

## Supporting Information

### **Ag(I) Energetic Metal-Organic Framework Assembled with the Energetic Combination of Furazan and Tetrazole: Synthesis, Structure and Energetic Performance**

**Xiao-Ni Qu,<sup>a§</sup> Sheng Zhang,<sup>a§</sup> Bo-Zhou Wang,<sup>b</sup> Qi Yang,<sup>a</sup> Jing Han,<sup>a</sup> Qing Wei,<sup>a</sup> Gang Xie,<sup>a</sup> and San-Ping Chen<sup>\*a</sup>**

<sup>a</sup> *Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an 710069, China.*

<sup>b</sup> *Xi'an Modern Chemistry Research Institute, Xi'an 710069, PR China.*

§ These authors have equal contribution to this work.

**\*Corresponding author**

**Prof. Sanping Chen**

**Tel.: +8602988302604**

**Fax: +8602988302604**

**E-mail: [sanpingchen@126.com](mailto:sanpingchen@126.com)**

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## 1.1. Chemicals and Equipments

All reagents were purchased commercially and used without further purification. Elemental analyses were carried out with an Elementar Vario EL III analyzer. IR spectra were recorded with a Tensor 27 spectrometer (Bruker Optics, Ettlingen, Germany). <sup>13</sup>C NMR spectra were recorded on a 500 MHz (Bruker AV500) nuclear magnetic resonance spectrometer operating at 300 MHz, by using DMSO-d<sub>6</sub> as solvent and locking solvent unless otherwise stated. Mass spectra were obtained on a GCMS-QP2010 instrument by using the EI<sup>+</sup> method. TG and DSC analysis was conducted on a Netzsch STA 449C instrument with the linear heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα, 1.5418 Å). The sensitivity to impact stimuli was determined by the standard staircase method applying fall hammer apparatus with a 2 kg drop weight. The results were reported in terms of height for 50% probability of explosion (*h*<sub>50%</sub>).<sup>[1]</sup> The friction sensitivity was determined on a Julius Peter's apparatus by following the BAM method.<sup>[2]</sup> The constant-volume combustion energy of the compound was determined with an RBC-type II rotating-bomb calorimeter.<sup>[3]</sup>

## 1.2. Synthesis the related compounds

### 1.2.1. Synthesis of 4'-oxybis[3,3'-(1*H*-5-tetrazol)]furazan (H<sub>2</sub>BTFOF)<sup>[4, 5]</sup>

#### Synthesis of 3-Cyano-4-nitrofurazan (CNNF)

Sodium tungstate dihydrate Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (66.0 g, 0.22 mol) was added to the H<sub>2</sub>O<sub>2</sub> (50%) (600.0 g, 8.8 mol) solution and stirred at -15 °C in an ice salt bath. Then, concentrated sulfuric acid (880.0 g, 8.8 mol) was slowly added (about 50 min) to the mixture under 5 °C. Subsequently, the temperature was heated up to 12 °C, and CNAF (22.0 g, 0.2 mol) was added in batches. After the mixture had been stirred for 2 h at 15 °C, the solution was extracted four times with dichloromethane (300 mL x 4), the combined organic phases were washed with caustic and water. The organic layer was dried with anhydrous magnesium sulfate. After removal of the solvent in vacuum, the pure pale yellow liquid (18.1 g, 64.6%, based on CNAF) was obtained. <sup>13</sup>C NMR (DMSO-d<sub>6</sub>), δ: 163.15, 130.76, 106.13. IR (KBr, cm<sup>-1</sup>): 2265, 1542, 1355, 1580, 1463, 1033. Anal. Calcd. for C<sub>3</sub>N<sub>4</sub>O<sub>3</sub> (140.07): C, 25.71; H, 0.00; N, 40.00. Found: C, 25.63; H, 0.02; N, 39.59.

#### Synthesis of 3,3'-Dicyanodifurazanyl ether (FOF-2)

CNNF (14.0 g, 0.1 mol) and anhydrous sodium carbonate (8.5 g, 0.08 mol) were dissolved in anhydrous acetonitrile (980 mL), and slowly heated to 78 °C. After the mixture had been stirred for 6 h, the light yellow precipitate (10.5g) was collected by filtration at room temperature. The ethanol (20 mL) was used to completely dissolve the precipitate, and for separating out product 140 mL water was added to the solution. The white solid was collected on a filter. After removal of the solvent in vacuum, the white solid (8.6 g, 84.3%, based on CNNF) was obtained. <sup>13</sup>C NMR (DMSO-d<sub>6</sub>), δ: 162.19, 127.34, 106.11. IR (KBr, cm<sup>-1</sup>): 2268, 1560, 1253, 1030. Anal. Calcd. for C<sub>6</sub>N<sub>6</sub>O<sub>3</sub> (204.53): C, 41.18; H, 0.00; N, 35.29. Found: C, 41.18; H, 0.00; N, 35.36.

