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We report the synthesis of $\text{Zn}(\text{C}_6\text{H}_4\text{N}_5)\text{N}_3$, a new three-dimensional metal-organic framework (MOF) that exhibits strong energetic properties with high thermostability. The compound is synthesized by the hydrothermal method with in situ ligand formation under controlled pH. Structural characterization is carried out by single-crystal XRD, elemental analysis and FTIR. Energetic properties are obtained from TGA and DSC measurements. This novel MOF structure is thermally stable up to 345 C and its heat of detonation is -400\$ kJ/g. The measured velocity and pressure of detonation are 4.66 km/s and 9.99 GPa, respectively.

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Azide-based high-energy metal-organic framework with enhanced thermal stability

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Abstract

We report the synthesis of $[\text{Zn}(\text{C}_6\text{H}_4\text{N}_5)\text{N}_3]_n$, a new three-dimensional metal-organic framework (MOF) that exhibits strong energetic properties with high thermostability. The compound is synthesized by the hydrothermal method with *in situ* ligand formation under controlled pH. Structural characterization is carried out by single-crystal XRD, elemental analysis and FTIR. Energetic properties are obtained from TGA and DSC measurements. This novel MOF structure is thermally stable up to 345°C and its heat of detonation is $\Delta H_{\text{det}} = -400$ kJ/g. The measured velocity and pressure of detonation are 4.66 km/s and 9.99 GPa, respectively.

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I. INTRODUCTION

Metal-organic frameworks (MOF) have attracted great interest in material science due to the large combination of organic ligands and inorganic building blocks that can be used to produce novel crystalline structures with desired properties. This structural diversity has enabled applications in gas storage [1–3], gas separation [4–6], nonlinear optics [7–9], drug delivery [10–12], catalysis [13, 14] and sensing [15, 16]. More recently, high-energy metal-organic frameworks (HE-MOF) have emerged as promising energetic materials due to their facile synthesis, higher density, better thermal stability and superior mechanical strength in comparison with conventional energetic compounds [17], which tend to have low photo and thermal stability, and in some cases present an extreme sensitivity to involuntary initiation by friction, impact and sparks [18–22].

High-performance HE-MOFs should have a high density, elevated heat of detonation, insensitivity to mechanical stress, and high thermal stability [23–25]. High heats of detonation can be reached with nitrogen-rich compound, with large average bond energies: C–N (273 kJmol⁻¹), N–N (160 kJmol⁻¹), N=N (418 kJmol⁻¹) and N≡N (954 kJmol⁻¹) [17]. One promising main strategy to achieve this goal in HE-MOFs involves the use of five-membered nitrogen heterocycles as ligands. In particular, pyrazole and tetrazole molecules are promising choices due to their high heats of formation, elevated nitrogen content, stability, and multiple coordination sites with commonly used transition metal ions. Azido ligands can also be used to assemble HE-MOFs, introducing a N≡N bond into the structure. However, azido ligands frequently decrease the thermal stability of the material, lowering the energetic performance [26]. In order to increase the thermal stability of HE-MOF crystals with azido groups, three-dimensional coordination geometries offer better structural reinforcement than low-dimensional MOFs [26].

In this work, we synthesize the high-energy MOF $[\text{Zn}(\text{C}_6\text{H}_4\text{N}_5)\text{N}_3]_n$, which has 3-pyridyltetrazole and azido ligands in its structure. Azide and tetrazole groups are known for having multiple coordination modes [27, 28], which enables the assembly of a diverse set of MOF structures [29]. This increases the possibility of obtaining a stable three-dimensional MOF under common hydrothermal synthesis conditions. Second, these nitrogen-rich ligands have a high heat of formation, which favours the release of a large amount of heat upon combustion. Finally, 3-pyridyltetrazole ligands can be synthesized *in situ* in the presence

of azide, via a Demko-Sharpless reaction involving Zn^{2+} as a Lewis acid [30]. This strategy avoids sequential synthesis steps and the use of non-environmentally friendly solvents or commonly used heavy metal ions frequently used such as Pb^{2+} and Ag^+ .

