Supporting Information

Solvent-free Dense Energetic Metal-organic Framework (EMOF): To Improve Stability and Energetic Performance *via* in *situ* Microcalorimetry

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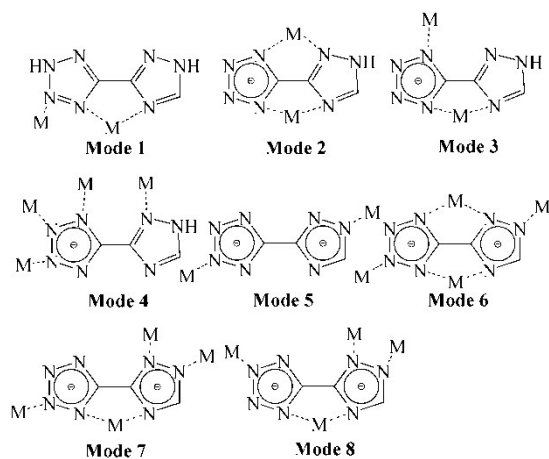
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Table of contents

Scheme S1. Coordination Modes of 3-(1*H*-tetrazol-5-yl)-1*H*-triazole ligand.
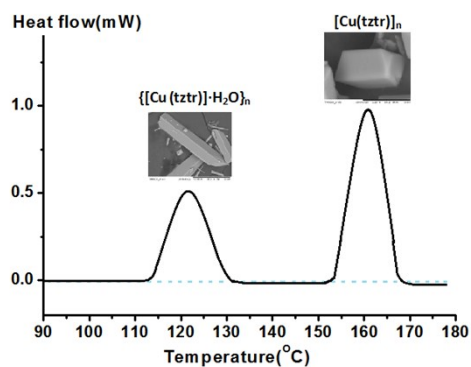
Fig. S1 Heat-flow curve of the mixture of $Cu(ClO_4)_2$, NaN_3 and H_2tztr *versus* water (heating rate = 0.15 ^oC min^{-1}).
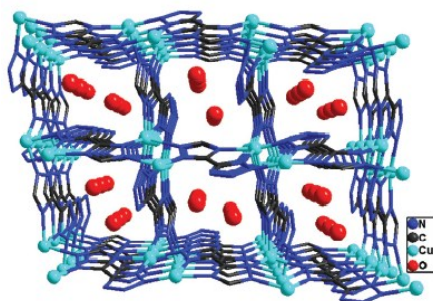
Fig. **S2** 3D porous structure of $\{[Cu(tztr)] \cdot H_2O\}_n$ (*Green Chem.*, 2015,**17**, 831-836). Hydrogen atoms are omitted for clarity).
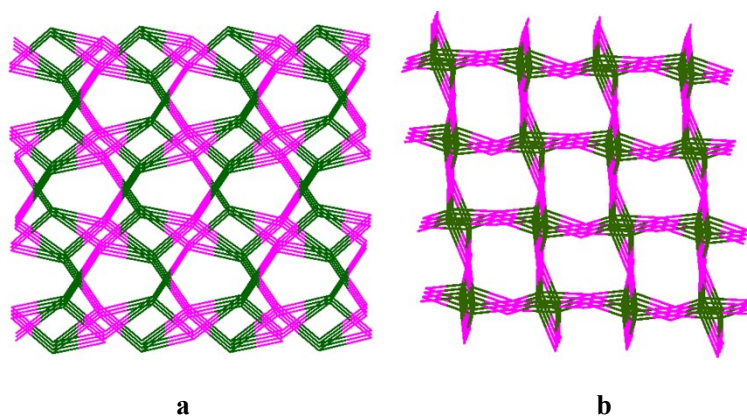

