

## Supplementary Information

### **Synthesis of energetic coordination compounds based on pyrazole and 4-chloropyrazole via Co-Melting Crystallization Method**

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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 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 ( $\text{Mo}_{\text{K}\alpha}$ , 0.71073 Å). The thermal behavior of the compounds was analyzed by differential scanning calorimeter (TGA/DSC 2, METTLER TOLEDO STAR<sup>e</sup> system), with the heating rate was 5 K·min<sup>-1</sup>, and the gas atmosphere was N<sub>2</sub>. Infrared (IR) spectra were measured on a Nicolet Is10 spectrometer (Equipped with KBr discs) with a measurement range of 4000–400 cm<sup>-1</sup>. 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.

### Hot needle 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.

### Cook-off tests

Approximately 20 mg of the compound was dispersed on the operating table in a powdered state. Use an alcohol lamp to slowly heat a metal spoon, while recording the deflagration process of the compound with a high-speed camera.

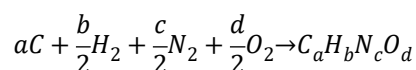
## Theoretical Calculation Section ESP calculation and visualization

Firstly, the geometry optimization and vibrational analysis of pyrazole and 4-chloropyrazole were performed under the M062X/def2TZVP level of theory, confirming them as minima without imaginary frequencies. Subsequently, the binary checkpoint (.chk) files generated from this task were converted to formcheck (.fchk) files using the formchk component in Gaussian 09. The fchk files were then processed

by the wavefunction post-processing program Multiwfn<sup>1</sup> to calculate the numerical values of Electrostatic Surface Potential (ESP) on grid points. Finally, the resulting .cube files and others were submitted to the VMD program<sup>2</sup> for visualization.

### Enthalpy of formation calculation

The enthalpy change of producing one mole of a compound from its simple substances in their standard states is defined as the standard molar enthalpy of formation of the compound. Taking the compound  $C_aH_bN_cO_d$  as an example, the corresponding general equation for its formation reaction is as follows:



By definition, the enthalpy of formation is the reaction enthalpy of the above equation. The enthalpy of reaction is determined by calculating the difference between the enthalpy of the products and the enthalpy of the reactants. To calculate the enthalpy of each species involved in the reaction, quantum chemistry computational programs such as Gaussian or ORCA can be used. Carbon is a solid at room temperature, but the enthalpy value obtained from quantum chemistry calculation corresponds to its formation in the gaseous state. Subtracting the sublimation enthalpy ( $H_{sub}(C)$ ) from the enthalpy value ( $H(C)$ ) obtained from quantum chemistry calculation is necessary to determine the enthalpy of carbon in its stable phase (solid).

In summary, the formula for calculating the enthalpy of formation using the definition method is as follows:

$$\Delta_f H_m^\theta = \Delta_r H_m^\theta = H(C_aH_bN_cO_d) - a[H(C) - H_{sub}(C)] - \frac{b}{2}H(H_2) - \frac{c}{2}H(N_2) - \frac{d}{2}H(O_2)$$

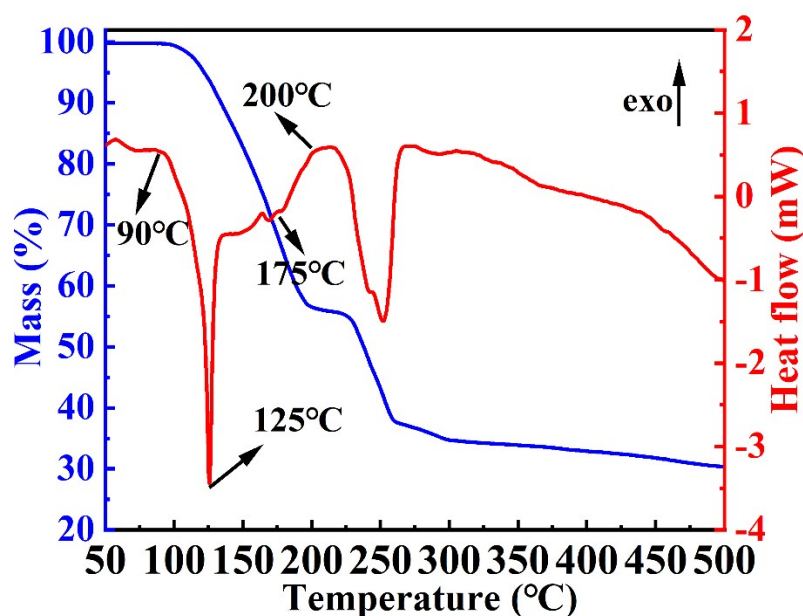
All the enthalpy values provided above are enthalpies at 298 K. The enthalpy represented by  $H(C_aH_bN_cO_d)$  corresponds to the enthalpy of a single molecule. Therefore, the final result denotes the gas-phase enthalpy of formation of the compound at 298 K.

