Supporting Information

Position-Oriented N-Methylation Engineering: Multidimensional Regulation of Energy-Safety Balance in Energetic Copper Complexes

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Experimental Section

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 = 635 nm. Frequency F = 1Hz.).

Synthesis of ligands

At room temperature, 0.1 mol of the starting ester was dissolved in 50 mL of methanol. Under continuous stirring, 0.15 mol of hydrazine hydrate (80%, $N_2H_4 \cdot H_2O$) was slowly added to the mixture. The reaction system was then heated to 80 °C and refluxed for approximately 10 hours. After completion, the mixture was cooled to room temperature, resulting in the precipitation of a substantial amount of white solid. The solid was collected by filtration and thoroughly washed with chilled methanol (3 × 30 mL) to remove any potential by-products and unreacted starting materials. The final products were air-dried to afford high-purity powdered target ligands, with isolated yields exceeding 80% for all compounds.

For 1M-3PCA, yield 83%. IR (KBr, ν/cm^{-1}): 3330 (m), 3185 (m), 1668 (s), 1626 (s), 1542 (m), 1357 (m), 1271 (s), 1204 (m), 1084 (m), 1099 (s), 842 (s), 743 (s), 694 (s), 636 (s). MS (ESI), m/z: 139.0623 [$C_5H_7N_4O^-$]. Elemental analysis (%) for $C_5H_8N_4O$ (Mr = 140.15 g mol^{-1}): calcd C 42.85, H 5.75, N 39.98; found C 42.67, H 5.57, N 40.11. ^{13}C NMR (400 MHz, DMSO-d_6): δ 161.64, 145.65, 132.63, 106.56, 39.32.

For 1M-5PCA, yield 92%. IR (KBr, ν/cm^{-1}): 3315 (m), 3258 (m), 1666 (s), 1626 (s), 1539 (m), 1477 (m), 1425 (m), 1335 (s), 1112 (m), 960 (s), 935 (s), 812 (s), 708 (s), 606 (s). MS (ESI), m/z: 139.0618 [$C_5H_7N_4O^-$]. Elemental analysis (%) for $C_5H_8N_4O$ (Mr = 140.15 g mol^{-1}): calcd C 42.85, H 5.75, N 39.98; found C 42.71, H 5.63, N 40.06. ^{13}C NMR (400 MHz, DMSO-d_6): δ 159.77, 137.70, 134.54, 107.15, 39.15.

For 1,5DM-3PCA, yield 85%. IR (KBr, ν/cm^{-1}): 3337 (m), 3220 (m), 1653 (s), 1531 (s), 1429

(m), 1272 (m), 1142 (s), 1045 (m), 918 (m), 874 (s), 810 (s), 749 (s), 641 (s), 538 (s). MS (ESI), m/z: 153.0779 [$C_6H_9N_4O^-$]. Elemental analysis (%) for $C_6H_{10}N_4O$ (Mr = 154.17 g mol^{-1}): calcd C 46.74, H 6.54, N 36.34; found C 46.62, H 6.46, N 36.42. ^{13}C NMR (400 MHz, DMSO-d_6): δ 161.83, 144.12, 140.59, 105.95, 36.78, 11.11.

For 1,3DM-5PCA, yield 90%. IR (KBr, ν/cm^{-1}): 3257 (m), 1710 (m), 1660 (s), 1622 (m), 1540 (s), 1518 (s), 1456 (s), 1314 (m), 1250 (s), 1150 (m), 1096 (m), 1036 (m), 949 (s), 817 (m), 786 (s) 720 (s), 678 (s), 608 (s). MS (ESI), m/z: 153.0775 [$C_6H_9N_4O^-$]. Elemental analysis (%) for $C_6H_{10}N_4O$ (Mr = 154.17 g mol^{-1}): calcd C 46.74, H 6.54, N 36.34; found C 46.58, H 6.41, N 36.55. ^{13}C NMR (400 MHz, DMSO-d_6): δ 159.80, 145.90, 134.86, 106.45, 38.74, 13.53.

Preparation of ECCs

The synthesized organic ligand and copper(II) perchlorate hexahydrate [$Cu(ClO_4)_2{\cdot}6H_2O$] were dissolved in a suitable amount of methanol in a 2:1 stoichiometric ratio and stirred at 60 °C to form a homogeneous supersaturated solution. After hot filtration to remove insoluble impurities, the clear filtrate was allowed to stand undisturbed at room temperature for slow solvent evaporation. Over a period of 2 to 3 days, high-quality blue single crystals suitable for X-ray diffraction analysis gradually formed in the solution.

ECC-1, yield: 77%. IR (KBr, ν/cm^{-1}): 1625 (s), 1564 (s), 1499 (m), 1389 (m), 1295 (s), 1176 (s), 1088 (m), 900 (m), 800 (m), 763 (s), 624 (m), 574 (m), 471 (s). Elemental analysis (%) for $C_{10}H_{16}N_8O_{10}Cl_2Cu$ (Mr = 542.73 g mol^{-1}): calcd. C 22.13, H 2.97, N 20.65; found C 22.01, H 2.88, N 20.76.

