Supplementary Information

Construction of Bowl-Shaped Copper Clusters and Nitrate-Selective Sensing

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Section S1: Materials and Instrumentation

Materials and Reagents. All chemicals and solvents obtained from suppliers were used without further purification. All solvents were of analytical grade.

Tetrakis(acetonitrile)copper(I) hexafluorophosphate $[Cu(MeCN)_4](PF_6)$ and triphenylphosphine (PPh_3) were purchased from Energy Chemical, Shanghai, China. 2-Ethynyl aniline(97%), Ethyl isocyanate(98%), $[Cu(MeCN)_4](BF_4)$, $Cu(HCOO)_2 \cdot 4H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Cu(ClO_4) \cdot 6H_2O$, Cu power was purchased from Anhui Senrise Technology Co., Ltd. Solvents of analytical grade were purchased from Sinopharm Chemical Reagent Beijing Co., Beijing, China.

Instrumentation. ^1H NMR and ^1H-^1H COSY NMR spectra were recorded on a Bruker DRX spectrometer operating at 600 MHz in CD_2Cl_2 and $CDCl_3$. X-ray powder diffraction (PXRD) patterns of the samples were recorded on a Rigaku MiniFlex diffractometer (Cu-Kα; λ = 1.54178 Å; 2θ range of 3-50°). Mass spectra (MS) were recorded on an X500R QTOF spectrometer. Fourier transform-infrared spectroscopy (FT-IR) were recorded using a Bruker ALPHA II FTIR spectrometer in the wavenumber range from 4000 to 400 cm^{-1} . Thermogravimetry analyses (TGA) were performed on a TGA Q50 system under a N_2 atmosphere (flow rate = 60 $mL \cdot min^{-1}$) in the temperature range of 25-800 °C at a heating rate of 10 °C min^{-1} . Element analyses (EA) were collected on a PerkinElmer 240 elemental analyzer. Absorption spectra of the solution were recorded on a Jasco V-750 UV-Vis spectrometer with a 1 cm quartz cell.

X-Ray crystallography. At room temperature, crystals with regular shape, good transparency, and no cracks (**Cu_4-BF_4**, **Cu_4-PF_6**, **Cu_4-HCOO**, and **Cu_4-NO_3** are colorless bar crystals; **Cu_4-ClO_4** crystals are colorless flake crystals) were picked out through a microscope, fixed on a special ring, and data collection was performed on a Rigaku XtaLAB Pro single-crystal diffractometer, and the ray source was chosen as Cu-Kα (λ = 1.54184 Å) or Mo-Kα (λ = 0.71073 Å), and the test temperature was 200 K. Data collection and reduction were performed by the *CrysAlisPro* program. The initial structure of the crystals was first solved by *SHELXT-2015*,[1] using the direct method, and then refined in *OLEX2* using the *SHELXL-2015* module with the full matrix least squares method.[2] When resolving the crystals, the non-hydrogen atoms were anisotropically refined and all hydrogen atoms were obtained by theoretical

hydrogenation. Structure refinements were performed with different strategies according to the electron density distribution. The least-squares refinement of the structural model was performed under hard geometry and displacement parameter restraints, such as SADI, ISOR, DFIX, FLAT, DELU, DANG and SIMU processing. Detailed information on the crystal data, data collection, and refinement results for all the complexes is summarized in Tables S2 and S3.

DFT calculation: With the help of Gaussian 16 software platform, the time-density flood theory (TD-DFT) calculations are implemented under the Perdew-Burke-Ernzerhof (PBE) exchange correlation generalization.[3] At the initial stage, a single-crystal structure is selected as the starting guess for the base state optimization calculations. In order to ensure the reliability of the calculation results, it was further analyzed by vibrational frequency analysis, based on the key criterion of the absence of negative eigenvalues in it, which strongly verified that all the reported standing points were true minima. The calculated absorption spectra were obtained by Multiwfn 3.8 (dev).[4]

Binding Energy DFT: All calculations were carried out with the Gaussian 16 software[1]. The PBE0 functional[5] was adopted for all calculations in combination with the D3BJ dispersion correction.[6] For geometry optimization and frequency calculations, SDD basis set[7, 8] was used for Cu and 6-31+G(d,p) for others.[9, 10]

Section S2: Synthesis

Synthesis of 1-ethyl-3-(2-ethynylphenyl)urea (L)

The ligand 1-ethyl-3-(2-ethynylphenyl)urea (**L**)[11] was synthesized by reviewing and referring to the literature as follows (Figure S1): a solution of 2-ethynylaniline (1.20 g, 10.0 mmol) and a solution of ethyl isocyanate (1.07 g, 15 mmol) were added dropwise to a solution of THF (30 mL) at room temperature. After the dropwise addition was completed, it was allowed to reflux at 70 ℃ for 10 h. After the reaction was completed, the solvent was removed under reduced pressure to obtain a brown oily crude product. In order to obtain the target product with high purity, it was purified by column chromatography, and ethyl acetate/hexane (v/v of 1/3) was selected as the eluent. After the crude product was sufficiently eluted and separated, the residual solvent in it was removed under reduced pressure, and then it was dried under vacuum to finally obtain the milky-white solid target product **L** (the yield was 0.79 g, 42%).^{1}H

NMR (600 MHz, CD_2Cl_2, 298 K): δ 8.19 (d, J = 12 Hz, 1H), 7.45 (d, J = 6 Hz, 1H), 7.35 (t, J = 9 Hz, 1H), 7.08 (s, 1H), 6.98 (t, J = 6 Hz, 1H), 4.94 (s, 1H), 3.55 (s, 1H). 3.35-3.28 (m, 2H), 1.21 (t, J = 6 Hz, 3H).ESI MS (CH_3OH): 187.10 Da (187.09 Da for $[C_{11}N_2OH_{11}]^-$).

Synthesis and Characterizations of Cu_4-X

$[Cu_4(PPh_3)_4(C{\equiv}CC_6H_4(NHCONHC_2H_5))_3](BF_4)$(**$Cu_4$-$BF_4$**):$[Cu(MeCN)_4](BF_4)$ (13 mg, 0.04 mmol), PPh_3 (10.5 mg, 0.04 mmol) and **L** (5.7 mg, 0.03 mmol) were dissolved in 2 mL of CH_3OH and 2 mL of acetone. Et_3N (40 μL, 0.29 mmol) was added and stirred for 5 min, then the resulting pale yellow solution was filtered. It was slowly evaporated at low temperature and protected from light to obtain colorless bar-shaped crystals of **Cu_4-BF_4**. Yield: 77% (15 mg) based on $[Cu(MeCN)_4](BF_4)$. The samples were vacuum-dried at 50 ℃ prior to testing to eliminate solvent interference. Elemental analysis: According to the molecular formula of $C_{105}H_{93}N_6BF_4P_4Cu_4O_3$ (molecular weight: 1951.78), the theoretical calculated value is (%): C 64.61, O 2.46, H 4.80; the experimentally determined value is (%): C 64.59, O 2.47, H 4.75. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ 7.98 (d, J = 12 Hz, 3H), 7.74 (s, 6H), 7.19 (s, 18H), 7.07 (s, 3H), 7.04-6.80 (m, 39H), 6.31 (dd, J = 6, 18 Hz, 6H), 5.61 (s, 3H). 3.11-3.01 (m, 6H), 1.09 (t, J = 6 Hz, 9H). ESI MS (CH_2Cl_2 and CH_3OH): 1865.33 Da (1865.34 Da for $[Cu_4(C_{11}N_2H_{11}O)_3((C_6H_5)_3P)_4]^+$; 1927.25 Da (1865.34 Da for $[Cu_5(C_{11}N_2H_{11}O)_2(C_{11}N_2H_{10}O)((C_6H_5)_3P)_4]^+$; 1989.17 Da (1865.34 Da for $[Cu_6(C_{11}N_2H_{10}O)_2(C_{11}N_2H_{11}O)((C_6H_5)_3P)_4]^+$; 1989.17 Da (2053.10 Da for $[Cu_7(C_{11}N_2H_{10}O)_3((C_6H_5)_3P)_4]^+$).

$[Cu_4(PPh_3)_4(C{\equiv}CC_6H_4(NHCONHC_2H_5))_3](PF_6)$(**$Cu_4$-$PF_6$**):$[Cu(MeCN)_4](PF_6)$ (15 mg, 0.04 mmol), PPh_3 (10.5 mg, 0.04 mmol) and **L** (5.7 mg, 0.03 mmol) were mixed in 3 mL of CH_3OH. Et_3N (40 μL, 0.29 mmol) was added, producing a large white precipitate. After stirring for 5 min, the resulting pale yellow solution was filtered. The white precipitate was dissolved with 2 mL of CH_2Cl_2, and then 2 mL of CH_3OH was added, and slowly evaporated at low temperature and light protection to obtain colorless needle-like crystals of **Cu_4-PF_6**. Yield: 76% (16 mg) based on $[Cu(MeCN)_4](PF_6)$. The samples were vacuum-dried at 50 ℃ prior to testing to eliminate solvent interference. Elemental analysis: Based on the molecular formula of $C_{105}H_{93}N_6F_6P_5Cu_4O_3$ (molecular weight: 2009.94), the theoretical calculated value is (%): C 62.74, O 2.39, H 4.66; the experimentally determined value is (%): C 62.77, O 2.41, H 4.63. ^{1}H NMR

(600 MHz, $CDCl_3$, 298 K): δ 7.86 (d, J = 12 Hz, 3H), 7.61 (s, 6H), 7.12 (s, 18H), 6.90 (d, J = 12 Hz, 36H), 6.79 (t, J = 9 Hz, 3H), 6.52 (s, 3H), 6.28 (d, J = 6 Hz, 3H), 6.23 (t, J = 6 Hz, 3H), 5.34 (s. 3H), 3.11-3.01 (m, 6H), 1.07 (t, J = 6 Hz, 9H). ESI MS (CH_2Cl_2 and CH_3OH): 1865.33 Da (1865.34 Da for $[Cu_4(C_{11}N_2H_{11}O)_3((C_6H_5)_3P)_4]^+$; 1927.25 Da (1865.34 Da for $[Cu_5(C_{11}N_2H_{11}O)_2(C_{11}N_2H_{10}O)((C_6H_5)_3P)_4]^+$; 1989.17 Da (1865.34 Da for $[Cu_6(C_{11}N_2H_{10}O)_2(C_{11}N_2H_{11}O)((C_6H_5)_3P)_4]^+$; 1989.17 Da (2053.10 Da for $[Cu_7(C_{11}N_2H_{10}O)_3((C_6H_5)_3P)_4]^+$).

