Supporting Information

New Method Synthesis of Urazine and Self-crystallization of Its Ag(I)-based Laser Energetic Coordination Polymers

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Experimental Section

Caution!

The new substances and raw materials used in the article are all potentially explosive materials. Although we did not encounter any danger in the process of handling these compounds during the synthetic procedure , the necessary protective equipment (leather gloves, face mask) is strongly recommended.

Materials and Equipments

During the experiment, the reagents (analytical grade) used were purchased from Aladdin and Titan and used without further purification. Single crystal X-ray diffraction data was collected by using Rigaku supernova single X-ray diffractometer area detector ($Mo_{K\alpha'}$, 0.71073 Å). Powder X-ray diffraction (PXRD) data of the product was tested using a Bruker D8 ADVANCE X-ray powder diffractometer ($Cu_{K\alpha'}$, 1.5418 Å). The thermal behavior of the compound was analyzed by differential scanning calorimeter (TGA/DSC2, METTLER TOLEDO STAR ^{e} system), with the heating rate was 5 $K \cdot min^{-1}$, and the gas atmosphere was N_2. Infrared (IR) spectra were measured on a Nicolet Is10 spectrometer (Equipped with KBr discs) with a measurement range of 4000 - 400 cm^{-1} . Elemental analyses (C,H,N or C,H,N,S) were carried out on an elemental analyzer (Vario EL Cube, Germany). The mechanical sensitivities (including impact sensitivity and friction sensitivity) of the material were determined by the standard step method of the drop weight device with a BAM DFH-10 device with a weight drop of 10 kg. The constant pressure reaction heat is measured by High Pressore Oxygen Calorimeter (BCA$^{@}$ 500), with the standard molar combustion enthalpy can be converted by the combustion equation. The experimental density is obtained by the powder densitometer test (Micromeritics AccuPyc II 1340). The morphologies and surface appearance of the samples were characterized using field emission scanning electron microscopy (FESEM, S-4800, Hitachi). The laser performance test is measured by Diode Laser (Changchun laser technology co., LTD. LR-ISP-980/1~1000mW. Spectral Line width (nm): < 3, Output Power (mW): 1~1000, Beam Diameter at Aperture (mm): 5.0 x 5.0, Modulating Repetition: 100KHz TTL / 10KHz Analogue).

Synthesis of hydrazodicarboxylate (2)

Diethyl hydrazodicarboxylate is commercially available and can also be prepared. 17.4 g (100 mmol) of diethyl azodicarboxylate (**1**) was added dropwise to a 250 ml reaction flask containing 100 ml water, and 5.88 g of 85 % hydrazine hydrate solution was slowly added. The reaction was carried out at room temperature for 2 h. After the reaction was completed, the reaction solution was placed in a refrigerator at 5 °C for 3 h to obtain white needle-like crystals. Suction filtration, washing with cold water, and drying to obtain 15.4 g of the target product (**2**) (yield 87.5%).

Synthesis of H_2ur (3)

Method 1: 1.62 g (30 mmol) of sodium methoxide was dissolved in 50 ml of anhydrous methanol. 5.28 g (30 mmol) of compound **2** were weighed and dissolved in the above reaction solution, and then 7 g of hydrazine hydrate (85 %) was slowly added. The white intermediate product Hur^{-} (**3'**) can be obtained by refluxing for 8 h. After the reaction was completed, white solid was obtained by filtration, and the solid was washed with anhydrous methanol. Then, the solid was dissolved in 30

mL of water, and concentrated hydrochloric acid was added to adjust the pH < 3 to obtain a large number of columnar crystals. The reaction solution was placed in a refrigerator at 4 °C for 5 hours, filtered and washed to obtain 2.32 g of the target product H2ur (**3**) (yield 66.7 %).