For our **ECCs-1** to **ECCs-4**, being zero-dimensional complexes, one can seamlessly apply the aforementioned method for enthalpy of formation calculations on

a single coordination unit. It is essential to note that, in our system, apart from the C element, Cu exists in a stable solid state. Therefore, the sublimation enthalpy (337.6 kJ/mol, source: <https://webbook.nist.gov/cgi/cbook.cgi?ID=C7440508&Units=SI&Mask=1#Thermo-Gas>) should be taken into account for Cu.

Optimization and vibrational analysis for ECCs were carried out at the TPSS0/def2TZVP level, and high-precision single-point energy calculations were performed using ORCA at the PWPB95D3/def2-QZVPP level. Adding the high-precision single-point energy to the enthalpy correction obtained from the vibrational analysis task yields the enthalpy values. Following the above-mentioned approach, the enthalpies of formation of ECCs can be determined.

### Supplementary Figures S1-S11



**Fig. S1** Thermogravimetric (TG) and DSC curves of  $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ .

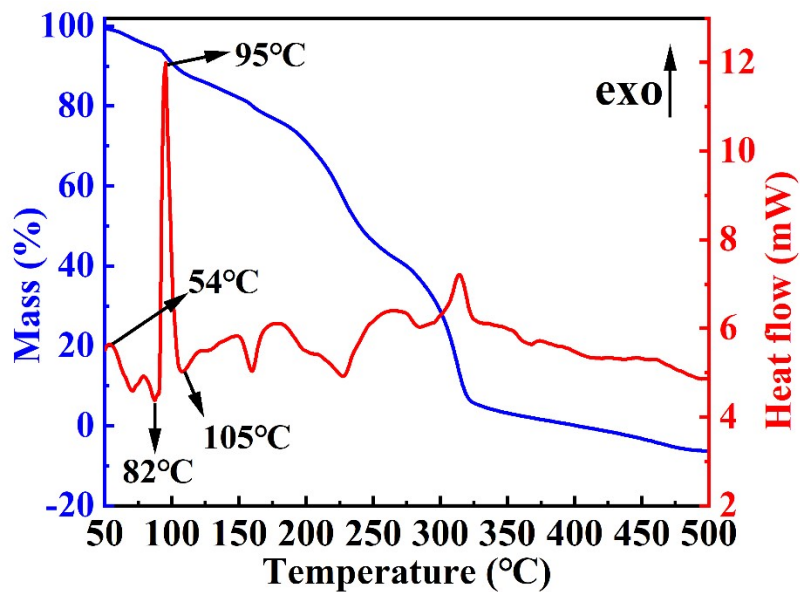


Fig. S2 Thermogravimetric (TG) and DSC curves of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

