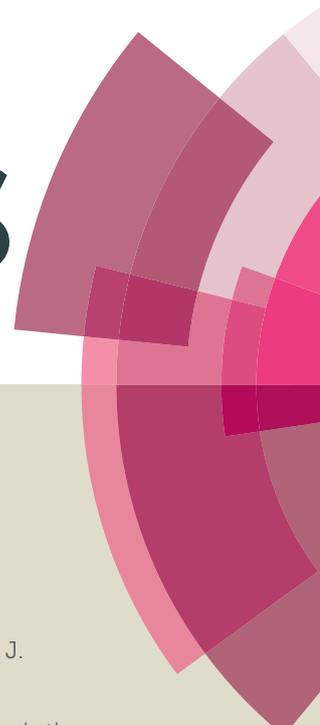


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High Performance 5-Aminotetrazole-based Energetic MOF and Its Catalytic Effect on Decomposition of RDX

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Abstract

An energetic metal-organic framework (EMOF) [Ag₂(5-ATZ)(N₃)] (**1**) was hydrothermally prepared and structurally characterized by single crystal X-ray diffraction analysis. **1** features a compacted three-dimensional framework structure and possesses the highest density ($\rho = 3.4 \text{ g cm}^{-3}$) in the known energetic compounds, in which each 5-ATZ ligand possesses μ_4 -1,2,3,4 coordination mode and each azide group adopts rare μ_4 -1,1,1,3 bridging mode. **1** exhibits considerably high thermal stability with the thermal decomposition temperature about 300.0 °C and insensitivity to external stimuli. Remarkably, the kinetic triplets (the apparent activation energy (E_a), the preexponential factor (A) and the mechanism function ($f(\alpha)$) are discussed in detail. In addition, the energetic performance and the catalytic effect of **1** on the thermal decomposition of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) were also examined.

Keywords: Energetic metal-organic framework (EMOF) / Energetic performance / Catalytic effect

Introduction

The past several decades have witnessed the rapid development of energetic metal-organic frameworks (EMOFs) not only ascribing to their intriguing architectures, but also the excellent energetic properties.^[1] In recent years, considerable efforts have been devoted to design and synthesis new-generation high-energy-density materials in order to balance the disharmony between sensitivity and heat of detonation, which closely relates to the compositions and inherent framework structures constructed by metal cations and energetic ligands.^[2]

Since the metal-based energetic compounds with different dimensionality are extensively studied, the relatively higher dimensional compounds have been demonstrated superior structural stability and detonation properties including high heat of detonation and insensitivity.^[3] From the perspective of the interior structure, the bonding modes of energetic ligands with metal cations play an extremely crucial role in achieving the dense gathering in a small space, aiming at enhancing the structure stability and energetic performance.^[4] As noticed, based on both energy and environment effects, energetic ligands among the energetic compounds previously reported were mostly focused on the furazan/triazole/tetrazole and their derivatives with -NH₂, -NO₂, -N₃ and -NNO₂ groups.^[5] Obviously, nitrogen-rich energetic ligands that nitrogen atoms potentially

were coordinated with metal cations to construct high dimensional energetic compounds, may greatly improve the detonation properties.

Although it is still challenging to construct high dimensional energetic compounds with these favored energetic groups, great progress has been achieved. In 2013, Pang *et al.*^[3a] synthesized two three-dimensional (3D) energetic compounds with 4,4'-azo-1,2,4-triazole (atrz) containing six potentially coordinating sites, $[\text{Cu}(\text{atrz})_3(\text{NO}_3)_2]_n$ and $[\text{Ag}(\text{atrz})_{1.5}(\text{NO}_3)]_n$, which show excellent energetic properties. Subsequently, our group^[3b] reported the synthesis and energetic characteristics of $[\text{Cu}(\text{Htztr})]_n$ with 3-(tetrazol-5-yl) triazole as ligand including seven potentially coordinating sites, exhibiting the highest heat of detonation among the known energetic compounds and common explosives. Recently, Zhang and co-workers^[3c] successfully encapsulated the energetic anions ($\text{N}(\text{NO}_2)_2^-$) in the known MOFs $[\text{Cu}(\text{atrz})_3(\text{NO}_3)_2]_n$ to obtain the energetic MOFs $\{\text{Cu}(\text{atrz})_3[\text{N}(\text{NO}_2)_2]_2 \cdot 0.46\text{H}_2\text{O}\}$ by one-step anion-exchange experiment at room temperature, which offers an effective strategy to develop new energetic materials. These above energetic compounds further promote the metal-based energetic compounds to serve as potential explosives with predictable structural stability and energetic properties.

