Supporting Information

Novel energetic pyridine-2-carbohydrazide copper perchlorate complex： synthesis, cationic ligand structure and properties

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1. Experimental details

The analytical grade reagents used in the experiment were bought from Aladdin and Azov and utilized without additional purification.

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). Infrared (IR) spectra were measured on a Nicolet Is10 spectrometer with a measurement range of 4000 - 400 cm^{-1}. On an elemental analyzer (Vario EL Cube, Germany), elemental analyses (C, H, N or C, H, N, O) were performed.

Thermal stability test: Thermogravimetry and synchrotron thermal analyzer (TGA/DSC3+, METTLER TOLEDO) and Differential thermal analyzer(DTA, OZM 552-Ex) were used to study the thermal behavior of synthesized compound under a nitrogen environment (80 $mL \cdot min^{-1}$) and a heating rate of 5 $℃ \cdot min^{-1}$.

Sensitivity test: By using a BAM DFH-10 device with a weight drop of 5 kg, the standard step approach of the drop weight device was used to assess the mechanical sensitivities of the material, including impact sensitivity and friction sensitivity.

Hot ignition test: Approximately 2 mg of the compound was dispersed on the filter paper. Light the filter paper, and then slowly ignite compounds, while recording the deflagration to detonation process of the compound with a high-speed camera.

Laser performance test: Weigh 2 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.

Detonation initiation test: 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 $Cu(TZCA)_2ClO_4$ or ECCs-1 (50

mg, pressure of fixation is 40 MPa); the second component is RDX (500 mg, charge pressure is 40 MPa). The lead plate has a thickness of 5 mm.

2. Calculation details

We hypothesize that the ECCs-1 has a similar crystal stacking pattern to its analogues, the perchlorate nitrate bis-anionic copper complex (**Fig.S7**). Therefore, we modelled the crystal structure of the copper perchlorate complex using Gaussview. By using the CP2K program, we firstly used the GFN1-xTB method to carry out the kinetic relaxation of the modelled structure in the NPT regime at 5 ps with a time step of 0.2 fs. The potential and kinetic energy curves of the kinetic simulation showed that the modelled structure was fully relaxed at 5 ps. The relaxed structure was taken out and the variable cell optimization was implemented under PBE/DZVP-MOLOPT-SR-GTH, also using CP2K. Finally, the optimized structure under DFT precision was taken out and the simulation results of powder XRD were given by using Powder Diffraction Pattern module of VESTA program.

The theoretical calculations of geometry optimization was performed using Gaussian 09 at the B3LYP 6-311+G** level of theory. Calculations of enthalpy of formation are performed based on its definition. Predictions of explosive performance, including detonation velocity and pressure, were conducted using EXPLO5 v6.04.