II. EXPERIMENTAL

Caution

Although no explosive behaviour was observed during the preparation and handling of the reported energetic MOF, azido complexes are known to be potentially explosive. Small-scale synthesis is strongly encouraged. Manipulations must be carried out in a hood behind a safety shield. Eye protection and leather gloves must be worn at all times.

Materials and methods

The crystal structures of both solvates were determined by X-ray diffraction at 293 K. Data collection was done on a SMART CCD diffractometer using ϕ and ω -scans as the data collection strategy. Data sets were reduced using SAINT[31], while the structures were solved by direct methods and completed by Difference Fourier Synthesis. Least-squares refinement was conducted by using SHELXL[32]. (Multi-scan absorption corrections were applied using SADABS.[31]) The hydrogen atom positions were calculated after each cycle of refinement with SHELXL using a riding model for each structure, with a C–H distance of 0.93 or 0.97 Å. $U_{\text{iso}}(\text{H})$ values were set equal to 1.2 U_{eq} of the parent carbon atom. The thermogravimetric analyses were done on a Mettler Toledo modelo Star TGA/DSC 2 equipment. The TGA curves were registered in the 20-600°C range, using a 10°C/min heating rate under nitrogen atmosphere (40 mL/min). DSC experiment were performed at 1, 5, 10, 15 and 20°C/min. IR spectra was recorded on a Spectrum Two FT-IR Spectrometer. The elemental analyses were done on a FLASH 2000 CHN Analyzer equipment. Powder X-ray diffraction analysis was done using a Shimadzu XRD 6000 diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5418$ Å) radiation for structural characterization and phase determination. Calculated PXRD patterns were generated using Mercury 3.10. The constant-volumen energy of combustion was measured in a oxygen-bomb calorimeter (Parr 6200, Parr instruments Company, Illinois, USA) and using samples of 0.55 g according to UNE-EN 14918 standard for biosolid fuels. Finally, all

reactants were used without purification and the pHmeter employed was a pH 2700 Oakton. Textural properties were obtained from the adsorption-desorption isotherm of N₂ at 77K which was carried out using a Micromeritics 3Flex instrument. The sample was previously degassed 10 h at 413K under vacuum using a Micromeritic SmartVacPrep instrument. All gas-intake simulations were performed assuming a rigid MOF structure using the Grand Canonical Monte Carlo (GCMC) molecular simulation scheme on the software RASPA [33]. A 2x4x3 supercell for calculation was set to use a 12 Å cutoff for the intermolecular interactions in the system. Five thousand cycles of initialization and another five thousand for the actual ensemble average simulations were done totalizing 10,000 cycles. Partial atomic charges for the atoms of the framework were obtained by the charge equilibration method (QEq). Generic MOFs and Trappe force field definitions were employed for the MOFs atoms and the N₂ and CO₂ gases, respectively. Temperatures for the isotherms estimation were 77 K in the N₂ case and 274 K for CO₂.

Synthesis of Zn(3-ptz)N₃ (1)

All the reactants and chemicals were purchased from Sigma-Aldrich and utilized without further purification. A mixture of 3-cyanopyridine (4 mmol), NaN₃ (8 mmol), and Zn(CH₃COO) (8 mmol) were dissolved in 6 mL of distilled water. The pH value was adjusted by using HNO₃ (66%) until reaching pH in the range 2.7 – 2.8. The mixture was transferred into a glass bottle and then put in a box furnace at 105 ° C for 24 h. The as-synthesized materials were taken out of the furnace after 24 h, filtered, and dried at room temperature prior to the structural analysis. Elem. anal. Calcd (%) for Zn(C₆H₄N₅)N₃ (253.52): C, 28.49; N, 44.17; H, 1.57. Found: C, 27.89; N, 42.08; H, 1.50.