Method 2: 1.62 g (30 mmol) of sodium methoxide was dissolved in 50 mL of anhydrous methanol. 5.22 g (30 mmol) of diethyl azodicarboxylate (**1**) was weighed and dissolved in the above reaction solution. Keep the temperature below 25 °C and slowly add 9 g of 85% hydrazine hydrate. The white intermediate product Hur^- (**3'**) can be obtained by refluxing for 8 h. The subsequent operation steps were the same as Method 1 (yield 60.6%). IR (KBr, ν/cm-1): 3332(s), 3001(m), 2794(m), 1740(m), 1673(s), 1487(s), 1246(s), 954(s), 781(s), 754(s), 671(s), 648(m). MS (ESI), m/z: 115.03 [C2H3N4O2-]. Elemental analysis (%) for C2H4N4O2 (Mr = 116.03 g mol-1): calcd. C 20.68, H 3.45, N 48.26; found C 20.71, H 3.41, N 48.14.

Synthesis of $Ag(H_2ur)NO_3$ (powder, 4)

Dissolve 10 mmol (1.16 g) H_2ur in 30 ml of 85 °C water, and consider it as solution A. Dissolve 10 mmol (1.67 g) of $AgNO_3$ in 5 ml of water, which is regarded as solution B. B was slowly added dropwise to A to obtain a large amount of white precipitate. The precipitate was filtered and dried to obtain 2.4 g of product. IR (KBr, ν/cm-1): 3221(m), 3077(m) 1712(s), 1655(s), 1607(s), 1455(s), 1416(s), 1343(s), 1283(s), 1092(s), 837(s), 758(s).

Synthesis of $Ag(H_2ur)NO_3$ (crystals, 5)

Method 1: Suspend 2.4 g of 4 in 20 ml of water at 85 °C, then add concentrated nitric acid to dissolve it until the solution is clear. Filter while hot to obtain mother liquor, cool and slowly volatilize and crystallize to obtain Ag(H2ur)NO3. Yield: 53.6 % (based on H2ur).

Method 2: In step of synthesizing 4, when B is added dropwise to A and a large amount of white precipitate is obtained, concentrated nitric acid solution can be directly added to dissolve the precipitate. The next steps are the same as method 1. Yield: 52.4% (based on H2ur). IR (KBr, ν/cm-1): 3221(m), 3077(m) 1712(s), 1655(s), 1607(s), 1455(s), 1416(s), 1343(s), 1283(s), 1092(s), 837(s), 758(s).

Oxygen bomb calorimetry

The constant pressure reaction heat ($\Delta_C U$) of **5** was measured by an oxygen bomb calorimeter, and the average value was obtained by three measurements independently. The standard molar combustion enthalpy ($\Delta_C H^\theta_m$) can be obtained from the constant pressure reaction heat ($\Delta_C U$) according to the equation 1. According to the principle of Hess' law, the complete combustion reaction equation of **5** were shown in equation 2 and 3, and the standard molar generation enthalpy ($\Delta_f H^\theta_m$) can be obtained based on the formulas 2, 3 and 4 [CO_2(g): -393.51 kJ mol^{-1}; Ag_2O(s): -30.56 kJ mol^{-1}; H_2O(l): -285.85 kJ mol^{-1}]. The final experimental results showed that the combustion heats of **5** is -726.9 kJ mol^{-1}.

$$\Delta cH^\theta m = \Delta cU + \Delta nRT \quad (1)$$

$\Delta_n = n_g$(products)-n_g(reactants), (n_g is the sum of the total moles of gas in the product or reactant, R = 8.314 J mol^{-1} K^{-1}, T = 298.15 K)

$$C_2H_4N_5O_5Ag(s) + \frac{3}{4}O_2(g) = 2CO_2\,(g) + 2H_2O(l) + \frac{5}{2}N_2(g) + \frac{1}{2}Ag_2O(s) \quad (2)$$

$$\Delta_f H^\theta m(compound) = \sum \Delta_f H^\theta m(products) - \Delta_c H^\theta m(compound) \quad (3)$$

The oretical simulation based on K-J equations

Detonation speed (D) and explosion pressure (P) are the main indicators for measuring energetic materials. The various detonation characteristics of the ECPs were predicted using the modified Kamlet-Jacbos (K-J) equations (eq 5-7) which is a commonly used equation for predicting the detonation velocity and pressure of high energy materials.

$$C_2H_4N_5O_5Ag(s) = \frac{3}{2}CO(g) + 2H_2O(g) + \frac{5}{2}N_2(g) + \frac{1}{2}CO_2 + \frac{1}{2}AgO(s) \quad (4)$$