3. Graphics

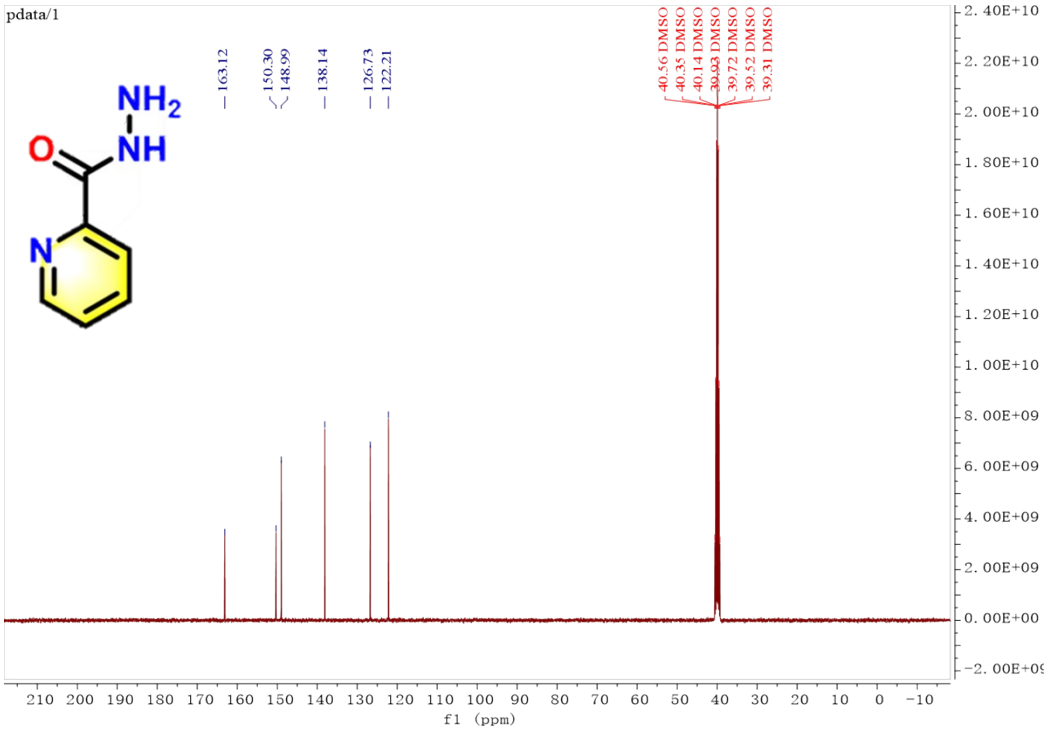

Figure S1. ^{13}C NMR of 2-PDCA

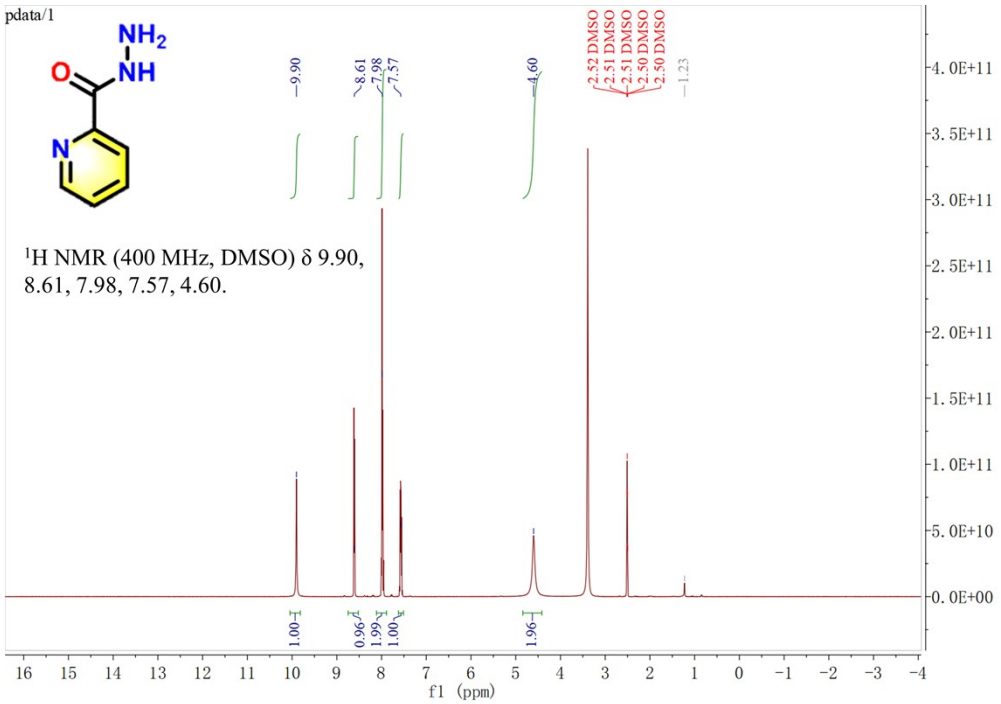

Figure S2. ^{1}H NMR of 2-PDCA

