Electronic Supplementary Information

Integrating three types of structure reinforcements abounding in heat-resistant explosives to construct a 3D solvent-free EMOF with superb stability

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1. Synthesis of H₂DAAT
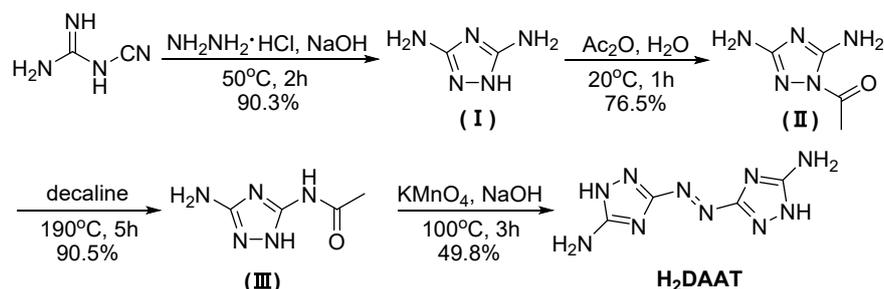
A. Synthesis of 1*H*-1,2,4-triazole-3,5-diamine (I)

Dicyandiamide (20.01 g, 0.24 mol) was dissolved in 60 mL water. Then, hydrazine dihydrochloride (27.62 g, 0.26 mol) was added to the solution slowly. The mixture was heated at 50°C for 2 h. Subsequently, the pH of the mixture was adjusted to 10.5 with NaOH solution (3.0 mol·L^{-1})[1]. The solvent was removed by vacuum evaporation to obtain a solid white powder **I** (21.22 g, 0.21 mol, 90.3%). ^{1}H NMR ([D$_6$] DMSO, 25°C): δ = 10.64 (s, 1H), 5.01 (s, 4H).

B. Synthesis of 1-acetyl-3,5-diamino-1*H*-1,2,4-triazole (II)

According to the literature[2], acetic anhydride (40.8 mL, 1.2 equiv.) was added dropwise under vigorous stirring to a solution of **I** (36.02 g, 0.36 mol) in 130 mL water at room temperature. After stirring for 1 h, the precipitate was filtered off, washed with water, and dried at room temperature to yield **II** as a colorless powder (38.83 g, 0.27 mol, 76.5%). ^{1}H NMR([D$_6$] DMSO): δ = 7.35 (s, 2 H), 5.66 (s, 2 H), 2.33 (s, 3 H). ^{13}C NMR ([D$_6$] DMSO): δ = 169.95, 161.60, 156.47, 23.03.

C. Synthesis of 3-acetylamino-5-amino-1*H*-1,2,4-triazole (III)

A mixture of **II** (10.00 g, 70.89 mmol) and decaline (100.0 mL) was heated to reflux with stirring at 187-190°C for 6 h. The solid was filtered off, washed with petroleum ether (100.0 mL) and diethyl ether (100.0 mL). White powder **III** (9.05 g, 64.15 mmol, 90.5%) was obtained by drying in the air. ^{1}H NMR (D$_2$O, NaOH, 25°C): δ= 2.05 (s, 3H). ^{13}C NMR (D$_2$O, NaOH): δ= 173.90, 161.89, 153.96, 22.49.

D. Synthesis of 5,5'-diamino-3,3'-azo-1*H*-1,2,4-triazole (H₂DAAT)

Potassium permanganate (1.54 g, 9.72 mmol) was added over a period of 10 minutes to the solution of **III** (2.00 g, 14.18 mmol) in sodium hydroxide (32%, 15.0 mL) at 0°C. After the addition, the mixture was allowed to reflux for 3 h. The generated

manganese oxide was removed by filtration, and the filtrate was acidified with concentrated hydrochloric acid to pH = 6. The precipitate was filtered and washed with water, and H_2DAAT was obtained as an orange solid (0.47 g, 2.42 mmol, 49.8%). ^{13}C NMR (D_2O, NaOH): δ= 169.80, 164.89.

2. Crystal structure determination
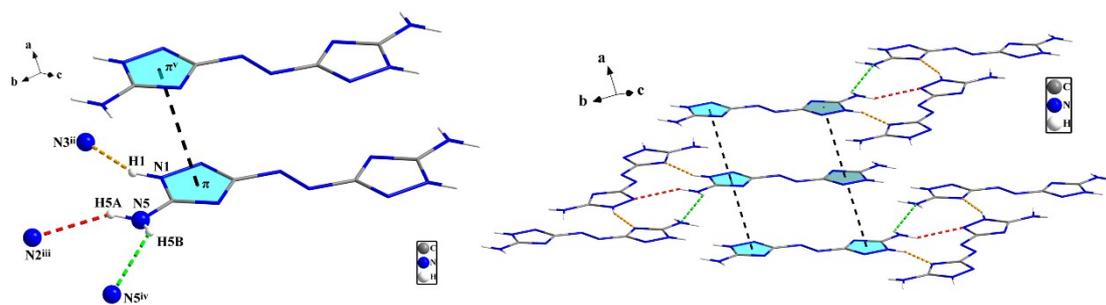
Fig. S1 View of the crystal packing for H_2DAAT showing hydrogen bonds, and π···π interactions.
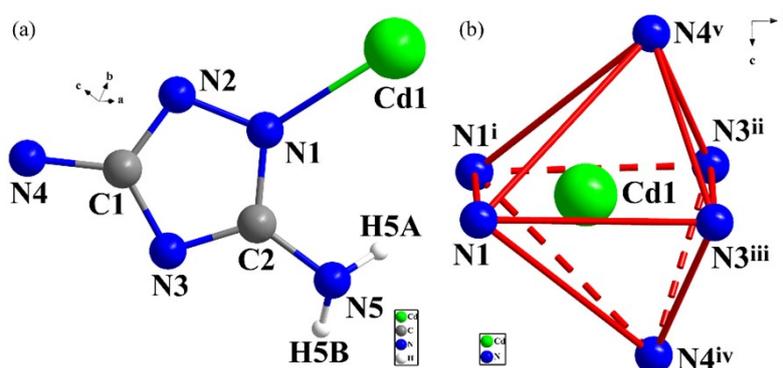
Fig. S2 (a) The asymmetric unit for **1**; (b) Distorted octahedral configuration of Cd1.

