Supporting Information

Optimization of Performance and Sensitivity: Preparation of Two Ag(I)-based ECPs by Using Isomeric Ligands

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Table of Contents

Experimental Section

Caution!

In the process of research, the chemicals we used, including raw materials and target products, are all potentially dangerous. Although we have not encountered any danger in the process of using these substances, we still strongly recommend taking necessary protective measures before touch these items, including the use of prescribed gloves, face shields, lab coats, and baffles. All operations must be performed in a fume-hood.

Materials and Equipment

During the experiment, the reagents (analytical grade) used were purchased from Aladdin and Azov 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 5 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 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. Operating parameters: theoretical maximal output power P_{max} = 30.15 W; theoretical pulse length τ_{max} = 49571 μs. wavelength λ = 915 nm. Frequency F = 1Hz.).

Synthesis of 1H imidazole -2- carbohydrazide (2-IZCA)

Take 14.1 g (0.1 mol) of ethyl 1H-imidazole-2-carboxylate, add it to a flask containing 50 ml of anhydrous methanol, keep the solution stirring rapidly, slowly add 8.8 ml (0.15 mol) of hydrazine hydrate (85 %), reflux the reaction at 80 ℃ for 5 hours, filter, wash, and dry to obtain a large amount of white solid product, **2-IZCA**. Yield: 83 %.

IR (KBr, ν/cm^{-1}): 3288 (m), 1685 (m), 1623 (m), 1542 (s), 1507 (s), 1457(s), 1436 (s), 1348 (s), 1238 (s), 1078 (s), 864 (s), 623 (s).

MS (ESI), m/z: 125.04 [$C_4H_5N_4O^-$].

Elemental analysis (%) for $C_4H_6N_4O$ (Mr = 126.05 g mol^{-1}): calcd. C 38.09, H 4.80, N 44.42; found C 37.88, H 4.69, N 44.91.

^{1}H NMR (400 MHz,DMSO-d_6): δ 4.52 (s, 2H), 6.84 (s, 1H), 7.18 (d, 1H), 7.63 (s, 1H), 10.02 (s, 1H).

^{13}C NMR (400 MHz, DMSO-d_6), (δ: ppm): 158.45, 140.66, 129.21, 119.78.

Synthesis of 1H imidazole -4- carbohydrazide (4-IZCA)

The synthesis method of **4-IZCA** is similar to that of **2-IZCA**, except that the raw material ethyl 1H imidazole -2- carboxylate is replaced by ethyl 1H imidazole -4- carboxylate. Yield: 77 %.

IR (KBr, ν/cm^{-1}): 3330 (m), 3289 (m), 1680 (m), 1617 (m), 1556 (s), 1514 (s), 1467(s), 1370 (s), 1297 (s), 1250 (s), 1033 (s), 864 (s), 796 (s), 626 (s).

MS (ESI), m/z: 125.04 [$C_4H_5N_4O^-$].

Elemental analysis (%) for $C_4H_6N_4O$ (Mr = 126.05 g mol^{-1}): calcd. C 38.09, H 4.80, N 44.42; found C 37.79, H 4.65, N 44.82.

^{1}H NMR (400 MHz,DMSO-d_6): δ 4.35 (s, 2H), 7.61 (s, 1H), 7.72 (d, 1H), 9.10 (s, 1H), 12.49 (s, 1H).

^{13}C NMR (400 MHz, D_2O/NaOH-d_6): δ 164.97, 146.09, 133.25, 129.83.

Synthesis of Synthesis of $[Ag(2\text{-}IZCA)ClO_4]_n$ (ECPs-1).

Weigh 1.26 g (10 mmol) of ligand **2-IZCA** and dissolve it in 20 ml of water at room temperature. After heating to 70 ℃, add 2.5 ml of self-made $AgClO_4$ solution (c = 4.0 mol/l), and a large number of white solids will appear immediately. Then slowly drop perchloric acid until the solids are completely dissolved. Filter the filtrate while it is hot, and stand it for 2 days to obtain the colorless transparent crystal of **ECPs-1**. Yield: 65 %.

IR (KBr, ν/cm^{-1}): 3293 (m), 1685 (m), 1617 (m), 1512 (s), 1466 (s), 1370 (s), 1300 (s), 1250 (s), 1030 (s), 864 (s), 797 (s), 618 (s).