Therefore, taking the nitrogen content and coordination chemistry into consideration, 5-amino-tetrazole (5-ATZ, $N = 82.3\%$) and azido groups come into our sight. Upon being deprotonated, the four electron-donating nitrogen atoms in 5-ATZ ring could be coordinated to metal cations, which is helpful for the construction of EMOFs.^[6] Moreover, the azido group has been attracting great interest both in magnetic science and energetic materials attributing from its diverse bridging modes^[7] and superior contribution to the enthalpy of formation.^[8] As anticipated, the target 3D energetic compound, $[\text{Ag}_2(5\text{-ATZ})(\text{N}_3)]$ (**1**), was obtained under the hydrothermal condition. Structural analysis illustrates that 5-ATZ and azido groups are bonded with Ag(I) cation *via* the dense stacking to yield a 3D framework structure. Thermal stability, the kinetic triplets (E_a , A and $f(\alpha)$), the self-accelerating decomposition temperature (T_{SADT}), the critical temperature of thermal explosion (T_b) and detonation performance are discussed in detail. Furthermore, the combustion catalytic effect of **1** on the thermal decomposition of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)^[9] was also measured, determining that **1** can effectively decrease the thermal decomposition of RDX down to 228.9 °C.

Experimental

General caution: 5-ATZ, NaN_3 , RDX and compound **1** are potentially explosives, and should be treated with more caution. Appropriate safety precautions such as protective clothing, safety glasses and face shields should be used, especially when the compounds are produced on a large scale. Only small amounts were used in our work.

Materials and methods

All the materials and reagents employed were commercially available and used without further purifications. The phase purity of the crystals and powder samples were verified by X-ray powder diffraction (XRPD) measurements carried out on a Rigaku RU200 diffractometer at 60 kV, 300 mA and Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), with a scan speed of 5° min^{-1} and a step size of 0.02° in 2θ . Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out by a CDR-4P thermal analyzer of Shanghai Balance Instrument factory and a Netzsch STA 449C instrument, respectively, by using dry oxygen-free nitrogen as the atmosphere, with a flowing rate of 10 mL min^{-1} . About 0.6 mg of sample was sealed in an aluminum pan in the temperature range of 25-500 °C for the TG and DSC experiments. The constant-volume combustion energies of the compounds were determined by a precise rotating-bomb calorimeter (RBC-type II).^[10] The sensitivity to impact stimuli was carried out by fall hammer apparatus applying standard staircase method by using a 2 kg drop weight and the results were reported in terms of height for 50% probability of explosion ($h_{50\%}$).^[11] The friction sensitivity was determined on a Julius Peter's apparatus by the BAM method.^[12]

Synthesis of $[\text{Ag}_2(5\text{-ATZ})(\text{N}_3)]$ (**1**)

A mixture of AgNO_3 (0.4 mmol), 5-ATZ (0.3 mmol), and NaN_3 (0.2 mmol) in 6 mL of distilled water was stirred for 30 min in air, and sealed in a Teflon-lined stainless steel autoclave (25 mL). Then the system was heated to 140 °C for 3 days under autogenous pressure and allowed to cool to room temperature at a rate of 3° C h^{-1} . Colorless needle-like single crystals were collected by filtration, washed sequentially with water and dried in air. Yield 50.8% based on Ag. Anal. calcd for $\text{Ag}_2\text{CH}_2\text{N}_8$ (%): H, 0.59; C, 3.53; N, 32.96. Found (%): H, 0.65; C, 3.49; N, 32.73; Main IR bands (cm^{-1}): 3430 s, 3334 m, 2926 m, 2854 m, 2632 m, 2033 s, 1619 m, 1535 m, 1493 m, 1377 m, 1319 m, 1235 m, 1157 m, 1050 m, 695 m, 611 m.