a   **b**

Fig. S3 Schematic representation of the 3D topology of **1** (a) and $\{[Cu(tztr)] \cdot H_2O\}_n$ (b).
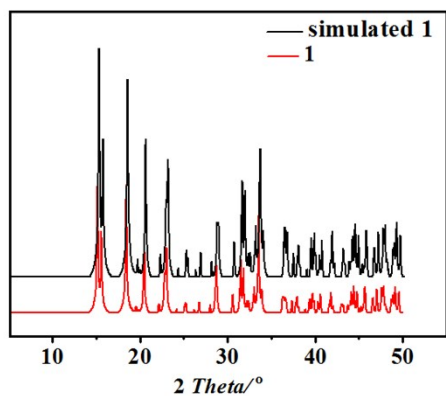
Fig. S4 X-ray powder diffraction (XRPD) curves of **1**.
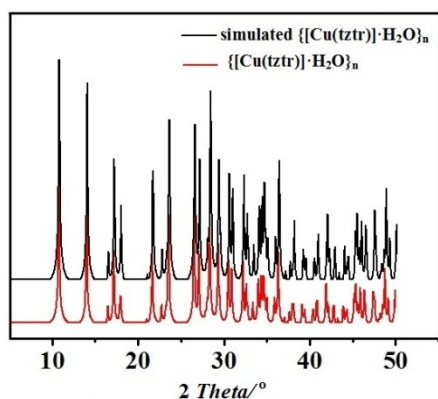
Fig. S5 X-ray powder diffraction (XRPD) curves of $\{[Cu(tztr)] \cdot H_2O\}_n$.
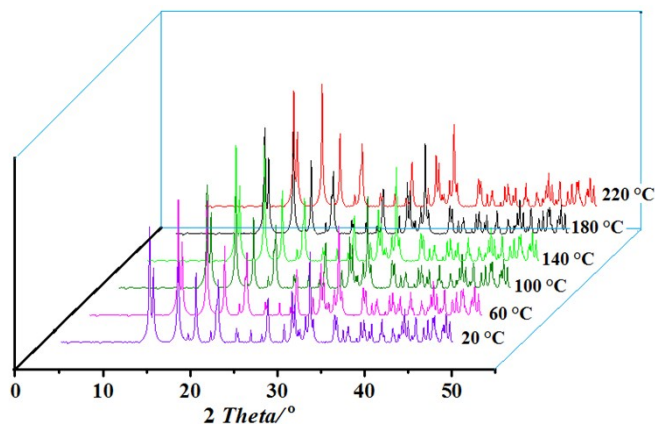
Fig. S6 Variable-temperature X-ray powder diffraction (XRPD) curves of **1**.

1. Instruments and reagents

All reagents used for the synthesis were purchased from commercial sources and used without further purification. Elemental analyses of C, H and N were performed on a Vario EL III analyzer. Infrared (IR) spectra were recorded on a Bruker FTTR instrument with KBr pellets (4000-400cm^{-1}). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a CDR-4P thermal analyzer of Shanghai Balance Instrument factory and a Netzsch STA 449C

instrument, respectively, using dry oxygen-free nitrogen as the atmosphere with a flowing rate of 10 mL·min $^{-1}$. The calorimetric experiment was performed by using a RD496-2000 type microcalorimeter.[1] Thermogravimetry-Fourier transform infrared spectrometry of the detonation products were carried out on a TG-209/Vector TM-22 instrument. The sensitivities to impact stimuli were determined by fall hammer apparatus applying standard staircase method using a 2 kg drop weight and the results were reported in terms of height for 50% probability of explosion ($h_{50\%}$).[2] The friction sensitivities were determined on a Julius Peter's apparatus by following the BAM method.[3] The purity of the bulk samples were verified by X-ray powder diffraction (XRPD) measurements performed on a Rigaku RU200 diffractometer at 60 kV, 300 mA and Cu Kα radiation (λ = 1.5406 Å), with a scan speed of 5°·min $^{-1}$ and a step size of 0.02° in 2θ. 1H NMR spectra was recorded on a Varian unity INOVA-400 instrument in [D6] DMSO at 25 ℃. The constant-volume combustion energy of the complex was determined using a precise rotating-bomb calorimeter (RBC-type II).

2. Synthetic procedures

General caution: H_2tztr and complexes are potentially explosive. Therefore, only small amounts of complexes should be prepared and they should be handled with care.