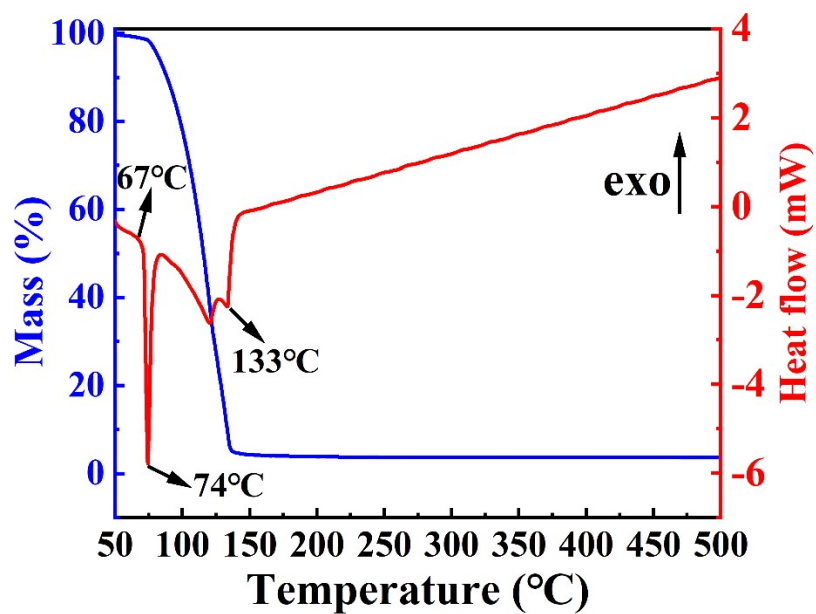
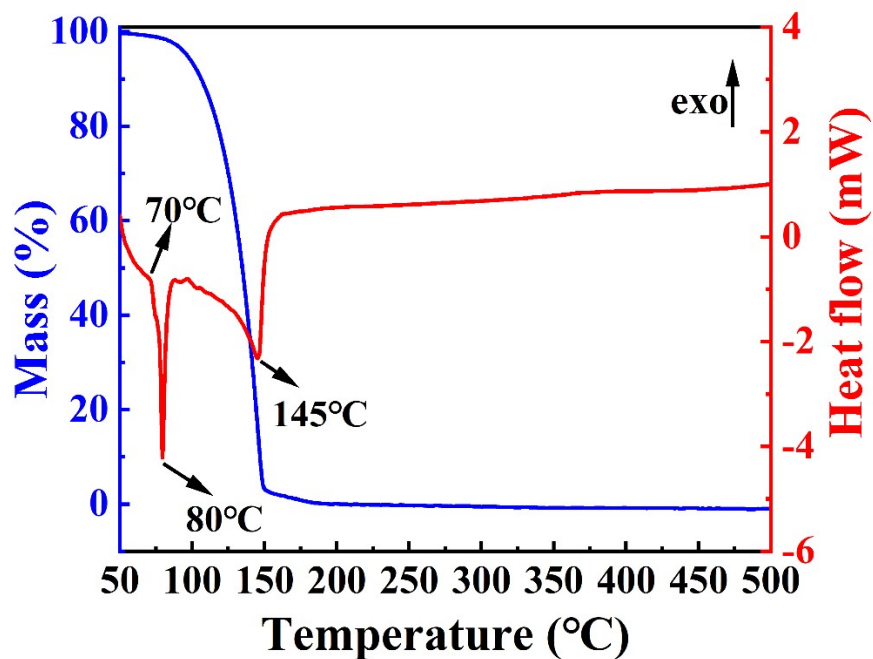
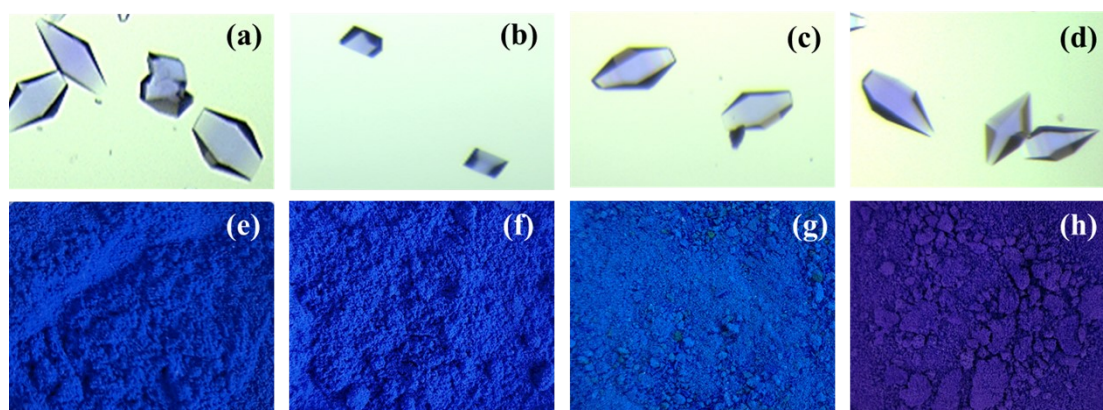


Fig. S3 Thermogravimetric (TG) and DSC curves of pyrazole.



**Fig. S4** Thermogravimetric (TG) and DSC curves of 4-Chloropyrazole.



**Fig. S5** (a-d) A small number of crystals obtained directly after co-melting and cooling: ECCs-1 (a); ECCs-2 (b); ECCs-3 (c); ECCs-4 (d). (e-h) crystals obtained after co-melting and cooling, washed with cold water and cold ethanol, and recrystallized in water: ECCs-1 (e); ECCs-2 (f); ECCs-3 (g); ECCs-4 (h).

