Supporting Information

Synthesize New Bi-structure Energetic Coordination Compounds by Using Ternary Components

Chao Zhang [a], Tingwei Wang [a], Meiqi Xu [a], Baolong Kuang [a], Zhiming Xie [a], Zujia Lu [a], Zhenxin Yi [b], Yan Li [b], Jianguo Zhang [a,*]

[a] State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing, 100081, China.

[b] School of Chemical Engineering, Nanjing University of Science and Technology, 200 Xiaolingwei Street, Xuanwu, Nanjing 210094, China.

Corresponding author: Jianguo Zhang,

E-mail: zjgbit@bit.edu.cn

Table of Contents

Experimental Section

Caution!

Although the raw materials we use are not energetic materials, the target compounds we have prepared are very dangerous. Even though we were very careful in using it, there were violent explosions during some tests. We strongly recommend that operators should take good safety precautions (masks, gloves, explosion-proof panels) when synthesizing and using these substances. All operations must be accompanied by peers and all operations must be carried out in professional equipment and protective equipment

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·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 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 = 808 nm. Frequency F = 1Hz.).

Synthesis of 1-APZ-5-CA

Under the influence of the 1,8-diazabicycloundec-7-ene (DBU) catalyst, 1H-pyrazole-5-carbohydrazide engages in an amination process with O-Tosylhydroxylamine (THA), resulting in the formation of 1-amino-1H-pyrazole-5-carbohydrazide. Compound **1** (10 mmol) and DBU (10 mmol) were suspended in anhydrous acetonitrile (50 mL), and the resulting mixture was stirred at room temperature for 0.5 h. Then, a freshly prepared THA solution (containing HClO$_4$, 2.3 M, 23 mmol) was added in batches within 5 minutes. The mixture was stirred for 5 hours and the solvent was removed under vacuum. The white solid **1-APZ-5-CA** was obtained via rapid chromatography. yield of 53%. IR ((KBr, ν/cm^{-1}): 3450 (s), 3354

(s), 3266 (m), 1664 (s), 1631 (s), 1581 (s), 1434 (s), 1247 (s), 1228 (s), 1101 (s), 1056 (s), 923 (s), 889 (s), 620 (s). MS (ESI), m/z: 140.04 [$C_4H_6N_5O^-$]. Elemental analysis (%) for $C_4H_7N_5O$ (Mr = 141.07 g mol^{-1}): calcd. C 34.0, H 4.9, N 49.6; found C 33.7, H 4.6, N 50.3. ^{13}C NMR (500 MHZ, DMSO-d_6): δ 155.85, 136.97, 121.54, 120.62

Synthesis of ECPs-1

To initiate the synthesis, **1-APZ-5-CA** (1.26 g, 10 mmol) was dissolved in water at room temperature. Upon reaching 70°C, 4.15 g (20 mmol) of solid AgClO$_4$ was introduced, resulting in the rapid generation of a notable quantity of white solid. The gradual addition of HClO$_4$ continued until the complete dissolution of the solid. Subsequent hot filtration was performed, and after allowing the mixture to stand for a period of 2-3 days, the desired crystals **ECPs-1** were obtained. Yield: 51 %. IR (KBr, v/cm^{-1}): 3325 (m), 1654 (s), 1622 (m), 1564 (m), 1534 (m), 1508 (m), 1363 (s), 1324 (s), 1282 (s), 1234 (s),1086 (s), 936 (s), 871 (s), 767 (s), 626 (s). Elemental analysis (%) for $C_8H_{16}Ag_2Cl_4N_{10}O_{18}$ (Mr = 897.85 g mol^{-1}): calcd. C 10.7, H 1.8, N 15.6; found C 10.4, H 1.5, N 21.3
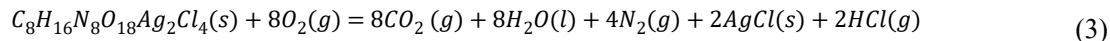
Oxygen bomb calorimetry