III. RESULTS AND DISCUSSIONS

Structural analysis

Single crystal X-ray diffraction shows that compound (1) possess a monoclinic crystal system and a C2/c spacegroup (see Table 1). The asymmetric unit is composed of a Zn atom, coordinated to both azide and 3-pyridyltetrazole molecules (Figure 1a). The zinc(II) cation presents a distorted trigonal bipyramidal orbital geometry, in which the nitrogens N1, N5 and

TABLE I: Crystallographic data for Zn(3-ptz)N₃

Empirical formula	Zn(C ₆ H ₄ N ₅)N ₃
Formula weight /g mol ⁻¹	253.52
Crystal system	Monoclinic
Space group	C2/c (N°15)
T /K	296
a /Å	20.519(4)
b /Å	7.6959(15)
c /Å	14.708(5)
beta/°	130.239(2)
Z	8
ρ_c /g cm ⁻³	1.900
$R(F)^a$	0.0219
$R_w(F^2)^b$	0.0563

$$a: R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$b: R_w(F^2) = [\sum_w (F_o^2 - F_c^2)^2 / \sum_w (F_o^2)^2]^{\frac{1}{2}}$$

N6 from tetrazolide, pyridyl and azido ligands, respectively, are displaced in the ecuatorial plane, involving a bond length ranging between 1.9837(16) and 2.0632(15)Å (see Table 2). Axial nitrogens N3 and N6 from azido and tetrazolide groups form coordination bonds with lengths in the range 2.1826(15) to 2.3585(16) Å. Figure 1b shows the presence of azido groups in the axial and ecuatorial positions leading to a symmetrical arrangement of two trigonal bipyrimidal units related by point symmetry and bonded through azido bridges by a μ -1,1 coordination mode. This structure shows a three-dimensional framework, in which the azido groups are oriented into the cavities when observed along the 010 direction (see Figure S1). Molecular dynamics modelling shows that compound (**1**) has a helium void fraction of 0.027, and is thus non-porous. This prediction was confirmed by performing N₂ gas adsorption experiments (ESI).

TABLE II: Selected geometrical parameters ($^{\circ}$, \AA) for $\text{Zn}(3\text{-ptz})\text{N}_3$

Zn1–N1	2.0233(16)
Zn1–N3 ⁱⁱ	2.1826(15)
Zn1–N5 ⁱ	2.0632(15)
Zn1–N6	1.9837(16)
Zn1–N6 ⁱⁱⁱ	2.3585(16)
N5 ⁱ –Zn1–N1	112.93(6)
N1–Zn1–N6	130.24(7)
N6–Zn1–N5	114.01(7)
N6–Zn1–N3 ⁱⁱ	97.83(6)
N6–Zn1–N6 ⁱⁱⁱ	77.18(7)

$i = x-1/2, -y+3/2, z-1/2$; $ii = -x+1/2, y+1/2, -z+1/2$; $iii = -x+1/2, y+3/2, -z$.

Thermal decomposition

Good thermal stability is a desired feature in energetic materials because low decomposition temperatures limit their performance in applications. In order to assess the thermal stability of **(1)**, we performed thermogravimetric (TG) and DSC analysis. The results are shown in figure 2. The TG curve shows that there is negligible mass loss up to 325°C , where about 49% of the initial weight is lost in an intense mass-loss process that occurs over a small temperature range. The DSC data shows a very intense exothermic peak at 345°C . In comparison with similar azide-based MOFs, such as $\text{Cu}(\text{DNBA})\text{N}_3$ [34] and $\text{Ag}_2(\text{ATZ})\text{N}_3$ [35], the detonation temperature of compound **(1)** is more than 65°C higher. In $\text{Ag}_2(\text{ATZ})\text{N}_3$, silver atoms coordinate with amino-tetrazole and azide ligands in a similar way as in **(1)**. However, the thermostability achieved in our work is better possibly due to a bipyramidal coordination environment, in contrast to the tetrahedral coordination geometry found in $\text{Ag}_2(\text{ATZ})\text{N}_3$. We compare the observed thermal stability found in compound **(1)** with common energetic materials.