Table S1 Crystallographic data for H_2DAAT and EMOF **1**

Compounds	H_2DAAT	**1**
CCDC number	2244766	2243170
Empirical formula	$C_4H_6N_{10}$	$C_4H_4CdN_{10}$
Formula weight	194.19	304.58
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pbcn$
a (Å)	3.5601(6)	7.9084(14)
b (Å)	12.1278(16)	10.8324(19)
c (Å)	8.6009(13)	9.4962(17)
α (°)	90	90
β (°)	96.628(6)	90
γ (°)	90	90

V (Å^3)	368.87(10)	813.5(2)
Z	2	4
D_c (g·cm^{-3})	1.748	2.487
μ (mm^{-1})	0.133	2.667
F (000)	200	581
Crystal size (mm^3)	0.15× 0.13 × 0.12	0.15 × 0.14 × 0.12
θ Range (°)	2.92-27.44	3.19-25.00
Reflections collected	4164	5668
Independent reflections	850 [R_{int} = 0.0899]	715 [R_{int} = 0.0478]
Reflections observed [$I > 2\sigma(I)$]	571	672
Data/restraints/parameters	850/0/70	715/0/76
Goodness-of-fit on F^2	1.1295	1.1072
R_1/wR_2 [$I > 2\sigma(I)$]	0.0481/0.1029	0.0163/0.0390
R_1/wR_2 (all data)	0.0809/0.1373	0.0171/0.0411
Max., Min. $\Delta\rho$ (e·Å^{-3})	0.3918, -0.4519	0.3315, -0.2994

Table S2 Selected bond lengths (Å) and angles (°) for H$_2$DAAT

H$_2$DAAT			
C1-N2	1.327(3)	C2-N1	1.337(3)
C1-N3	1.359(3)	C2-N5	1.351(3)
C1-N4	1.392(4)	N1-N2	1.371(3)
C2-N3	1.334(3)	N4-N4^i	1.274(4)
N2-C1-N3	115.6(2)	N1-C2-N5	124.7(2)
N2-C1-N4	117.4(2)	C2-N1-N2	110.3(2)
N3-C1-N4	127.1(2)	C1-N2-N1	101.5(2)
N3-C2-N1	110.2(2)	C2-N3-C1	102.4(2)
N3-C2-N5	125.0(2)	N4^i-N4-C1	112.7(2)

Symmetry code: i) 1-x, 1-y, 1-z.

Table S3 Hydrogen-bonding geometry and π···π interactions (Å, °) for H$_2$DAAT

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠D-H···A
N1-H1···N3^{ii}	0.879	1.958	2.779(3)	155
N5-H5A···N2^{iii}	0.888	2.404	3.168(3)	144
N5-H5B···N5^{iv}	0.856	2.687	3.326(3)	133
π (C1,C2,N1~N4)···π (C1,C2,N1~N4)^v			3.222(3)	0

Symmetry codes: ii) 1/2+x, 3/2-y, z-1/2; iii) 3/2-x, 1/2+y, 1/2-z; iv) 1- x, 2-y, 1-z; v) 1+x, y, z.

Table S4 Selected bond lengths (Å) and angles (°) for EMOF **1**

EMOF **1**			
Cd1-N1	2.262(2)	Cd1-N4^{iv}	2.494(3)
Cd1-N3^{ii}	2.358(2)	N4-N4^{vi}	1.292(4)
N1-N2	1.373(2)	C1-N4	1.379(3)
N1^{i}-Cd1-N1	93.43(9)	N1-Cd1-N4^{iv}	101.30(6)
N1-Cd1-N3^{iii}	93.06(6)	N4^{iv}-Cd1-N4^{v}	135.37(8)
N3^{iii}-Cd1-N4^{v}	78.75(6)	N1-Cd1-N4^{v}	108.95(6)
N3^{iii}-Cd1-N4^{iv}	67.33(8)	N1-Cd1-N3^{ii}	173.10(6)
N3^{ii}-Cd1-N3^{iii}	80.55(8)	Cd1-N4^{v}-N4^{ii}	115.4(2)
N3-C1-N4	125.43(18)	N2-N1-Cd1	123.66(13)

Symmetry codes: i) 1-*x*, *y*, 1/2-*z*; ii) 1/2+*x*, 1/2+*y*, 1/2-*z*; iii) 1/2-*x*, 1/2+*y*, *z*; iv) 1/2+*x*, 3/2-*y*, 1-*z*; v) 1/2-*x*, 3/2-*y*, *z*-1/2; vi) -*x*, 1-*y*, 1-*z*.