ECC-2, yield: 77%. IR (KBr, ν/cm^{-1}): 1634 (m), 1594 (s), 1563 (m), 1348 (m), 1213 (s), 1123 (s), 1063 (s), 938 (m), 891 (m), 800 (s), 750 (s), 712 (s), 623 (s). Elemental analysis (%) for $C_{10}H_{16}N_8O_{10}Cl_2Cu$ (Mr = 542.73 g mol^{-1}): calcd. C 22.13, H 2.97, N 20.65; found C 22.05, H 2.81, N 20.87.

ECC-3, yield: 77%. IR (KBr, ν/cm^{-1}): 1623 (s), 1566 (s), 1515 (m), 1435 (m), 1382 (s), 1358 (s), 1301 (m), 1185 (m), 1088 (m), 912 (s), 768 (s), 624 (s), 589 (m), 529 (m), 479 (m). Elemental analysis (%) for $C_{12}H_{20}N_8O_{10}Cl_2Cu$ (Mr = 569.00 g mol^{-1}): calcd. C 25.25, H 3.53, N 12.42; found C 25.12, H 3.41, N 12.52.

ECC-4, yield: 77%. IR (KBr, ν/cm^{-1}): 1661 (m), 1591 (s), 1559 (m), 1543 (m), 1271 (s), 1230 (s), 1096 (s), 1050 (s), 890 (m), 820 (m), 621 (s). Elemental analysis (%) for $C_{12}H_{20}N_8O_{10}Cl_2Cu$ (Mr = 569.00 g mol^{-1}): calcd. C 25.25, H 3.53, N 12.42; found C 25.07, H 3.43, N 12.61.

Predicted detonation parameters

The standard enthalpies of formation (HOF) for ECC-1 to ECC-4 were calculated using the EM-STUDIO software (***J. Mater. Chem. A***, 2023,**11**, 25031-25044), yielding values of -397.87 kJ/mol, -396.64 kJ/mol, -496.00 kJ/mol, and -512.59 kJ/mol, respectively. These data, along with molecular formulas and room-temperature densities, were subsequently input into the EXPLO5 software (v6.04) to compute their detonation parameters, with the resulting detonation velocities and pressures summarized in **Table 1** in manuscript.

Supplementary Figures S1-S18

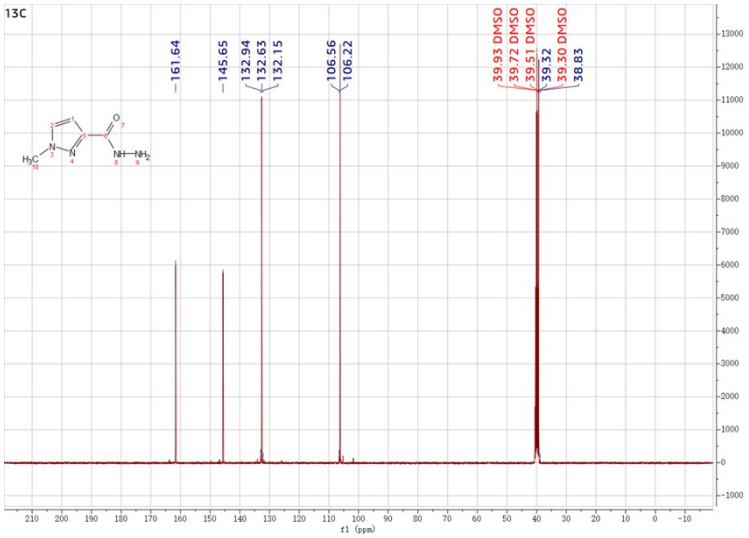

Fig. S1 $^{13}C\{^{1}H\}$ NMR spectrum of 1M-3PCA in DMSO-d6 at 400 MHz.

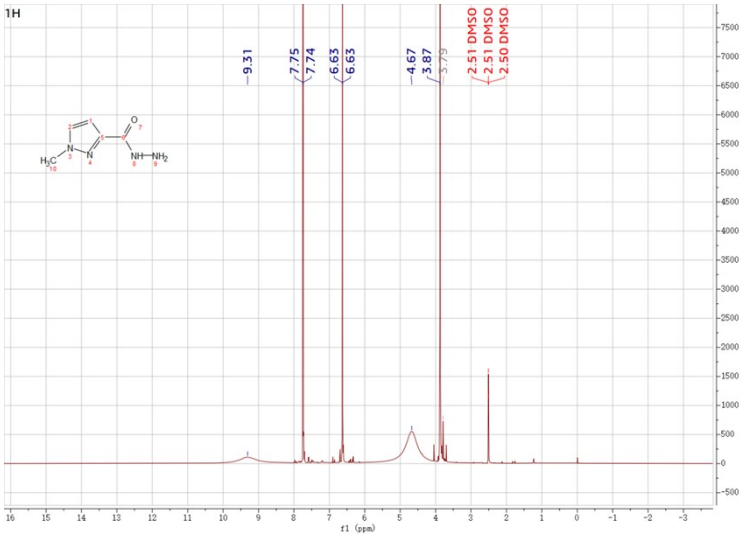

Fig. S2 ^{1}H NMR spectrum of 1M-3PCA in DMSO-d6 at 400 MHz.

