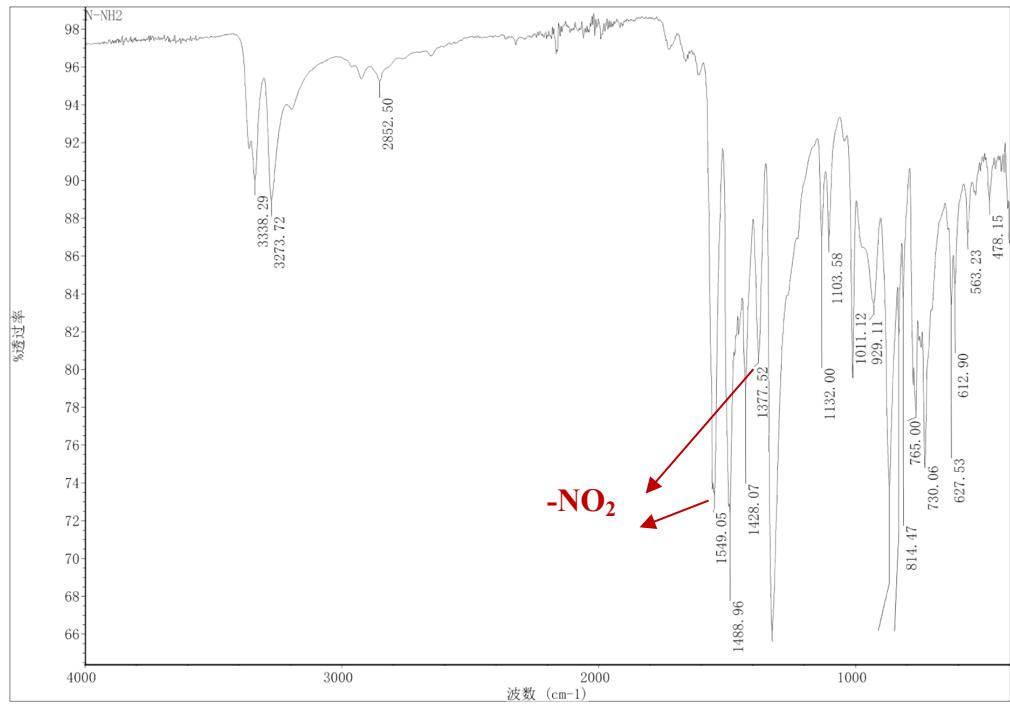
**Figure S9**  $^{13}\text{C}$  NMR spectrum of TNBP-2 in d6-DMSO.



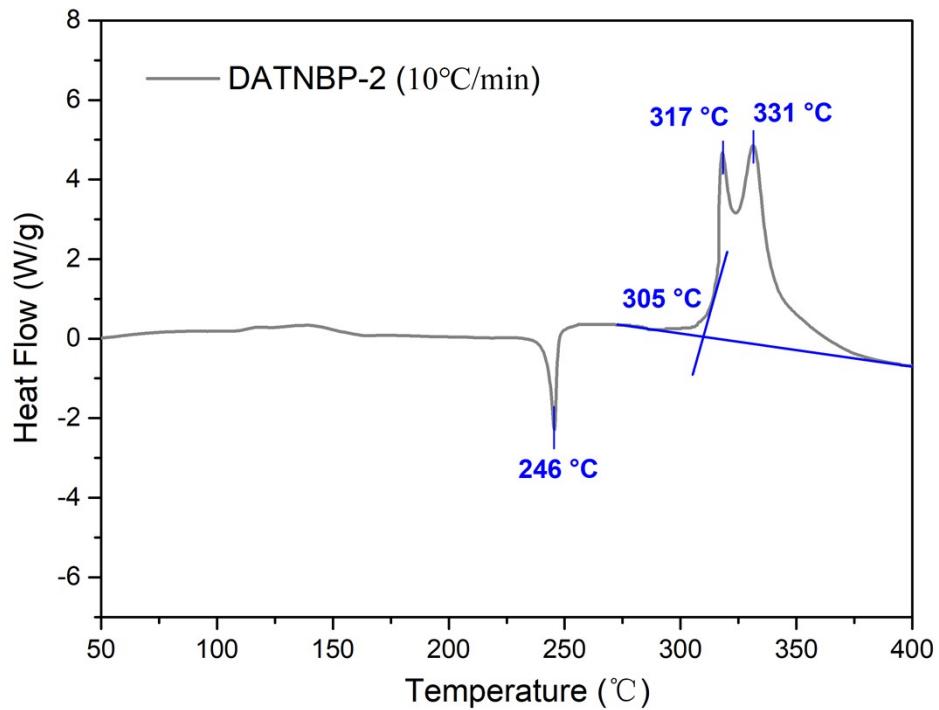
**Figure S10** <sup>1</sup>H NMR spectrum of DATNBP-2 in d<sub>6</sub>-DMSO.