Elemental analysis (%) for $C_4H_6N_4O_5AgCl$ (Mr = 333.45 g mol^{-1}): calcd. C 14.41, H 1.81, N 16.80; found C 14.29, H 1.71, N 16.91.

Synthesis of Synthesis of $[Ag(4\text{-}IZCA)ClO_4]_n$ (ECPs-2).

The method of cultivating crystals of **ECPs-2** is similar to that of **ECPs-1**, as long as the ligand is **4-IZCA**. Yield: 65 %.

IR (KBr, ν/cm^{-1}): 3327 (m), 1664 (m), 1623 (m), 1522 (s), 1431 (s), 1343 (s), 1235 (s), 1066 (s), 935 (s), 852 (s), 758 (s), 621 (s).

Elemental analysis (%) for $C_4H_6N_4O_5AgCl$ (Mr = 333.45 g mol^{-1}): calcd. C 14.41, H 1.81, N 16.80; found C 14.33, H 1.67, N 16.95.

Oxygen bomb calorimetry

The constant pressure reaction heat ($\Delta_C U$) of **ECPs-1** and **ECPs-2** 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 **ECPs-1** and **ECPs-2** were shown in equation (**2**), and the standard molar generation enthalpy ($\Delta_f H^\theta_m$) can be obtained based on the formulas (**2**) and (**3**) [$\Delta_f H^\theta_m$: CO_2(g): -393.51 kJ mol^{-1}; H_2O(l): -285.83 kJ mol^{-1}; HCl(g): -92.31 kJ mol^{-1}; AgCl(s): -127.04 kJ mol^{-1}]. The final experimental results showed that the combustion heats of **ECPs-1** and **ECPs-2** are 2608 kJ mol^{-1} and 2759 kJ mol^{-1} respectively.

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

Δ_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)

$$C_4H_6N_4O_5ClAg(s) + 3O_2(g) = 4CO_2\,(g) + 3H_2O(l) + 2N_2(g) + AgCl(s) \quad (2)$$

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

Theoretical simulation based on K-J equations

The constant pressure reaction heat ($\Delta_C U$) of compounds were measured by an oxygen bomb calorimeter, Detonation speed (D) and explosion pressure (P) are the main indicators for measuring energetic materials. The various detonation characteristics were predicted by using the modified Kamlet-Jacbos (K-J) equations (eq 4-7) which is a commonly used equation for predicting the detonation velocity and pressure of high energy materials.

$$C_4H_6N_4O_5ClAg(s) = 2CO(g) + 2C(s) + 3H_2O(g) + 2N_2(g) + AgCl(s) \quad (4)$$

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

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

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

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

Detonation initiation

The test device used to breakdown of the lead plate, the material inside can be divided into two parts: the first part is filled with compound **ECPs-1** or **ECPs-2** (100 mg, pressure of fixation is 25 MPa); the second component is RDX (400 mg, charge pressure is 40 MPa). The lead plate has a thickness of 2 mm.

Laser performance test

Weigh 10 mg samples (pressure of fixation is 20 MPa), 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.

Theoretical decomposition mechanism study

All the structures are optimized under the level of M06-2X with the basis set of def2tzvp in Gaussian 16 package. The optimized structures are summarized in **Fig. S7**, and the discussions of Wiberg bond index and Mayer bond order (MBO) are performed at the same theoretical level in Multiwfn 3.7 program. Based on the gas-phase structures, we build 30 × 30 × 30 Å boxes for all the molecules in order to understand the stabilities and the decomposition pathways with a raised temperature by applying CPMD (Car-Parrinello Molecular Dynamic) methods. All the dynamic calculations are performed with Quantum Espresso 6.0 package. The time step is set as 4.0 a.u (~ 0.1 fs) for all complexes in the simulations. The kinetic energy cutoff for wave functions is 40 Ry (544 eV) with the effective electron mass of 600 D0 for **ECCs-1**. The PBE exchange-correlation functional is chosen, and core electrons are taken into account using PBE-type ultrasoft pseudopotentials, with valence states Ag($4d^{10}5s^{1}$), C($2s^{2}2p^{2}$), N($2s^{2}2p^{3}$), O($2s^{2}2p^{4}$), Cl($3s^{2}3p^{5}$) and H($1s^{1}$) used to describe the valence electrons. In the simulation of CPMD, the time of simulation is set as 1.93 ps (20000 steps). An NVT ensemble is employed and the external temperature directly increased to 1500 K with the step of 0.1 fs. The oscillation frequency of the Noše thermostat is set as 550 ~ 750 THz. The simulation curves of time (step) - potential energy (a.u) relationship.