#### Synthesis of 4,4'-oxybis[3,3'-(1*H*-5-tetrazol)]furazan (H<sub>2</sub>BTFOF)

FOF-2 (0.55 g, 2.7 mmol), 25 mL deionized water, NaN<sub>3</sub> (0.50 g, 7.7 mmol), and ZnCl<sub>2</sub>·2H<sub>2</sub>O (0.46 g, 2.7 mmol), were mixed and refluxed 4 h in flask. Cooling to room temperature, 10% of dilute hydrochloric acid was dropped into the mixture until pH=1. The solution was extracted with the ethyl acetate extract (15 mL x 4) and the combined organic phases were dried with anhydrous magnesium sulfate. The solvent was removed in vacuum, the light yellow solid were obtained. The crude product was recrystallized with water to give white solid (0.41 g, 76%, based on FOF-2). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>), δ: 161.23, 147.02, 139.22. IR (KBr, cm<sup>-1</sup>): 3453, 1592, 1238, 1048. Anal. Calcd. for C<sub>6</sub>H<sub>2</sub>N<sub>12</sub>O<sub>3</sub> (290.16): C, 24.83; H, 0.69; N, 57.93. Found: C, 25.19; H, 0.97; N, 57.43. MS (EI), m/z (%): 247 (0.53), 232 (1.87), 204 (8.53), 137 (11.17), 69 (18.07), 30 (100.00).

#### 1.2.2. Synthesis of [Ag<sub>16</sub>(BTFOF)<sub>9</sub>]<sub>n</sub>·[2(NH<sub>4</sub>)]<sub>n</sub> (**1**)

A mixture of AgNO<sub>3</sub> (0.0510 g, 0.3 mmol), H<sub>2</sub>BTFOF (0.0145 g, 0.5 mmol) and NH<sub>3</sub>·H<sub>2</sub>O (60 μL) in H<sub>2</sub>O (6 mL) was sealed in a 10 mL Teflon-lined stainless autoclave and heated at 130 °C under autogenous pressure for 3 days, then cooled at the rate of 5 °C h<sup>-1</sup> to room temperature. The colorless crystals of **1** were isolated by filtrating, washing with aqueous methanol solution. (yield 42%, based on Ag). Anal. Calcd for C<sub>54</sub>H<sub>8</sub>Ag<sub>16</sub>N<sub>110</sub>O<sub>27</sub> (4355.62): C, 14.88; N, 35.36; H, 0.18 %. Found: C, 15.11; N, 35.52; H, 0.29 %. Main IR (KBr, cm<sup>-1</sup>): 2356w, 2132w, 1646s, 1534s, 1393s, 1207m, 1076w, 1029w, 992s, 880m, 684m, 761m, 515m.