Table S5 Hydrogen-bonding geometry, N-H···π, and *p*···π interactions (Å, °) for EMOF **1**

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠D-H···A
N5-H5A···N2^{v}	0.888	2.182	3.052(2)	166
N5-H5B···π (C1,C2,N1~N4)^{vii}	0.844	2.598	3.065(2)	138
p(N5)···π (C1,C2,N1~N3)^{i}			3.111(2)	

Symmetry codes: i) 1-*x*, *y*, 1/2-*z*; v) 1/2-*x*, 3/2-*y*, *z*-1/2; vii) *x*, 1-*y*, *z*-1/2.
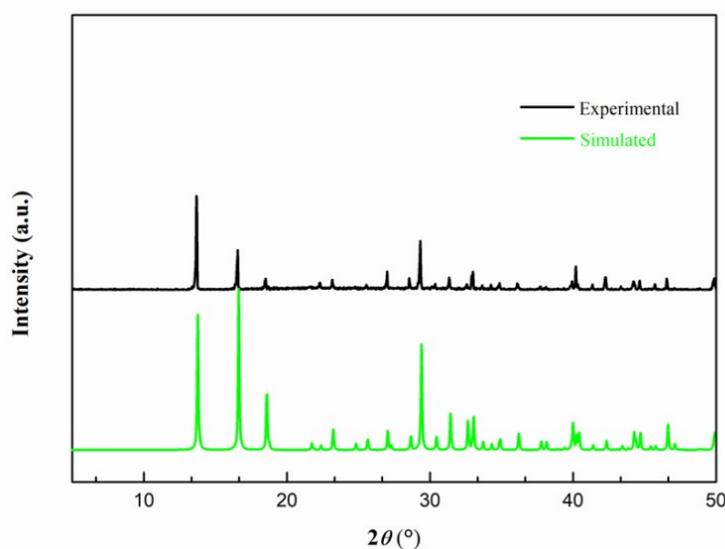
Fig. S3 Powdered X-ray diffraction (PXRD) pattern of EMOF **1**.