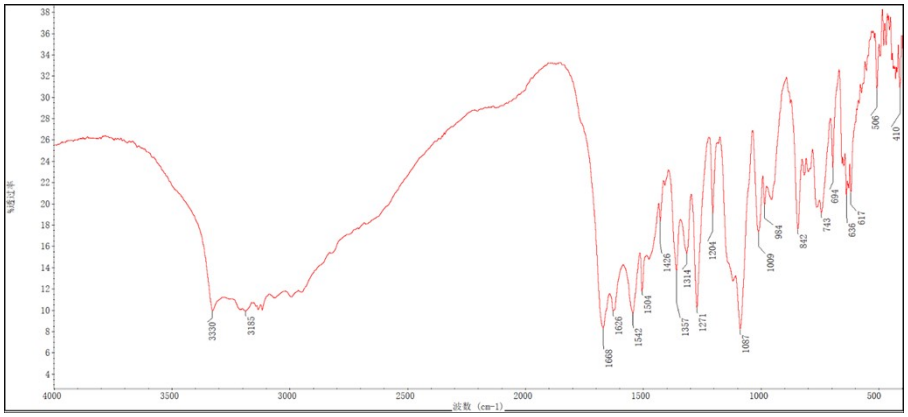

Fig. S3 IR spectra of 1M-3PCA.

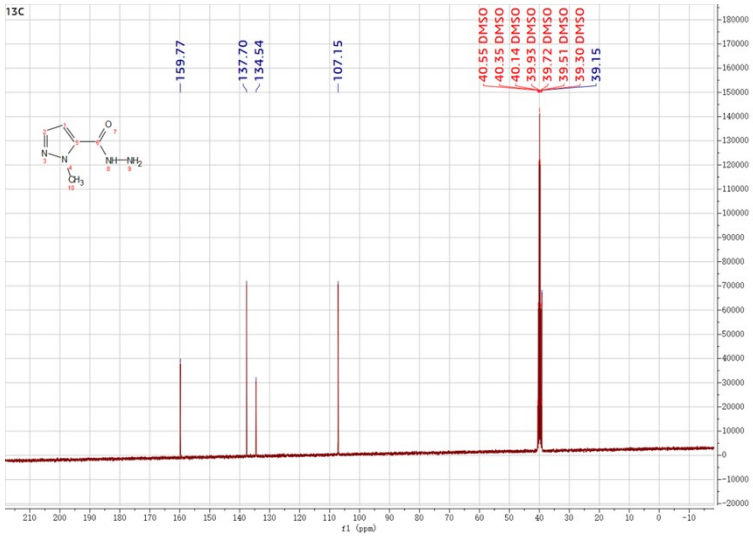

Fig. S4 $^{13}C\{^{1}H\}$ NMR spectrum of 1M-5PCA in DMSO-d6 at 400 MHz.

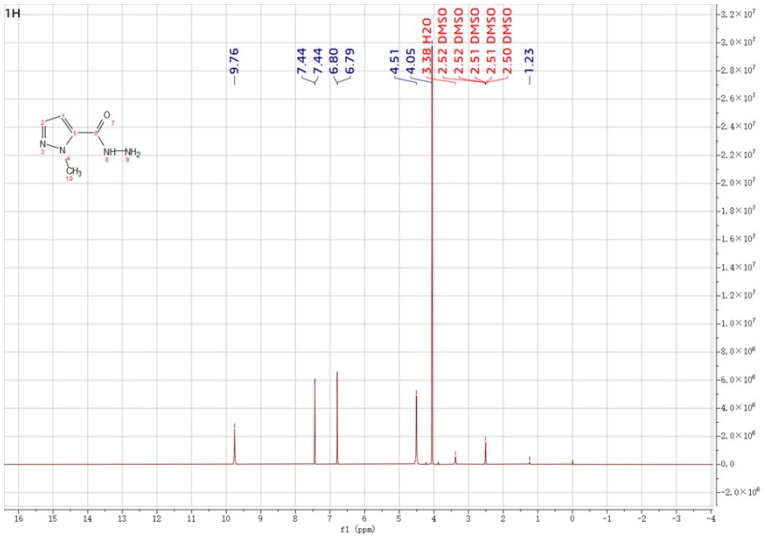

Fig. S5 ^{1}H NMR spectrum of 1M-5PCA in DMSO-d6 at 400 MHz.