The constant pressure reaction heat ($\Delta_C U$) of **ECPs-1** 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 equations were shown in equation **1** to **4**, and the standard molar generation enthalpy ($\Delta_f H^{\theta}_m$) can be obtained based on the formulas **1** and **2** [$CO_2(g)$: -393.51 kJ mol^{-1}; AgCl(s): -127.04 kJ mol^{-1}; HCl(g): -92.31 kJ mol^{-1}; H_2O(l): -285.85 kJ mol^{-1}]. The final experimental results showed that the standard molar enthalpy of formation ($\Delta_f H^{\theta}_m$) of **ECPs-1** is -288 kJ mol^{-1}.
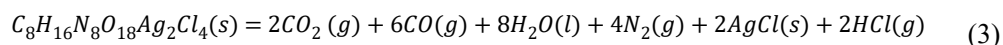
$$\Delta c H^{\theta} m = \Delta c U + \Delta n R T \tag{1}$$

$\Delta_n = n_g$(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)

$$\Delta_f H^{\theta} m(compound) = \sum \Delta_f H^{\theta} m(products) - \Delta_c H^{\theta} m(compound) \tag{2}$$

$$C_8H_{16}N_8O_{18}Ag_2Cl_4(s) + 8O_2(g) = 8CO_2(g) + 8H_2O(l) + 4N_2(g) + 2AgCl(s) + 2HCl(g) \tag{3}$$

Theoretical 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 EIsCCs-1 were predicted 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 [$CO_2(g)$: -393.51 kJ mol^{-1};CO(g):110.525 kJ mol^{-1}; AgCl(s): -127.04 kJ mol^{-1}; H_2O(g): -241.82 kJ mol^{-1}; HCl(g): -92.31 kJ mol^{-1}].

$$C_8H_{16}N_8O_{18}Ag_2Cl_4(s) = 2CO_2(g) + 6CO(g) + 8H_2O(l) + 4N_2(g) + 2AgCl(s) + 2HCl(g) \tag{3}$$

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

$$P = 1.55\rho^2 NM^{1/2}Q^{1/2} \tag{6}$$

$$Q = \frac{-[\Delta H_f(\text{detonation production}) - \Delta H_f(\text{explosive})]}{\text{formula weight of explosive}} \tag{7}$$

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-ignition tests (0 MPa)

Approximately 5 mg of the compound was dispersed on the operating table in a powdered state (the pressure is 0 MPa). 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.

Hot-ignition tests (3 MPa)

The samples were compressed into a plate-like shape (the pressure is 3 MPa). Approximately 5 mg of the compound was dispersed on the filter paper. Light the filter paper, and then slowly ignite compounds, 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 LA or ECCs (80 mg, pressure of fixation is 20

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

Laser performance test

Weigh 3 mg samples (pressure of fixation is 0 MPa or 3 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.