3. SEM
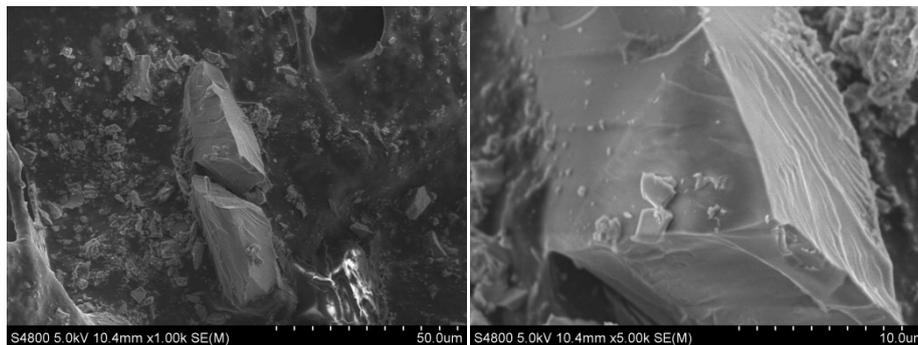
Fig. S4 SEM of EMOF **1**.

4. TG-DSC of H$_2$DAAT
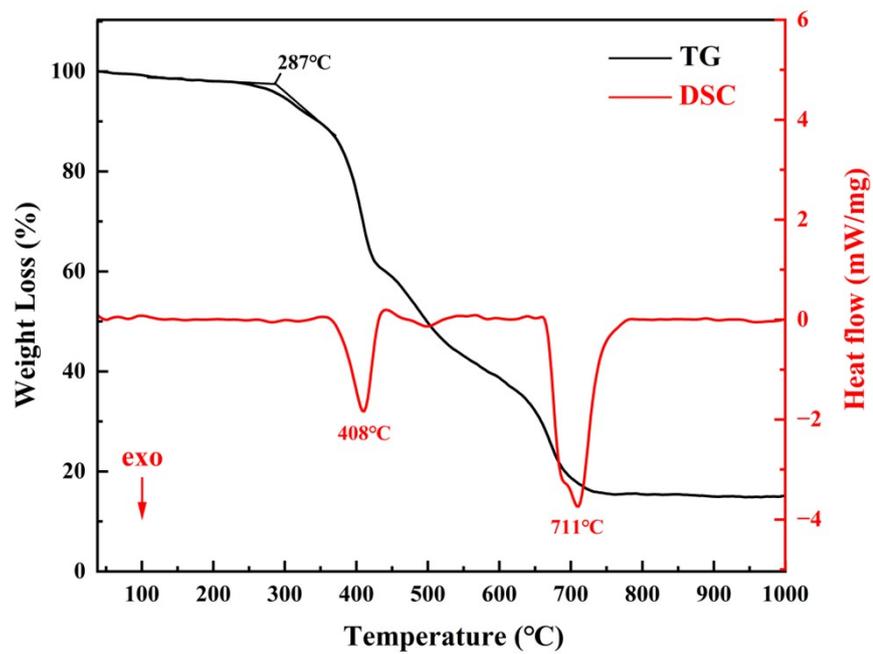
Fig. S5 The TG-DSC curves of H$_2$DAAT.

5. Spectra of TG-DSC-MS-IR
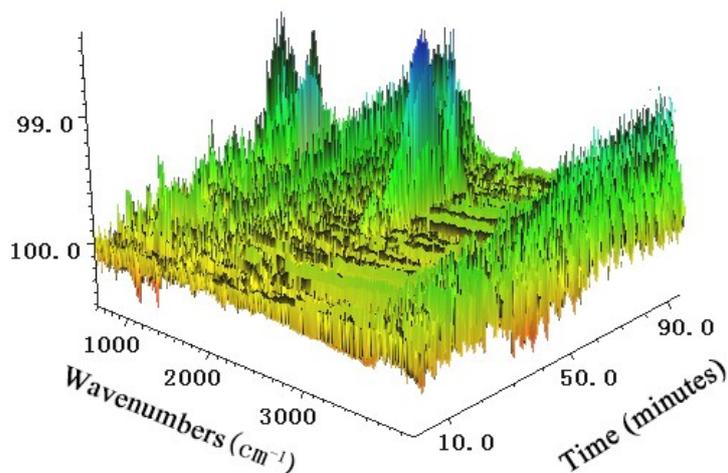
Fig. S6 IR spectra.
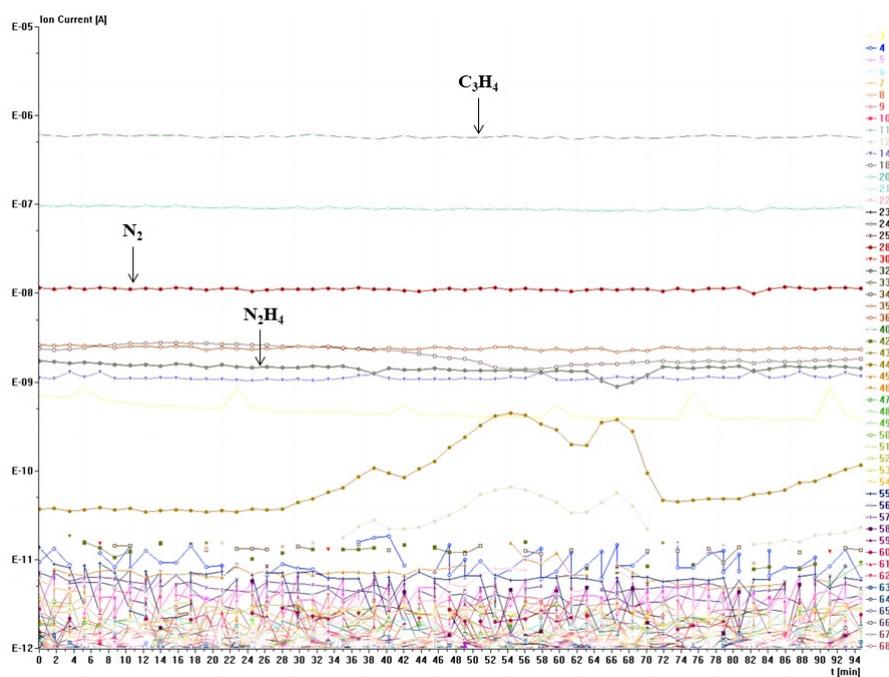
Fig. S7 Mass spectra.

6. Sensitivity

Impact sensitivity was determined by the Fall Hammer Apparatus. Twenty milligrams of EMOF **1** was compacted to a copper cap under the press of 39.2 MPa and hit by a 2 kg drop hammer, and the calculated value of h_{50} represents the drop height of 50% initiation probability. Friction sensitivity of EMOF **1** was measured by applying a

Julius Peter's machine using a 20 mg sample.

7. Oxygen bomb calorimetry

The constant-volume combustion energy of EMOF **1** and H_2DAAT were investigated by a precise C200 calorimeter (Germany IKA)[3]. Approximately 200 mg of the samples were pressed with a well-defined amount of benzoic acid to form a tablet to ensure better combustion. The recorded data are the average of six single measurements. The calorimeter was calibrated by the combustion of certified benzoic acid (Standard Reference Material, 39i, NIST) in an oxygen atmosphere at a pressure of 30.5 bar.

The experimental results for the constant volume combustion energy ($\Delta_c U$) of the EMOF **1** and H_2DAAT are -4075.28 $kJ \cdot mol^{-1}$, and -3972.54 $kJ \cdot mol^{-1}$, respectively. According to the formula, $\Delta_c H_m^\theta = \Delta_c U_m^\theta + \Delta n_g RT$ (n_g is the total molar amount of gases in the products or reactants, R = 8.314 $J \cdot mol^{-1} \cdot K^{-1}$, T = 298.15 K), the standard molar enthalpies of combustion ($\Delta_c H_m^\theta$) can be derived as being -4066.58 $kJ \cdot mol^{-1}$, and -3963.87 $kJ \cdot mol^{-1}$ for equation S1-S2, respectively. The combustion reaction equations are listed as follows:

$$C_4H_4CdN_{10} \text{ (s)} + 11/2 \ O_2 \text{ (g)} \rightarrow CdO \text{ (s)} + 4 \ CO_2 \text{ (g)} + 2 \ H_2O \text{ (l)} + 5 \ N_2 \text{ (g)} \qquad \text{(S1)}$$

$$C_4H_6N_{10} \text{ (s)} + 11/2 O_2 \text{ (g)} \rightarrow 4CO_2 \text{ (g)} + 3H_2O \text{ (l)} + 5N_2 \text{ (g)} \qquad \text{(S2)}$$
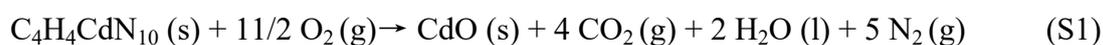
Based on the calculated enthalpies of combustion and known enthalpies of formation of the combustion products determined experimentally, $\Delta_f H_m^\theta(CdO)$ = -258.35 $kJ \cdot mol^{-1}$, $\Delta_f H_m^\theta(CO_2)$ = -393.51 $kJ \cdot mol^{-1}$, $\Delta_f H_m^\theta(H_2O)$ = -285.83 $kJ \cdot mol^{-1}$ are obtained from literature[4]. On the basis of Hess's law in thermochemical equation, the standard enthalpies of formation ($\Delta_f H_m^\theta$) of EMOF **1** and H_2DAAT are calculated as 1662.53 $kJ \cdot mol^{-1}$, and 1532.34 $kJ \cdot mol^{-1}$, respectively.