**Table S1.** Selected bond lengths (Å) and angles (°) for **1**.

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**Compound 1**

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Ag(1)-N(1)#1	2.265(7)	N(7)-Ag(1)-N(2)	96.0(3)
Ag(1)-N(4)#2	2.331(6)	N(8)#2-Ag(2)-N(8)#3	87.5(3)
Ag(1)-N(7)	2.342(8)	N(8)#2-Ag(2)-N(8)	87.5(3)
Ag(1)-N(2)	2.391(7)	N(8)#3-Ag(2)-N(8)	87.5(3)
Ag(2)-N(8)#2	2.457(8)	N(8)#2-Ag(2)-N(3)#3	92.0(3)
Ag(2)-N(8)#3	2.457(8)	N(8)#3-Ag(2)-N(3)#3	90.3(2)
Ag(2)-N(8)	2.457(8)	N(8)-Ag(2)-N(3)#3	177.8(3)
Ag(2)-N(3)#3	2.481(6)	N(8)#2-Ag(2)-N(3)#2	90.3(2)
Ag(2)-N(3)#2	2.481(6)	N(8)#3-Ag(2)-N(3)#2	177.8(3)
Ag(2)-N(3)	2.481(6)	N(8)-Ag(2)-N(3)#2	92.0(3)
N(1)-Ag(1)#1	2.265(7)	N(3)#3-Ag(2)-N(3)#2	90.2(2)
N(4)-Ag(1)#3	2.331(6)	N(8)#2-Ag(2)-N(3)	177.8(3)
N(1)#1-Ag(1)-N(4)#2	127.1(3)	N(8)#3-Ag(2)-N(3)	92.0(3)
N(1)#1-Ag(1)-N(7)	122.2(3)	N(8)-Ag(2)-N(3)	90.3(2)
N(4)#2-Ag(1)-N(7)	97.6(3)	N(3)#3-Ag(2)-N(3)	90.2(3)
N(1)#1-Ag(1)-N(2)	110.2(2)	N(3)#2-Ag(2)-N(3)	90.2(2)
N(4)#2-Ag(1)-N(2)	97.2(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z    #2 -x+y+1,-x+1,z    #3 -y+1,x-y,z

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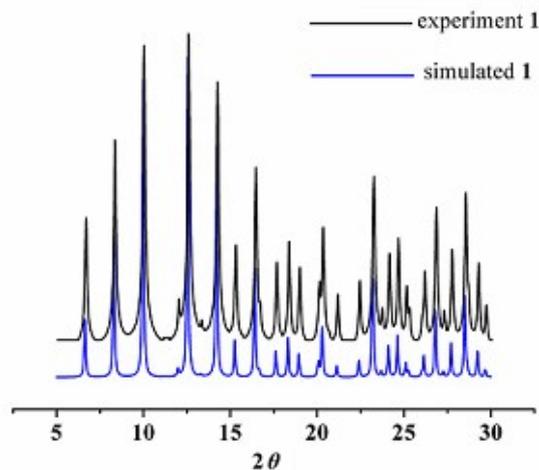


Figure S1. PXRD curve of **1**.

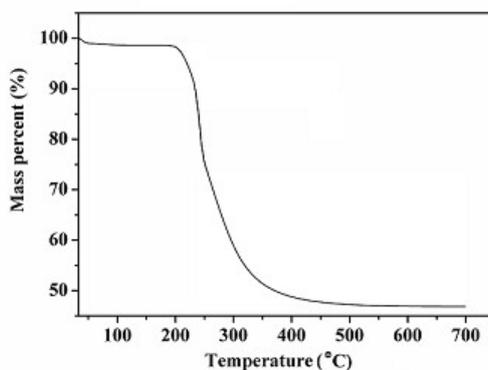


Figure S2. TG curve of **1**.

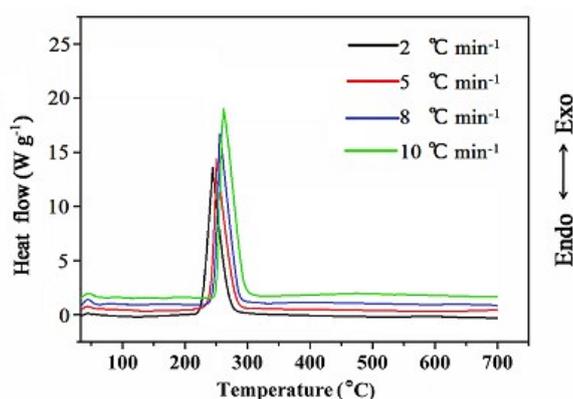


Figure S3. DSC curves of **1** under different heating rates.

### 1.3 The detection of the ammonium cations

The crystals of **1** were put into a tube with aqueous solution of potassium hydroxide. A mixed solution was boiled. Furthermore, a filter paper was soaked by Nessler's reagent<sup>[6]</sup> and put in the tube mouth to detect the escape of gas from the mixed solution. The color of filter changes into yellow, indicating the existence of the ammonium cations.

### 1.4 Non-isothermal kinetics

In this work, we employed Kissinger's method<sup>[7]</sup> and Ozawa-Doyle's method<sup>[8,9]</sup> to perform the apparent activation energy ( $E$ ) and the pre-exponential factor ( $A$ ), which could be applied to estimate the thermokinetics stability of **1**. The Kissinger equations (1) and Ozawa equations (2)

are as follows, respectively.