$[Cu_4(PPh_3)_4(C{\equiv}CC_6H_4(NHCONHC_2H_5))_3](HCOO)$ (**Cu_4-HCOO**): $Cu(HCOO)_2{\cdot}4H_2O$ (4.6 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), excess Cu powder (4 mg, 0.04 mmol) and **L** (5.7 mg, 0.03 mmol) were mixed in 3 mL of CH_3OH. Et_3N (40 μL, 0.29 mmol) was added and stirred vigorously for two days before the resulting pale yellow solution was filtered. It was slowly volatilized at low temperature and protected from light to obtain colorless needle-like crystals of **Cu_4-HCOO**. Yield: 47% (9 mg) based on $Cu(HCOO)_2{\cdot}4H_2O$. The samples were vacuum-dried at 50 ℃ prior to testing to eliminate solvent interference. Elemental analysis: according to the molecular formula of $C_{106}H_{94}N_6P_4Cu_4O_5$ (molecular weight: 1909.99), the theoretically calculated value is (%): C 66.66, O 4.19, H 4.96; the experimentally determined value is (%): C 66.62, O 4.18, H 4.95. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ 8.68 (s, 1H), 8.11-7.97 (m, 6H), 7.75 (t, J = 9 Hz, 6H), 7.44 (s, 3H), 7.29 (t, J = 9 Hz, 3H), 7.24 - 7.16 (m, 15H), 7.02-6.09 (m, 36H), 6.88 (t, J = 9 Hz, 3H), 6.29 (t, J = 9 Hz, 6H), 6.17 (d, J = 6 Hz, 3H), 3.06-2.98 (m, 6H), 1.05 (t, J = 6 Hz, 9H). ESI MS (CH_2Cl_2 and CH_3OH): 1865.33 Da (1865.34 Da for $[Cu_4(C_{11}N_2H_{11}O)_3((C_6H_5)_3P)_4]^+$; 1927.25 Da (1865.34 Da for $[Cu_5(C_{11}N_2H_{11}O)_2(C_{11}N_2H_{10}O)((C_6H_5)_3P)_4]^+$; 1989.17 Da (1865.34 Da for $[Cu_6(C_{11}N_2H_{10}O)_2(C_{11}N_2H_{11}O)((C_6H_5)_3P)_4]^+$; 1989.17 Da (2053.10 Da for $[Cu_7(C_{11}N_2H_{10}O)_3((C_6H_5)_3P)_4]^+$).

$[Cu_4(PPh_3)_4(C{\equiv}CC_6H_4(NHCONHC_2H_5))_3](ClO_4)$(**$Cu_4$-$ClO_4$**): $Cu(ClO_4){\cdot}6H_2O$ (7.5 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), excess Cu powder (4 mg, 0.04 mmol) and **L** (5.7 mg, 0.03 mmol) were mixed in 2 mL of CH_3OH and 2 mL of acetone. Et_3N (40 μL, 0.29 mmol) was added and stirred vigorously for two days, then the resulting pale yellow solution was filtered. It was slowly evaporated at low temperature away from light to obtain colorless flaky crystals of **Cu_4-ClO_4**. Yield: 51% (10 mg) based on $Cu(ClO_4){\cdot}6H_2O$. The samples were vacuum-dried at 50 ℃ prior to testing to eliminate solvent interference. Elemental analysis: calculated according to the molecular formula

of $C_{105}H_{93}N_6ClP_4Cu_4O_7$ (molecular weight: 1964.43), the theoretically calculated value is (%): C 64.20, O 5.70, H 4.77; the experimentally determined value is (%): C 64.20, O 5.68, H 4.76. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ 8.00 (d, J = 12 Hz, 3H), 7.75 (s, 6H), 7.20 (d, J = 30 Hz, 18H), 7.04 (s, 3H), 7.03-6.77 (m, 39H), 6.35-6.25 (m, 6H), 5.62 (t, J = 3 Hz, 3H), 3.12-3.02 (m, 6H), 1.12-1.01 (m, 9H). ESI MS (CH_2Cl_2 and CH_3OH): 1865.33 Da (1865.34 Da for $[Cu_4(C_{11}N_2H_{11}O)_3((C_6H_5)_3P)_4]^+$; 1927.25 Da (1865.34 Da for $[Cu_5(C_{11}N_2H_{11}O)_2(C_{11}N_2H_{10}O)((C_6H_5)_3P)_4]^+$; 1989.17 Da (1865.34 Da for $[Cu_6(C_{11}N_2H_{10}O)_2(C_{11}N_2H_{11}O)((C_6H_5)_3P)_4]^+$; 1989.17 Da (2053.10 Da for $[Cu_7(C_{11}N_2H_{10}O)_3((C_6H_5)_3P)_4]^+$).

$[Cu_4(PPh_3)_4(C{\equiv}CC_6H_4(NHCONHC_2H_5))_3](NO_3)$(**$Cu_4$-$NO_3$**):$Cu(NO_3)_2{\cdot}3H_2O$ (4.9 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), excess Cu powder (4 mg, 0.04 mmol) and **L** (5.7 mg, 0.03 mmol) were mixed in 2 mL of CH_3OH and 2 mL of acetone. Et_3N (40 μL, 0.29 mmol) was added and stirred vigorously for two days, then the resulting pale yellow solution was filtered. Slowly volatilized at low temperature and light protection, to obtain colorless strip crystals **Cu_4-NO_3**. yield: 42% (8 mg), based on $Cu(NO_3)_2{\cdot}3H_2O$. The samples were vacuum-dried at 50 ℃ prior to testing to eliminate solvent interference. Elemental analysis: according to the molecular formula of $C_{105}H_{93}N_7P_4Cu_4O_6$ (molecular weight: 1926.98), the theoretically calculated value is (%): C 65.45, O 4.98, H 4.86; the experimentally determined value is (%): C 65.44, O 4.96, H 4.85. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ 8.02 (s, 3H), 7.96 (s, 3H), 7.75-7.70 (m, 6H), 7.32 (t, J = 9 Hz, 3H), 7.17 (dd, J = 6, 18 Hz, 15H), 6.92 (dt, J = 6, 18 Hz, 36H), 6.83 (t, J = 9 Hz, 3H), 6.30 (s, 1H), 6.17 (t, J = 9 Hz, 3H), 5.98 (d, J = 12 Hz, 3H), 3.02-2.97 (m, 6H), 1.01 (t, J = 6 Hz, 3H). ESI MS (CH_2Cl_2 and CH_3OH): 1865.39 Da (1865.34 Da for $[Cu_4(C_{11}N_2H_{11}O)_3((C_6H_5)_3P)_4]^+$; 1950.37 Da (1950.32 Da for $Cu_4(C_{11}N_2H_{12}O)_3((C_6H_5)_3P)_4(NO_3)Na]^+$).

Section S3: Supplementary Figures

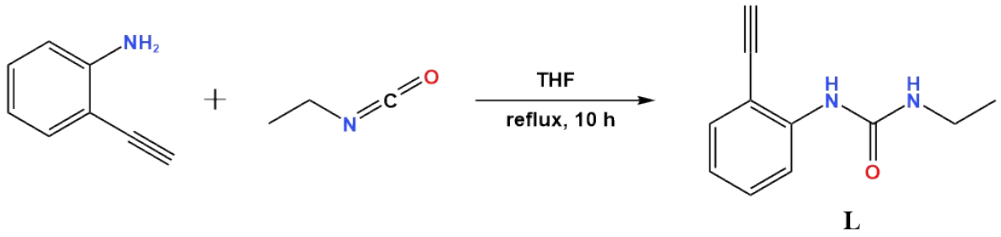

Figure S1. Synthetic procedures for ligand **L**.

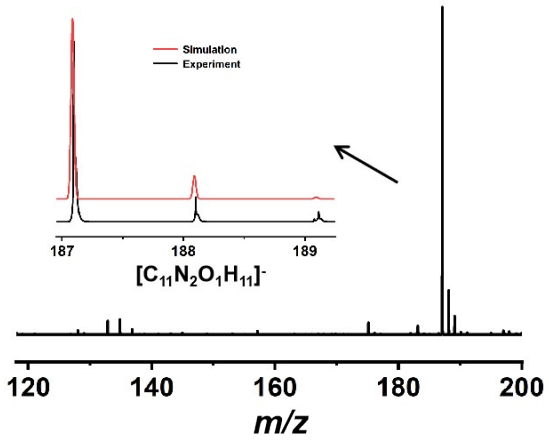

Figure S2. Negative ion mode ESI-MS spectrum of ligand **L** in CH_3OH solution; inset: isotopic distribution for simulations (red), isotopic distribution for experimental tests (black).

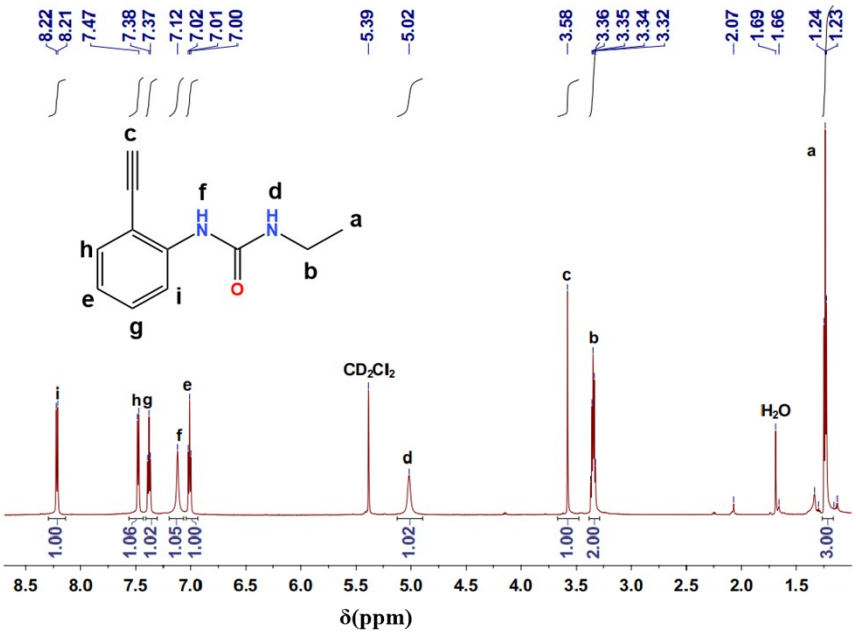

Figure S3. ^{1}H NMR spectrum of **L** (600 MHz, CD_2Cl_2, 298 K).