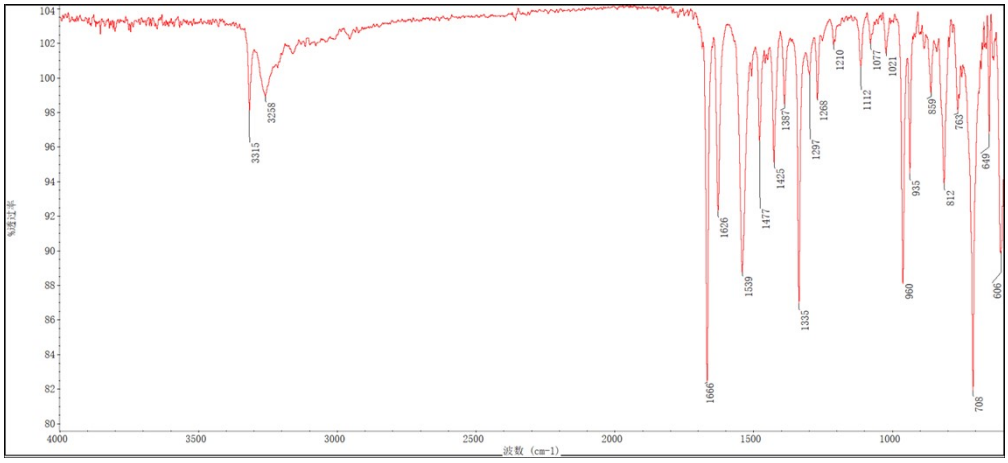

Fig. S6 IR spectra of 1M-5PCA.

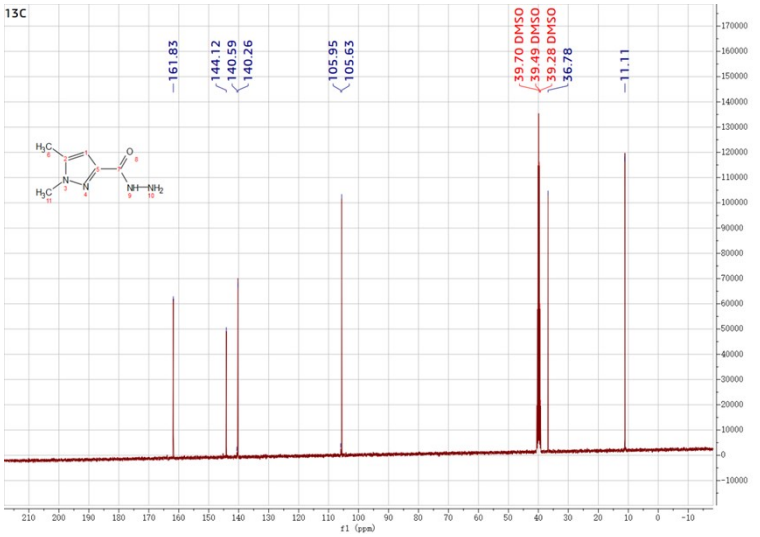

Fig. S7 $^{13}C\{^{1}H\}$ NMR spectrum of 1,5DM-3PCA in DMSO-d6 at 400 MHz.

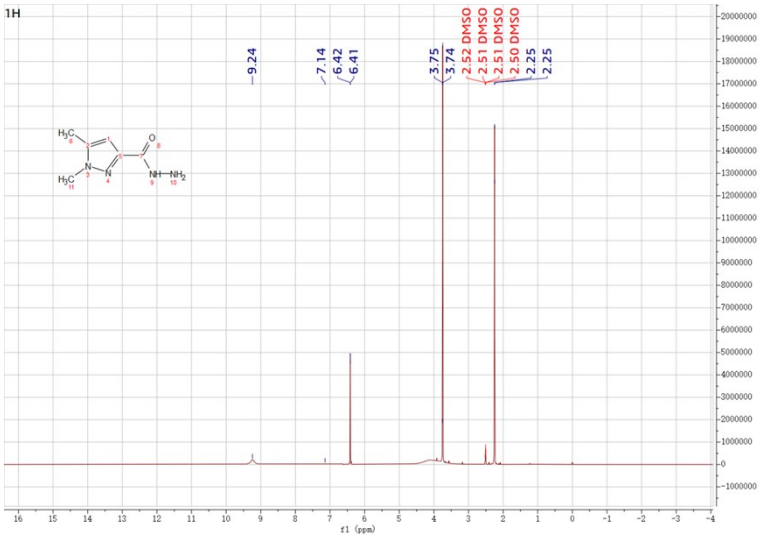

Fig. S8 ^{1}H NMR spectrum of 1,5DM-3PCA in DMSO-d6 at 400 MHz.