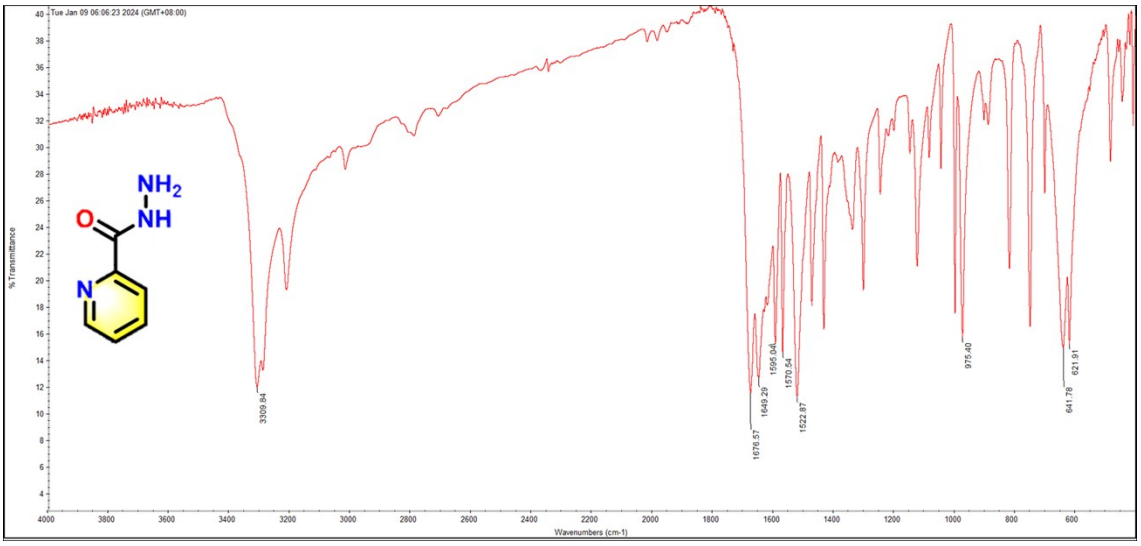

Figure S3. The IR spectra of 2-IMTO.

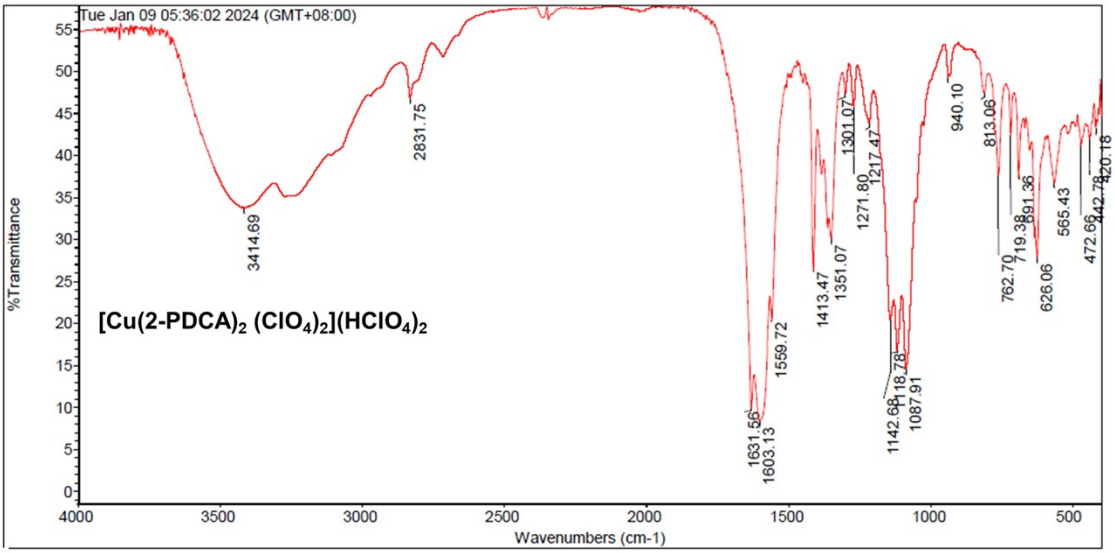

Figure S4. The IR spectra of **ECCs-1**.