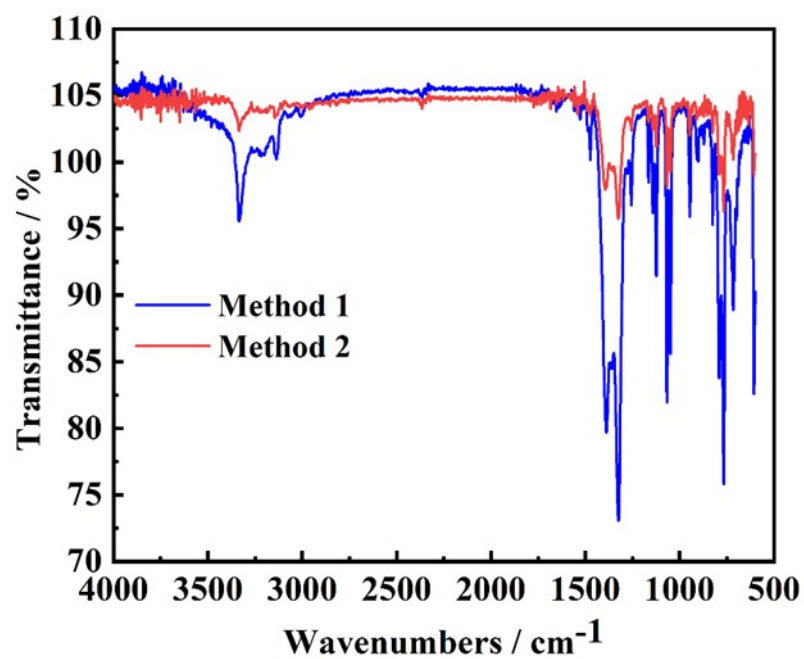


Fig. S6 Comparison of IR of ECCs-1.

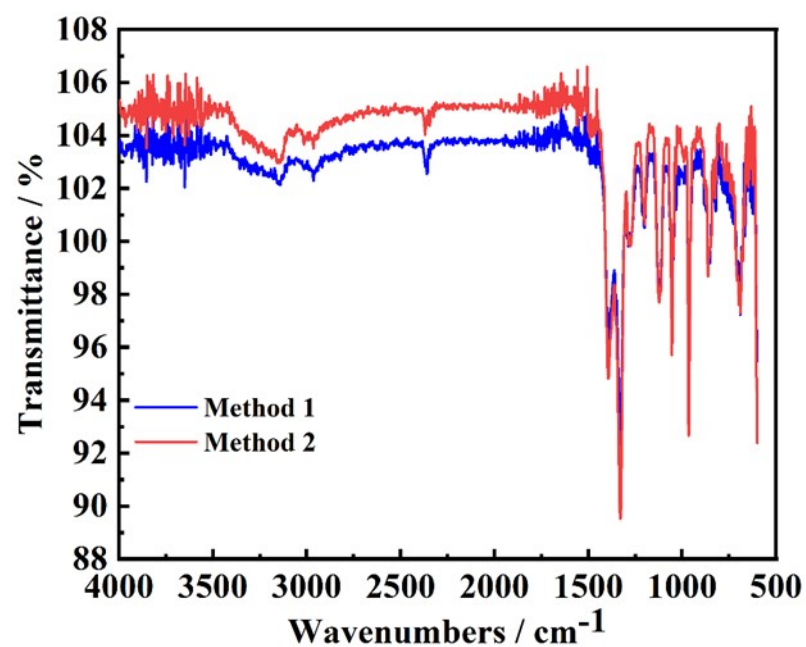


Fig. S7 Comparison of IR of ECCs-2.

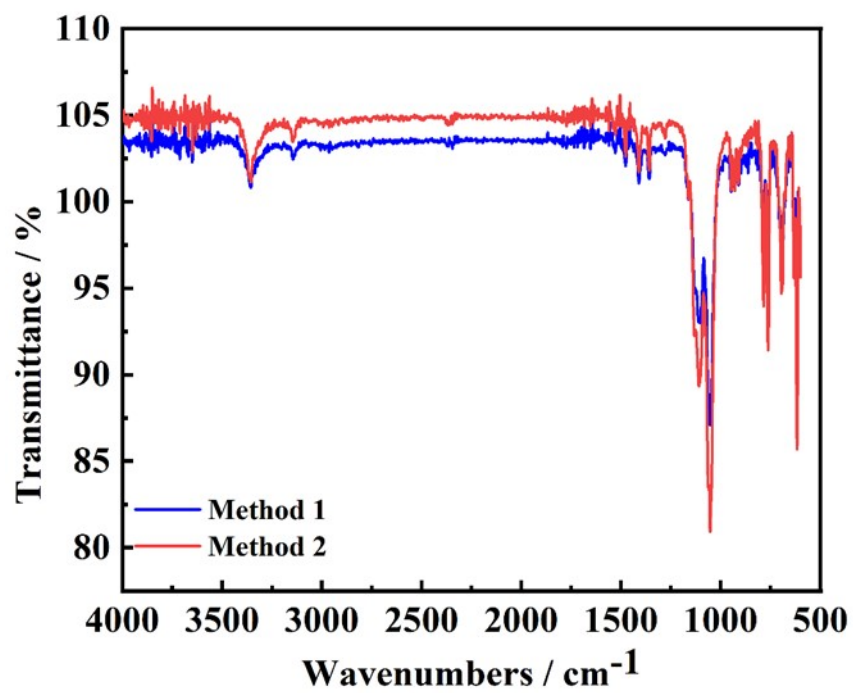


Fig. S8 Comparison of IR of ECCs-3.