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\frac{AR}{E} - \frac{E}{RT_p} \quad (1)$$

$$\log\beta + \frac{0.4567E}{RT_p} = C \quad (2)$$

where  $T_p$  is the peak temperature ( $^{\circ}\text{C}$ );  $A$  is the pre-exponential factor ( $\text{s}^{-1}$ );  $E$  is the apparent activation energy ( $\text{kJ mol}^{-1}$ );  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ );  $\beta$  is the linear heating rate ( $^{\circ}\text{C min}^{-1}$ ) and  $C$  is a constant.

According to the exothermic peak temperatures measured at four different heating rates of 2, 5, 8 and  $10 \text{ }^{\circ}\text{C min}^{-1}$ , the thermokinetics parameters of exothermal processes for **1** was investigated by Kissinger and Ozawa-Doyle methods. It is obvious that the exothermic peaks,  $T_p$ , shift to higher temperatures as the heating rate increases and the kinetic parameters for the thermal decomposition reactions of the solid materials are in the normal ranges.<sup>[10,11]</sup> Additionally, the calculated  $E$  values using both methods are quite close, and the obtained the values of  $E_a$  (the average of  $E_k$  and  $E_o$ ) are  $275.04 \text{ kJ mol}^{-1}$  for **1**. Especially, the linear correlation coefficients  $R$  are very close to 1 and thus it is proved that the results are extremely credible. On the basis of the calculated values of  $E_a$  and  $\ln A$ , the Arrhenius equations can be expressed as follows:  $\ln k = 25.5880 - 275.035 \times 10^3 / (RT)$  for **1**, which can be used to estimate the rate constants of the thermal decomposition processes of compound **1**.

The values ( $T_{00}$ ,  $T_{e0}$  and  $T_{p0}$ ) of the initial temperature point corresponding to  $\beta \rightarrow 0$  are obtained by equation (3).<sup>[12]</sup> Especially, two considerably important parameters, the self-accelerating decomposition temperature ( $T_{\text{SADT}}$ ) and critical temperature of thermal explosion ( $T_b$ ), are necessary for energetic compounds in order to ensure the safety during storage and operations. The equations (4) and (5) are applied to obtain the values of  $T_{\text{SADT}}$  and  $T_b$  for **1**. The  $T_{\text{SADT}}$  and  $T_b$  are respectively  $228.2$  and  $241.2 \text{ }^{\circ}\text{C}$ , revealing more perfect thermal stability in the exothermic decomposition stage than common explosives and the known energetic compounds.

$$T_{(0, e \text{ or } p)i} = T_{(00, e0 \text{ or } p0)i} + n\beta_i + m\beta_i^2 \quad i = 1 - 4 \quad (3)$$

$$T_{\text{SADT}} = T_{e0} \quad (4)$$

$$T_b = \frac{E_0 - \sqrt{E_0^2 - 4E_0RT_{e0}}}{2R} \quad (5)$$

The entropies of activation ( $\Delta S^\ddagger$ ), enthalpies of activation ( $\Delta H^\ddagger$ ), and free energies of activation ( $\Delta G^\ddagger$ ) of **1** can be calculated from equations (6)-(8)<sup>[12]</sup> corresponding to  $T = T_{po}$ , and  $A = A_k$ , which are the crucial parameters in the main exothermic decomposition reaction. The  $\Delta S^\ddagger$ ,  $\Delta H^\ddagger$ ,  $\Delta G^\ddagger$  of **1** are respectively 240.49 J mol<sup>-1</sup> K<sup>-1</sup>, 270.78 kJ mol<sup>-1</sup>, 147.59 kJ mol<sup>-1</sup>, which reveal that **1** is thermo-kinetically inert and the exothermic decomposition reaction of **1** would occur in the heating condition.

$$A = \frac{k_B T}{h} e^{\Delta S^\ddagger / R} \quad (6)$$

$$\Delta H^\ddagger = E - RT \quad (7)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (8)$$

where  $k_B$  is the Boltzmann constant and  $h$  is the Planck constant.

## 1.5 Sensitivity test

Impact sensitivities were determined by Fall Hammer Apparatus. Twenty milligrams of two compounds were compacted to a copper cap under the press of 39.2 MPa, and were hit by 2 kg drop hammer, and the calculated values of  $h_{50}$  represent the drop height of 50% initiation probability. The impact sensitivity value of **1** is measured to be 200 cm, which correspond to the impact energies of 40 J.