**Figure 11** <sup>13</sup>C NMR spectrum of DATNBP-2 in d<sub>6</sub>-DMSO.



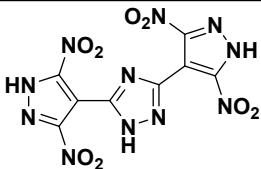
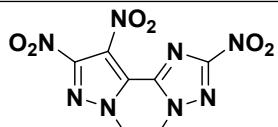
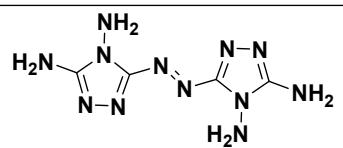
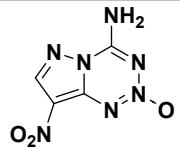
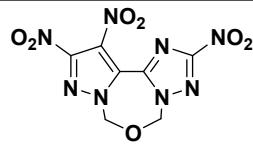
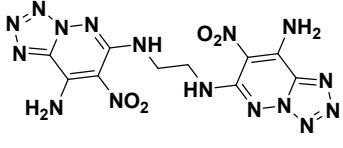
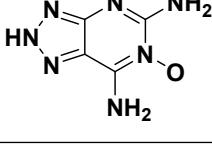
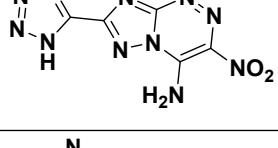
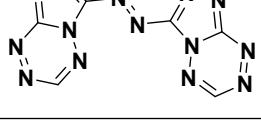
**Figure S12** IR spectrum of compound **DATNBP-2**.

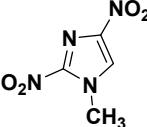
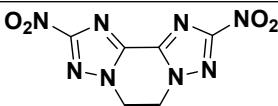
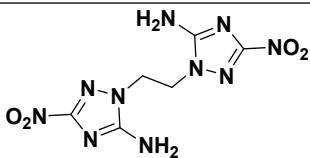
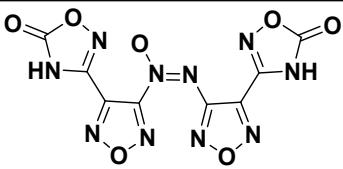
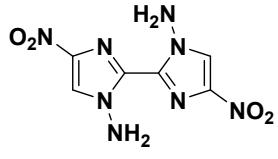
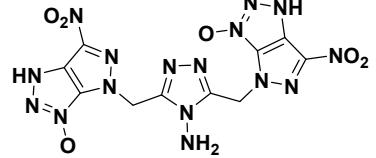
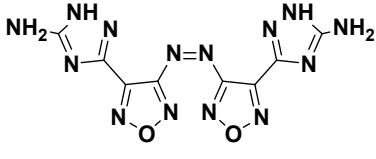
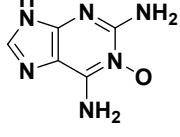
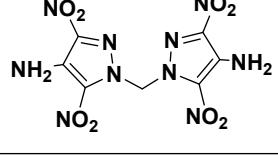
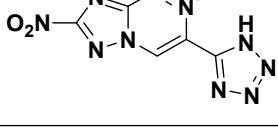