A brief description of the test process (see Figure S5 for schematic diagram): The whole test system consists of four parts: laser generator, explosive device, photoelectric sensor and terminal. After the experimental preparation is completed, we are ready to start the experiment. First, set the power and pulse time of the laser transmitter, then turn on the laser switch (at the same time, we will get an electrical signal which time will be recorded as t0). After the laser is transmitted through the optical fiber, it will irradiate the sample in the explosive device, and the sample will ignite with fire (the photoelectric sensor will capture the light and get an electrical signal, which time will be recorded as t1). The curves of the two electrical signals will be displayed on the terminal, and the time difference t1-t0 will be read out as ΔT or τ, which is the delay time. When processing data, the laser power x delay time is equal to the ignition energy.
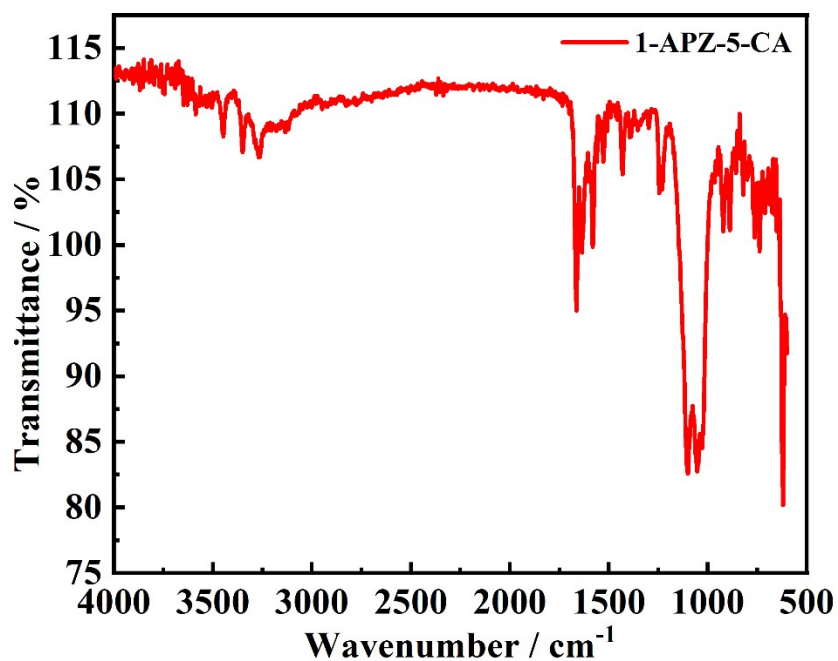
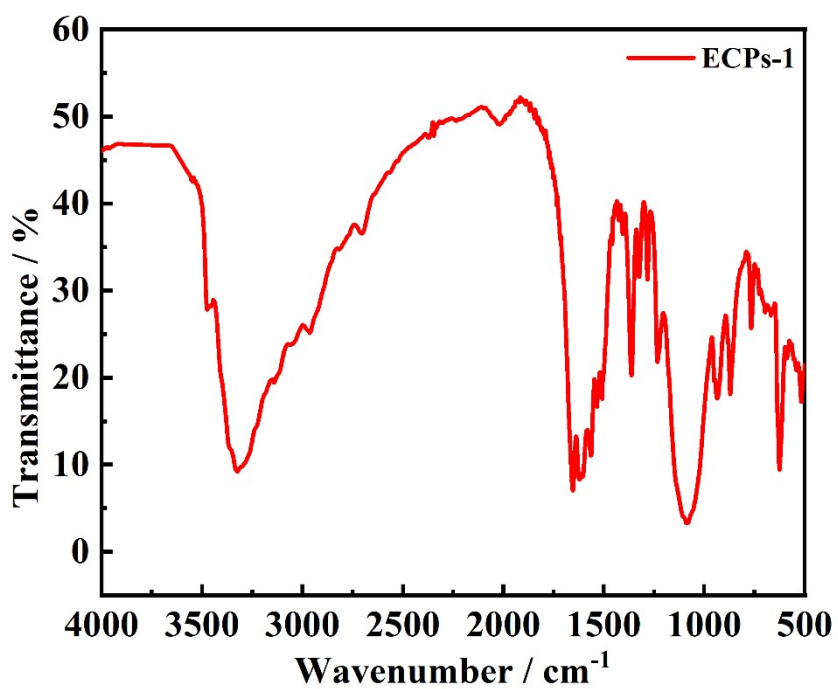**Figure S1.** Infrared spectra of 1-APZ-5-CA.

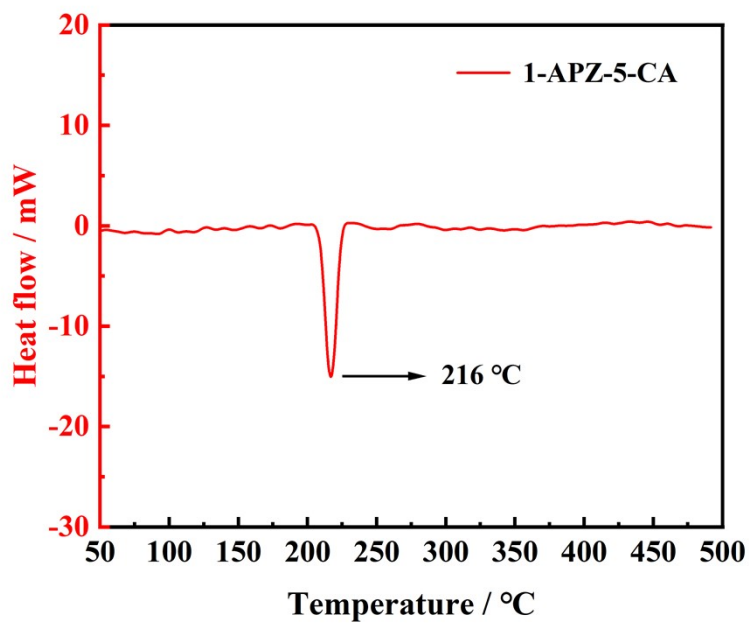
Figure S2. Infrared spectra of ECPs-1.