8. Detonation property

As described in ref.5, the new and efficient method, which employed the hypothesis of Becker-Kistiakowsky-Wilson (BKW) equation and arbitrary theory of the K-J method, could be applied to perform the detonation performances of metal

compounds containing special elements. The overall calculation process can be described as follows: for the explosives composed of C, H, N, and O elements, all N atoms are converted to N_2; O atoms form H_2O with H atoms first and then form CO_2 with C atoms; the remaining C atoms are retained in solid state; if there are O atoms left, they will form O_2. To preserve Kamlet's method, the developed theory is employed to determine the detonation products from metal-containing explosives. In most cases, metal atoms are converted to their oxidation states, emitting more heat after detonation. Otherwise, metal atoms can be treated as their reduction states, if the heat of formation (HOF) of metallic oxides is higher than that of H_2O, or there is no O atom in the molecule. Besides, O atoms form H_2O with H atoms first and the remaining ones then form CO_2 with C atoms. However, if the amount of O atoms is not sufficient to oxidize all H atoms, the remaining H atoms can produce NH_3 with N atoms, and the rest of the N atoms are released as N_2 gas. On the other hand, the remaining C atoms are retained in the solid state if they are not completely oxidized by O atoms. If there are redundant O atoms, however, they can be expelled as O_2. The detonation reactions of EMOF **1** and H_2DAAT estimated by the new method for compounds are described by the equation S3-S4. Detonation velocity (D) and detonation pressure (P) are of two compounds are investigated by Kamlet-Jacbos (K-J) equations, following as Equations (S5-S8)

$$C_4H_4CdN_{10} \text{ (s)} \rightarrow Cd \text{ (s)} + 4 \text{ C (s)} + 13/3 \text{ } N_2 \text{ (g)} + 4/3 \text{ } NH_3 \text{ (g)} \tag{S3}$$

$$C_4H_6N_{10} \text{ (s)} \rightarrow 4C \text{ (s)} + 4N_2 \text{ (g)} + 2NH_3 \text{ (g)} \tag{S4}$$
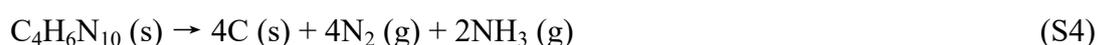
$$D = 1.01\varphi^{1/2}(1 + 1.30\rho) \tag{S5}$$

$$P = 1.558\varphi\rho^2 \tag{S6}$$

$$\Phi = 31.68N(MQ)^{1/2} \tag{S7}$$

$$Q = \frac{-\left[\Delta H_f(\text{detonation products}) - \Delta H_f(\text{energetic compound})\right]}{\text{formula weight of energetic compound}}$$

(S8)

where D is detonation velocity (km·s^{-1}), P is detonation pressure (GPa), Q is heat of detonation (kcal·g^{-1}), N is moles of detonation gases per gram of explosive, M is average molecular weight of the gases, ρ is density of explosive (g·cm^{-3}).

The N and M of detonation reaction are given by equations (S7-S8)

$$N = \frac{\sum n_g}{\text{formula weight of explosive}} \qquad \text{(S9)}$$

$$M = \frac{\sum(n_g \times M_g)}{\sum n_g}$$
(S10)

where n_g is the moles of each detonation gas per mole of explosive, M_g is the molecular weight of each detonation gas per mole of explosive. Utilizing the above equations, and the above experimentally determined $\Delta_f H_m^\theta$ values of **1** and the known NH_3 (g, -45.94 kJ·mol⁻¹), the detonation velocity and detonation pressure for compounds can be obtained.