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \quad (5)$$

$$P = 1.55\rho^2 NM^{1/2}Q^{1/2} \quad (6)$$

$$Q = \frac{-[\Delta H_f(detonation\ production) - \Delta H_f(explosive)]}{formulaweightof\ explosive} \quad (7)$$

D: detonation velocity, km s^{-1}); P: detonation pressure, GPa; ρ: density, g cm^{-3}; ΔH_f: heat of formation, kJ mol^{-1}); Q: heat of detonation, J g^{-1}); N: moles of detonation gases per gram of explosive, mol g^{-1}); M: average molecular weight of gases, g mol^{-1})

Hot needle (HN) tests

Approximately 20 mg of the compound was dispersed on the operating table in a powdered state. The tiny iron needle is heated, and then slowly approached the compound, while recording the deflagration process of the compound with a high-speed camera.

Laser performance test

Weigh 10 mg samples, a total of 5 parts, and place them in sample tubes. Use a semiconductor laser to trigger the sample. Determine the minimum trigger energy by adjusting the action time and power.. Take the average value as the final test value.

Supplementary Figures S1-S9

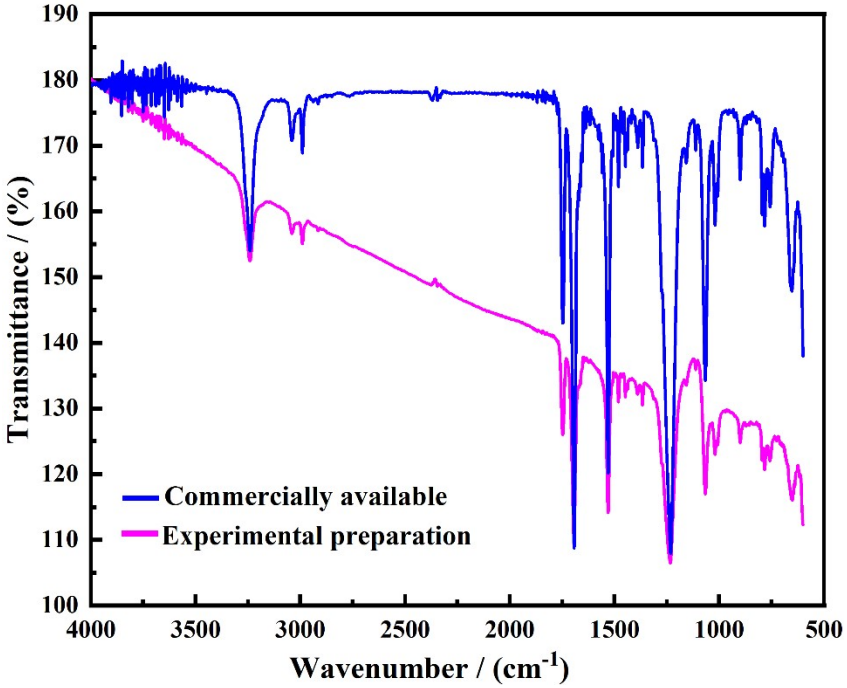

Figure S1 Infrared spectra of diethyl hydrazodicarboxylate.