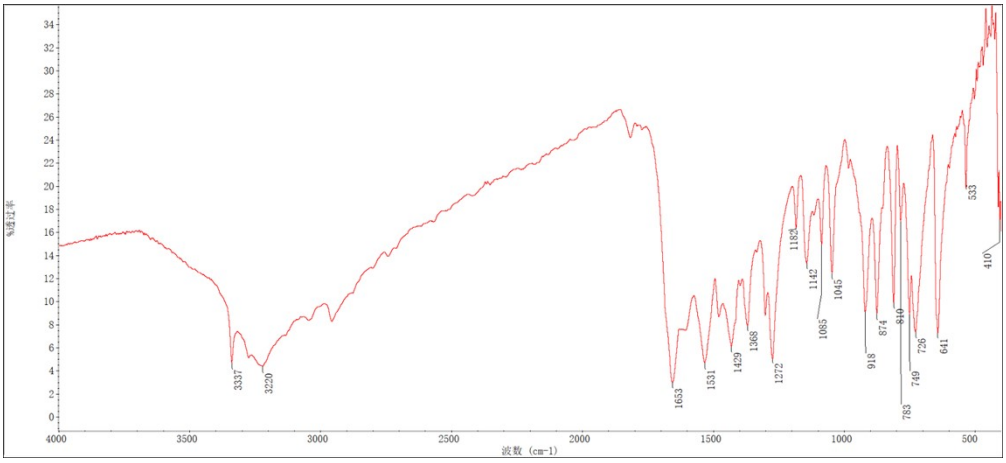

Fig. S9 IR spectra of 1,5DM-3PCA.

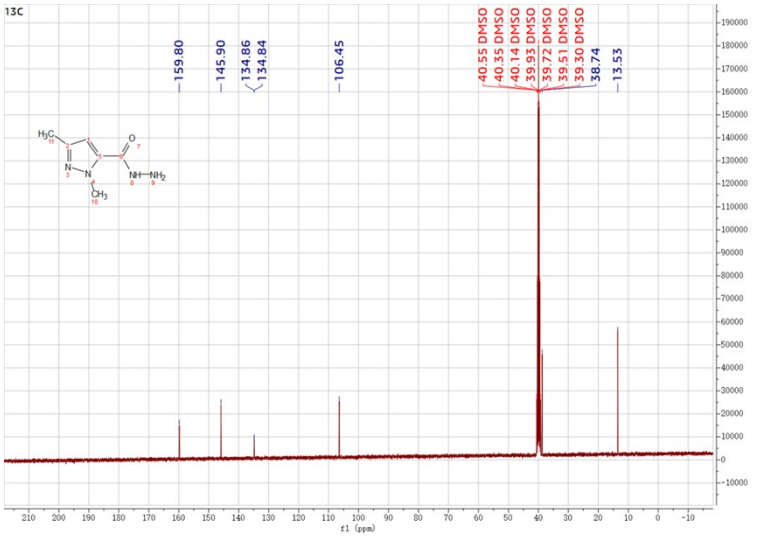

Fig. S10 $^{13}C\{^{1}H\}$ NMR spectrum of 1,3DM-5PCA in DMSO-d6 at 400 MHz.

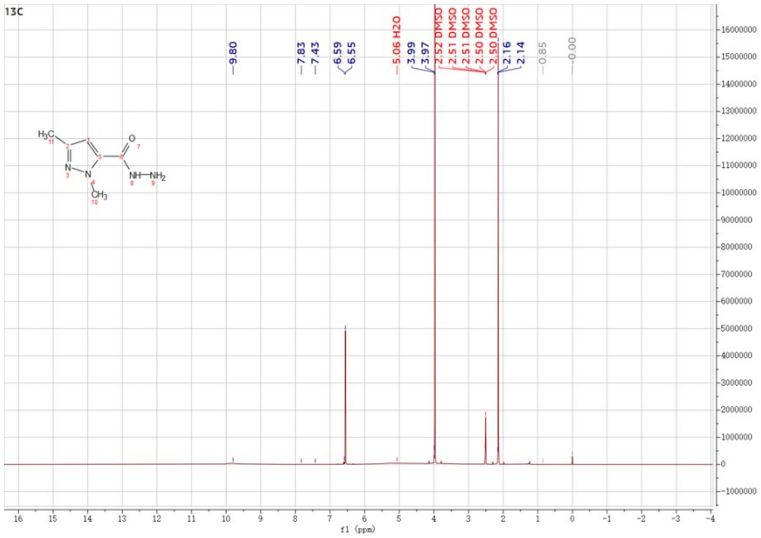

Fig. S11 ^{1}H NMR spectrum of 1,3DM-5PCA in DMSO-d6 at 400 MHz.