For EMOF **1**

ρ = 2.487 g·cm⁻³

Q = ΔH_{det} = -[4/3×(-45.94)-1662.53]/304.58 = 5.66 kJ·g⁻¹ = 1.36 kcal·g⁻¹

N = (13+4)/(3×304.58) = 0.0186 mol·g⁻¹

M = (17.03×4+28.01×13)/17 = 25.43 g·mol⁻¹

Φ = 31.68×0.0186×(25.43×1.36)¹ᐟ²=3.47

P = 1.558×(2.487)²×3.47 = 33.44 GPa

D = 1.01×(3.47)¹ᐟ²×(1+1.30×2.487) = 7.964 km·s⁻¹

For **H₂DAAT**

ρ = 1.748 g·cm⁻³

Q = ΔH_{det} = -[2×(-45.94)-1532.34]/194.19 = 8.36 kJ·g⁻¹ = 1.998 kcal·g⁻¹

N = (4+2)/194.19 = 0.0309 mol·g⁻¹

M = (28×4+17×2)/6 = 24.33 g·mol⁻¹

Φ = 31.68×0.0309×(24.33×1.998)¹ᐟ² = 6.83

P = 1.558×(1.748)²×6.83 = 32.51 GPa

D = 1.01×(6.83)¹ᐟ²×(1+1.30×1.748) = 8.638 km·s⁻¹

9. NMR spectra
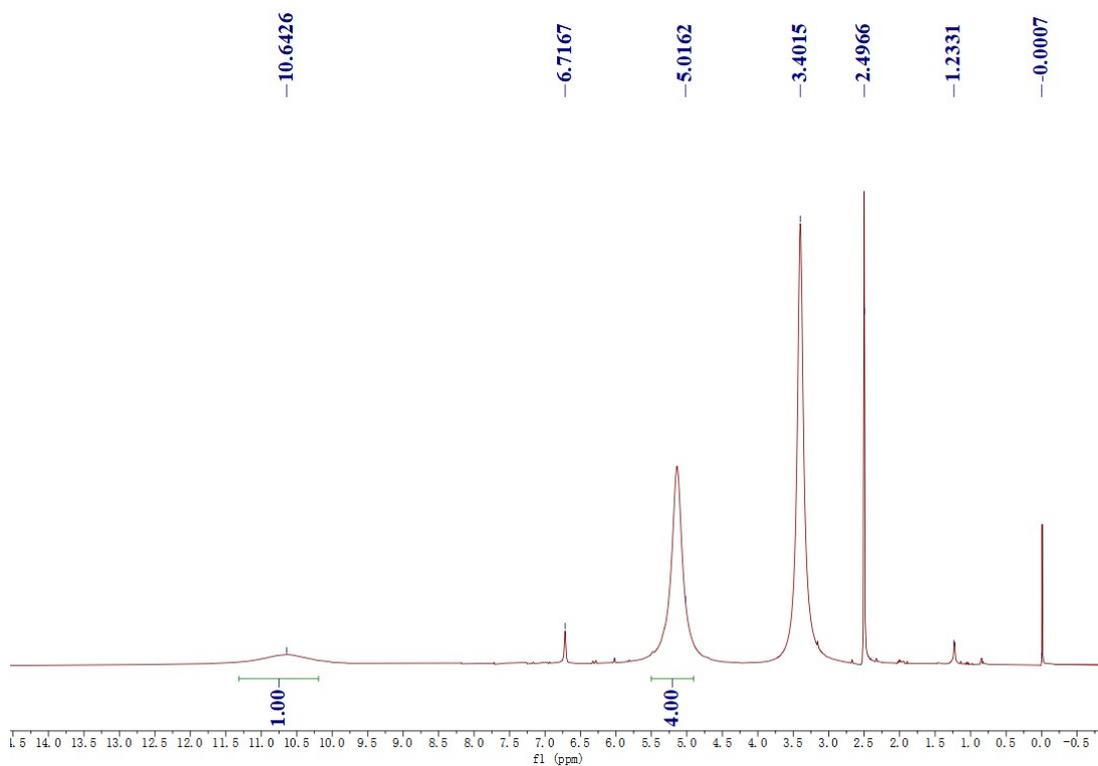
Fig. S8 ^{1}H NMR ([D$_6$] DMSO, 400 MHz) of **I**
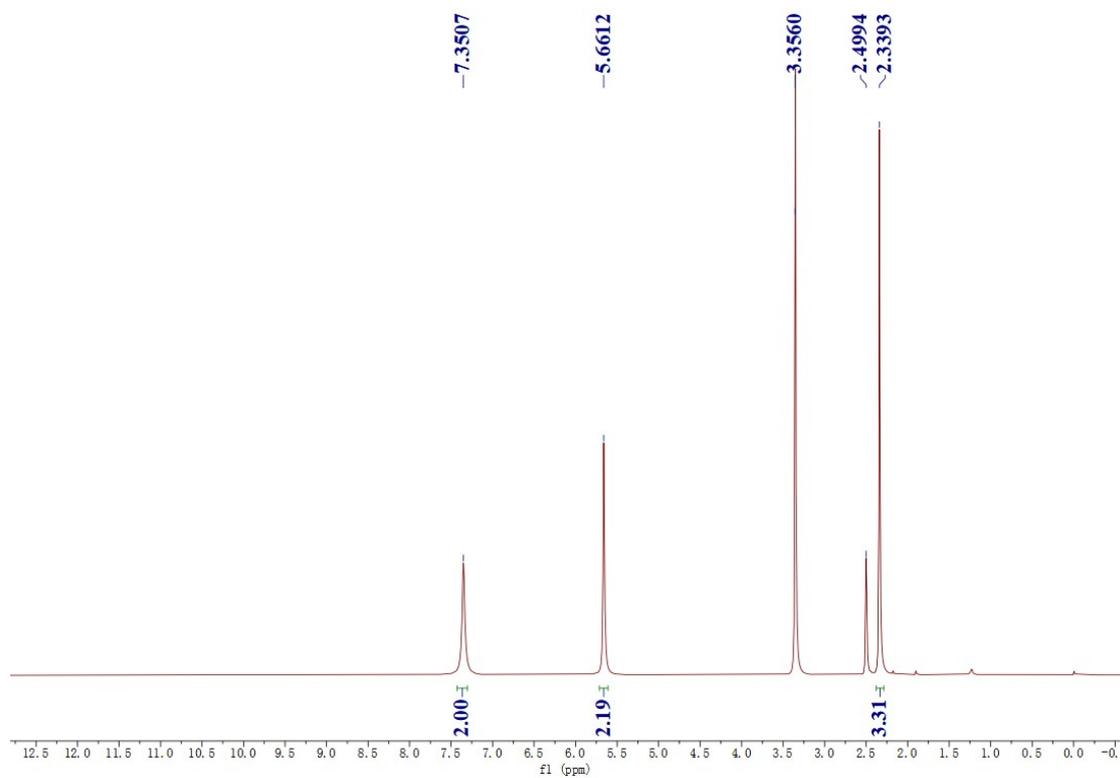
Fig. S9 ^{1}H NMR ([D$_6$] DMSO, 400 MHz) of **II**
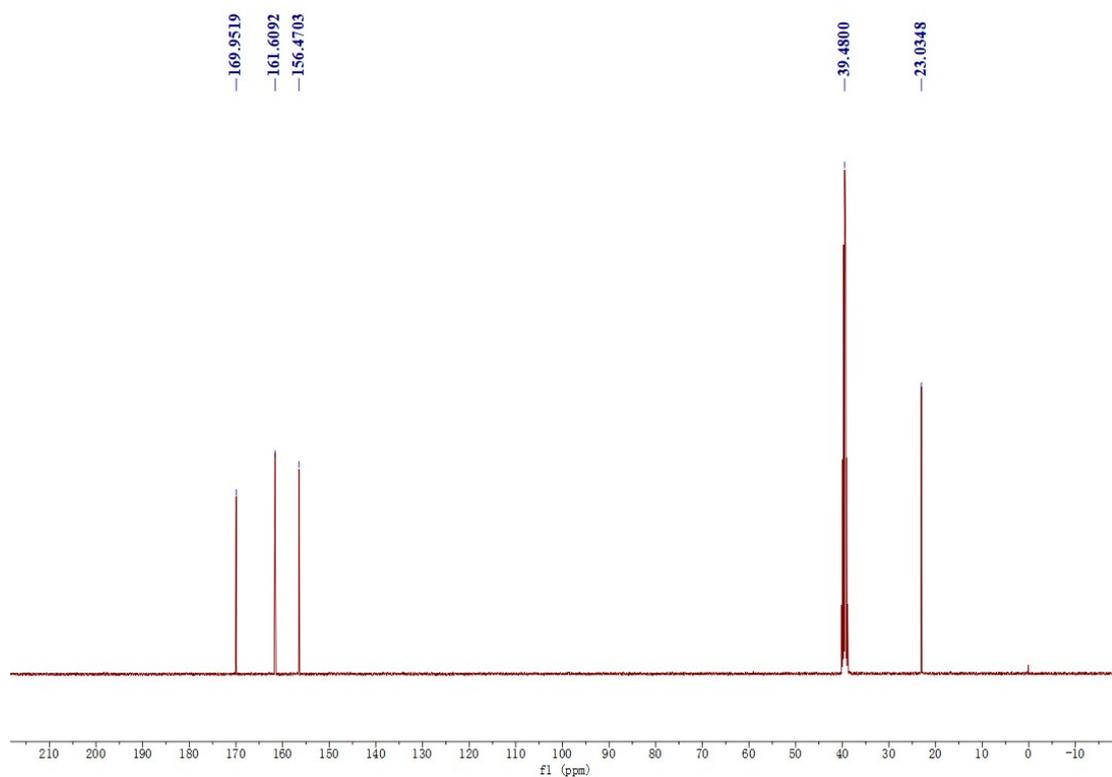