Synthesis of 3-(1*H*-tetrazol-5-yl)-1*H*-triazole (H_2tztr). 5-cyano-1*H*-1,2,4-triazole (2.24 g, 23.9 mmol), sodium azide (1.71 g, 26.3 mmol), and zinc chloride (4.0 g, 29.3 mmol) were suspended in water (120 mL) and the reaction mixture was refluxed for 16 h. After cooling to room temperature, 2M HCl (20 mL) were added to avoid precipitation of zinc hydroxide. The precipitate was collected by filtration, washed with water, and dried in air to yield 3-(1*H*-tetrazol-5-yl)-1*H*-triazole (Yield 85%, based on 5-cyano-1H-1,2,4-triazole) as colorless solid. For $C_3H_3N_7$ (137.08): C, 26.26; H, 2.18; N, 71.49%. Found: C, 26.23; H, 2.14; N, 71.40%. 1H NMR (400 MHz, [D6] DMSO, ppm): δ=8.88 (s, Htriazole/ tetrazole). IR (cm-1, KBr): 3453w, 3219s, 2973w, 1878m, 1616m, 1458s, 1340m, 1266s, 1224s, 1077m, 1035m, 947m, 801m, 699w, 626m, 482s.

Microcalorimetry of reaction system. The temperature calibration curve in the working range (20.0-200.0 ℃) was built on the basis of the melting points of references (gallium-indium-tin). A linear temperature programming mode (0.15 ℃ min^{-1}) was employed in the work. The H_2tztr, NaN_3 and $Cu(ClO_4)$ aqueous solution were placed into a stainless steel sample cell in separated 15 mL containers. The H_2tztr and NaN_3 aqueous solution was put into a small glass tube above the

Cu(ClO$_4$) aqueous solution which was in a larger one. After the establishment of equilibrium, the small glass tube with H$_2$tztr and NaN$_3$ aqueous solution was pushed down simultaneously, leading to the mixing of the two solutions. The change of thermoelectric power was recorded by means of a microcalorimeter to get the microcalorimetric heat flow curve.

Guided by the information of in situ microcalorimetry, we have obtained two complexes by means of hydro-thermal reaction as follows.

Synthesis of {[Cu(tztr)]·H$_2$O}$_n$. A mixture of H$_2$tztr (0.0133 g, 0.1 mmol) and Cu(ClO$_4$)$_2$ (0.02081 g, 0.1 mmol) and NaN$_3$ (0.0064g, 0.1 mmol) were dissolved in 8 mL water. The solution was put into a 15 mL Teflon liner, heated to 120 °C for 72h, and then cooled to room temperature at a rate of 5 °C·h^{-1}. The green prism-shaped crystals were obtained (Yield 61 %, based on Cu). The bulk materials of {[Cu(tztr)]·H$_2$O}$_n$ are measured by X-ray powder diffraction (XRPD), which is consistent with the reported complex in our group (X. Y. Liu, W. J. Gao, P. P. Sun, Z. Y. Su, S. P. Chen, Q. Wei, G. Xie and S. L. Gao. *Green Chem.*, 2015, **17,** 831-836).

Synthesis of [Cu(tztr)]$_n$ (1). A mixture of H$_2$tztr (0.0133 g, 0.1 mmol) and Cu(ClO$_4$)$_2$ (0.02081 g, 0.1 mmol) and NaN$_3$ (0.0064g, 0.1 mmol) were dissolved in 8 mL water. The solution was put into a 15 mL Teflon liner, heated to 160 °C for 72h, and then cooled to room temperature at a rate of 5 °C·h^{-1}. The black-blue rod-shaped crystals were obtained (Yield 43 %, based on Cu). Anal. Calcd. For CuC$_3$HN$_7$ (198.65): C, 18.14; H, 0.5074; N, 49.36%. Found: C, 18.13; H, 0.5065; N, 49.34%. IR (cm^{-1}, KBr): 3109w, 2925w, 2850w, 1508s, 1429s, 1389s, 1321m, 1283w, 1224m, 1176w, 1145m, 1090m, 1007m, 868w, 708m, 665m, 536w, 473w.

3. X-ray crystallography

For complex **1**, selected single crystals were performed on a Bruker Smart Apex CCD diffractometer equipped with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) using ω and φ scan mode. The single-crystal structure of **1** was both solved by direct methods and refined with full-matrix least-squares refinements based on F^2 using SHELXS 97 and SHELXL 97.[4,5] All non-hydrogen atoms were located using subsequent Fourier-difference methods. Hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms. Crystallographic data were summarized in table S1, and selected bond lengths and angles were showed in table S2.