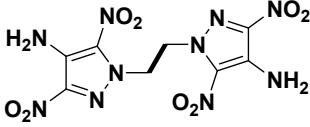
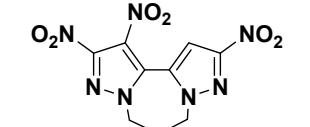
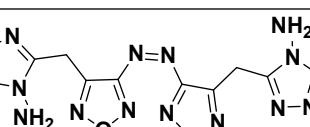
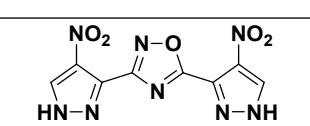
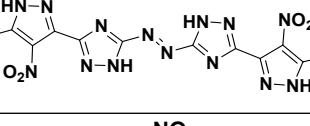
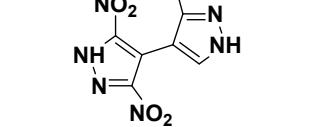
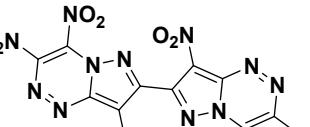
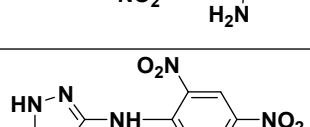
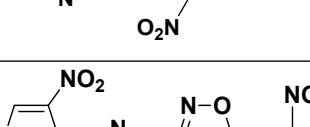
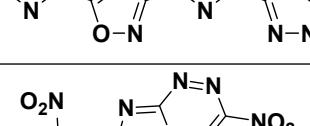
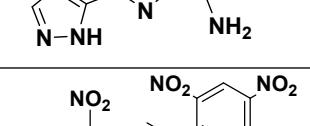
**Figure S13** DSC curve of **DATNBP-2**

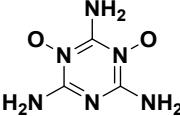
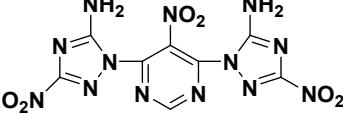
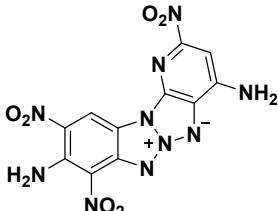
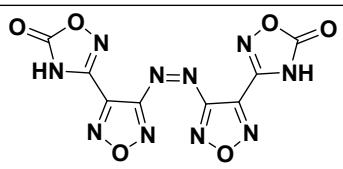
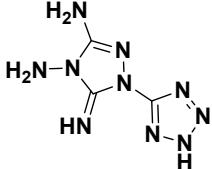
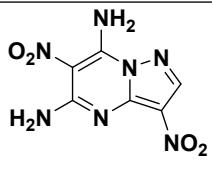
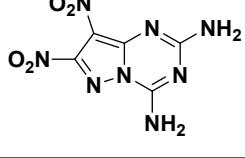
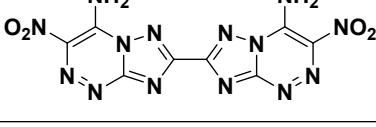
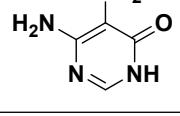
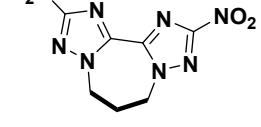
**6. 90 neutral energetic compounds with a  $T_d > 300^\circ\text{C}$  were collected and summarized**

**Table S7** 90 neutral energetic compounds with a  $T_d > 300^\circ\text{C}$  were collected and summarized

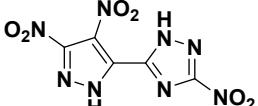
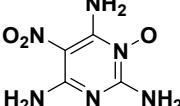
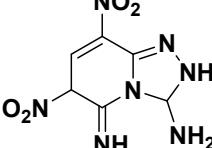
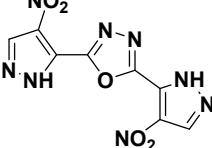
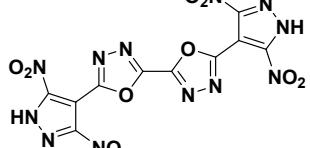
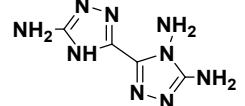
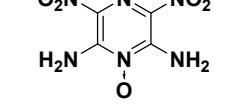
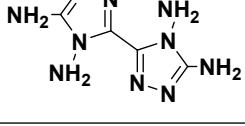
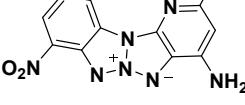
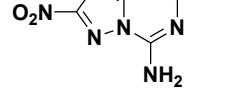
Compound	D (g·cm <sup>-3</sup> )	$T_d$ (°C)	D (m·s <sup>-1</sup> )	P (GPa)	IS (J)	FS (N)	Ref.
	1.860	300	8813	33.08	22	300	9
	1.816	302	8285	29.2	23	>360	10
	1.683	302	8742	26.9	>40	>360	11
	1.874	302	8935	34.5	>20	>360	12
	1.825	303	8304	29.8	21	>360	10
	1.840	303	8809	29.3	19	288	13
	1.72	303	7854	21.5	>40	>360	14
	1.82	305	8312	27	>80	>360	15
	1.91	305	9200	34.8	16	>360	16