Supplementary Figures S1 – S9

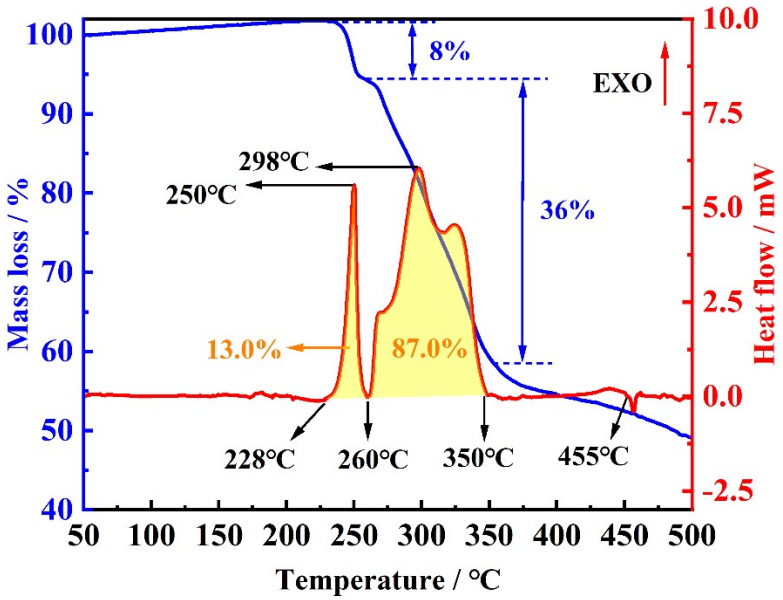

Figure S1 DSC-TG of **ECPs-1**.

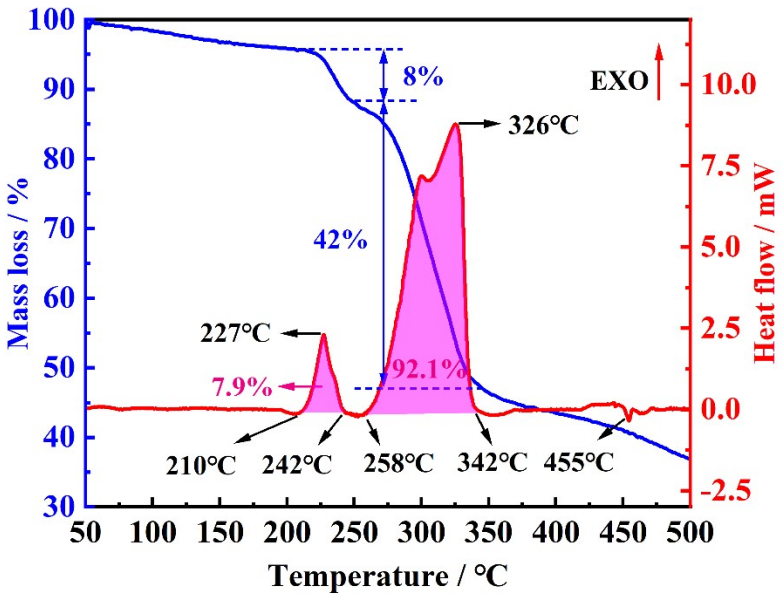

Figure S2 DSC-TG of **ECPs-2**.