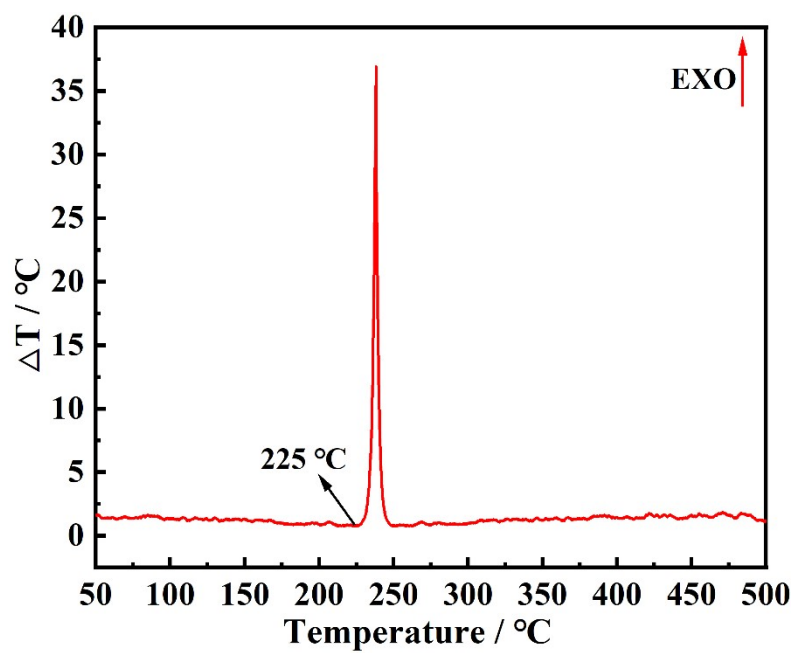**Figure S3   DSC testing result of 1-APZ-5-CA.**

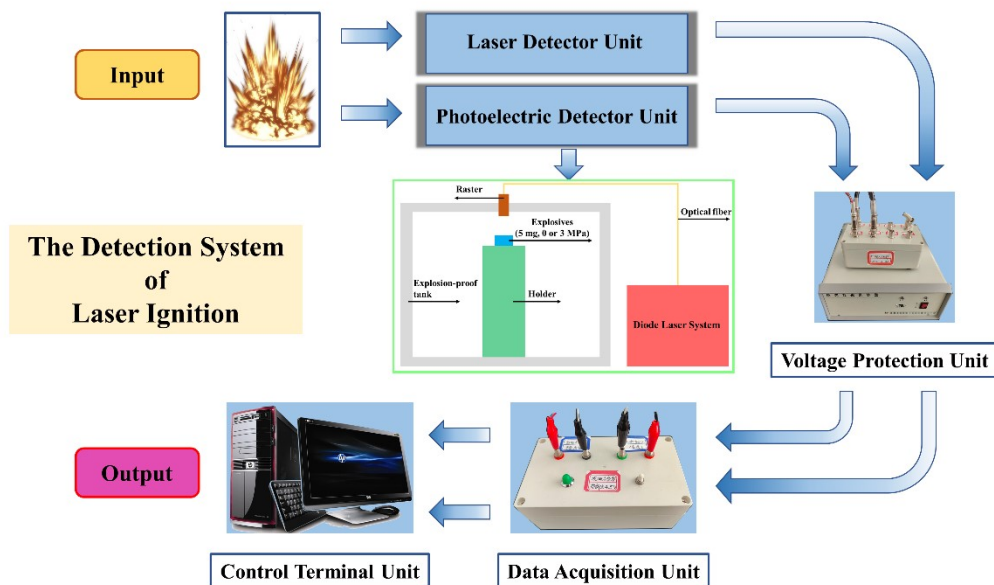**Figure S4   DTA testing result of ECPs-1.**