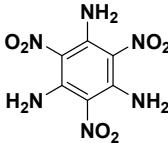
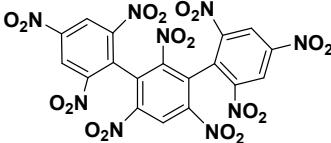
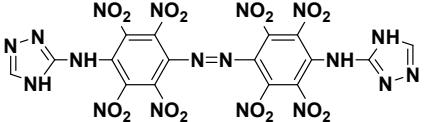
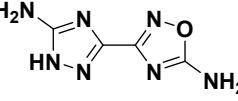
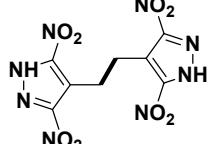
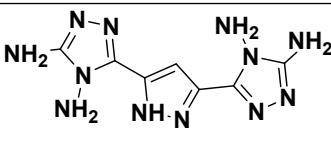
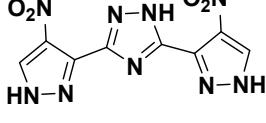
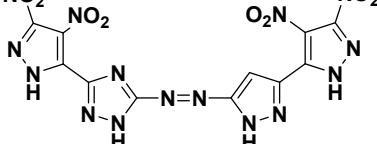
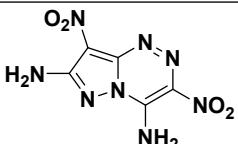
	1.613	305	7244	21.75	23	360	17
	1.733	307	7838	24.1	22	>360	18
	1.72	307	8069	24.5	>40	360	19
	1.95	307	8844	34.4	13	160	20
	1.75	308	7939	25.6	>40	-	21
	1.745	308	8329	27.9	18	240	22
	1.79	309	8458	26.2	>40	360	23
	1.66	309	6609	13.9	>40	>360	14
	1.802	310	8332	29.6	11	>360	24
	1.81	310	9047	34.0	25	360	25

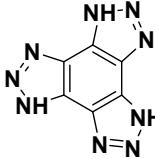
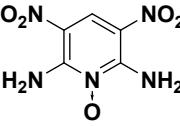
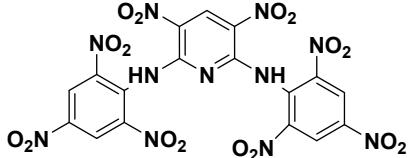
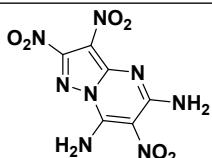
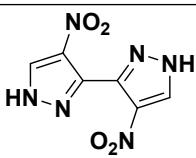
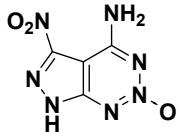
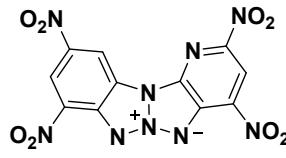
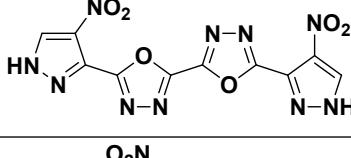
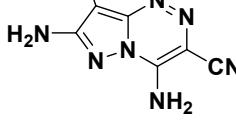
	1.77	311	8189	27.9	>40	>360	26
	1.69	312	7698	23.4	32	>360	10
	1.68	313	7756	23.6	>40	>360	27
	1.77	314	8027	26.4	>40	>360	28
	1.882	314	8889	34.3	18	240	29
	1.855	314	8256	28.6	20	>360	30
	1.85	315	8572	31.4	>60	>360	31
	1.94	316	7850	31.3	40	360	32
	1.782	317	7991	25.2	>40	>360	28
	1.79	317	8165	26.37	>40	>360	33
	1.74	318	7612	24.3	5	240	33