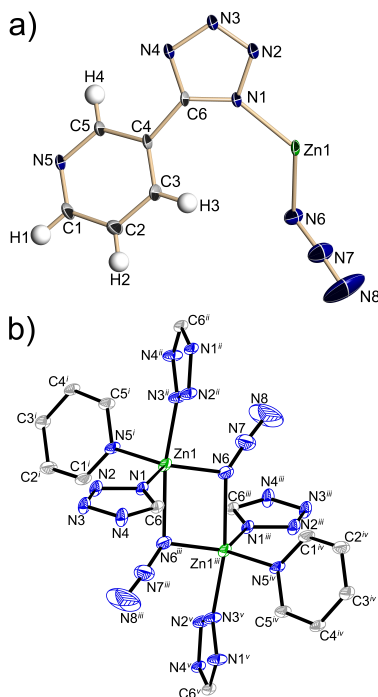
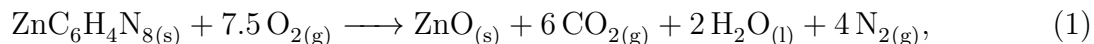


FIG. 1: (a) Thermal ellipsoid plot of asymmetric unit of compound (1) with the 50% of probability level while hydrogen atoms are drawn as sphere of arbitrary radii. (b) Thermal ellipsoid plot of symmetrical molecular arrangement. Hydrogens are omitted for clarity. Symmetry codes: (i): $1/2+x, 3/2-y, -1/2+z$; (ii): $1/2-x, 1/2+y, 1/2-z$; (iii): $1/2-x, 3/2-y, -z$; (iv): $1-x, y, 1/2-z$; (v): $x, 1-y, -1/2+z$.

Energy of combustion and enthalpy of formation

The constant-volume energy of combustion of (1) was measured to be (-3623 ± 15) kJmol^{-1} with a oxygen-bomb calorimeter. From $\Delta H = Q_p = Q_v + \Delta nRT$, we infer a bomb combustion equation of the form



giving an enthalpy of combustion $\Delta_c H = -3623 \text{ kJmol}^{-1}$, which is higher than commercial explosives such as TNT (-3406 kJmol^{-1})[36], RDX (-2120 kJmol^{-1}) and HMX (-2820 kJmol^{-1})[37]. This high enthalpy can be understood from the oxidation involved in the aromatic ring breaking. According to Hess law, the the enthalpy of formation can be calculated to give $\Delta_f H_{298}^\circ(\mathbf{1}, \text{s}) = 339 \text{ kJmol}^{-1}$ [45]

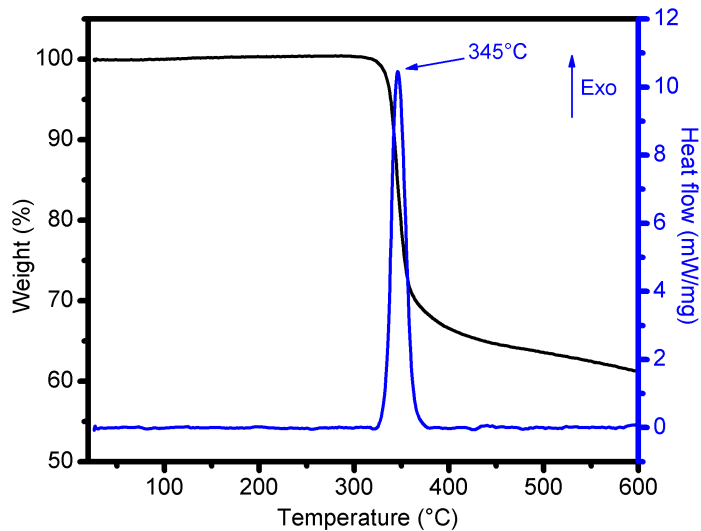


FIG. 2: Thermogravimetric and DSC curves of compound (1).