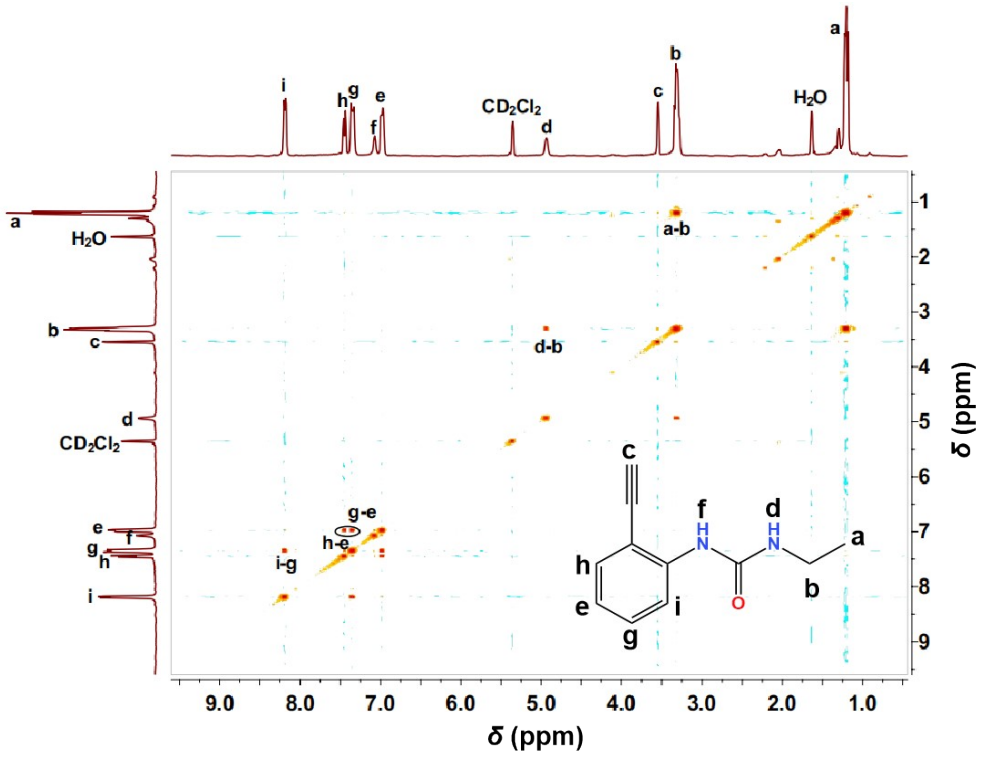

Figure S4. ^{1}H-^{1}H COSY NMR spectrum of **L** (600 MHz, CD_2Cl_2, 298 K).

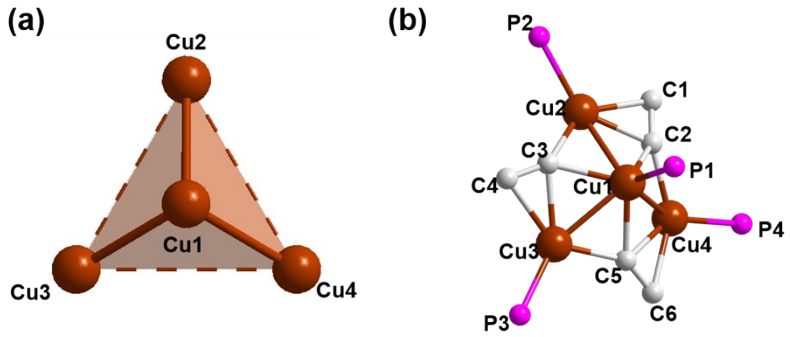

Figure S5. (a) Cu_4 tetrahedral core structure; (b) Cu_4 structural unit with alkyne and P atom coordination. Color code: Cu, brown; P, purple; C, light gray.

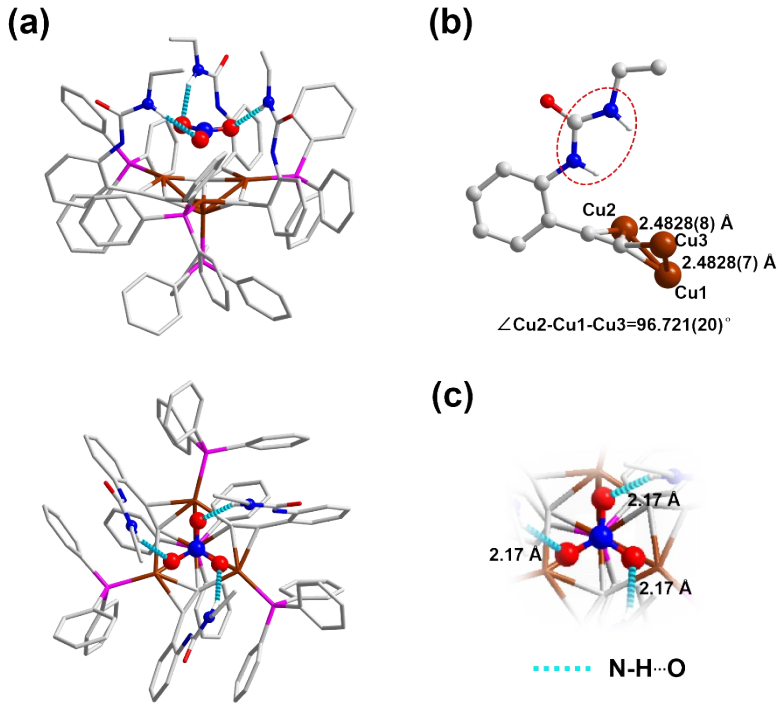

Figure S6. (a) Overall structure of **Cu_4-NO_3**; (b) Coordination pattern of the urea-based acetylene ligand **L** with Cu in **Cu_4-NO_3**; (c) Intramolecular hydrogen bonding pattern in **Cu_4-NO_3**. Color code: Cu, brown; P, pink; C, light gray; N, blue; O, red; H, white.

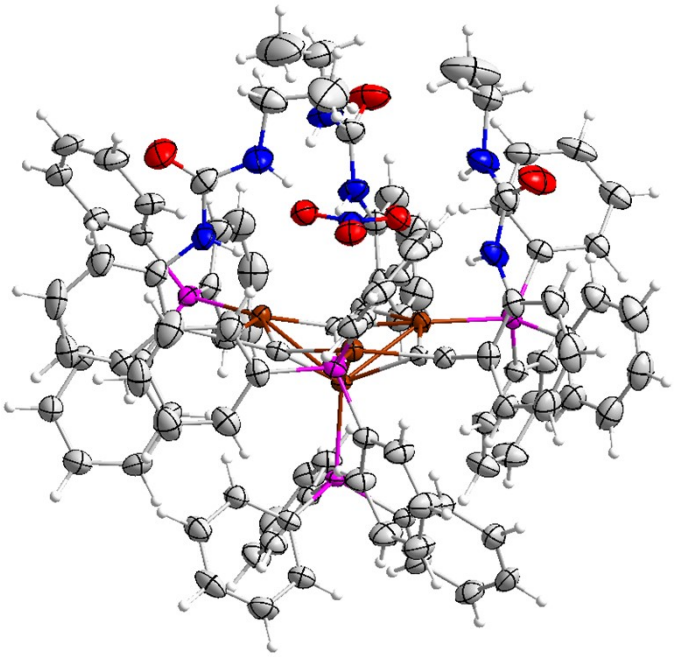

Figure S7. Crystal structure of **Cu_4-NO_3**. Thermal ellipsoids set at 50% probability. Color code: Cu, brown; P, pink; C, light gray; N, blue; O, red; H, white.

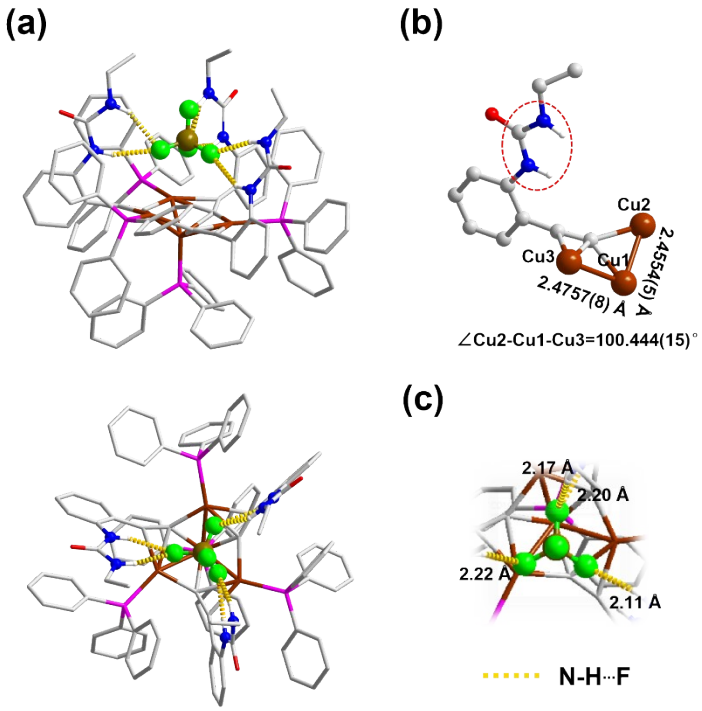

Figure S8. (a) Overall structure of **Cu_4-BF_4**; (b) Coordination pattern of ureidoalkyne ligand **L** with Cu in **Cu_4-BF_4**; (c) Intramolecular hydrogen bonding mode of action in **Cu_4-BF_4**. Color code: Cu, brown; P, pink; C, light gray; N, blue; O, red; F, bright green; B, gray-brown; H, white.

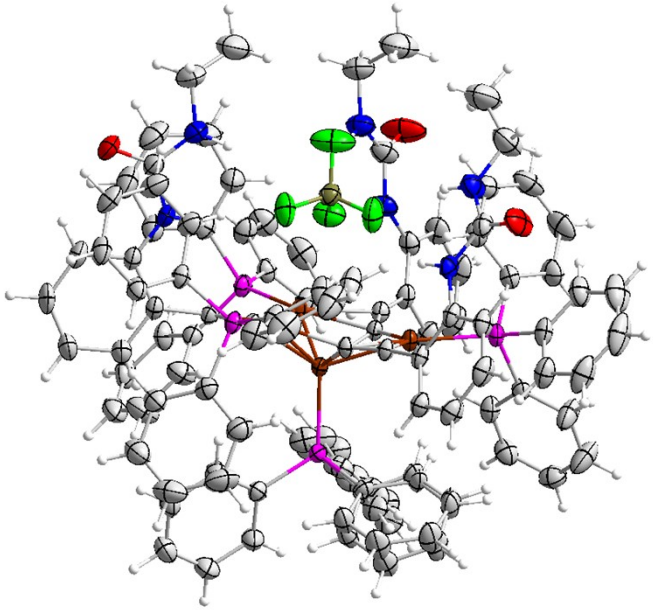

Figure S9. Crystal structure of **Cu_4-BF_4**. Thermal ellipsoids set at 50% probability. Color code: Cu, brown; P, pink; C, light gray; N, blue; O, red; F, bright green; B, gray-brown; H, white.