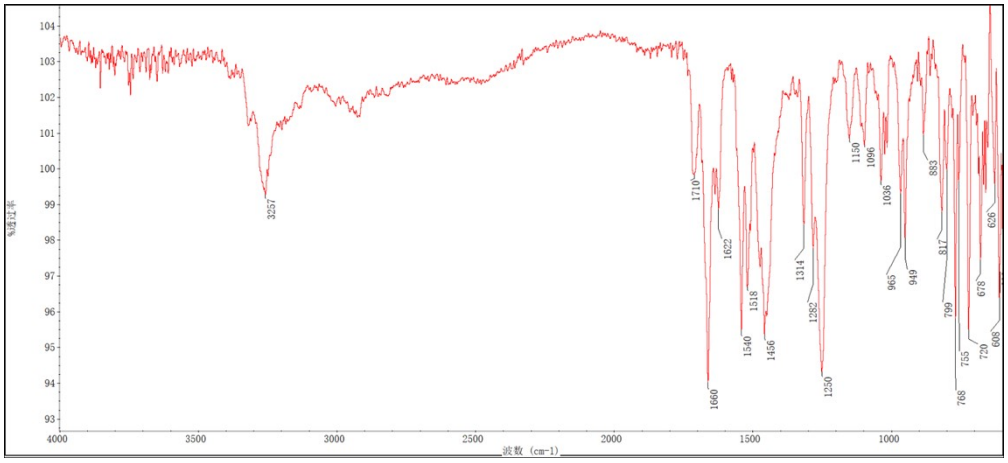

Fig. S12 IR spectra of 1,3DM-5PCA.

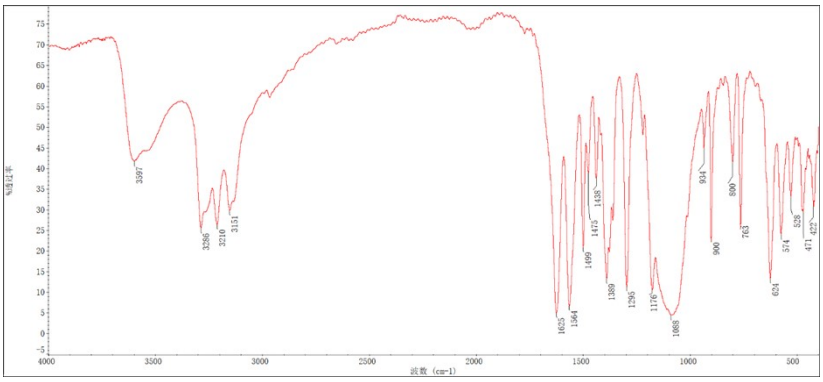

Fig. S13 IR spectra of ECC-1.

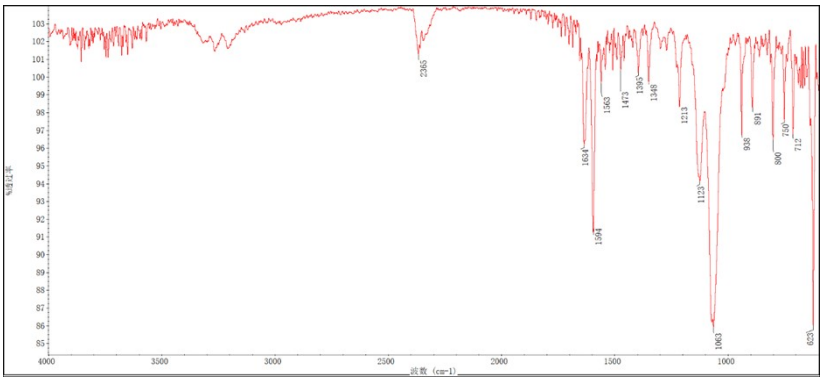

Fig. S14 IR spectra of ECC-2.

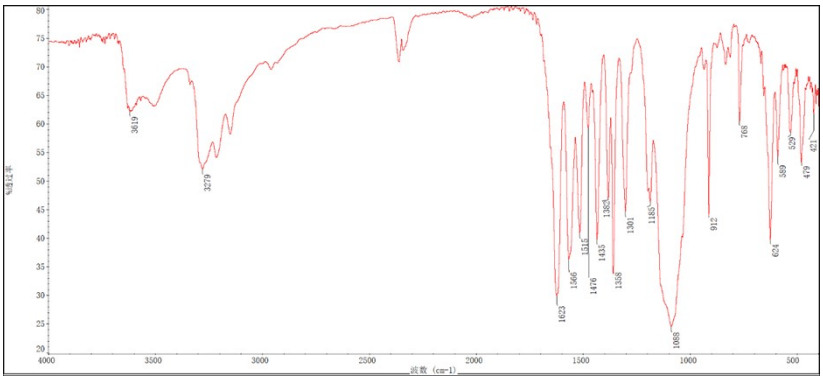

Fig. S15 IR spectra of ECC-3.