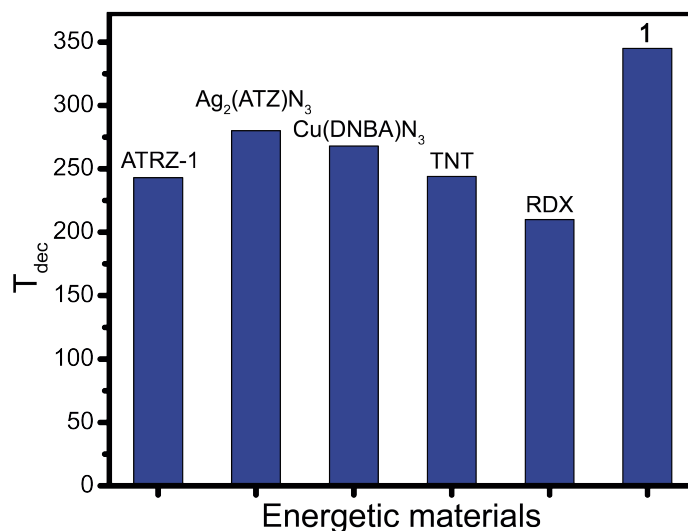


FIG. 3: Detonation temperature of different MOFs and commercial energetic materials, in comparison with compound (1)

Detonation parameters

The energy of detonation is one of the most important parameters used to evaluate the performance of an energetic material. According to the method proposed in refs. [38] and [39], the detonation reaction for compound (1) can be expressed as

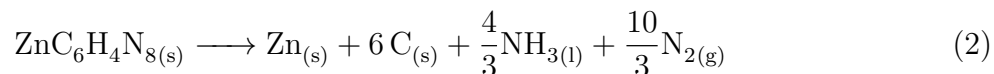


TABLE III: Physico-chemical properties of $\text{Zn}(\text{}_{298}\text{3-ptz})\text{N}_3$ and other energetic materials.

Compound	ρ^a (gcm^{-3})	N^b (%)	Ω^c (%)	T_{dec}^d ($^\circ\text{C}$)	$\Delta_f H_{298}^\circ$ (kJmol^{-1})	Q^e (kcalg^{-1})	D^f (km s^{-1})	P^g (GPa)
$\text{Zn}(\text{3-ptz})\text{N}_3$	1.900	44.20	-94.86	345	339	0.36	4.66	9.99
$\text{Cd}(\text{atz})_4(\text{N}_3)_2$	2.517	40.89	-40.33	372	1330	0.480	5.92	18.61
$\text{Ag}(\text{Mtta})$	2.995	29.34	-4.68	354	206	0.316	5.26	15.83
RDX	1.806	37.80	-21.60	210	93	1.44	8.91	34.1
TNT	1.654	18.50	-73.96	295	-67	1.22	7.18	20.50

^a Calculated by single X-ray diffraction. ^b Nitrogen content. ^c Oxygen balance. ^d Decomposition temperature. ^e Heat of detonation. ^f Detonation velocity ^g Detonation pressure. Mtta:

5-methyltetrazole. atz: 5-aminotetrazole.

We estimate the energy of detonation from the enthalpies of formation using the relation

$$\Delta H_{det} = \frac{\sum \Delta H_f(\text{products}) - \Delta H_f(\text{MOF})}{\text{MW}}, \quad (3)$$

where MW is the molecular weight of $\text{ZnC}_6\text{H}_4\text{N}_8$. The estimated enthalpy of detonation is -0.36 kcalg^{-1} (-400 kJg^{-1}). Additionally, using ΔH_{det} and the semi-empirical equations in ref. [38], the detonation velocity and detonation pressure of **(1)** are given by

$$D = 1.01 \left(NM^{\frac{1}{2}} Q^{\frac{1}{2}} \right)^{\frac{1}{2}} (1 + 1.30\rho) \quad (4)$$