Results and discussion

Structural description

Compound **1** crystallizes in a form of colorless needles and single crystal X-ray diffraction experiment was performed at 153 K. The single crystal X-ray diffraction study has revealed that compound **1** crystallizes in the orthorhombic *Pbam* space group (Table S1). The asymmetric unit contains two crystallographically independent Ag(I) centres, one completely deprotonated 5-ATZ ligand and one azido group. Just having a glance at the present compound, the same coordination modes, geometry configuration of Ag(I) centre and 3D framework structure were reported previously by Zhang *et al.*^[6d] Although two Ag(I) centers are all four coordinated by four N atoms from two different 5-ATZ ligands and two different azido groups to complete a distorted tetrahedral geometry, the differences exist in the coordination environments as seen in Fig. 1a. The Ag-N bond lengths are in the range of 2.229(5) Å–2.501(8) Å, and the corresponding N-Ag-N angles range from 83.5(2)° to 150.3(3)°, which are very close to those of the known Ag-based compounds.^[13] The Ag1-N and Ag2-N bond lengths (Ag1–N 2.256(4) (N1, N1A), 2.383(5) (N4, N4A), Ag2–N 2.229(5) (N2, N2A), 2.496(7) (N4B) 2.501(8) (N6)) imply that N atoms of 5-ATZ ligand have stronger coordination interactions with the Ag2(I) atoms, while N atoms of azido group have stronger coordination interactions with the Ag1(I) atoms. The selected bond lengths and angles are listed in Table S2. In Fig. 1b, each 5-ATZ ligand features $\mu_4-1,2,3,4$ mode to bond four Ag(I) atoms forming a 1D $[\text{Ag}_2(5\text{-ATZ})]^+$ ribbon (Fig. 1c(top right)), and each azide group adopts rare $\mu_4-1,1,1,3$ bridging mode to connect four Ag(I) atoms, resulting in a 2D $[\text{Ag}_2(\text{N}_3)]^+$ layer (Fig. 1c(bottom right)). These two different units are further each other interlaced to generate a compacted 3D framework structure, as displayed in Fig. 1d.

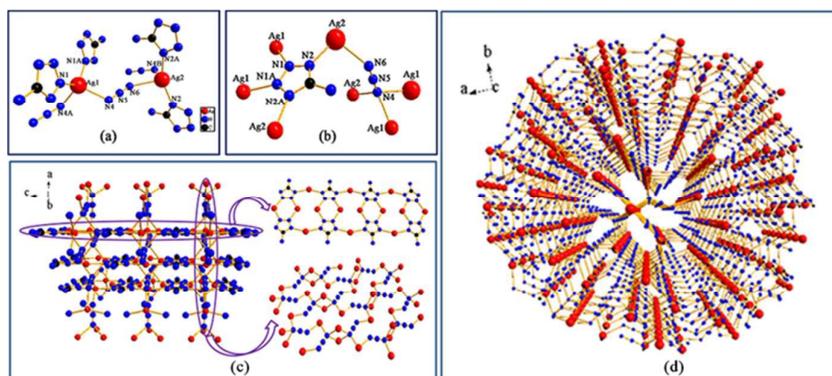


Fig. 1. (a) Coordination environment of Ag(I) centres; (b) coordination mode of 5-ATZ ligand and azido group; (c) (left) the 3D interleaving structure of **1**; (top right) the 1D $[\text{Ag}_2(5\text{-ATZ})]^+$ ribbon; (bottom right) the 2D $[\text{Ag}_2(\text{N}_3)]^+$ layer; (d) the 3D framework structure of **1**. (Hydrogen atoms are omitted for clarity)

Thermal decomposition and non-isothermal kinetics analysis of **1**.