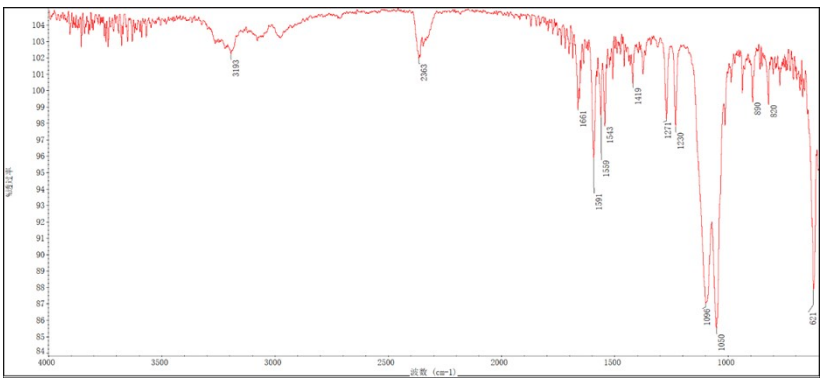

Fig. S16 IR spectra of ECC-4.

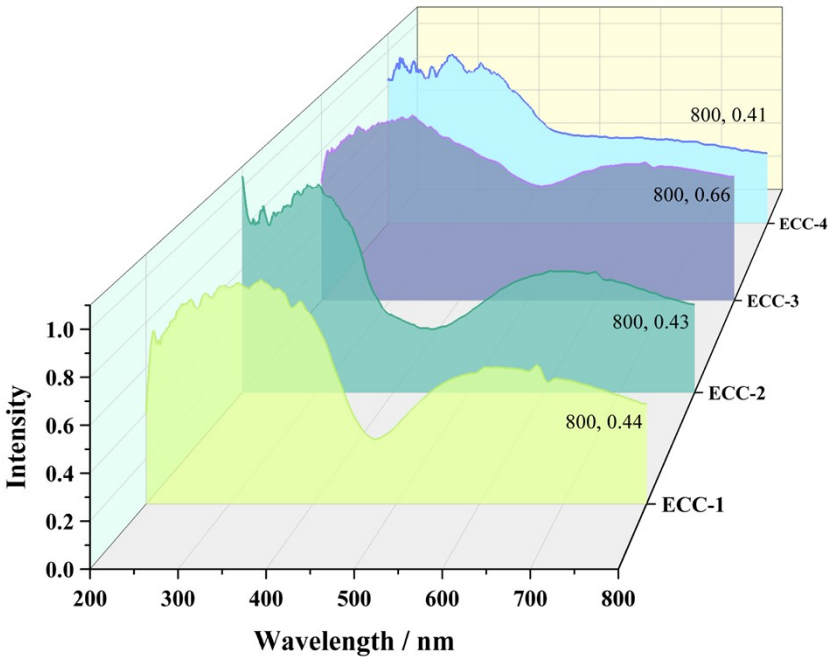

Fig. S17 UV-Vis spectra of ECC-1 to ECC-4.

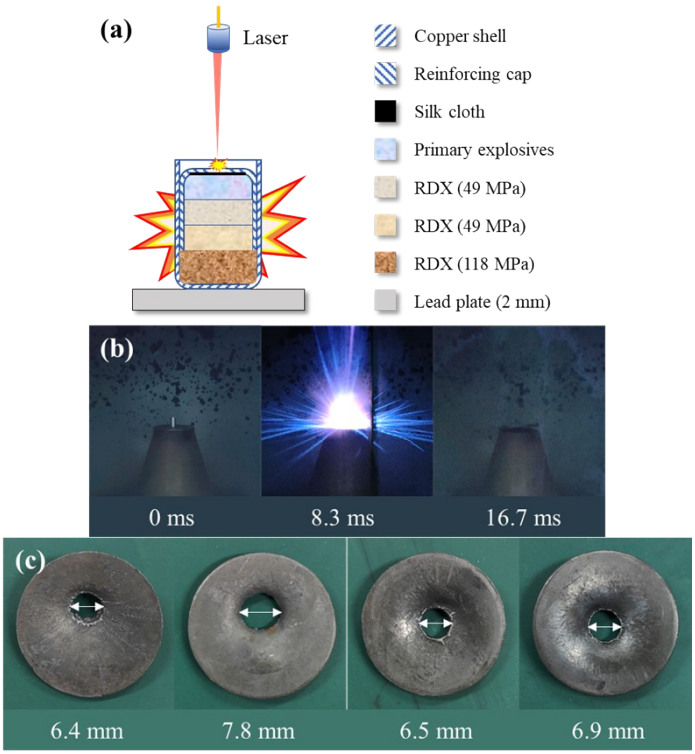

Fig. S18 Lead plate perforation test.