Figure S5. Illustration of setup of Laser Initiation Tests.
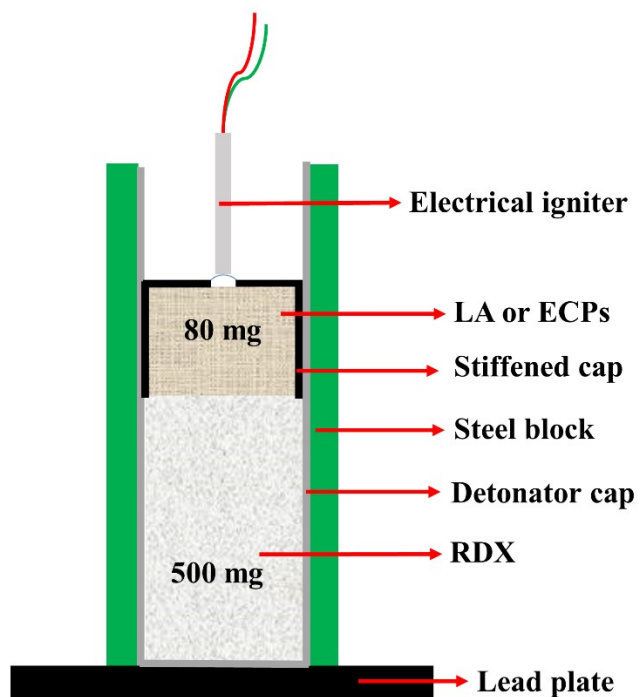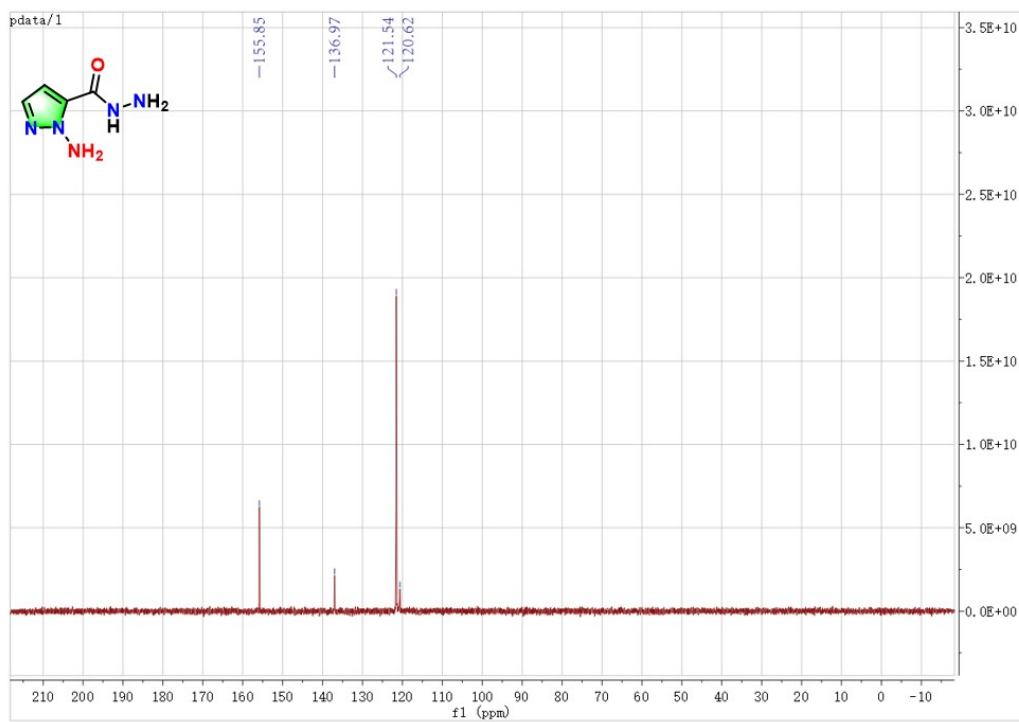

Figure 6. The illustration of test setup.

Figure S6. ^{13}C NMR spectra of 1-APZ-5-CA.

Supplementary Table S1

Table S1. Crystallographic data for **ECPs-1**

Formula	$C_4H_8N_5O_9Cl_2Ag$
Temperature [K]	116.55
M_w[g mol^{-1}]	448.91
Crystal size [mm^3]	0.23 x 0.21 x 0.2
Crystal system	monoclinic
Space group	P2$_1$/c
unit cell dimensions	a= 4.8338(2) Å, b= 29.2273(14) Å, c[Å]= 8.7843(4) Å
	α[°]= 90.00, β[°]= 96.134(4), γ[°]= 90.00
V[[Å^3]	1233.94(10)
Z	4
ρ_{calc}[g cm^{-3}]	2.416
μ[mm^{-1}]	2.126
F(000)	878.2
2θ range[°]	6.26 – 52
Reflections collected	5748
Index ranges	-4 ≤ h ≤ 5, -34 ≤ k ≤ 37, -11 ≤ l ≤ 11
R_{int}	0.0285
Data/restraints/parameters	2353 / 8 / 197
Final R index [$I > 2\sigma(I)$]	R1 = 0.0511, wR2 = 0.1163
Final R index [all data]	R1 = 0.0618, wR2 = 0.1237
GOF on F^2	1.087
CCDC	2279788