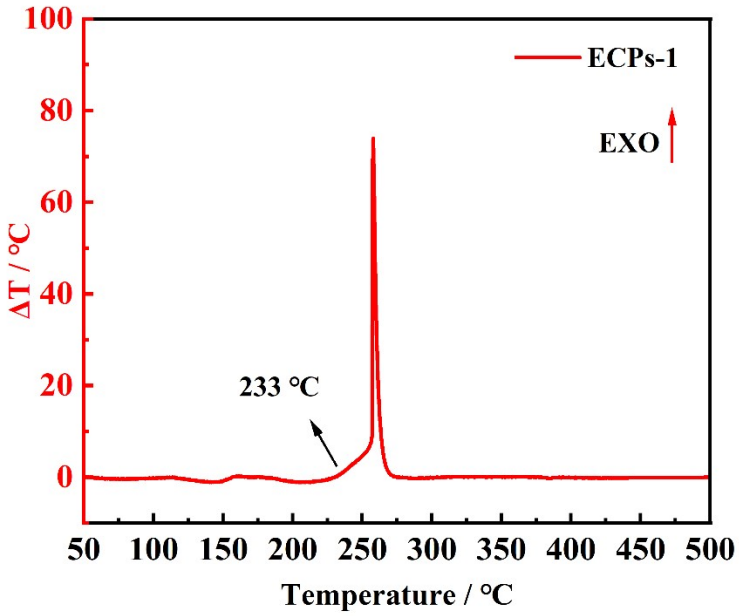

Figure S3 DTA of **ECPs-1**.

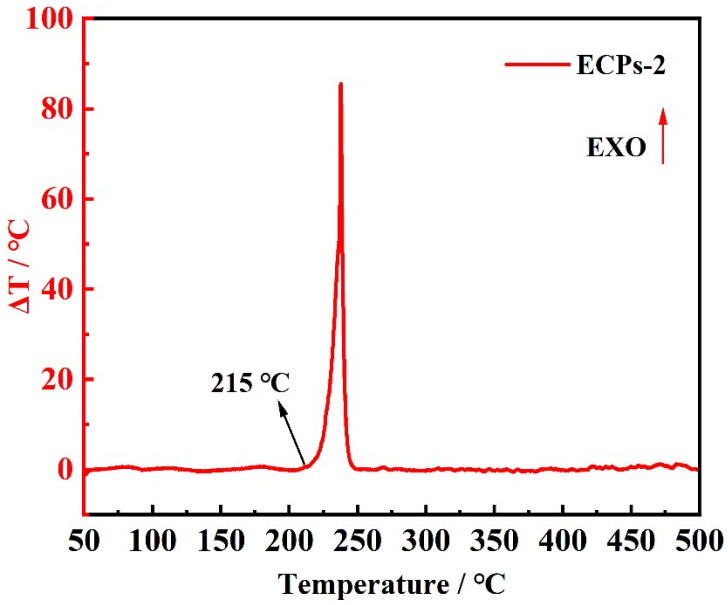

Figure S4 DTA of **ECPs-2**.