and

$$P = 1.558N (MQ)^{\frac{1}{2}} \rho^2, \quad (5)$$

respectively. The detonation velocity D in eq. (4) is in units of km/s, and the detonation pressure P is in GPa. ρ is the density of the energetic material in g/cm^3 , N is the number of gaseous detonation products per gram of energetic material, M average of molecular weight of gases and Q is the combustion heat of the reaction in kcal/g. From eqs. (4) and (5) we obtain $D = 4.66 \text{ km/s}$ and $P = 9.99 \text{ GPa}$ (see also Table 3). These parameters are consistent with the relatively low energy of formation and low oxygen content of **(1)**, which decrease the enthalpy of detonation and the molar mass average of the gas products. Despite the low oxygen content, the obtained heat of detonation of **(1)** is higher than other energetic MOFs that have tetrazole ligands (e.g., $\text{Ag}(\text{Mtta})$) as well as other commercial explosives such as

mercury fulminate (1.735 kJg^{-1}), lead sthepnate (1.453 kJg^{-1}) [40] and lead azide (1.569 kJg^{-1}) [41].

Kinetics analysis

In order to study the kinetic behavior of (1), we perform DSC measurements at different heating rates $\beta = 1, 5, 10, 15$ and $20^\circ\text{C}/\text{min}$. The DSC peak displaces to higher temperatures as the β increases, until reaching a plateau for $\beta \geq 10^\circ\text{C}/\text{min}$. At the highest heating rates, additional smaller peaks peaks temperatures beyond the main decomposition temperature. The scaling of the decomposition temperature with β could not be fitted using the Kissinger and Ozawa-Doyle kinetic models for first-order reactions [42–44], which points out to a temperature-dependent multi-step decomposition mechanism.

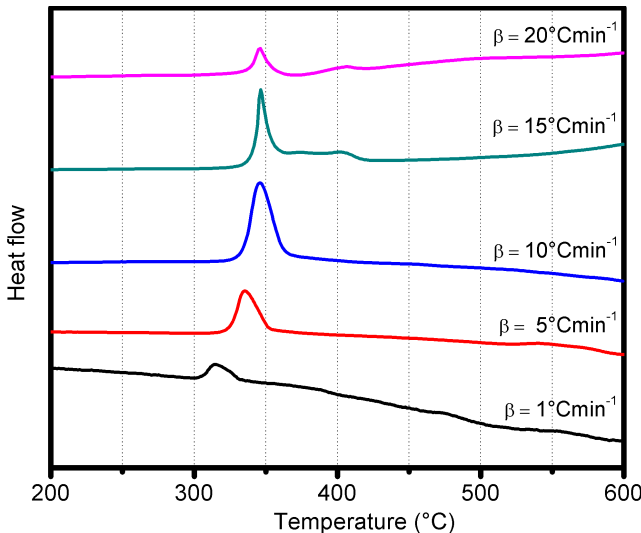


FIG. 4: DSC curves for different heating rates $\beta = 1, 5, 10, 15$ and $20^\circ\text{C}/\text{min}^{-1}$.

Conclusions

We report a new three-dimensional high energy MOF with excellent thermal stability up to 345°C that contains azido and tetrazole ligands in its structure. The compound is synthesized via a hydrothermal method with *in situ* ligand formation. The reported MOF exhibits a thermostability higher than typical explosives and other three-dimensional MOFs. The measured enthalpy of combustion is $\Delta_c H = -3623 \text{ kJ}/\text{mol}$, which exceeds the reported

values for TNT, RDX and HMX. The reported MOF has a moderate heat of detonation due to a relatively low oxygen content, but still higher than commercial explosives. The detonation velocity was found to be $D = 4.66$ km/s and the pressure of detonation $P = 9.99$ GPa. Finally, DSC measurements reveals that the kinetic behavior cannot be explained by Kissinger and Ozawa-Doyle models, indicating that complex decomposition mechanisms are promoted at high temperatures.

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