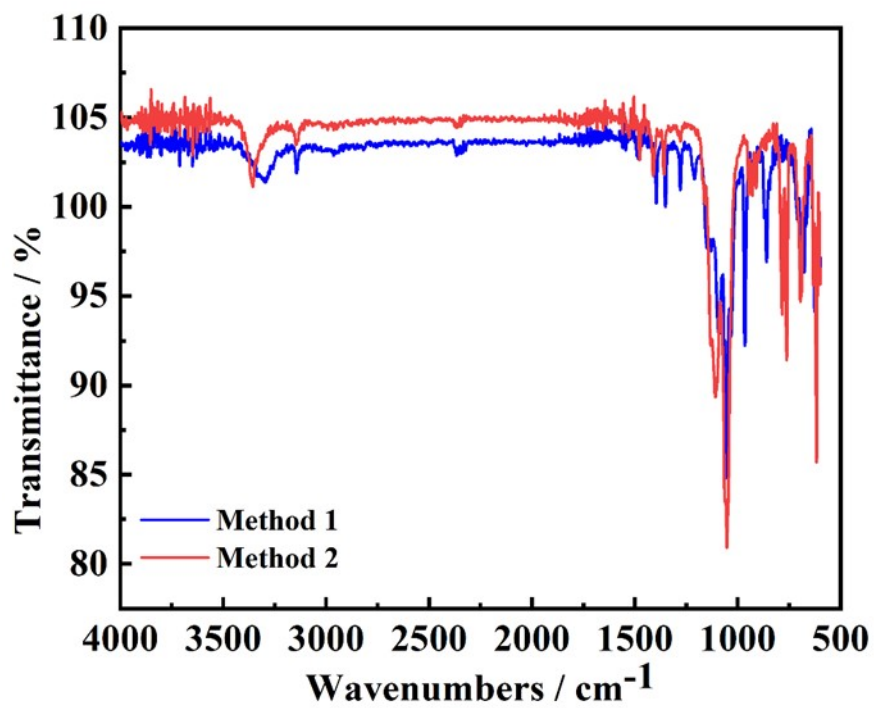


Fig. S9 Comparison of IR of ECCs-4.



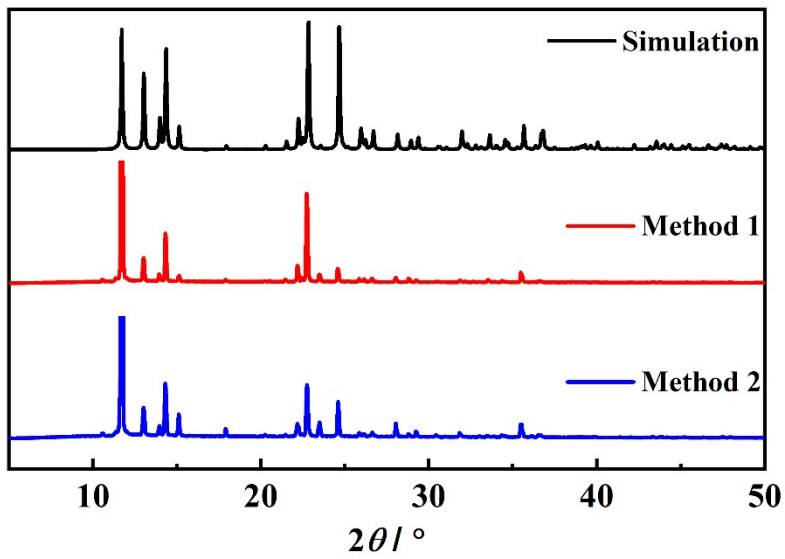


Fig. S10 Comparison of P-XRD of ECCs-1.