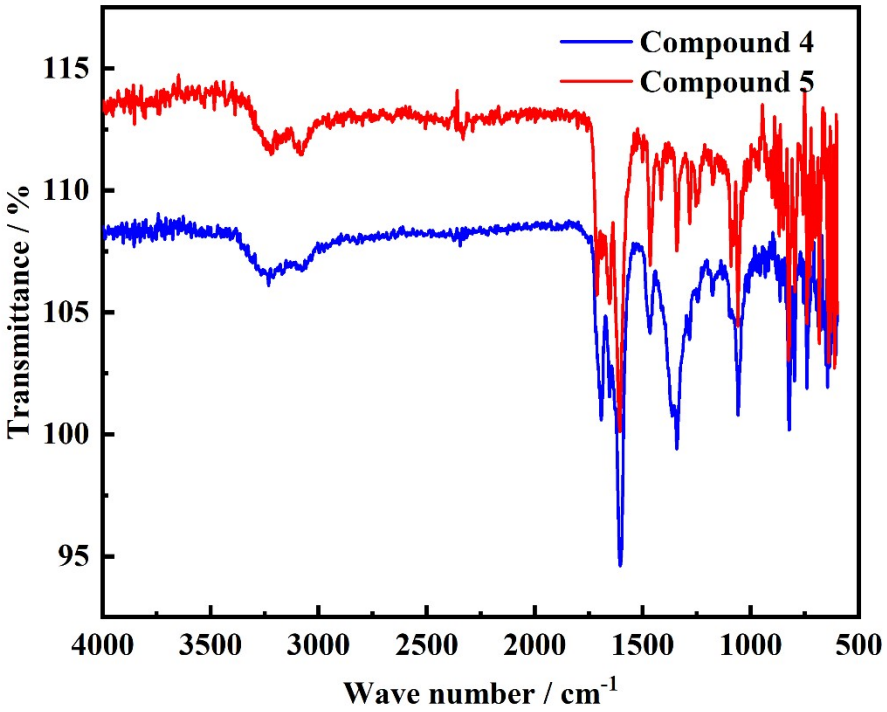

Figure S2 Infrared spectra of compounds **4** and **5.**

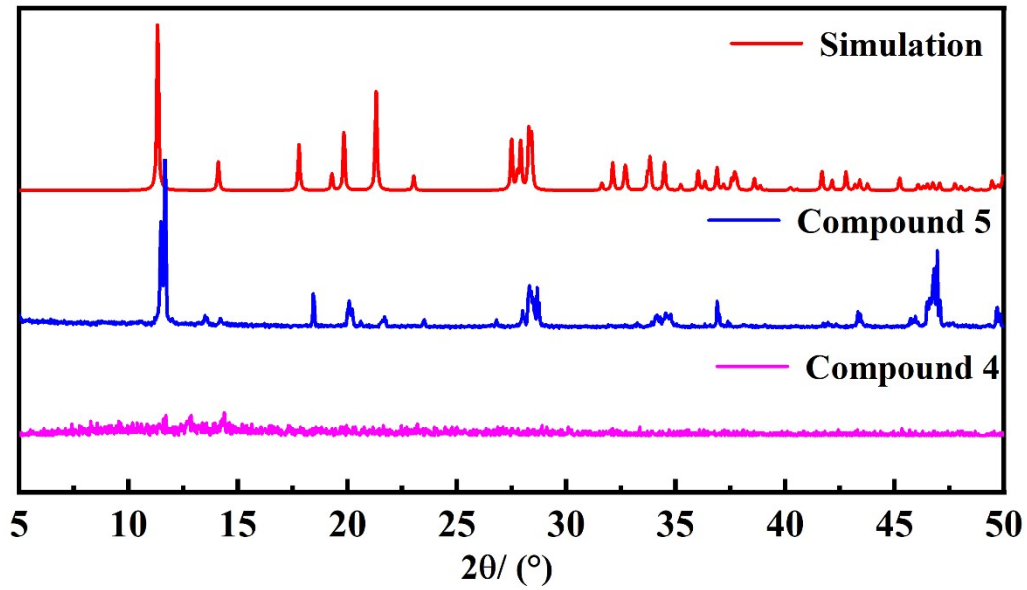

Figure S3 Comparison of single crystal and powder X-ray diffraction of **4** and **5**