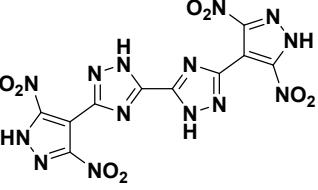
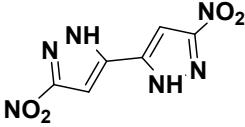
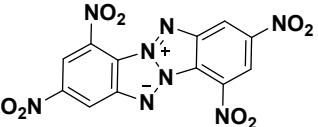
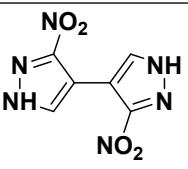
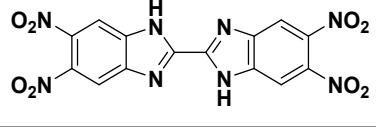
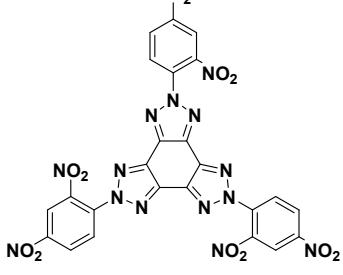
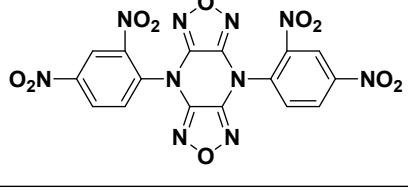
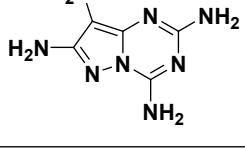
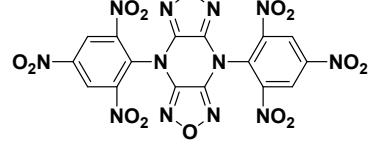
	1.71	319	6988	21.4	>40	>360	34
	1.84	320	8120	-	50	-	35
	1.84	320	7933	24.6	>15	360	36
	1.89	322	8507	30.7	16	160	37
	1.685	324	8423	24.16	>60	-	38
	1.88	325	8338	30.7	40	360	39
	1.825	326	8551	29.8	35	>360	40
	1.90	327	8837	32.9	>40	>360	41
	1.804	328	7535	19.2	>40	>360	42
	1.634	328	7336	19.7	30	>360	18

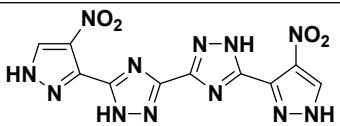
	1.812	328	8002	28.52	>70	-	43
	1.86	329	7853	24.5	>40	-	44
	1.88	329	7720	24.33	8.2	>360	45
	1.87	331	9075	30.7	>80	>360	46
	1.887	332	8538	30.4	>40	>360	47
	1.85	332	8476	30.24	>40	>360	33
	1.88	332	7840	27.91	20	-	48
	1.84	335	8030	27.3	5	>360	49
	1.872	335	8657	27.82	>60	>360	50
	1.85	336	8250	27.4	15	160	51

	1.851	336	8568	31.4	19	240	52
	1.76	337	7970	23.88	>40	>360	53
	1.81	337	8227	26.3	>40	>360	54
	1.80	338	8099	27.14	>40	>360	55
	1.865	341	8517	30.6	22	352	56
	1.68	341	7818	20.4	>40	>360	57
	1.92	342	8639	31.7	20	360	60
	1.68	342	8944	25.8	40	360	58
	1.78	343	7547	21.9	10	240	36
	1.743	348	7849	22.16	>80	>360	59

	1.73	348	8102	25	18	>360	60
	1.93	350	8176	27.72	50	>360	71
	1.78	350	7721	26.58	60	-	60
	1.97	350	8320	34.1	87	36	61
	1.772	351	7871	21.8	>40	>360	62
	1.805	351	8234	28.6	10	352	56
	1.78	353	9275	28.7	>80	>360	63
	1.786	354	7558	22.29	>30	>360	64
	1.855	354	8404	29.2	19	240	52
	1.90	355	8727	32.6	>60	>360	65

	1.77	356	7160	19.4	18	-	15
	1.878	358	7842	27.5	15	>360	66
	1.76	360	7757	25.1	10	360	71
	1.87	364	8359	26.5	>60	>360	67
	1.83	365	8120	26.9	>40	>360	68
	1.82	365	8528	29.4	20	>360	60
	1.67	365	7426	18.16	>40	>360	69
	1.94	366	7670	24.2	9	>360	36
	1.81	368	8054	26.53	>40	>360	55
	1.794	370	7891	22.7	60	>360	70

	1.877	372	8705	32.25	26	>360	9
	1.81	376	8026	26.2	>40	>360	68
	1.64	378	7250	21.0	69	>360	71
	1.794	382	7528	22.1	30	>360	30
	1.75	394	6198	14.5	15	>360	71
	1.69	400	7032	19.9	19	-	15
	1.74	405	7200	23.0	16	300	16
	1.78	406	7789	21.8	>40	>360	72
	1.82	415	7874	28.2	10	240	73



1.794      425      7503      21.37      >30      >360      64

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