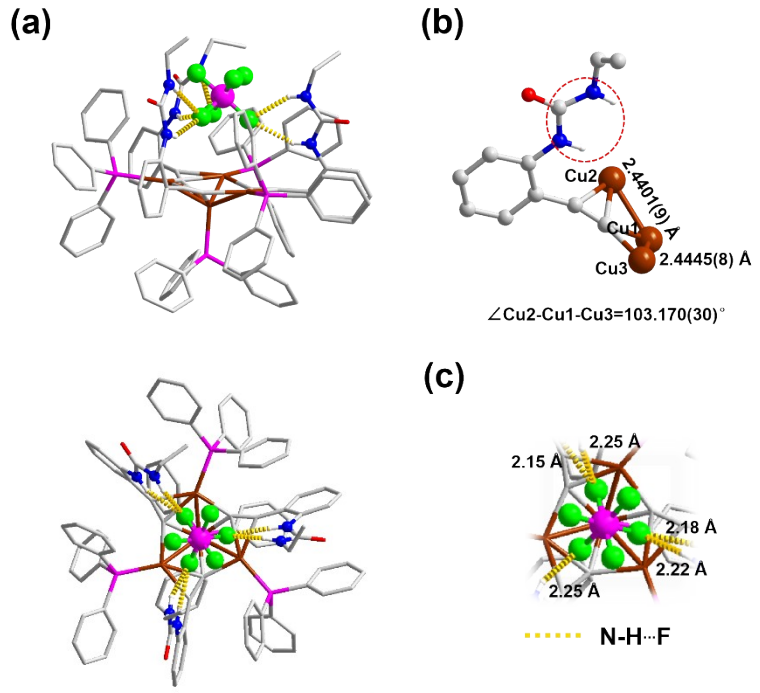

Figure S10. (a) Overall structure of **Cu_4-PF_6**; (b) Coordination pattern of ureidoalkyne ligand **L** with Cu in **Cu_4-PF_6**; (c) Intramolecular hydrogen bonding mode of action in **Cu_4-PF_6**. Color code: Cu, brown; P, pink; C, light gray; N, blue; O, red; F, bright green; H, white.

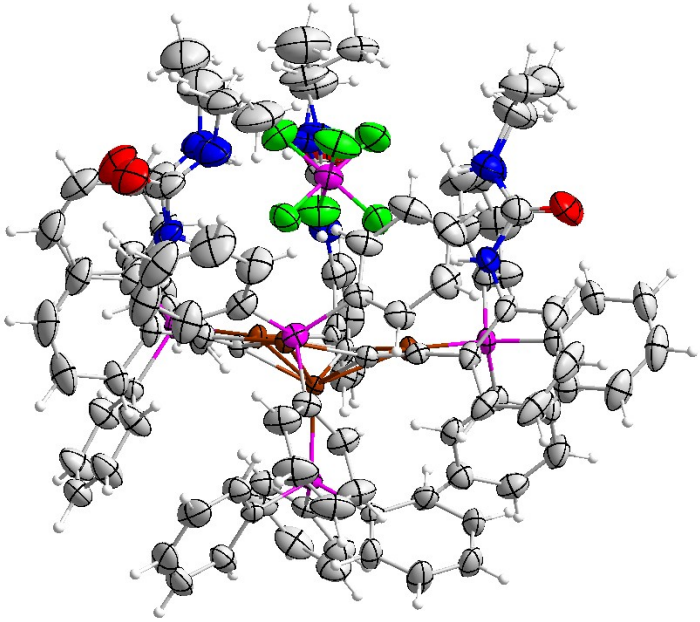

Figure S11. Crystal structure of **Cu_4-PF_6**. Thermal ellipsoids set at 50% probability. Color code: Cu, brown; P, pink; C, light gray; N, blue; O, red; F, bright green; H, white.

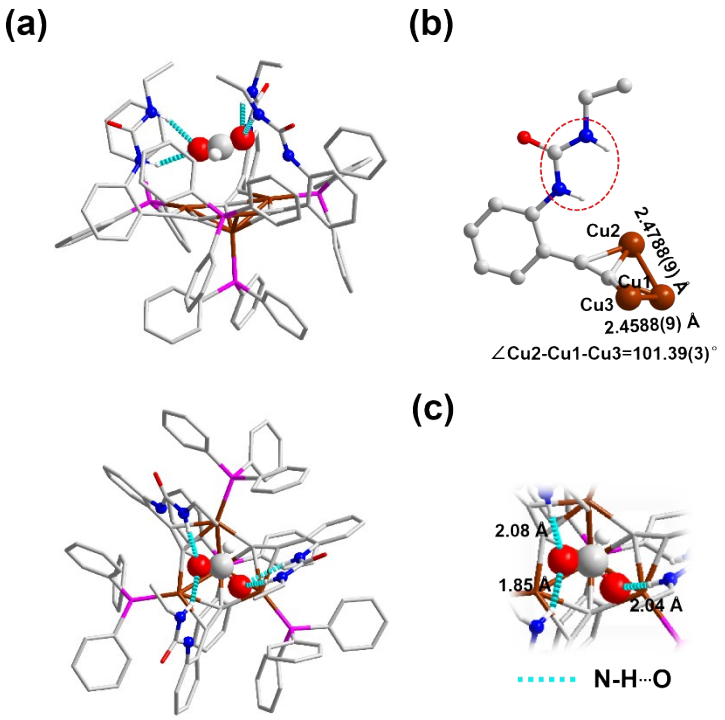

Figure S12. (a) Overall structure of **Cu_4-HCOO**; (b) Coordination pattern of ureidoalkyne ligand **L** with Cu in **Cu_4-HCOO**; (c) Intramolecular hydrogen bonding mode of action in **Cu_4-HCOO**. Color code: Cu, brown; P, pink; C, light gray; N, blue; O, red; H, white.

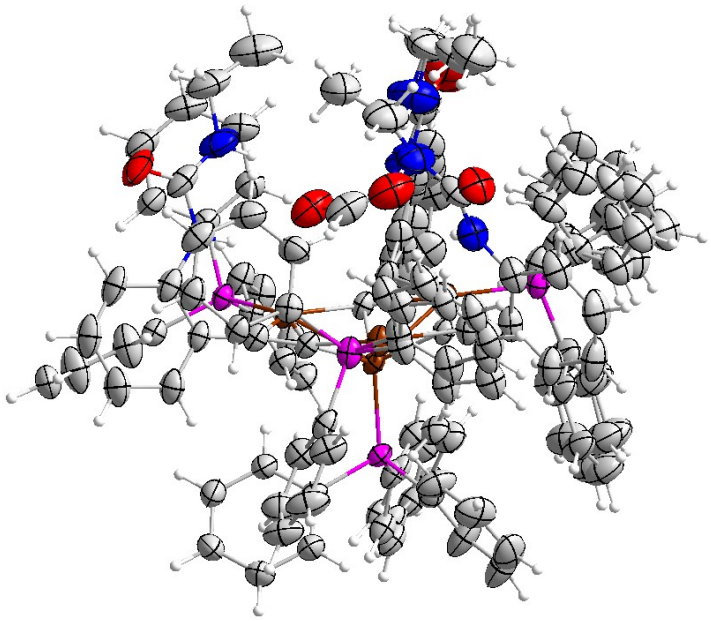

Figure S13. Crystal structure of **Cu_4-HCOO**. Thermal ellipsoids set at 50% probability. Color code: Cu, brown; P, pink; C, light gray; N, blue; O, red; H, white.

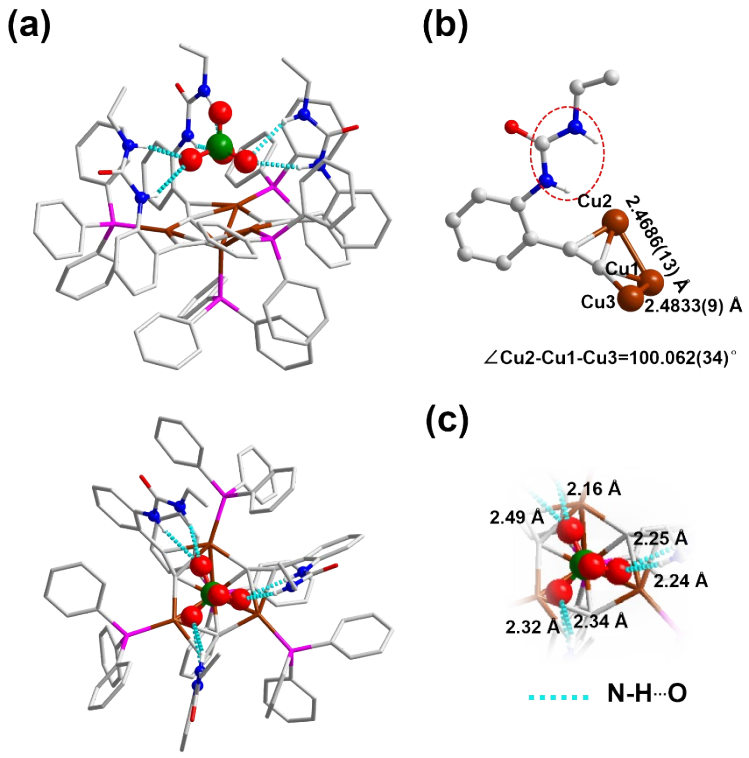

Figure S14. (a) Overall structure of **Cu_4-ClO_4**; (b) Coordination pattern of ureidoalkyne ligand **L** with Cu in **Cu_4-ClO_4**; (c) Intramolecular hydrogen bonding mode of action in **Cu_4-ClO_4**. Color code: Cu, brown; P, pink; C, light gray; N, blue; O, red; Cl, green; H, white.

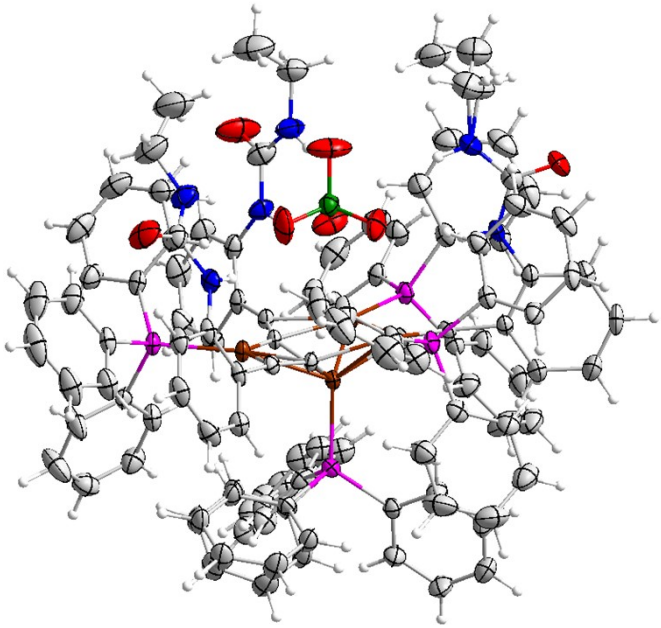

Figure S15. Crystal structure of **Cu_4-ClO_4**. Thermal ellipsoids set at 50% probability. Color code: Cu, brown; P, pink; C, light gray; N, blue; O, red; Cl, green; H, white.