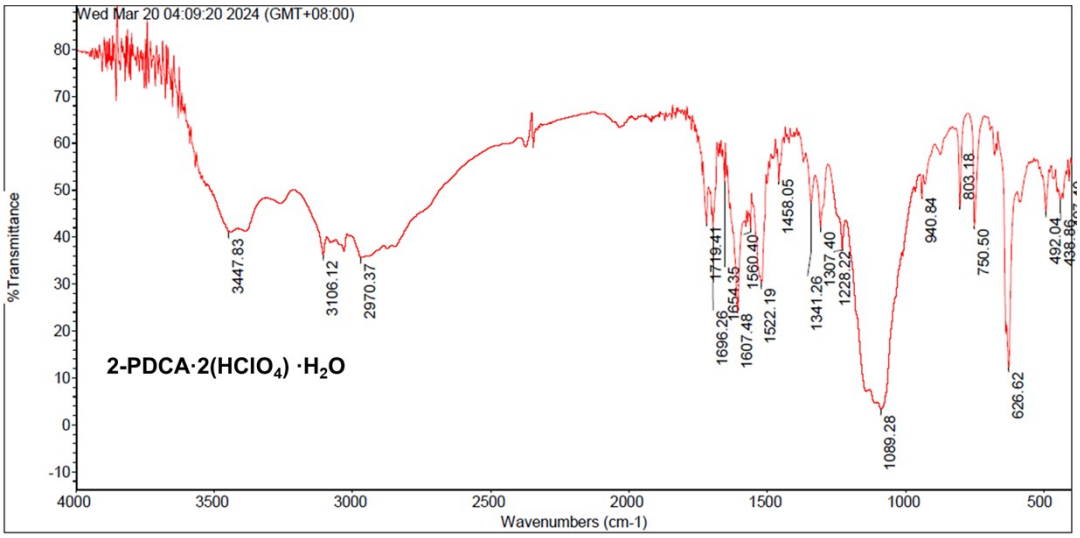

Figure S5. The IR spectra of **4-PDCA·2HClO$_4$·H$_2$O**.