Friction sensitivities of two compounds were measured by applying a Julius Peter's machine using 20 mg sample. No friction sensitivities are observed up to 36 kg (360 N) for **1**.

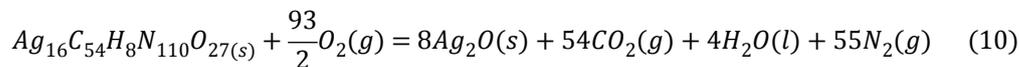
## 1.6 Oxygen bomb calorimetry

The constant-volume combustion energies of **1** was investigated by a precise rotating-oxygen bomb calorimeter (RBC-type II).<sup>[3]</sup> Approximately 200 mg of the samples were pressed with a well-defined amount of benzoic acid (Calcd. 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. The experimental constant volume combustion energies ( $\Delta_c U$ ) of **1** is  $(-7505.04 \pm 1.43)$  J g<sup>-1</sup>, from which the standard molar combustion enthalpy ( $\Delta_c H_m^\theta$ ) of **1** can be calculated as being  $(-32534.17 \pm 6.23)$  kJ mol<sup>-1</sup> by the equation (9). The combustion

reaction equation is listed as equation (10):

$$\Delta_c H_m^\theta = \Delta_c U + \Delta n RT \quad (9)$$

where  $\Delta n = n_g(\text{products}) - n_g(\text{reactants})$ , ( $n_g$  is the total molar amount of gases in the products or reactants,  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $T = 298.15 \text{ K}$ ).

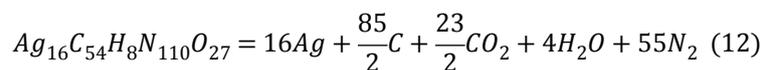


$$\Delta_f H_m^\theta(s) = 8\Delta_f H_m^\theta(Ag_2O,s) + 54\Delta_f H_m^\theta(CO_2,g) + 4\Delta_f H_m^\theta(H_2O,l) - 4\Delta_c H_m^\theta(1,s) \quad (11)$$

Based on the calculated enthalpies of combustion and known enthalpies of formation of the combustion products<sup>[11]</sup> determined experimentally,  $Ag_2O(s)$ ,  $\Delta_c H_m^\theta (Ag_2O, s) = (-31) \text{ kJ mol}^{-1}$ ,  $CO_2 (g)$ ,  $\Delta_c H_m^\theta (CO_2, g) = (-393.51 \pm 0.13) \text{ kJ mol}^{-1}$ ,  $H_2O (l)$ ,  $\Delta_c H_m^\theta (H_2O, l) = (-285.830 \pm 0.040) \text{ kJ mol}^{-1}$ , the standard enthalpy of formation of **1**,  $\Delta_f H_m^\theta$ , was back-calculated from the combustion equations.<sup>[13]</sup> On the basis of Hess's law in thermochemical equation (11), the standard enthalpy of formation ( $\Delta_f H_m^\theta$ ) of **1** is calculated as  $(9893.31 \pm 8.45) \text{ kJ mol}^{-1}$ .

## 1.7 Heat of detonation

In the current work, on the basis of the largest exothermic principle proposed by Kamlet-Jacobs,<sup>[14]</sup> we employed a new empirical method previously reported<sup>[15]</sup> to investigate the energetic performances of metal-containing explosives without depending on sophisticated computer programs. As in ref. 15, the new and efficient method, which employed the hypothesis of BKW equation and arbitrary theory of the K-J method, could be applied to perform the detonation performances of metal compounds containing special elements such as Cd and Ag. The Kamlet-Jacobs equations and detonation reaction of **1** are as shown in equation (12-15).<sup>[15]</sup> Furthermore, the heat of detonation value ( $Q/J \text{ g}^{-1}$ ) of **1** was calculated as  $0.8535 \text{ kcal g}^{-1}$ .



$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \quad (13)$$

$$P = 1.55\rho^2NM^{1/2}Q^{1/2} \quad (14)$$

$$Q = \frac{-[\Delta H_f(\text{detonation products}) - \Delta H_f(\text{explosive})]}{\text{formula weight of explosive}} \quad (15)$$

The detonation pressure ( $P$ ) and detonation velocity ( $D$ ) of compound **1** were calculated to be  $65.29 \text{ GPa}$  and  $11.81 \text{ km s}^{-1}$  by Kamlet-Jacobs (K-J) equations.

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