Table S1. Crystallographic data   for **1**.

complex	**1**
Formula	$C_3 H Cu N_7$
Formula weight	198.65
T/K	296(2)
Crystal system	Orthorhombic
Space group	$Pbca$
a/Å	8.934(4)
b/Å	9.067(5)
c/Å	14.698(7)
α/°	90.00
β/°	90.00
γ/°	90.00
V/Å^3	1190.6(10)
Dcalc/(g/cm^3)	2.216
Z	8
Cystal size/mm	$0.23 \times 0.21 \times 0.18$
Measured data	6102
Unique data	1265
R_{int}	0.0956
θ Range (°)	2.77 to 26.77
$F(000)$	776
Absorption coefficient /mm	3.596
Final R indices [I>2sigma (I)]	$R_1 = 0.0446$ $wR_2 = 0.1101$
R indices (all data)	$R_1 = 0.0823$ $wR_2 = 0.1360$

Table S2. Selected bond lengths (Å) and bond angles (°) in **1**.

Cu(1)-N(1)	2.009(5)	Cu(1)-N(6b)	1.985(5)
Cu(1)-N(3a)	1.969(5)	Cu(1)-N(7)	2.314(5)
Cu(1)-N(5c)	2.027(5)		
N(1)-Cu(1)-N(5c)	86.8(2)	N(5c)-Cu(1)-N(7)	92.13(19)
N(1)-Cu(1)-N(7)	76.61(19)	N(6b)-Cu(1)-N(5c)	93.6(2)
N(3a)-Cu(1)-N(1)	90.1(2)	N(6b)-Cu(1)-N(7)	96.53(19)
N(3a)-Cu(1)-N(5c)	159.1(2)	N(6b)-Cu(1)-N(1)	173.1(2)
N(3a)-Cu(1)-N(6b)	92.0(2)		

Symmetry transformations used to generate equivalent atoms: a *-0.5+x, y,1.5-z*; b *1-x, 1-y, 1-z*; c *0.5-x, -0.5+y, z.*

4. Thermal decomposition

The curves of TG and DSC under the linear heating rate of 5 °C·min^{-1} with nitrogen atmosphere are shown in Figs. S7and S8 to demonstrate the thermal decomposition processes of **1**.

The thermostability of **1** was investigated using thermogravimetric analysis. As shown in Fig. S7, there is one step of mass loss from 360 °C to 398 °C. The curve for **1** shows weight loss found for 48.85% (the calculated is 49.87%), which means that **1** completely converts to the mixture of Cu (s) and C (s) with mass percentage of 49.88% (the calculated value is 50.13%). The abrupt curve of weight loss reveals the rapid release of energy, which correspond to the exothermic processes in the DSC curve (see Fig. S8). There is only one exothermic peak from 360 °C to 400 °C in the DSC curve.
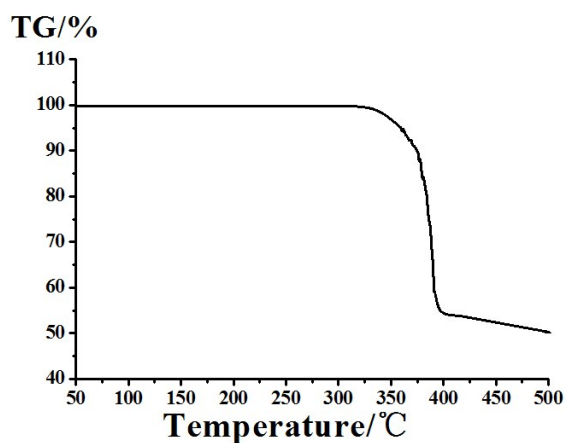