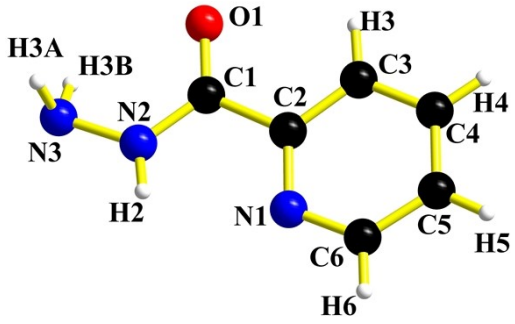

Figure S6. The single crystal of **2-PDCA.**

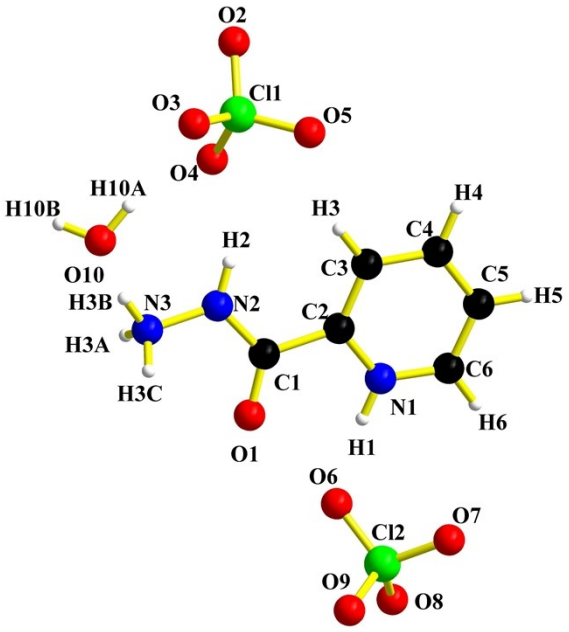

Figure S7. The single crystal of **2-PDCA·2HClO$_4$·H$_2$O.**

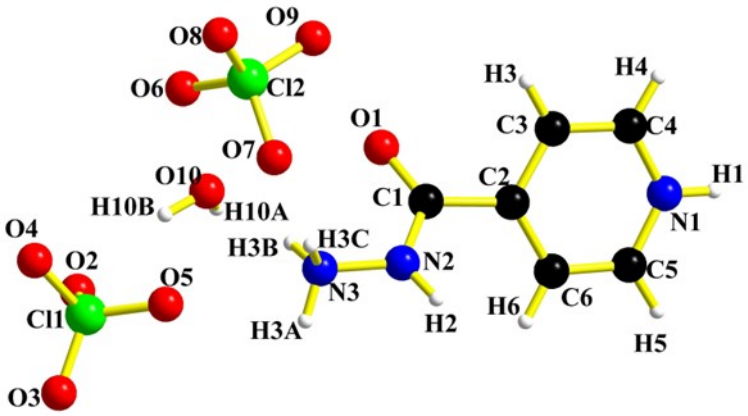

Figure S8. The single crystal of **4-PDCA·2HClO$_4$·H$_2$O.**

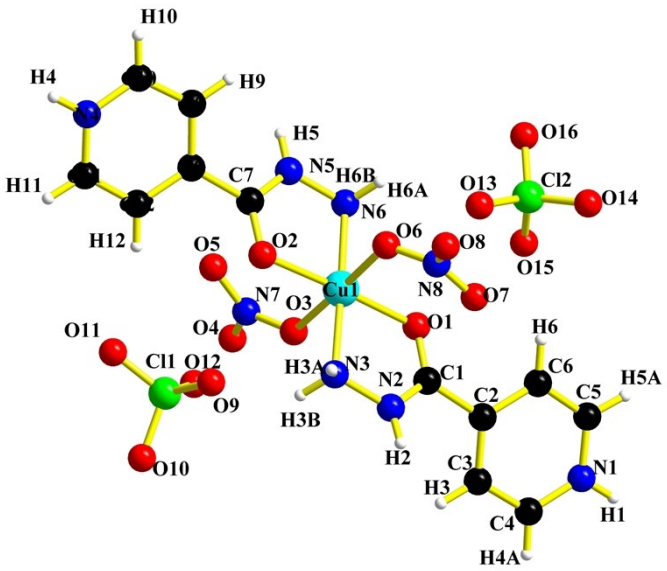

Figure S9. The single crystal of **$Cu(4\text{-}PDCA)_2(NO_3)_2\cdot 2HClO_4$.**

4. Tables

Table S1. Crystal data of **$4\text{-}PDCA\cdot 2HClO_4\cdot H_2O$, $Cu(4\text{-}PDCA)_2(NO_3)_2\cdot 2HClO_4$.**

$4\text{-}PDCA\cdot 2HClO_4\cdot H_2O$	**$Cu(4\text{-}PDCA)_2(NO_3)_2\cdot 2HClO_4$**
2326909	2325143
$C_6H_{11}Cl_2N_3O_{10}$	$CuC_{12}H_{16}Cl_2N_8O_{16}$
356.08	662.77
115.5	115.3
monoclinic	monoclinic
$P2_1$	$P2_1/c$
Colorless	Blue
4.9151(6)	10.1057(8)
10.5757(16)	15.7064(10)
12.470(3)	141.8468(11)
90	90
94.788(16)	105.467(7)
90	90
645.93(19)	2271.2(3)
2	4
1.831	1.938
364	1340
3.28~`25.99	2.96~`26
-6≤h≤6,	-10≤h≤12,
-13≤k≤13,	-11≤k≤19,
-15≤l≤15	-17≤l≤17