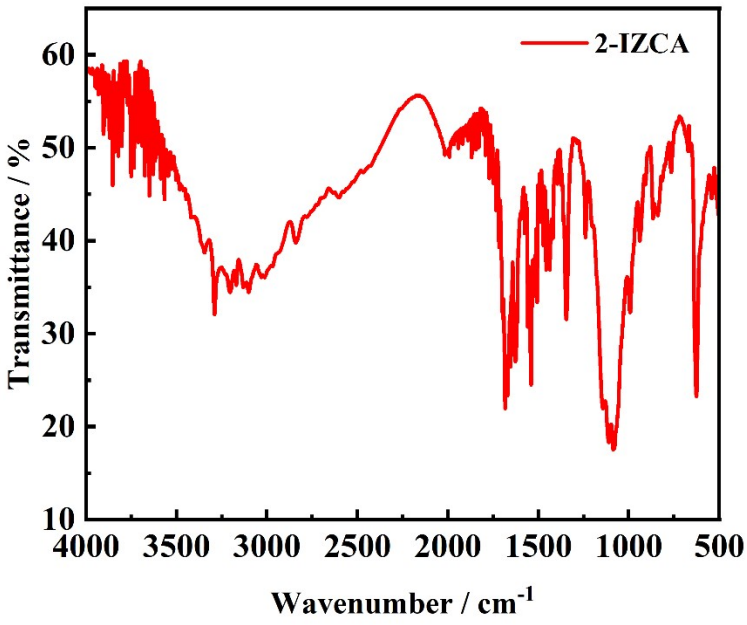

Figure S5 IR of **2-IZCA.**

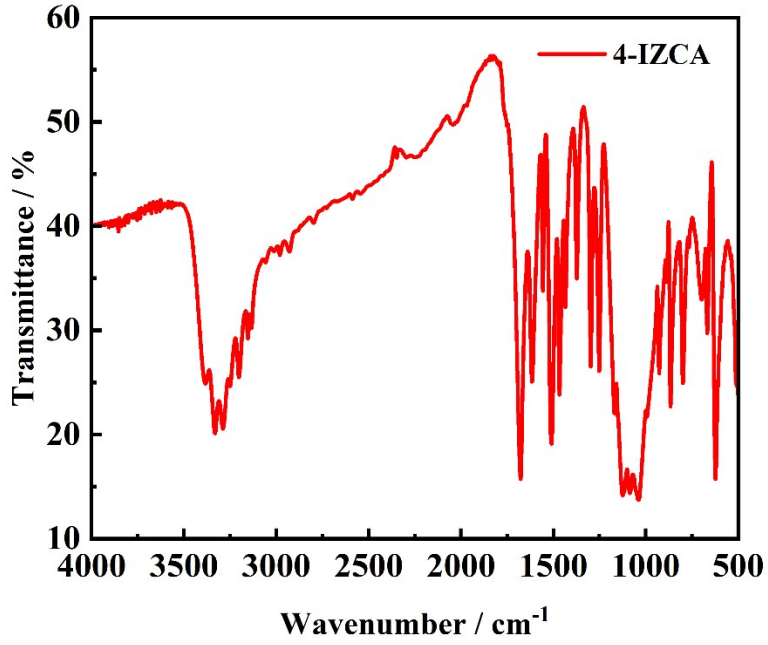

Figure S6 IR of **4-IZCA.**

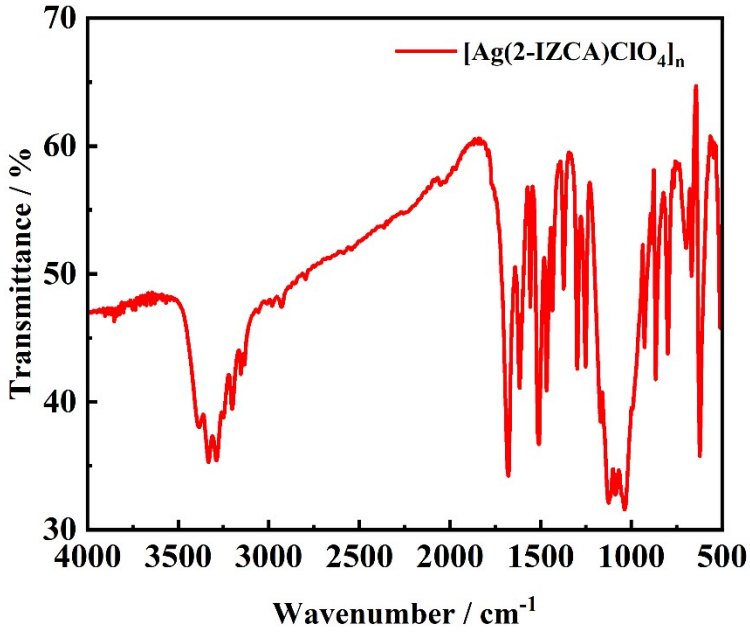

Figure S7 IR of **ECPs-1.**

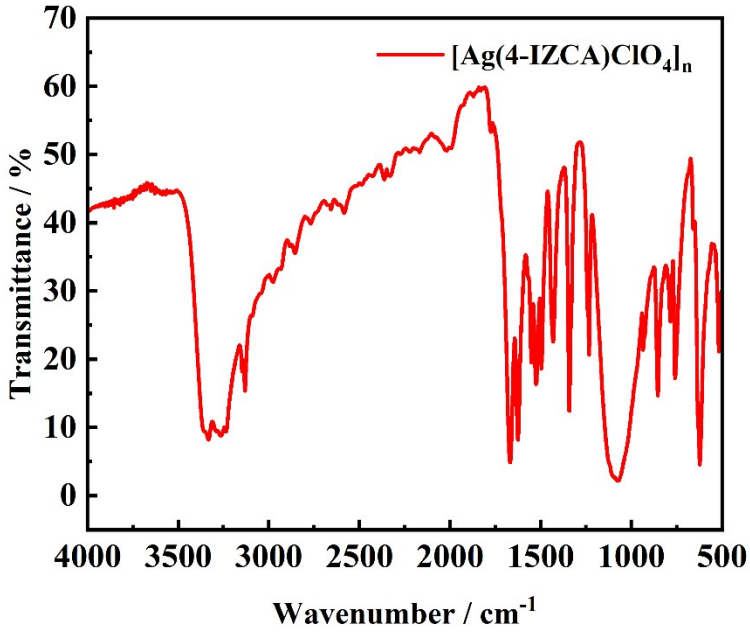

Figure S8 IR of **ECPs-2.**

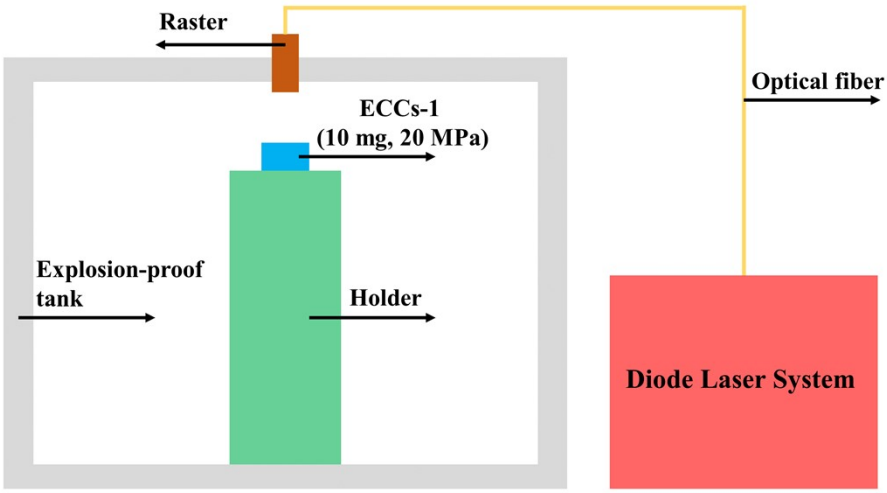

Figure S9 Illustration of setup of Laser Initiation Tests.

Supplementary Table S1 – S2

Table S1. Crystallographic data for **[Ag(2-IZCA)ClO_4]$_n$**

Formula	$C_4H_6N_4O_5ClAg$
Temperature [K]	293(2)
M_w[g mol^{-1}]	333.45
Crystal size [mm^3]	0.13 x 0.07 x 0.05
Crystal system	Monoclinic
Space group	$P2_1/c$
unit cell dimensions	a[Å]=7.1250(7), b[Å]=9.8501(9), c[Å]=13.4002(12)
	α[°]=90.00, β[°]=105.020(4), γ[°]=90.00
V[[Å^3]	908.32(15)
Z	4
ρ_{calc}[g cm^{-3}]	2.438
μ[mm^{-1}]	2.523
F(000)	648.0
2θ range[^{o}]	5.2 – 50.04
Reflections collected	4220
Index ranges	-8 ≤ h ≤ 3, -11 ≤ k ≤ 11, -14 ≤ l ≤ 15