TG and DSC experiments were performed with a linear heating rate of $5\text{ }^\circ\text{C min}^{-1}$ in N_2 gas flowing under a rate of 20 ml min^{-1} to explore the thermal stability of the title compound **1**. About 0.6 mg of sample was sealed in an aluminum pan in the temperature range of 25–500 $^\circ\text{C}$ for the TG and DSC experiments. As shown in Fig. S2, **1** undergoes one-step obvious weight loss from 295.3 $^\circ\text{C}$ to 318.7 $^\circ\text{C}$ corresponding to the whole collapse of the main frameworks shown in the TG curve and the intense exothermic process appears at 284.4 $^\circ\text{C}$ and ends at 336.2 $^\circ\text{C}$ with a peak temperature of 309.5 $^\circ\text{C}$ in the DSC curve, which implies that **1** possesses considerably higher thermal stability above 300.0 $^\circ\text{C}$ compared with 5-ATZ ligand (245.0 $^\circ\text{C}$),^[14] attributing to the inherently compacted 3D framework structure.

Significantly, the TG-DTG data under different heating rates (2, 5, 8 and 10 $^\circ\text{C min}^{-1}$) were collected in Table S3. In our present work, based on the iso-conversional kinetic method,^[15,16] the kinetic triplets (the apparent activation energy (E_a), the preexponential factor (A) and the mechanism function ($f(a)$, a is the degree of conversion/reaction)) are discussed in detail seen in Supporting Information. The T - a curves with different heating rates and E_a - a curves by using different methods are plotted in Fig. S3-S4. As shown in Ref. 15 and 16, the average E_a , $\log A$ and the linear correlation coefficient R are respectively 291.8 kJ mol^{-1} , 24.0402 s^{-1} and 0.9655 calculated by five kinetic analysis methods. The linear correlation coefficient R is very close to 1, proving that the results are extremely credible. Thus, the Arrhenius equation can be expressed as $\ln k = 55.2925 - 291.8 \times 10^3 / (RT)$, which can be used to estimate the rate constant (k) of the thermoexplosive process of **1** from the perspective of thermokinetics.

Furthermore, DSC curves with the heating rates of 2, 5, 8 and 10 $^\circ\text{C min}^{-1}$ were plotted in Fig. S6. The basic data of the main exothermic decomposition process for **1**, including the beginning temperature ($T_0/^\circ\text{C}$), extrapolated onset temperature ($T_e/^\circ\text{C}$), and peak temperature ($T_p/^\circ\text{C}$) under the different heating rates ($\beta/^\circ\text{C min}^{-1}$), are listed in Table 1. The self-accelerating decomposition temperature (T_{SADT}) and critical temperature of thermal explosion (T_b), are crucial parameters for energetic materials to guarantee the safety during use and storage. Based on the obtained T_0 , T_e

and T_p under different heating rate in DSC, these values of the initial temperature points (T_{00} , T_{e0} and T_{p0}) (corresponding to $\beta \rightarrow 0$), are calculated in Table 1 by the equations^[17] shown in Supporting Information. The T_{SADT} and T_b are further obtained respectively as 280.3 °C and 289.2 °C, signifying that **1** performs more excellent thermal stability in the process of thermal decomposition reaction than FOX-7 (206.0 and 207.1 °C)^[18] and $[\text{Cu}(\text{NH}_3)_4](\text{DNANT})_2$ (217.9 and 221.0 °C).^[17a]

Table 1. The thermokinetics parameters of the thermoexplosive processes at different heating rates.

β (°C min ⁻¹)	T_0 (°C)	T_e (°C)	T_p (°C)	T_{00} (°C)	T_{e0} (°C)	T_{p0} (°C)	T_{SADT} (°C)	T_b (°C)
2	263.6	284.4	302.3					
5	270.5	290.6	309.5	258.5	280.3	298.3	280.3	289.2
8	274.4	295.2	318.6					
10	277.2	298.9	325.3					

Detonation properties

As to the safety evaluation for **1**, the impact and friction sensitivities were carried out respectively. Impact sensitivity was measured by Fall Hammer Apparatus. Twenty milligrams of the title compound was compacted to a copper cap by 39.2 MPa press, then hit by 2 kg drop hammer. The calculated value of h_{50} shows in terms of height for 50% probability of explosion. The impact sensitivity value of **1** is measured to be 200 cm, corresponding to the impact energies of 40 J. No friction sensitivity is observed up to 360 N for **1**. This indicates that **1** features superior insensitive compared with other nitrogen-rich compounds due to the stable and compacted framework structure.