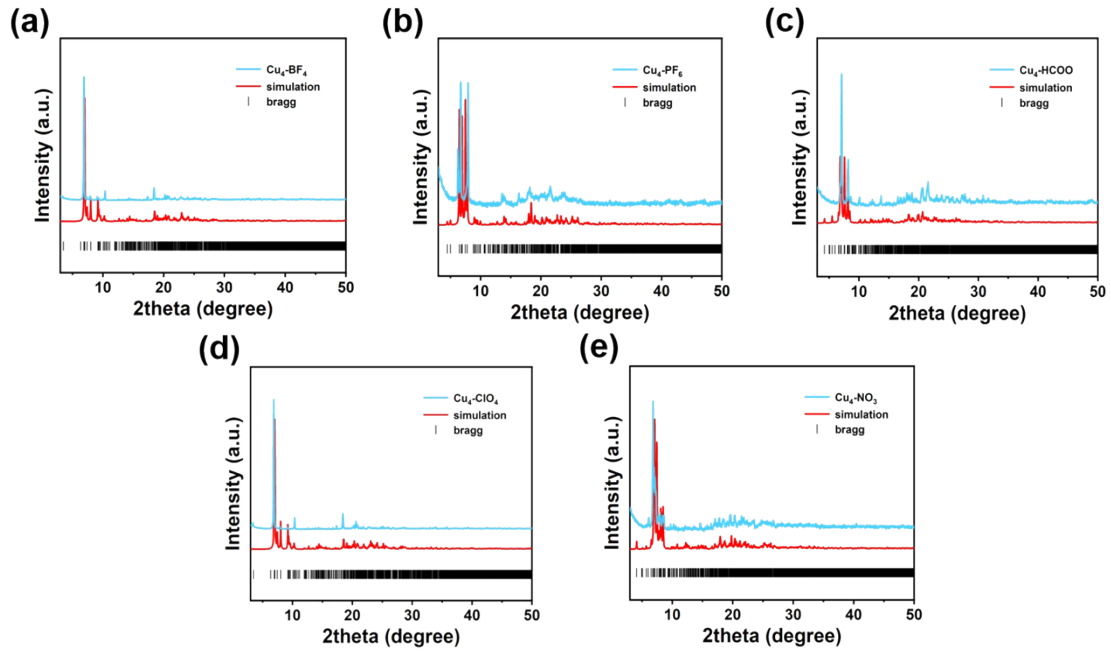

Figure S16. Comparison of experimental PXRD patterns and simulated data results for **Cu_4-BF_4** (a), **Cu_4-PF_6** (b), **Cu_4-HCOO** (c), **Cu_4-ClO_4** (d), and **Cu_4-NO_3** (e) at room temperature.

To demonstrate the chemical composition of the five **Cu_4-X** crystals, we dissolved them with CD_2Cl_2 and $CDCl_3$ reagents, respectively, measured their ^1H NMR spectra, and combined the crossover signals in the ^1H-^1H COSY spectra to determine the positions of the two neighboring hydrogen atoms in the aromatic and aliphatic regions. As shown in Figures S12 and S13, we attribute peaks a and b to the H atoms in the fat region on alkyne ligand **L**, with a peak area ratio of 3:2, and find that peaks c and b have a cross signal in the COSY spectrum, and peak g does not show a cross signal with the other peaks and is a singular peak, so we can determine the location of the H atoms on **L**. The rest of the peaks can be attributed to the H atoms on all aromatic rings of the alkyne ligands **L** and PPh_3. Since these five Cu_4 clusters have the same basic composition, the area of the peaks as well as the attribution of the peaks can be judged in this way for the other four copper clusters in addition to the anion. As shown in Figures S12-S21, the ratio of the number of alkyne ligands to PPh_3 on **Cu_4-BF_4**, **Cu_4-PF_6**, **Cu_4-HCOO**, **Cu_4-ClO_4**, and **Cu_4-NO_3** is 3:4, and the ratio of the peak areas is about 11:20, which is close to the theoretical value, proving the high purity of the resulting crystals.

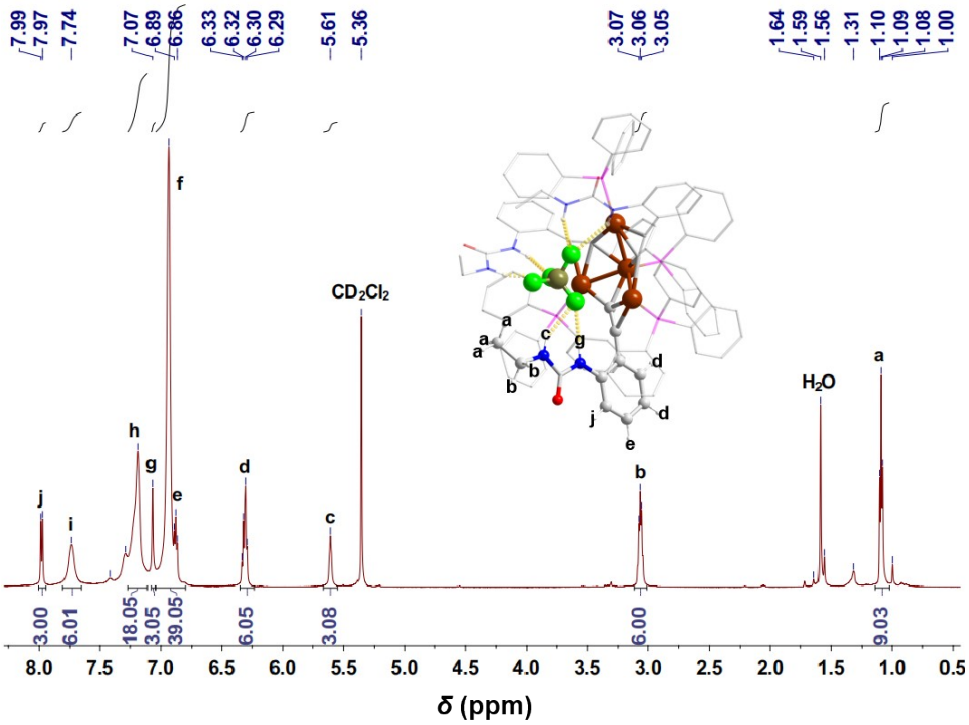

Figure S17. ^{1}H NMR spectrum of **Cu_4-BF_4** (600 MHz, CD_2Cl_2, 298 K).

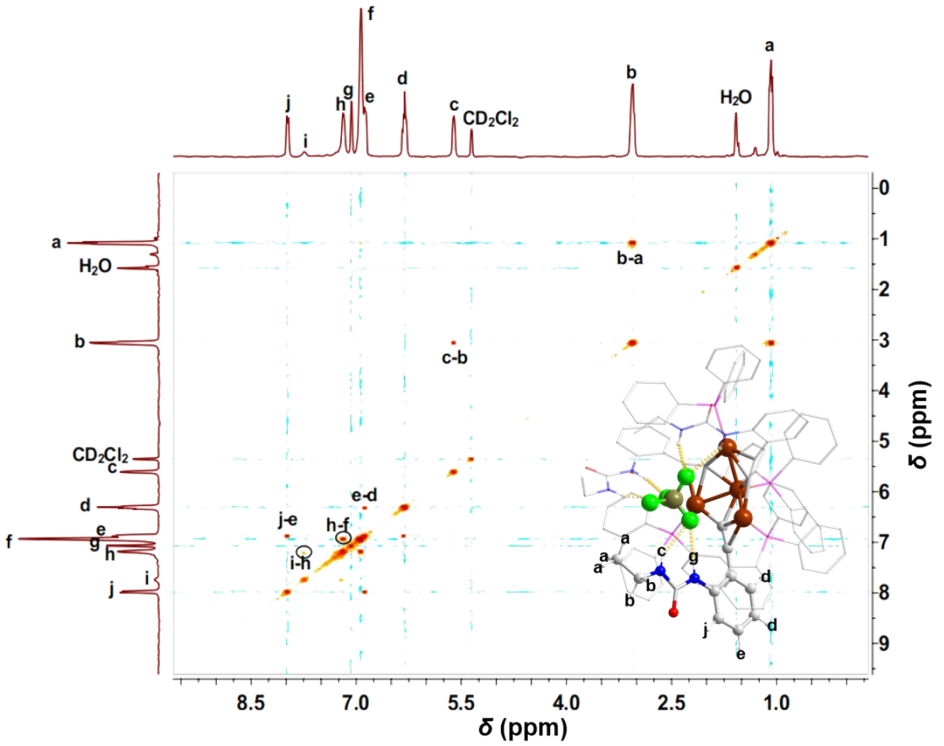

Figure S18. ^{1}H-^{1}H COSY NMR spectrum of **Cu_4-BF_4** (600 MHz, CD_2Cl_2, 298 K).

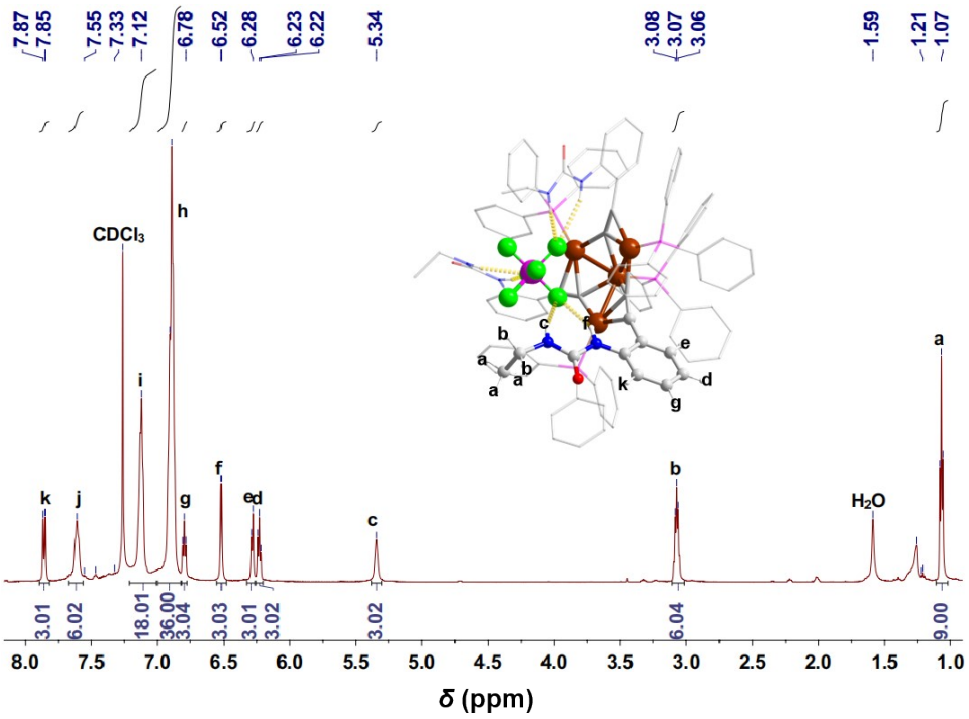

Figure S19. ^{1}H NMR spectrum of **Cu_4-PF_6** (600 MHz, $CDCl_3$, 298 K).