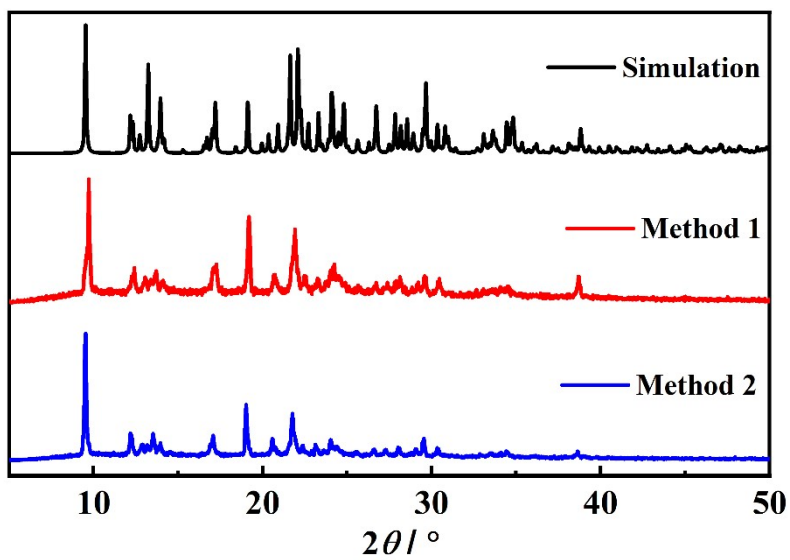


Fig. S11 Comparison of P-XRD of ECCs-2.

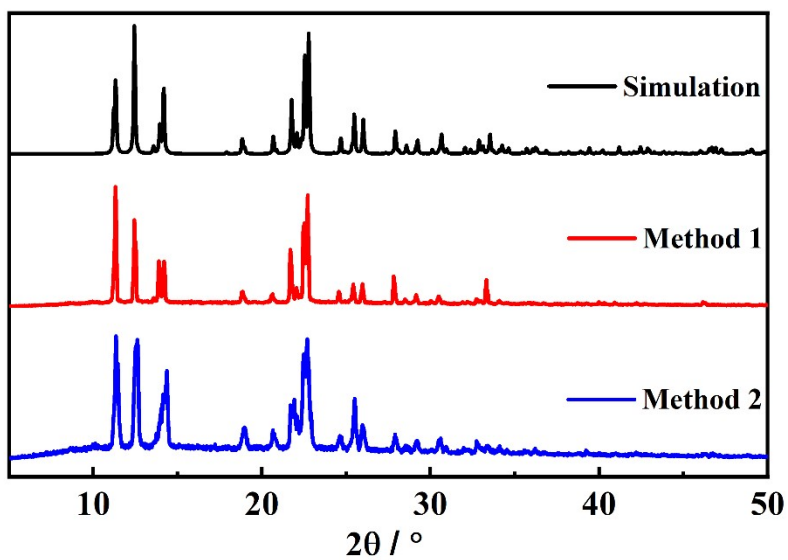


Fig. S12 Comparison of P-XRD of ECCs-3.

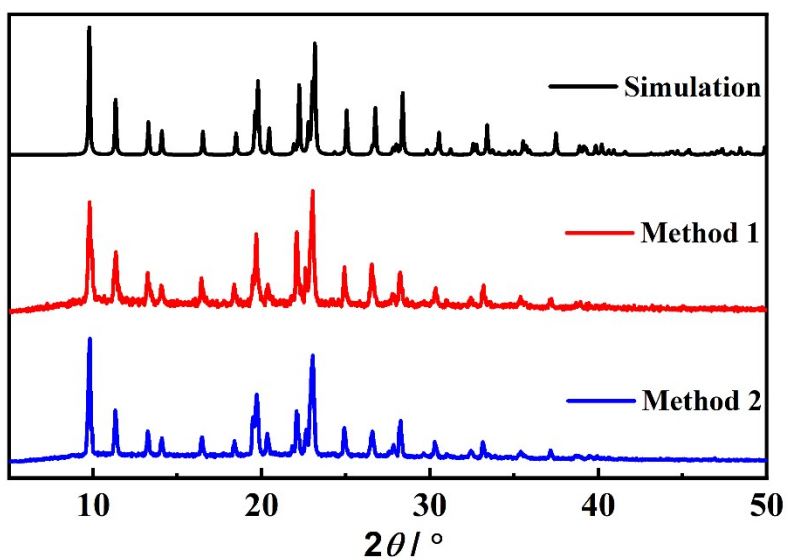
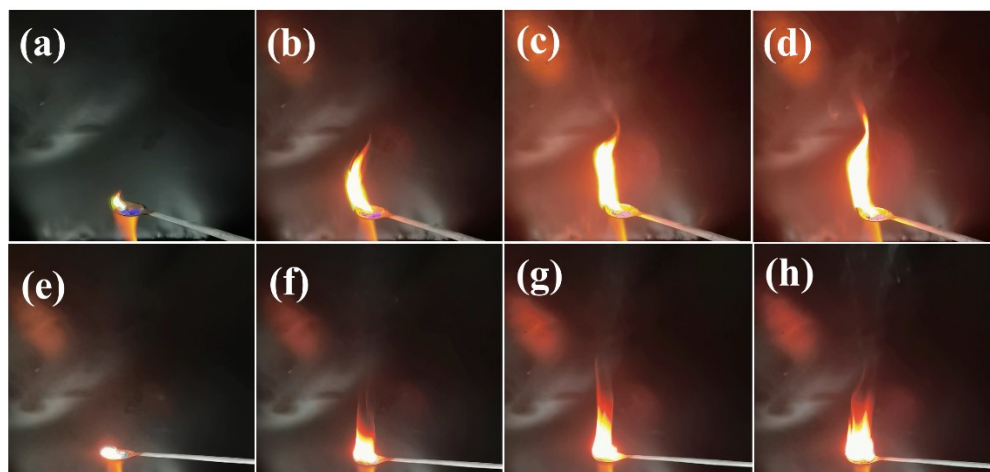