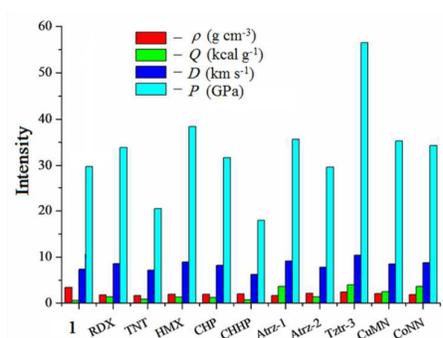


Fig. 2. Bar chart representation of the literature parameters for the common explosives and energetic compounds. (RDX = Hexogen;^[1a] TNT = Trinitrotoluene;^[1a] HMX = Octogen;^[1a] CHP = Cobalt hydrazine perchlorate;^[1a] CHHP = Cobalt hydrazine hydrazinecarboxylate perchlorate;^[2i] Atr-1 = Copper 4,4'-azo-1,2,4-triazole;^[3a] Atr-2 = Silver 4,4'-azo-1,2,4-triazole;^[3a] Tztr-3 = Copper 3-(tetrazol-5-yl) triazole;^[3b] CuMN = Copper melamine azide; Co = Cobalt 3-amine-1*H*-1,2,4-triazole azide^[2b].) Red for density ($\rho/\text{g cm}^{-3}$), green for heat of detonation ($Q/\text{kcal g}^{-1}$), dark blue for detonation velocity ($D/\text{km s}^{-1}$) and blue for detonation pressure (P/GPa)

A precise rotating-oxygen bomb calorimeter (RBC-type II)^[10] was used to investigate the constant-volume combustion energy of **1**. The detailed measurement process was shown in Supporting Information. The experimental value of the constant volume combustion energies ($\Delta_c U$) for **1** was $(-4522.45 \pm 2.47) \text{ J g}^{-1}$. Then the enthalpies of combustion ($\Delta_c H_m^0$) was calculated as $(-1539.46 \pm 0.84) \text{ kJ mol}^{-1}$ on the basis of the formula $\Delta_c H_m^0 = \Delta_c U_m^0 + \Delta n RT$, $\Delta n = n_g(\text{products}) - n_g(\text{reactants})$, (n_g is the total molar amount of gases in the products or reactants, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, $T = 298.15 \text{ K}$). Subsequently, according to combustion reaction equation, Hess's law (seen in Supporting Information) and the known enthalpies of formation of the combustion products^[19] $\text{Ag}_2\text{O}(\text{s})$, $\Delta_c H_m^0(\text{Ag}_2\text{O}, \text{s}) = -31 \text{ kJ mol}^{-1}$, $\text{CO}_2(\text{g})$, $\Delta_c H_m^0(\text{CO}_2, \text{g}) = (-393.51 \pm 0.13) \text{ kJ mol}^{-1}$, $\text{H}_2\text{O}(\text{l})$, $\Delta_c H_m^0(\text{H}_2\text{O}, \text{l}) = (-285.830 \pm 0.040) \text{ kJ mol}^{-1}$, the standard enthalpies of formation for **1** ($\Delta_f H_m^0$) is obtained as $(829.12 \pm 0.84) \text{ kJ mol}^{-1}$, evidencing that N-N, N=N bonds and azido group in structure make a decisive contribution to the enthalpy of formation of **1**.

For energetic compounds, heat of detonation ($Q/\text{kcal g}^{-1}$), detonation velocity ($D/\text{km s}^{-1}$) and detonation pressure (P/GPa) become pivotal reference points. In the current work, we adopted an empirical method to estimate the energetic properties of metal-based compounds containing Ag without depending on sophisticated computer programs.^[3a,19a] Based on the largest exothermic principle reported by Kamlet-Jacobs,^[20] the values of Q , D and P of **1** are respectively calculated as 0.6 kcal g^{-1} , 7.0 km s^{-1} and 29.5 GPa . The detailed detonation reaction and empirical Kamlet-Jacobs equations are described in Supporting Information. In terms of the calculated Q , it exhibits the extremely low heat of detonation compared with other known energetic compounds (Fig. 2), probably resulted from the little energy contribution of explosive products (just 3.5 %) as shown in the detonation reaction. And the relatively high D and P are probably attributed to the highest density (3.384 g cm^{-3}) determined by the compacted framework structure.