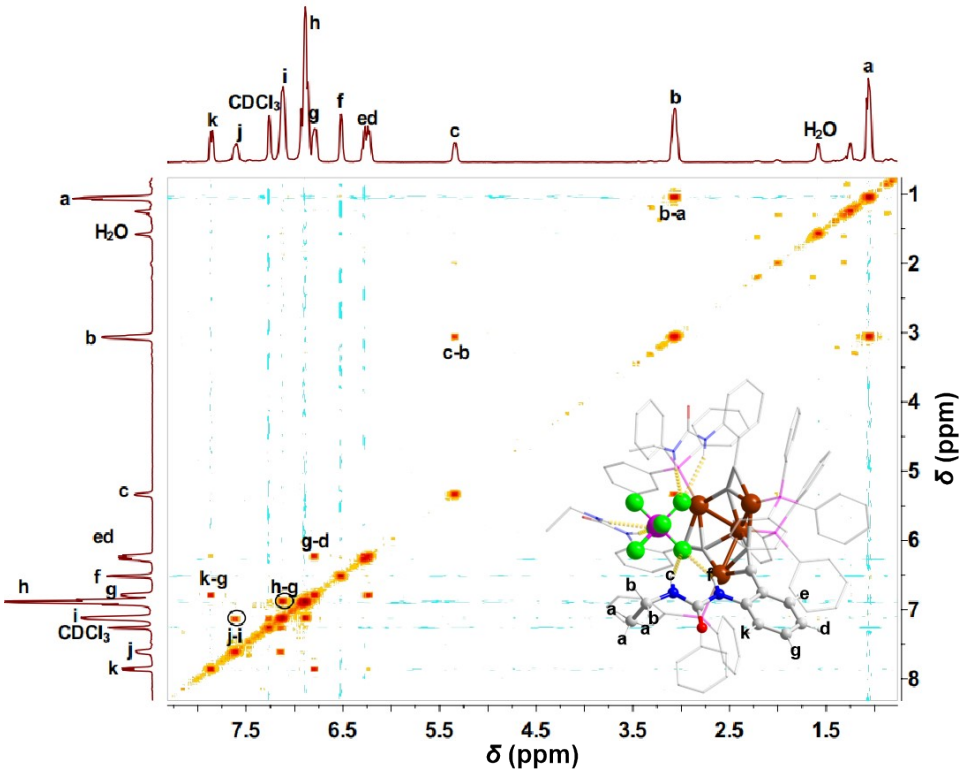

Figure S20. ^{1}H-^{1}H COSY NMR spectrum of **Cu_4-PF_6** (600 MHz, $CDCl_3$, 298 K).

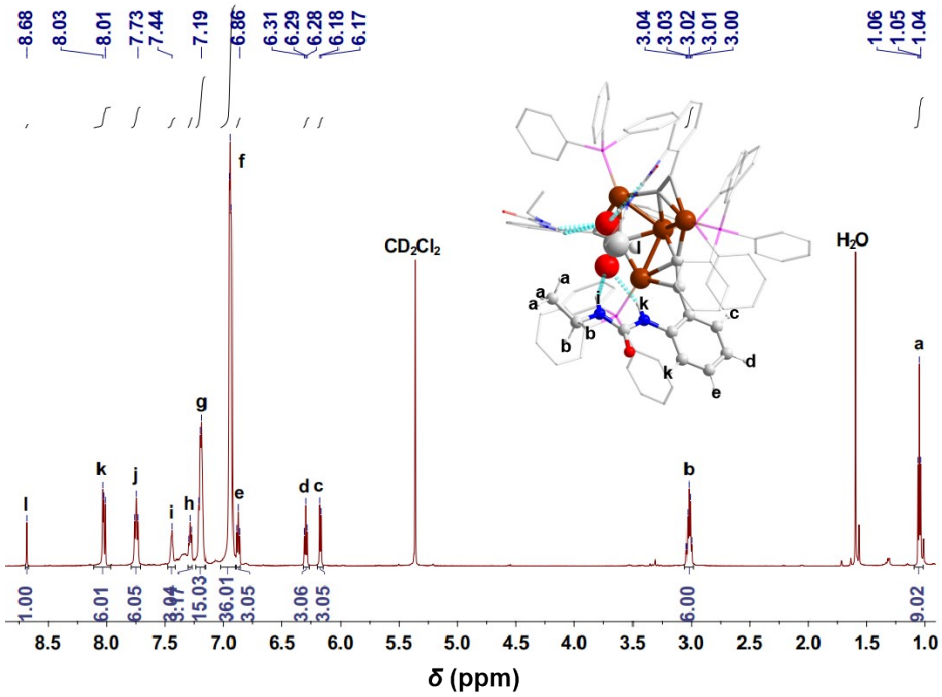

Figure S21. ^{1}H NMR spectrum of **Cu_4-HCOO** (600 MHz, CD_2Cl_2, 298 K).

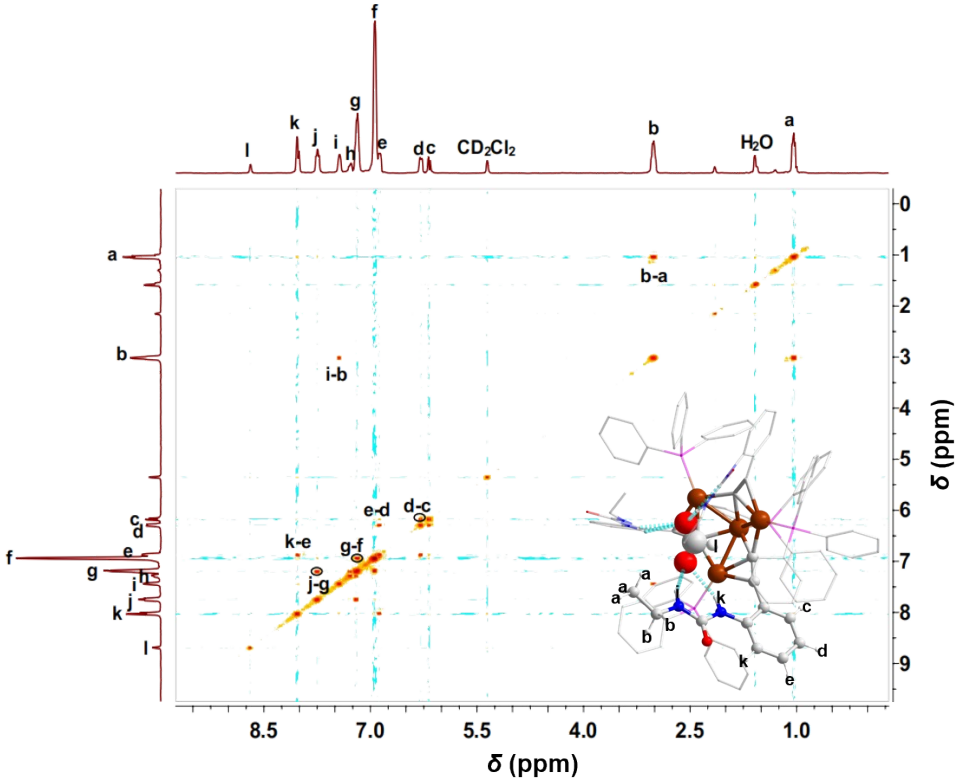

Figure S22. ^{1}H-^{1}H COSY NMR spectrum of **Cu_4-HCOO** (600 MHz, CD_2Cl_2, 298 K).

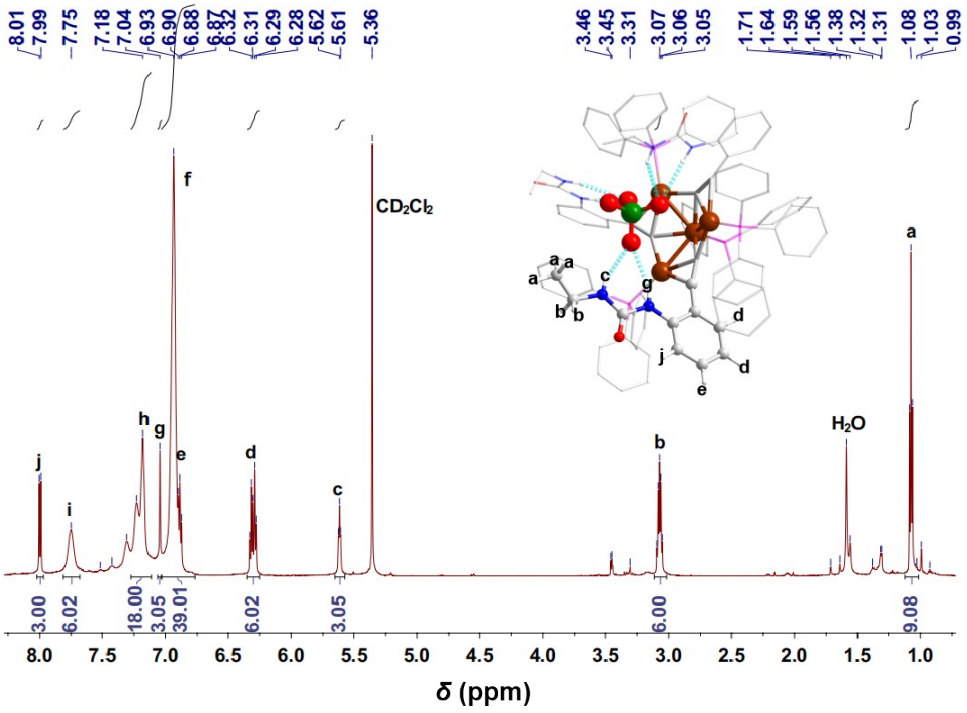

Figure S23. ^{1}H NMR spectrum of **Cu_4-ClO_4** (600 MHz, CD_2Cl_2, 298 K).

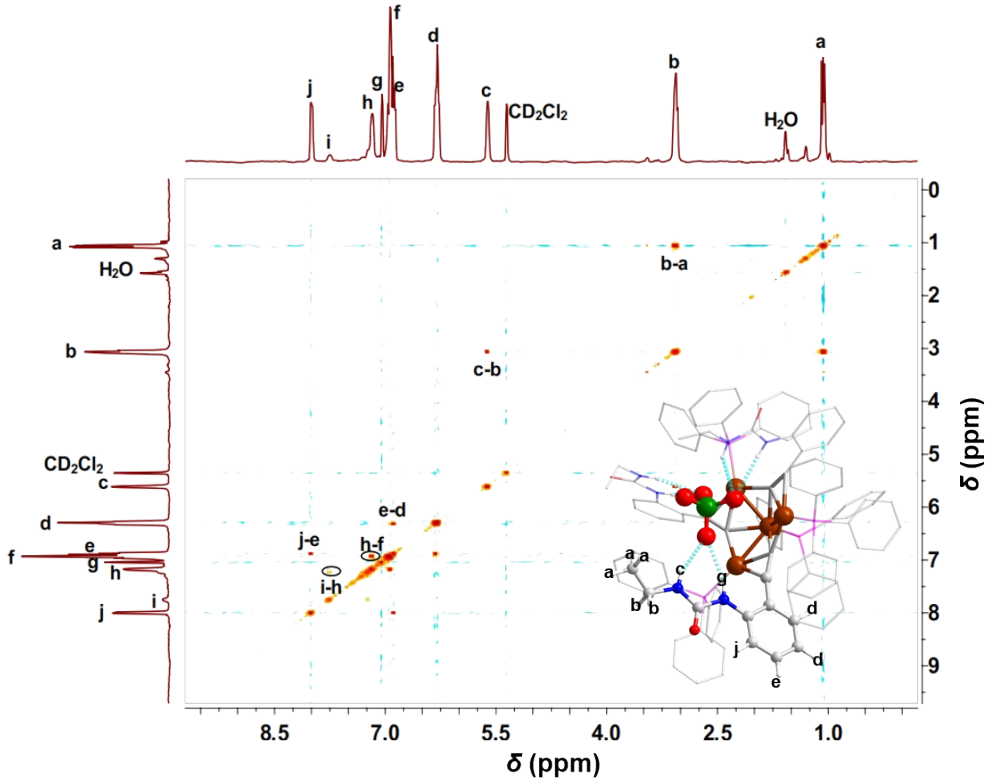

Figure S24. ^{1}H-^{1}H COSY NMR spectrum of **Cu_4-ClO_4** (600 MHz, CD_2Cl_2, 298 K).