Fig. S13 Comparison of P-XRD of ECCs-4.





**Fig. S16** The combustion behavior of **ECCs-1** (a-d) and **ECCs-2** (e-h) under the cook-off tests.

## Supplementary Table S1-S5

**Table S1** Crystallographic data for ECCs-1

Formula	C <sub>12</sub> H <sub>16</sub> N <sub>10</sub> O <sub>6</sub> Cu
<i>M<sub>w</sub></i> [g mol <sup>-1</sup> ]	459.870
Crystal size [mm <sup>3</sup> ]	0.4 x 0.24 x 0.22
Crystal system	Monoclinic
Space group	<i>C2/C</i>
unit cell dimensions	<i>a</i> =13.6445(13)Å, <i>b</i> =9.8750(9)Å, <i>c</i> =14.6405(14)Å <i>α</i> =90°, <i>β</i> =112.024(5)°, <i>γ</i> =90°
<i>V</i> [[Å <sup>3</sup> ]	1828.7(3)
<i>Z</i>	4
<i>ρ</i> <sub>calc</sub> [g cm <sup>-3</sup> ]	1.670
<i>μ</i> [mm <sup>-1</sup> ]	1.251
<i>F</i> (000)	941.9
2 <i>θ</i> range[°]	5.24 – 50.04
Reflections collected	5441
Index ranges	-18 ≤ <i>h</i> ≤ 17, -10 ≤ <i>k</i> ≤ 13, -15 ≤ <i>l</i> ≤ 19
<i>R</i> <sub>int</sub>	0.0385
Data/restraints/parameters	1604 / 18 / 134
Final <i>R</i> index [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0439, <i>wR</i> <sub>2</sub> = 0.1210
Final <i>R</i> index [all data]	<i>R</i> <sub>1</sub> = 0.0514, <i>wR</i> <sub>2</sub> = 0.1298
GOF on <i>F</i> <sup>2</sup>	1.061
CCDC	2301433

**Table S2** Crystallographic data for ECCs-2

Formula	C <sub>12</sub> H <sub>12</sub> N <sub>10</sub> O <sub>6</sub> Cl <sub>4</sub> Cu
<i>M<sub>w</sub></i> [g mol <sup>-1</sup> ]	597.66
Crystal size [mm <sup>3</sup> ]	0.27 x 0.2 x 0.13
Crystal system	Monoclinic
Space group	<i>C2/c</i>
unit cell dimensions	<i>a</i> =38.031(3)Å, <i>b</i> =7.9094(8)Å, <i>c</i> =14.7249(11)Å <i>α</i> =90°, <i>β</i> =102.767°, <i>γ</i> =90°
<i>V</i> [[Å <sup>3</sup> ]	4319.8(7)
<i>Z</i>	8
<i>ρ</i> <sub>calc</sub> [g cm <sup>-3</sup> ]	1.838
<i>μ</i> [mm <sup>-1</sup> ]	1.561
<i>F</i> (000)	2392
2 <i>θ</i> range[°]	4.4 – 50.04
Reflections collected	10045
Index ranges	-45 ≤ <i>h</i> ≤ 43, -7 ≤ <i>k</i> ≤ 9, -11 ≤ <i>l</i> ≤ 17
<i>R</i> <sub>int</sub>	0.0494
Data/restraints/parameters	3800 / 173 / 336
Final <i>R</i> index [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0759, <i>wR</i> 2 = 0.1878
Final <i>R</i> index [all data]	<i>R</i> 1 = 0.0916, <i>wR</i> 2 = 0.1948
GOF on <i>F</i> <sup>2</sup>	1.125
CCDC	2301815