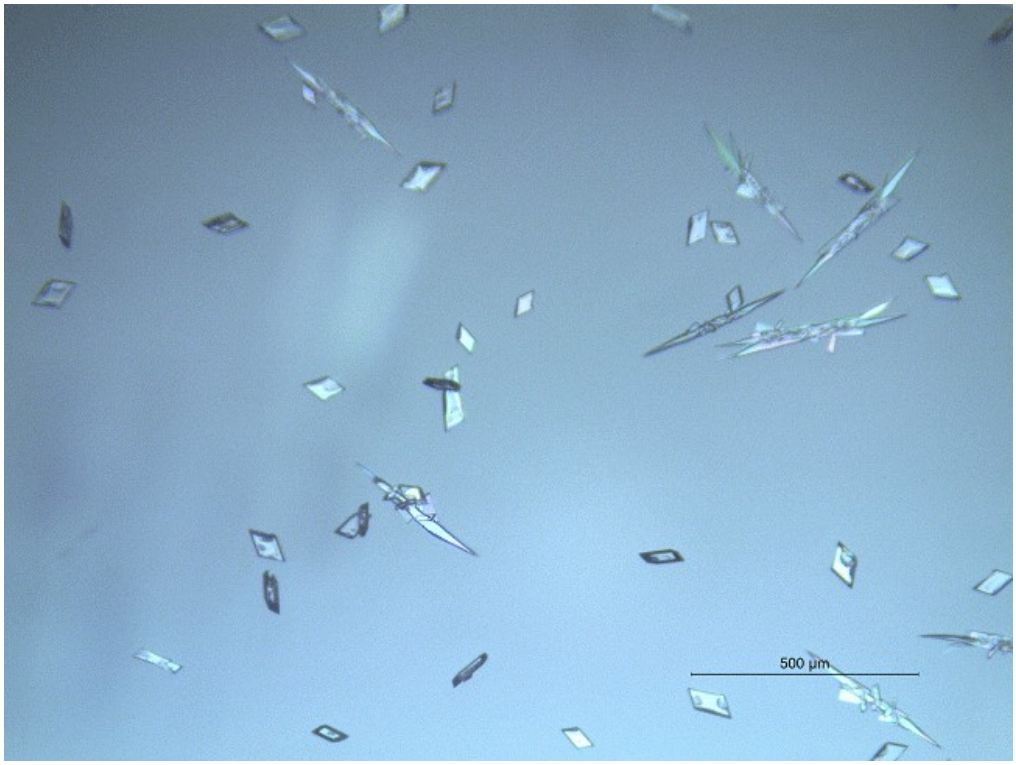

Figure S4 Self-crystallization process of **3** under the control of perchloric acid.