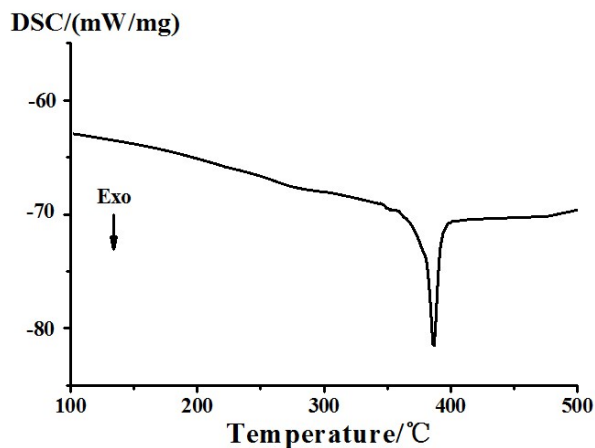**Fig. S7** TG curve of **1.**

Fig. S8 DSC curve of **1**.

5. Oxygen bomb calorimetry

The constant-volume combustion energies of the compounds were determined with a precise rotating-oxygen bomb calorimeter (RBC-type II).[6] Approximately 200 mg of the samples were

pressed with a well-defined amount of benzoic acid (calculated: 800 mg) 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. After six single measurements, the experimental result for the constant-volume combustion energies (Q_v) of **1** is -21854.69±6.79J g^{-1}. The combustion reaction of the complex **1** is equation (1).

$$CuC_3HN_7(s) + (15/4)O_2(g) \rightarrow CuO(s) + 3CO_2(g) + (1/2)H_2O\ (l) + (7/2)\ N_2\ (g) \tag{1}$$
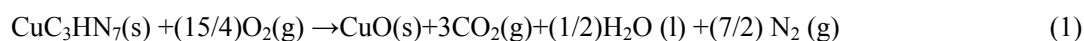
The standard molar enthalpy of combustion ($\Delta_c H_m^\theta$) is given by equation (2)

$$\Delta_c H_m^\theta = Q_p = Q_v + \Delta n_g RT \tag{2}$$

where Δn_g is the change in the number of gas constituents in the reaction process, R = 8.314 J mol^{-1} K^{-1}, T=298.15 K. So the standard molar enthalpy of combustion ($\Delta_c H_m^\theta$) can be calculated to be -4348.25±1.35kJ mol^{-1} for **1**. The standard molar enthalpy of formation of **1** was back-calculated from the energy of combustion on the basis of equation (1) and with the Hess law, as given in equation (3). With the known enthalpies of formation of CuO(s) (-156.06kJ mol^{-1}), CO_2 (g) (-393.51±0.13kJ mol^{-1}) and H_2O (l)(-285.83±0.04kJ mol^{-1}), [7] the standard enthalpy of formation ($\Delta_f H_m^\theta$) of **1** was calculated to be 2868.75 ±1.41 kJ mol^{-1} via equation (3). $\Delta_f H_m^\theta(CuC_3HN_7, s) =$

$$\Delta_f H_m^\theta(CuO, s) + 3\Delta_f H_m^\theta(CO_2, g) + (1/2)\Delta_f H_m^\theta(H_2O, l)$$

$$- \Delta_c H_m^\theta(CuC_3HN_7, s) \tag{3}$$

6. Detonation property

Heat of detonation, detonation velocity and detonation pressure are the most important parameters reflecting the performance of explosives, which can be estimated based on several empirical methods.[8] Herein, we use three different methods to evaluate the detonation properties of **1**.

1). EXPLO5 v6.01. Based on the calculated standard enthalpy of formation, the measured molecular formula and density at ambient temperature, the commercial program EXPLO5 v6.01[9] was employed to determine the detonation properties of **1**. The calculated heat of detonation, detonation velocity and detonation pressure for **1** are listed in table S4.

2). Kamlet-Jacobs (K-J) equations. On the basis of the largest exothermic principle proposed by