**Table S3** Crystallographic data for **ECCs-3**

Formula	C <sub>12</sub> H <sub>16</sub> N <sub>8</sub> O <sub>8</sub> Cl <sub>2</sub> Cu
<i>M<sub>w</sub></i> [g mol <sup>-1</sup> ]	534.77
Crystal size [mm <sup>3</sup> ]	0.3 x 0.2 x 0.17
Crystal system	Monoclinic
Space group	<i>C2/c</i>
unit cell dimensions	<i>a</i> =14.4222(15)Å, <i>b</i> =9.8977(11)Å, <i>c</i> =15.7318(16)Å <i>α</i> =90°, <i>β</i> =115.349(16)°, <i>γ</i> =90°
<i>V</i> [[Å <sup>3</sup> ]	2029.4(4)
<i>Z</i>	4
<i>ρ</i> <sub>calc</sub> [g cm <sup>-3</sup> ]	1.750
<i>μ</i> [mm <sup>-1</sup> ]	1.400
<i>F</i> (000)	1084
2 <i>θ</i> range[°]	5.16 – 50.04
Reflections collected	10045
Index ranges	-11 ≤ <i>h</i> ≤ 17, -11 ≤ <i>k</i> ≤ 10, -18 ≤ <i>l</i> ≤ 18
<i>R</i> <sub>int</sub>	0.0334
Data/restraints/parameters	1786 / 60 / 142
Final <i>R</i> index [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0428, <i>wR</i> 2 = 0.1140
Final <i>R</i> index [all data]	<i>R</i> 1 = 0.0537, <i>wR</i> 2 = 0.1202
GOF on <i>F</i> <sup>2</sup>	1.072
CCDC	2294247

**Table S4** Crystallographic data for **ECCs-4**

Formula	C <sub>12</sub> H <sub>12</sub> N <sub>8</sub> O <sub>8</sub> Cl <sub>6</sub> Cu
<i>M<sub>w</sub></i> [g mol <sup>-1</sup> ]	672.54
Crystal size [mm <sup>3</sup> ]	0.32 x 0.3 x 0.18
Crystal system	Orthorhombic
Space group	<i>Fddd</i>
unit cell dimensions	<i>a</i> =36.169(3)Å, <i>b</i> =9.9451(9)Å, <i>c</i> =13.4069(16)Å <i>α</i> =90°, <i>β</i> =90°, <i>γ</i> =90°

$V$ [[Å <sup>3</sup> ]	4822.5(8)
$Z$	8
$\rho_{\text{calc}}$ [g cm <sup>-3</sup> ]	1.853
$\mu$ [mm <sup>-1</sup> ]	1.62.7
$F(000)$	2680
$2\theta$ range[°]	4.5 – 50.04
Reflections collected	5437
Index ranges	-42 ≤ h ≤ 42, -11 ≤ k ≤ 11, -8 ≤ l ≤ 15
$R_{\text{int}}$	0.1068
Data/restraints/parameters	1069 / 43 / 99
Final R index [ $I > 2\sigma(I)$ ]	R1 = 0.0950, wR2 = 0.2492
Final R index [all data]	R1 = 0.1103, wR2 = 0.2642
GOF on F <sup>2</sup>	1.105
CCDC	2301817

**Table S5** Crystallographic data for CCs-1

Formula	C <sub>27</sub> H <sub>33</sub> Cu <sub>3</sub> N <sub>19</sub> O <sub>4</sub>
$M_w$ [g mol <sup>-1</sup> ]	878.34
Crystal size [mm <sup>3</sup> ]	0.32 x 0.17 x 0.14
Crystal system	trigonal
Space group	$R\bar{3}$
unit cell dimensions	$a=12.1710(13)\text{Å}$ , $b=12.1710(13)\text{Å}$ , $c= 43.960(4)\text{Å}$ $\alpha=90^\circ$ , $\beta=90^\circ$ , $\gamma= 120^\circ$
$V$ [[Å <sup>3</sup> ]	5639.5(10)
$Z$	6
$\rho_{\text{calc}}$ [g cm <sup>-3</sup> ]	1.552
$\mu$ [mm <sup>-1</sup> ]	1.742
$F(000)$	2682
$2\theta$ range[°]	3.98 – 50.04
Reflections collected	9447
Index ranges	-12 ≤ h ≤ 14, -14 ≤ k ≤ 14, -47 ≤ l ≤ 52
$R_{\text{int}}$	0.0606
Data/restraints/parameters	2223 / 0 / 160
Final R index [ $I > 2\sigma(I)$ ]	R1 = 0.0560, wR2 = 0.1606
Final R index [all data]	R1 = 0.0675, wR2 = 0.1678
GOF on F <sup>2</sup>	1.117
CCDC	2301818

1 T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580–592.

2 W. Humphrey, A. Dalke and K. Schulten, *J. Mol. Graph.*, 1996, **14**, 33–38.