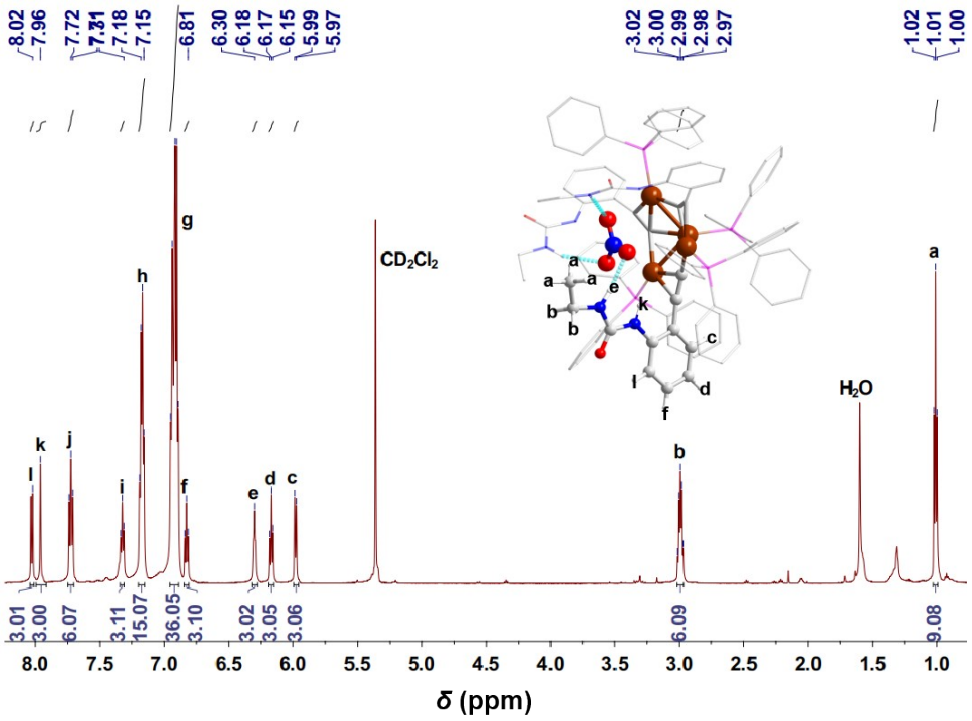

Figure S25. ^{1}H NMR spectrum of **Cu_4-NO_3** (600 MHz, CD_2Cl_2, 298 K).

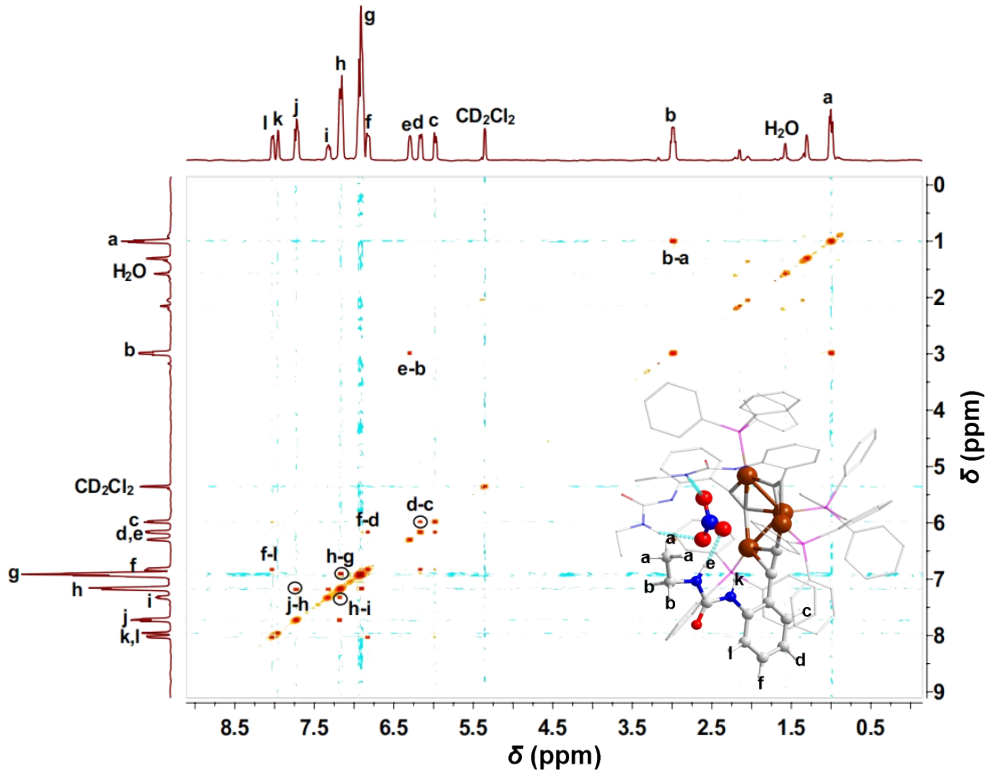

Figure S26. ^{1}H-^{1}H COSY NMR spectrum of **Cu_4-NO_3** (600 MHz, CD_2Cl_2, 298 K).

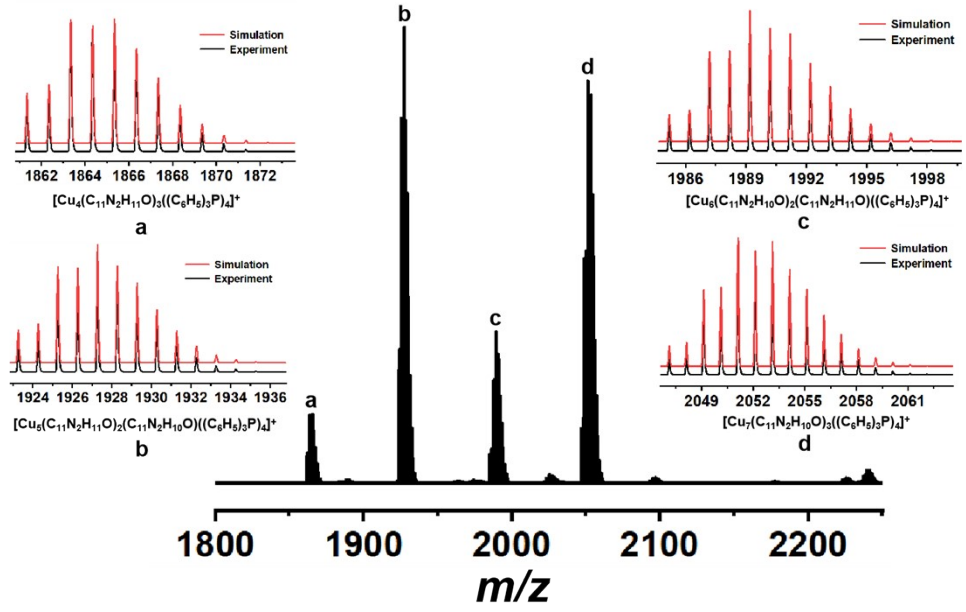

Figure S27. Positive ion mode ESI-MS spectra of **Cu_4-BF_4** clusters in a mixture of CH_3OH and CH_2Cl_2; insets: simulated isotopic distribution (red) and experimental isotopic distribution (black).

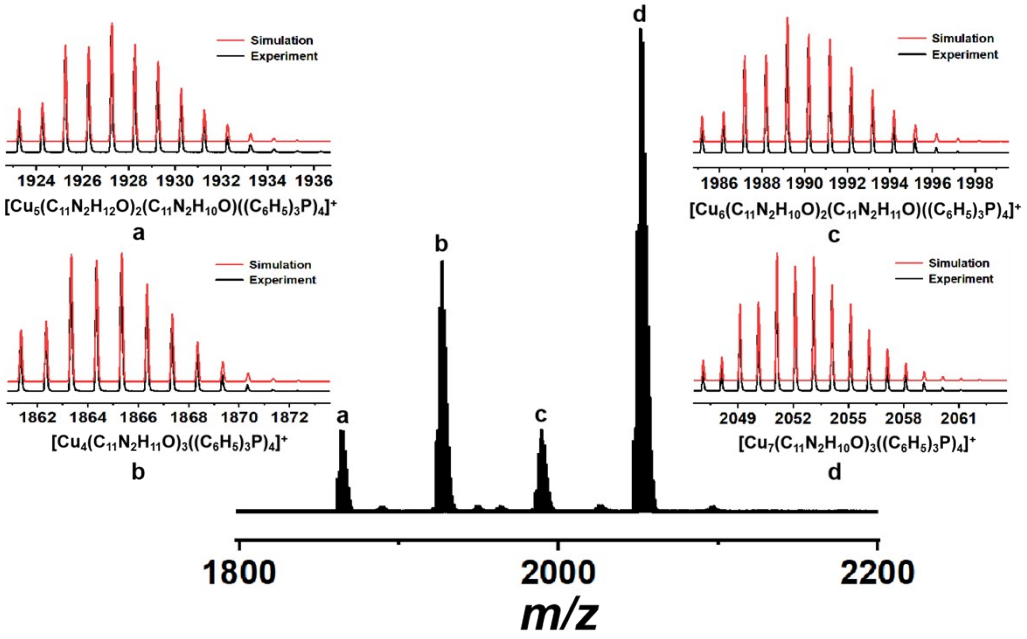

Figure S28. Positive ion mode ESI-MS spectra of **Cu_4-PF_6** clusters in a mixture of CH_3OH and CH_2Cl_2; insets: simulated isotopic distribution (red) and experimental isotopic distribution (black).