Fig. S10 ^{13}C NMR ([D$_6$] DMSO, 100 MHz) of **II**
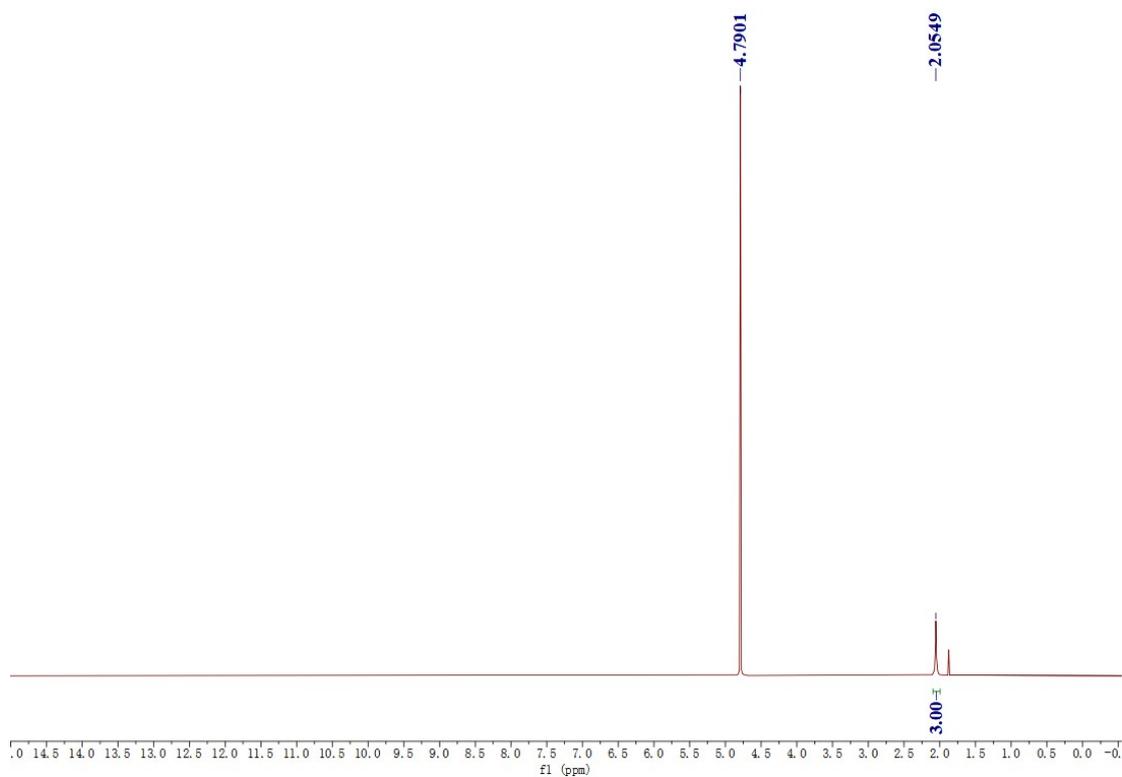
Fig. S11 ^1H NMR (D$_2$O, NaOH, 400 MHz) of **III**
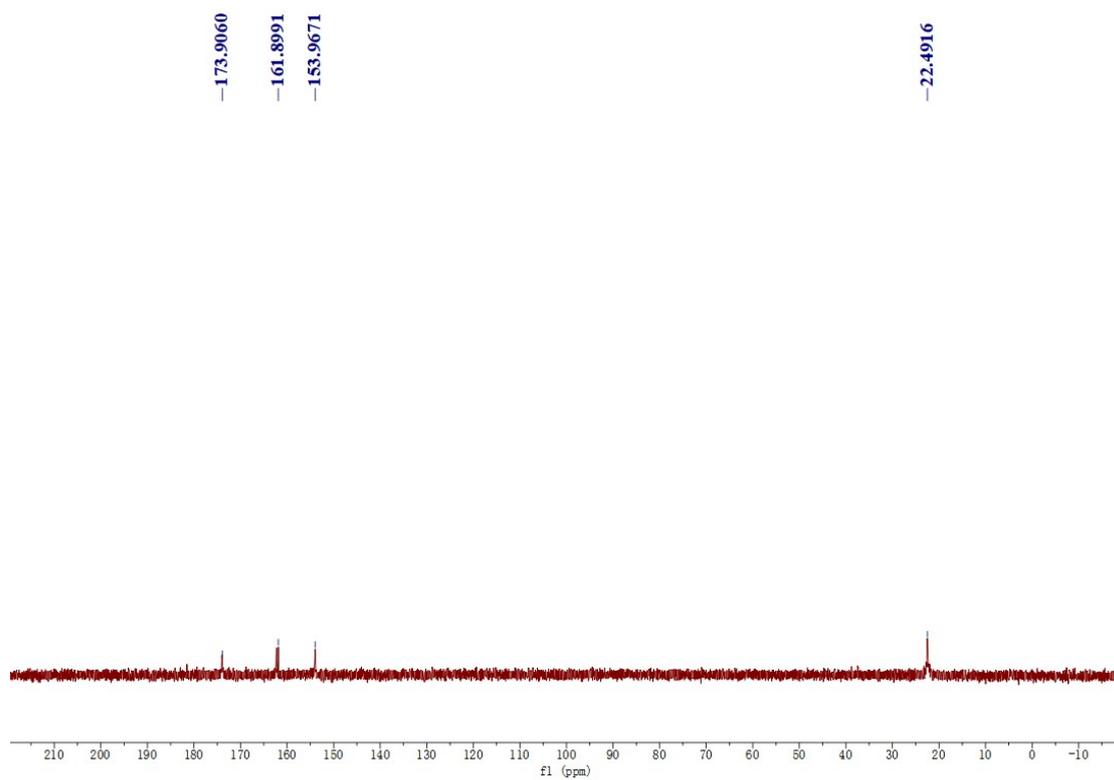
Fig. S12 ^{13}C NMR (D$_2$O, NaOH, 100 MHz) of **III**
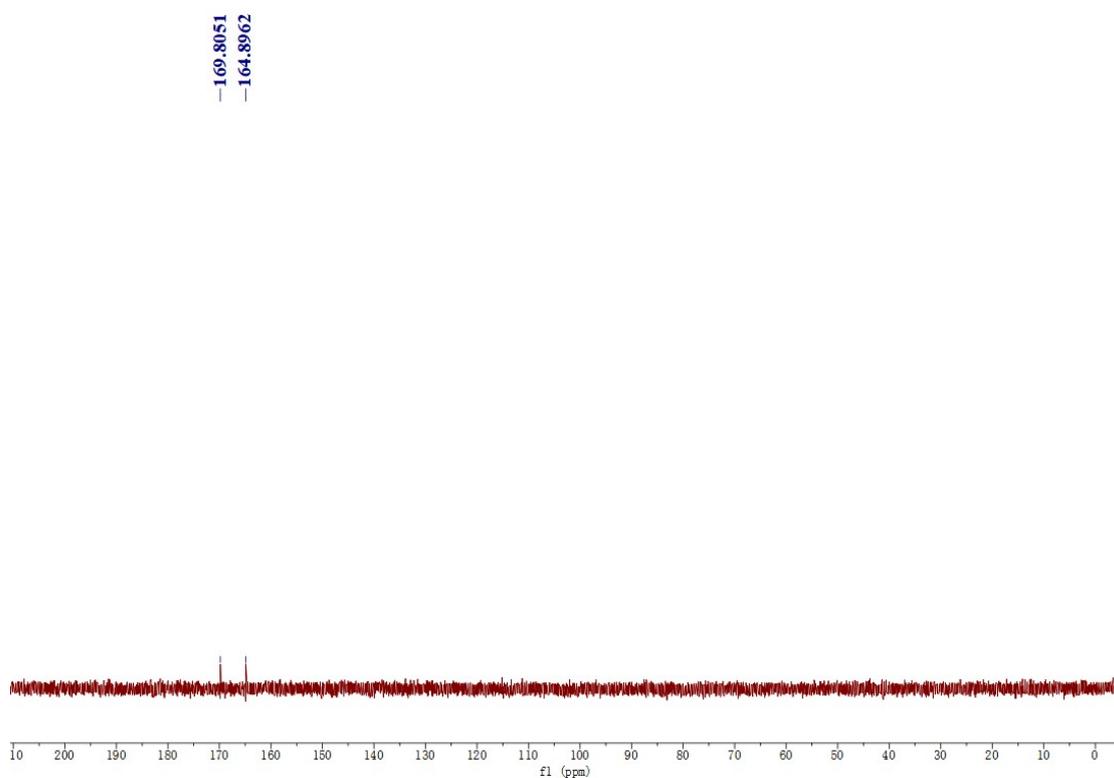
Fig. S13 ^{13}C NMR (D$_2$O, NaOH, 100 MHz) of **H$_2$DAAT**

10. References

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