Kamlet-Jacobs, [10] we employed a new empirical method previously reported [11] to investigate the detonation properties of metal-containing explosives. As in ref.11, the new and efficient method, which employed the hypothesis of BKW equation and arbitrary theory of the Kamlet-Jacobs method, could be applied to perform calculation of the detonation properties. For systems with metals, the most stable products of detonation reaction were assumed under the constraints of stoichiometrically available oxygen.[12] For **1**, nitrogen, carbon, and ammonia were assumed to be the final products of decomposition of the organic part of the framework and the formation of metallic state was assumed to be governed by the deficiency of oxygen.[11] The complete detonation reaction considered is described by equation (4), and the detonation properties are calculated by Kamlet–Jacobs equations[10] (5-8) as follows:

$$CuC_3HN_7(s) \rightarrow Cu(s) + 3C(s) + (10/3)N_2(g) + 1/3NH_3(g) \tag{4}$$

$$D = 1.01\Phi^{1/2}(1+1.30\rho) \tag{5}$$

$$P = 1.558\Phi\rho^2 \tag{6}$$

$$\Phi = 31.68N(MQ)^{1/2} \tag{7}$$

$$Q = \frac{-[\Delta_f H_m^\theta(detonation\ products) - \Delta_f H_m^\theta(explosive)]}{formula\ weight\ of\ explosive}$$

(8)

where D is detonation velocity (km·s^{-1}). P is detonation pressure (GPa). Φ, N, M and Q are characteristic parameters of an explosive. N is moles of detonation gases per gram of explosive. M is average molecular weight of the gases. Q is chemical energy of detonation (kcal·g^{-1}). $\Delta_f H_m^\theta$ is the standard molar enthalpy of formation. ρ is density of explosive (g·cm^{-3}).

The N and M of detonation reaction are given by equations (9-10).

$$N = \frac{\sum n_g}{formula\ weight\ of\ explosive} = 0.01846\ mol.g^{-1} \tag{9}$$

$$M = \frac{\sum(n_g \times M_g)}{\sum n_g} = 27.012\ g.mol^{-1} \tag{10}$$

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. According to the known enthalpies of formation, including NH$_3$(g) (-46 kJ mol^{-1}), H$_2$O(g) (-242 kJ mol^{-1}), [7] and CuC$_3$H$_3$N$_7$O(s)(2868.75 kJ mol^{-1}),

the calculated heat of detonation (Q/ kcal·g^{-1}) for **1** is 3.761 kcal·g^{-1}(8.33 kcal·cm^{-3}). Utilizing the above equations (5-7), and the known values of N, M and Q, the detonation velocity and detonation pressure can be obtained (see table S4).

3). Density functional theory and Kamlet−Jacobs (K−J) equations. In order to give qualitative observations of explosive power of **1**, and compare with other energetic MOFs and classical energetic materials, density functional theory (DFT) is used to calculate the energy of detonation of the geometry-optimized structures ($\Delta E_{DFT, det}$). $\Delta E_{DFT, det}$ is defined as the difference between the energies of formation of the explosive and the detonation products, from which the heat of detonation (ΔH_{det}) is estimated by using a linear correlation equation ($\Delta H_{det} = 1.127\Delta E_{DFT,det} + 0.046$, r=0.968). [12] As in Ref. 13, the DFT calculation for energetic MOF was performed with the code DMOl3[14] under 3D periodic boundary conditions employing the Monkhorst–Pack multiple K-point sampling of the Brillouin zone[15] and the Perdew–Becke–Ezerhoff (PBE) exchange-correlation function.[16] The detonation reaction is described by equation (4), and the calculated parameters see table S3.

Table S3. Calculated parameters used in the detonation reaction for **1**

[Cu(tztr)]$_n$	Cu	N$_2$	C	NH$_3$	ΔE_{det}	ΔE_{det}	ΔH_{det}	ΔH_{det}
(hartree)	(hartree)	(hartree)	(hartree)	(hartree)	(hartree)	(kcal·g^{-1})	(kcal·g^{-1})	(kcal·cm^{-3})
-694.0932	-196.1132	-109.447	-37.738	-56.5045	1.1079	3.4997	3.9902	8.8418

Calculation processes of ΔE_{det} and ΔH_{det} are shown in the following:

$\Delta E_{DFT,det}$=-196.1132+3×(-37.738)+(10/3)×(-109.447)+(1/3)×(-56.5045)-(-694.0932)

      =1.1079 hartree =3.4997 kcal·g^{-1}

$Q = \Delta H_{det}$=1.127$\Delta E_{DFT,det}$ + 0.046=1.127×3.4997+0.046=3.9902 kcal·g^{-1}

$Q = \Delta H_{det}$=3.9902 kcal·g^{-1}×2.216 g/cm^3=8.8418 kcal·cm^{-3}

According to above equations (4-7), detonation pressure (P) and detonation velocity (D) of **1** are respectively calculated, and their values are shown in table S4.