Supplementary Table S1-S4

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

Formula	C10 H16 N8 O10 Cl2 Cu
Temperature [K]	122
M_w[g mol^{-1}]	542.75
Crystal size [mm^3]	0.33 × 0.32 × 0.02
Crystal system	orthorhombic
Space group	*Pbca*
unit cell dimensions	*a*= 7.2382(4) Å, *b*= 15.0414(17) Å, *c*[Å]= 18.6792(11) Å
	α= 90.00 °, β[Å]= 90.00 °, γ[Å]= 90.00 °
V[[Å^3]	2033.7(3)
Z	4
ρ_{calc}[g cm^{-3}]	1.773
μ[mm^{-1}]	4.580
F(000)	1100
2θ range[^{o}]	9.46 – 132.62
Reflections collected	4088
Index ranges	-7 ≤ h ≤ 8, -17 ≤ k ≤ 10, -21 ≤ l ≤ 13
R_{int}	0.0467
Data/restraints/parameters	1755/0/143
Final R index [$I > 2\sigma(I)$]	R1 = 0.0426, wR2 = 0.1186
Final *R* index [all data]	R1 = 0.0488, wR2 = 0.1261
GOF on F^2	1.059
CCDC	2505079

Table S2. Crystallographic data for **ECC-2**

Formula	C10 H16 N8 O10 Cl2 Cu
Temperature [K]	298
M_w[g mol^{-1}]	542.75
Crystal size [mm^3]	0.33 × 0.21 × 0.18
Crystal system	monoclinic
Space group	$P2_1/n$
unit cell dimensions	a= 10.5426(12) Å, b= 7.6257(9) Å, c[Å]= 12.2240(13) Å
	α= 90.00 °, β[Å]= 97.387(2) °, γ[Å]= 90.00 °
V[[Å^3]	974.59(19)
Z	2
ρ_{calc}[g cm^{-3}]	1.850
μ[mm^{-1}]	1.466
F(000)	550
2θ range[^{o}]	4.81 – 57.21
Reflections collected	4449
Index ranges	-12 ≤ h ≤ 8, -9 ≤ k ≤ 9, -14 ≤ l ≤ 14
R_{int}	0.0375
Data/restraints/parameters	1714/0/142
Final R index [$I > 2\sigma(I)$]	R1 = 0.0335, wR2 = 0.0910
Final R index [all data]	R1 = 0.0393, wR2 = 0.0937
GOF on F^2	1.074
CCDC	2417984

Table S3. Crystallographic data for **ECC-3**

Formula	C12 H20 N8 O10 Cl2 Cu
Temperature [K]	293
M_w[g mol^{-1}]	570.80
Crystal size [mm^3]	0.27 × 0.15 × 0.10
Crystal system	triclinic
Space group	P_{-1}
unit cell dimensions	a= 7.5238(6) Å, b= 7.7132(7) Å, c[Å]= 9.2288(9) Å
	α= 99.585(3) °, β[Å]= 98.663(3) °, γ[Å]= 96.642(2) °
V[[Å^3]	516.60(8)
Z	1
ρ_{calc}[g cm^{-3}]	1.835
μ[mm^{-1}]	1.388
F(000)	291
2θ range[^{o}]	5.54 – 56.81
Reflections collected	2501
Index ranges	-8 ≤ h ≤ 8, -7 ≤ k ≤ 9, -10 ≤ l ≤ 10
R_{int}	0.0282
Data/restraints/parameters	1784/0/153
Final R index [$I > 2\sigma(I)$]	R1 = 0.0654, wR2 = 0.1582
Final R index [all data]	R1 = 0.0856, wR2 = 0.1671
GOF on F^2	1.054
CCDC	2501356

Table S4. Crystallographic data for **ECC-4·2H$_2$O**

Formula	C12 H24 N8 O12 Cl2 Cu
Temperature [K]	116
M_w[g mol^{-1}]	606.83
Crystal size [mm^3]	0.43 × 0.40 × 0.12
Crystal system	triclinic
Space group	P_{-1}
unit cell dimensions	a= 7.1171(9) Å, b= 7.7155(8) Å, c[Å]= 10.8431(13) Å
	α= 99.405(9) °, β[Å]= 96.746(10) °, γ[Å]= 98.364(10) °
V[[Å^3]	575.05(12)
Z	1
ρ_{calc}[g cm^{-3}]	1.752
μ[mm^{-1}]	1.258
F(000)	311
2θ range[^{o}]	6.52 – 51.98
Reflections collected	4058
Index ranges	-8 ≤ h ≤ 8, -9 ≤ k ≤ 8, -13 ≤ l ≤ 12
R_{int}	0.0470
Data/restraints/parameters	2210/3/168
Final R index [I > 2σ(I)]	R1 = 0.0463, wR2 = 0.1055
Final R index [all data]	R1 = 0.0557, wR2 = 0.1140
GOF on F^2	1.083
CCDC	2417985