Catalytic effect on thermal decomposition of RDX

The catalytic effect of **1** on thermal decomposition of RDX was tested by DSC experiment

under the heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. Compound **1** and RDX were mixed at a mass ratio of 1: 3 and the sample mass were not exceeding 0.8 mg when measurement was performed. As depicted in Fig. 3, the compound **1** has one exothermic peak at $325.3\text{ }^{\circ}\text{C}$ with the whole collapse of the main frameworks. While pure RDX possesses one endothermic peak at $204.7\text{ }^{\circ}\text{C}$ corresponding to its melting and one exothermic peak at $246.4\text{ }^{\circ}\text{C}$ due to its decomposition.^[9] When mixing compound **1** with RDX, the mixture still occupies the endothermic peak at $204.7\text{ }^{\circ}\text{C}$ while the exothermal peak is reduced to $228.9\text{ }^{\circ}\text{C}$, probably attributing to the formation of the micron-scale or nanoscale metal silver when the decomposition reaction performs. This indicates that **1** can be used as an effective additive to accelerate the thermal decomposition of RDX.

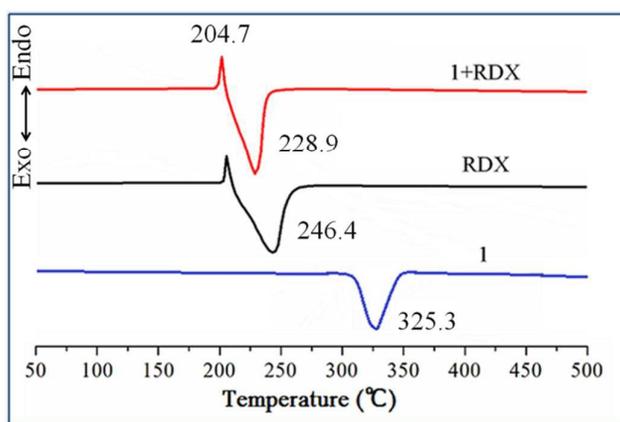


Fig. 3. DSC curves of the compound **1**, pure RDX and **1**+RDX mixed with a mass ratio of 1: 3 under the heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

Conclusions

In this work, a 3D Ag-based EMOF was successfully synthesized and structurally characterized ($N = 32.7\%$), verifying the compacted framework structure interlaced with the 1D $[\text{Ag}_2(5\text{-ATZ})]^+$ ribbon and 2D $[\text{Ag}_2(\text{N}_3)]^+$ layer.^[6d] Significantly, the compacted structure possesses the highest density ($\rho = 3.4\text{ g cm}^{-3}$) among the known EMOFs and good thermal stability with the decomposition temperature of $300.0\text{ }^{\circ}\text{C}$. The self-accelerating decomposition temperature and critical temperature of thermal explosion are respectively $280.3\text{ }^{\circ}\text{C}$ and $289.2\text{ }^{\circ}\text{C}$, further confirming the excellent thermal stability of **1**. The evaluated detonation properties reveal that **1** features the promising insensitivity, detonation velocity and detonation pressure attributing from the stable framework structure and superior density. However, the unsatisfied heat of detonation is

relatively low compared to the known explosives due to the little energy contribution of explosive products. Remarkably, **1** can accelerate effectively the thermal decomposition of RDX and make the decomposition temperature down to 228.9 °C. This work demonstrates that EMOFs with purposively selecting energetic ligands could effectively improve the detonation properties based on metal-induced coordination self-assembly.

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Graphical Abstract

Synopsis:

The energetic compound $[\text{Ag}_2(5\text{-ATZ})(\text{N}_3)]$ (**1**) features an impacted 3D framework structure and the highest density ($\rho = 3.4 \text{ g cm}^{-3}$) in the known energetic compounds. **1** possesses remarkable thermostability above $300 \text{ }^\circ\text{C}$, insensitivity, detonation velocity and detonation pressure (7.0 km s^{-1} and 29.5 GPa). Remarkably, **1** can accelerate effectively the thermal decomposition of RDX and make the decomposition temperature down to $228.9 \text{ }^\circ\text{C}$.