Table S4. The detonation properties of **1**

complex	ρ^a (g·cm^{-3})	$\Delta_f H_m^{\theta\,b}$ (kJ mol^{-1})	N^c (mol·g^{-1})	M^d (g·mol^{-1})	Q^e (kcal·g^{-1})	Q^e (kcal·cm^{-3})	D^f (km·s^{-1})	P^g (GPa)
1	2.216	2868.75	0.01846	27.012	3.761 [h](14213.9kJ/kg) [h]	8.33 [h]	9.51 [h]	45.08 [h]
					3.9902 [i]	8.84 [i]	9.66 [i]	46.44 [i]
			-	-	3.397 [j]	7.53 [j]	8.429 [j]	40.02 [j]

[a] From X-ray diffraction. [b] Standard molar enthalpy of formation. [c] Moles of detonation gases per gram of explosive. [d] Average molecular weight of the gases per gram of explosive. [e] Heat of detonation. [f] Detonation velocity. [g] Detonation pressure. [h] Heat of detonation, detonation velocity, detonation pressure calculated using RBC-type II and K-J equations. [i] Heat of detonation, detonation velocity, detonation pressure calculated using DFT and K-J equations. [j] Heat of detonation,

detonation velocity, detonation pressure calculated using RBC-type II and EXPLO5 v6.01.

7. Sensitivity

Impact sensitivity is determined by Fall Hammer Apparatus. Twenty milligrams of **1** is compacted to a copper cap under the press of 39.2 MPa and is hit by 2 kg drop hammer, and the calculated value of h_{50} represents the drop height of 50% initiation probability. Friction sensitivity of **1** is measured by applying a Julius Peter's machine using 20 mg sample.

8. References

[1]   M. Ji, M.Y. Liu, S.L. Gao, *Instrum. Sci. Technol.*, 2001, **29**, 53-57.

[2]   R. Meyer, J. Köhler (Eds.), Explosives, 4th ed. Revised and extended, VCH Publishers, New York, 1993, 149.

[3]   R. Meyer, J. Köhler (Eds.), Explosives, 4th ed. revised and extended, VCH Publishers, New York, 1993, 197.

[4]   G. M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Determination, Göttingen University, Germany, 1997.

[5]   G. M. Sheldrick, SHELXL-97, Program for X-ray Crystal Structure Refinement, Göttingen University, Germany, 1997.

[6]   X. W. Yang, S. P. Chen, S. L. Gao, H. Li and Q. Z. Shi, *Instrum. Sci. Technol.*, 2002, **30**, 311-321.

[7]   D. R. Lide, Standard Thermodynamic Properties of Chemical Substances. CRC Handbook of Chemistry and Physics, Internet Version 2007, Taylor and Francis, Boca Raton, FL, 87th edn, 2007.

[8]   C. Shen, P. C.Wang, M. Lu. *J. Phys. Chem. A*, 2015, **119**, 8250-8255

[9]   M. Sućeska, EXPLO5 6.01, Brodarski Institute, Zagreb, Croatia, 2013.

[10] M. J. Kamlet, S. Jacobs, *J. Chem. Phys.*, 2003, **48**, 23-35.

[11] Y. Wang, J.C. Zhang, H. Su, S.H. Li, S.W. Zhang, S.P. Pang, *J. Phys. Chem. A*, **2014**, *118*, 4575–4581.

[12] O. S. Bushuyev, P. Brown, A. Maiti, R. H. Gee, G. R. Peterson, B. L. Weeks, L. J. Hope- Weeks, *J. Am. Chem. Soc.*, 2012, **134**, 1422-1425.

[13] S. Li, Y. Wang, C. Qi, X. Zhao, J. Zhang, S. Zhang and S. P. Pang, *Angew. Chem. Int. Ed.*, 2013, **52**, 14031-14035.

[14] B. J. Delley, *J. Chem. Phys.*, 1990, **92**, 508-517.

[15] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B*., 1976, **13**, 5188-5197.

[16] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.