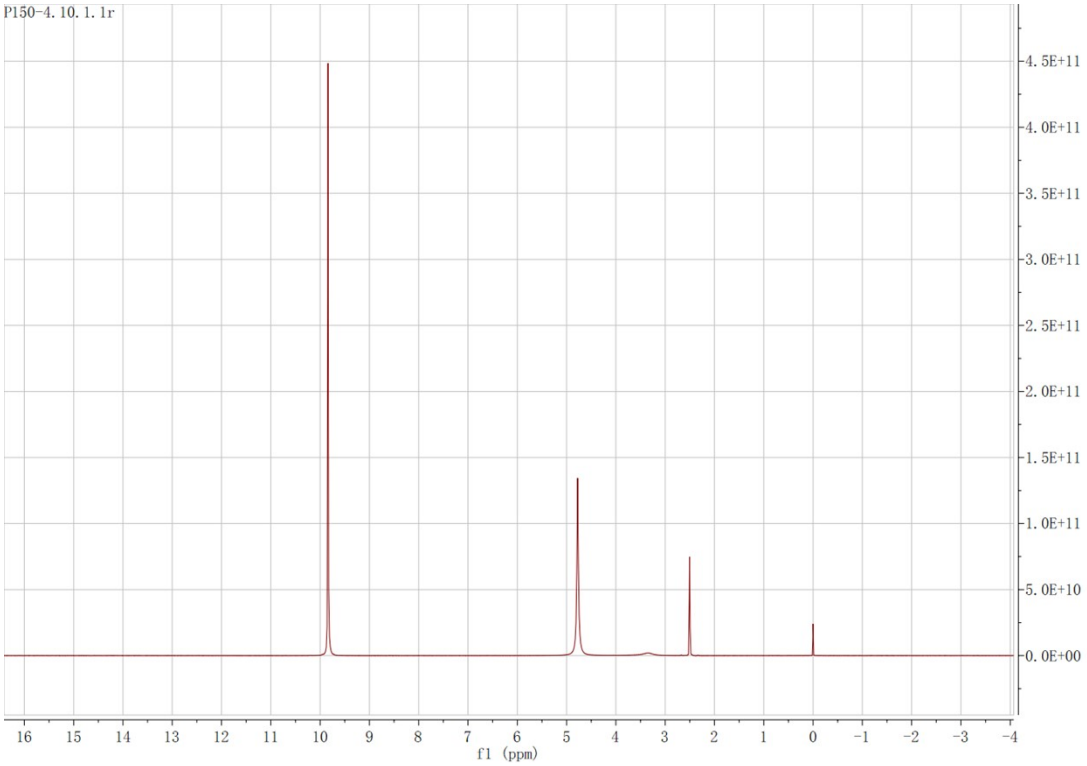

Figure S5 ^{1}H NMR spectra of H_2ur

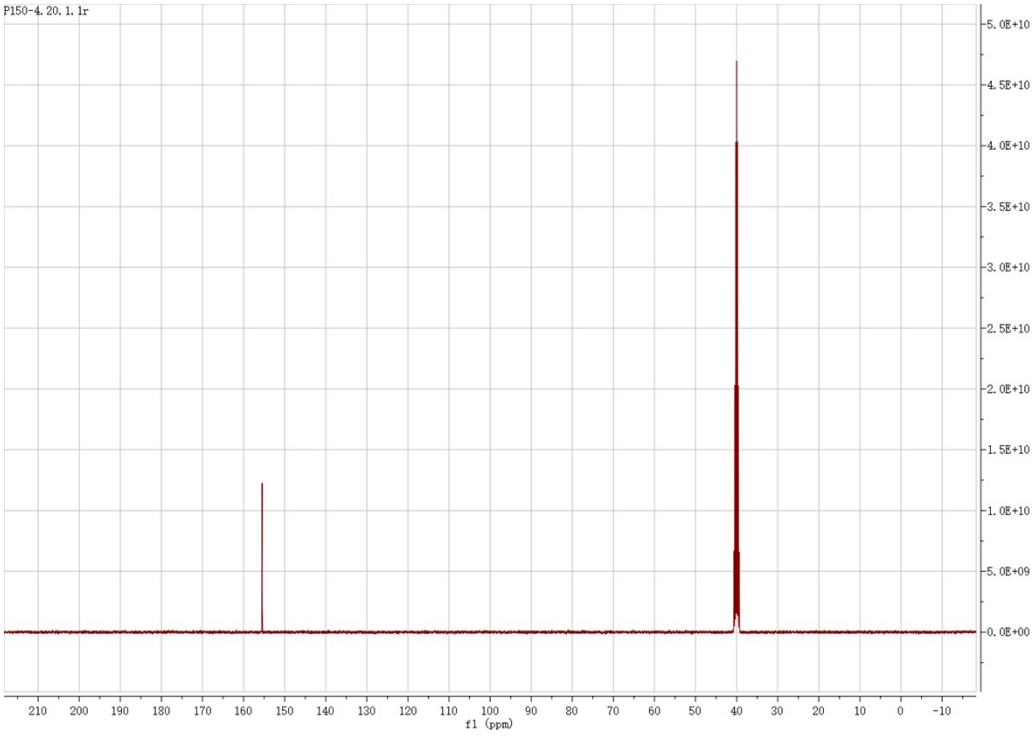

Figure S6 ^{13}C NMR spectra of H_2ur

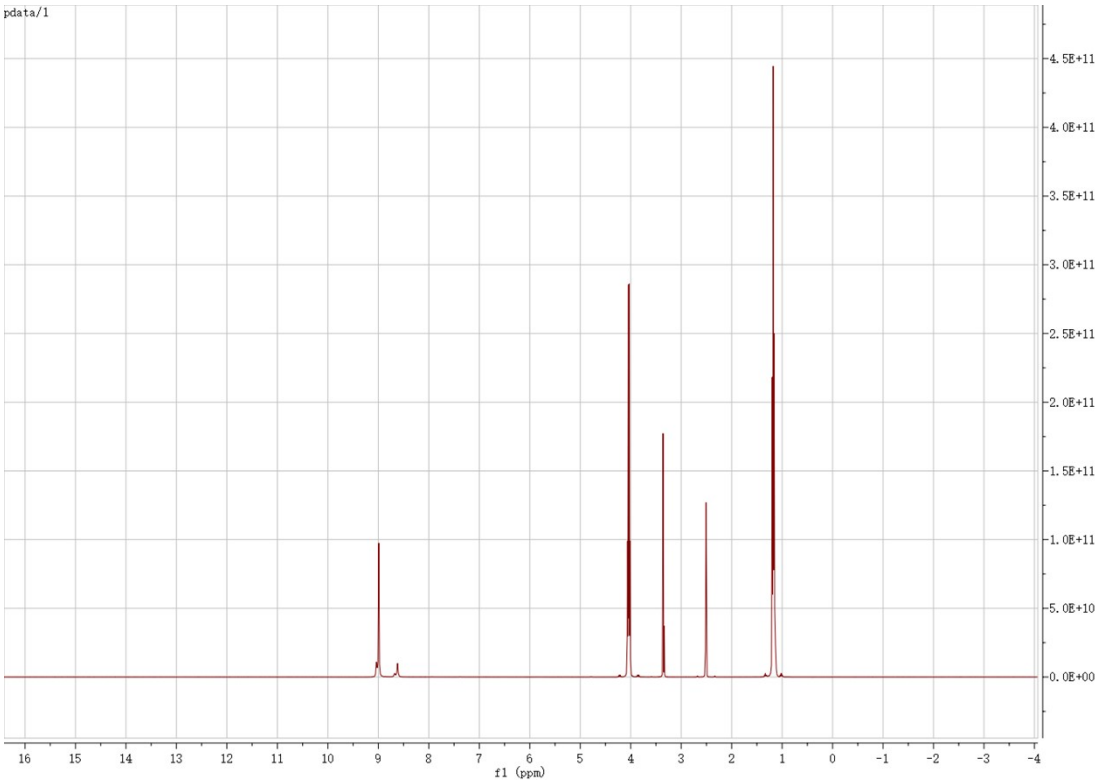

Figure S7 ^{1}H NMR spectra of 2•H_2O

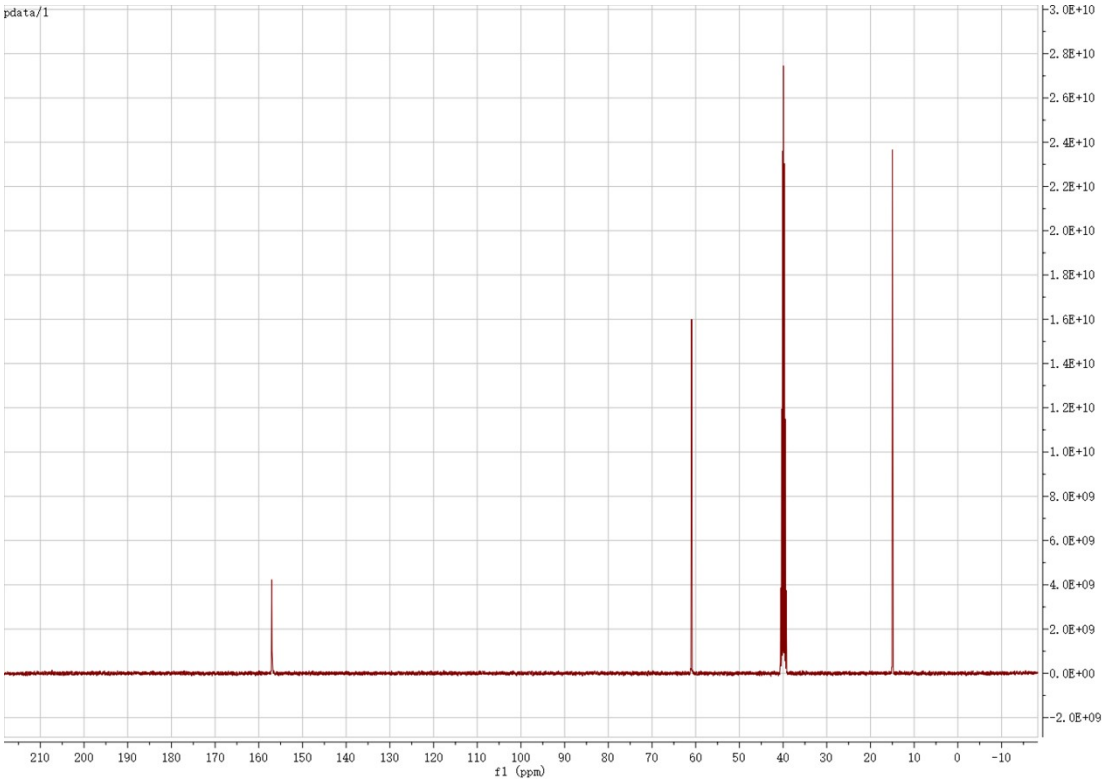

Figure S8 ^{13}C NMR spectra of 2•H_2O

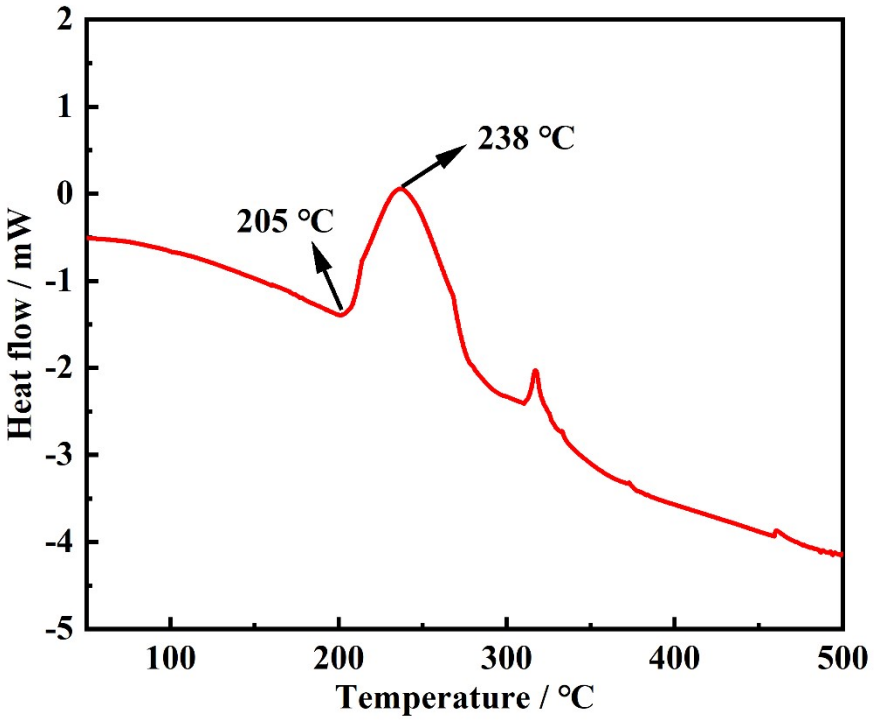

Fig.S9 DSC curves of 4.

Supplementary Table S1

Table S1. Crystallographic data for **3**

Formula	$C_2H_4N_5O_5Ag$
M_w[g mol^{-1}]	285.953
Crystal size [mm^3]	0.4 x 0.16 x 0.13
Crystal system	Monoclinic
Temperature [K]	298.15
Space group	*C2/c*
unit cell dimensions	*a*=9.9723(9) Å, *b*=12.5561(12)Å, *c*[Å]=5.5731(6)Å
	α[Å]=90, β[Å]=92.159(3), γ[Å]=90
V[[Å^3]	697.33(12)
Z	4
ρ_{calc}[g cm^{-3}]	2.724
μ[mm^{-1}]	2.894
F(000)	548.8
2θ range[^{o}]	5.22 – 49.98
Reflections collected	2081
Index ranges	-13≤ h ≤ 12, -16 ≤ k ≤ 13, -7 ≤ l ≤ 7
R_{int}	0.0647
Data/restraints/parameters	1086 / 8 / 119
Final R index [$I > 2\sigma(I)$]	R1 = 0.0516, wR2 = 0.1393
Final *R* index [all data]	R1 = 0.0520, wR2 = 0.1397
GOF on F^2	1.048
CCDC	2133311