R_{int}	0.1155
Data/restraints/parameters	1579 / 61 / 146
Final R index [$I > 2\sigma(I)$]	R1 = 0.0808, wR2 = 0.2086
Final R index [all data]	R1 = 0.0942, wR2 = 0.2190
GOF on F^2	1.066
CCDC	2277705

Table S2. Crystallographic data for **[Ag(4-IZCA)ClO_4]$_n$**

Formula	$C_4H_6N_4O_5ClAg$
Temperature [K]	298.15
M_w[g mol^{-1}]	333.45

Crystal size [mm^3]	0.32 x 0.23 x 0.12
Crystal system	Orthorhombic
Space group	P_{nma}
unit cell dimensions	a[Å]=9.4181(9), b[Å]=6.6865(6), c[Å]=14.2531(13)
	α[°]=90.00, β[°]=90.00, γ[°]=90.00
V[[Å^3]	897.58(14)
Z	4
ρ_{calc}[g cm^{-3}]	2.468
μ[mm^{-1}]	2.553
F(000)	648.0
2θ range[^{o}]	5.18 – 50.02
Reflections collected	4005
Index ranges	$-11 \leq h \leq 10$, $-7 \leq k \leq 7$, $-16 \leq l \leq 13$
R_{int}	0.0690
Data/restraints/parameters	866 / 37 / 89
Final R index [$I > 2\sigma(I)$]	R1 = 0.0610, wR2 = 0.1511
Final R index [all data]	R1 = 0.0858, wR2 = 0.1624
GOF on F^2	1.111
CCDC	2277708