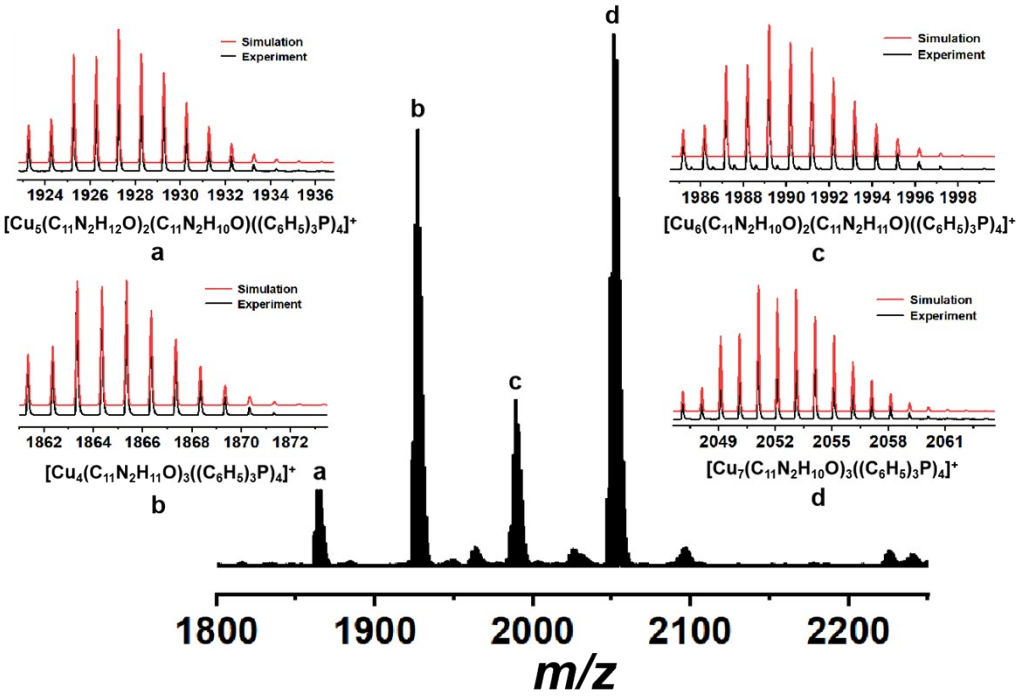

Figure S29. Positive ion mode ESI-MS spectra of **Cu_4-ClO_4** clusters in a mixture of CH_3OH and CH_2Cl_2; insets: simulated isotopic distribution (red) and experimental isotopic distribution (black).

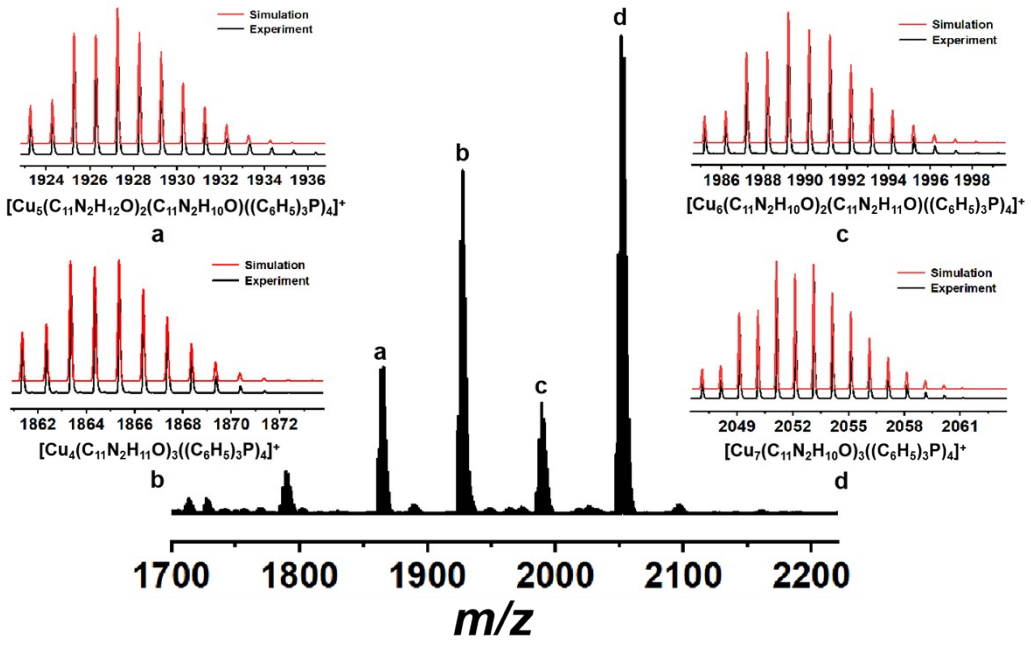

Figure S30. Positive ion mode ESI-MS spectra of **Cu_4-HCOO** clusters in a mixture of CH_3OH and CH_2Cl_2; insets: simulated isotopic distribution (red) and experimental isotopic distribution (black).

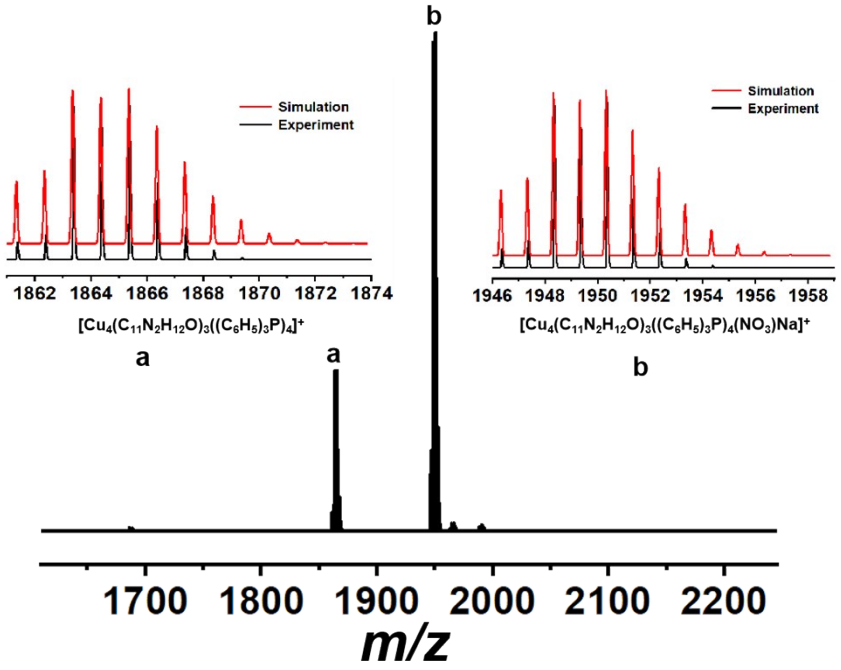

Figure S31. Positive ion mode ESI-MS spectra of **Cu_4-NO_3** clusters in a mixture of CH_3OH and CH_2Cl_2; insets: simulated isotopic distribution (red) and experimental isotopic distribution (black).

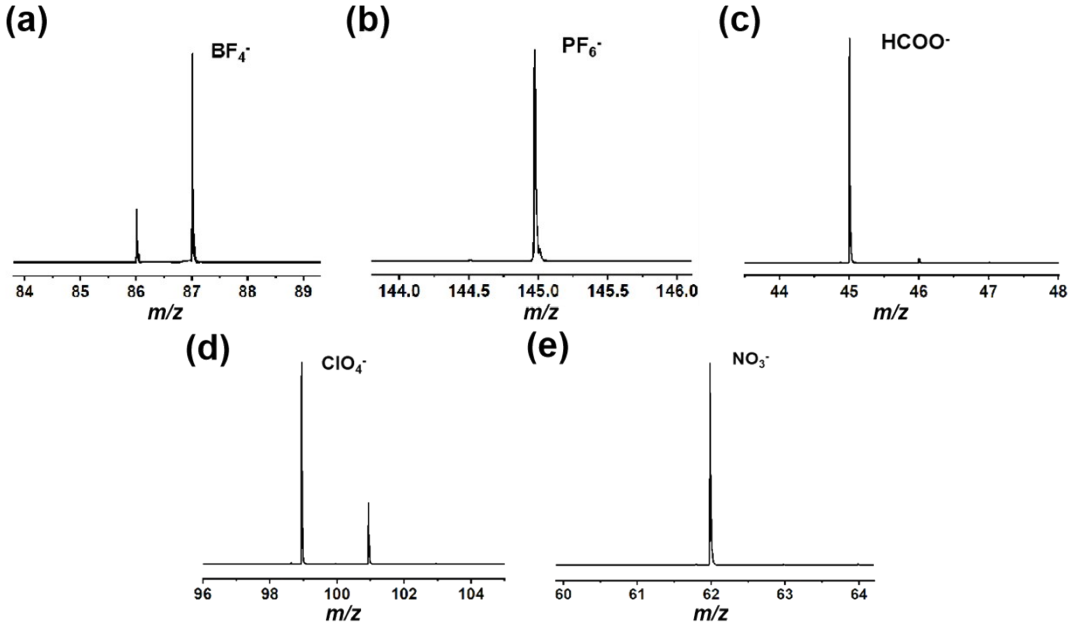

Figure S32. Negative ion mode ESI-MS spectrum of **Cu_4-X** clusters in a mixed solution of CH_3OH and CH_2Cl_2, confirming the presence of BF_4^- (a), PF_6^- (b), $HCOO^-$ (c), ClO_4^- (d) and NO_3^- (e).

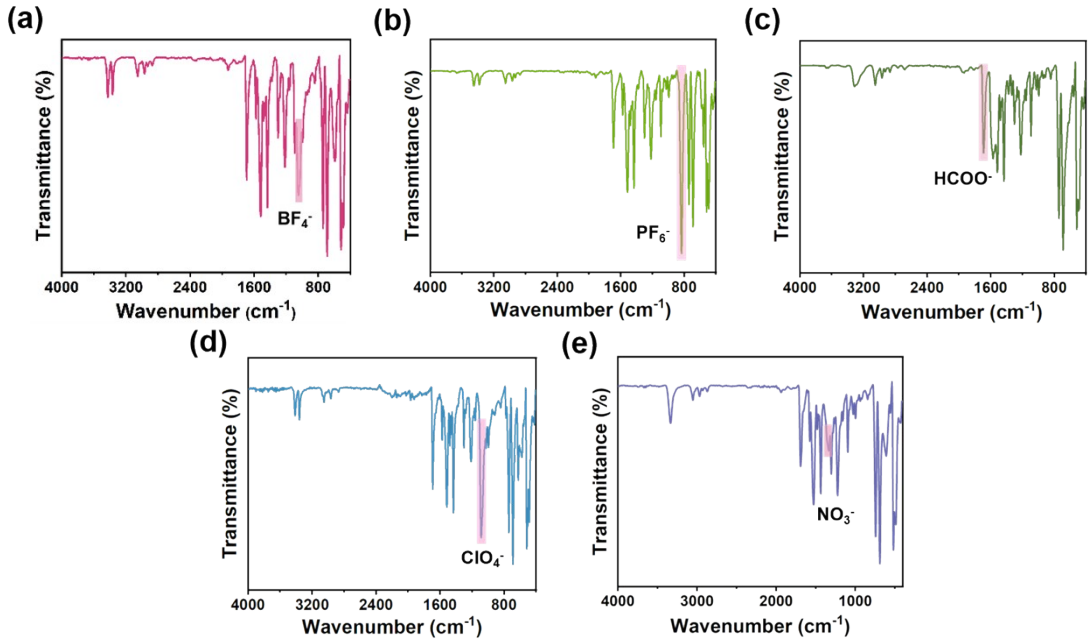

Figure S33. FT-IR spectra of **Cu_4-BF_4** (a), **Cu_4-PF_6** (b), **Cu_4-HCOO** (c), **Cu_4-ClO_4** (d), and **Cu_4-NO_3** (e).The peak at 1047 cm^{-1} is attributed to the BF_4^-, the peak at 834 cm^{-1} is attributed to the PF_6^-, the peak at 1691 cm^{-1} is attributed to the $HCOO^-$, the peak at 1087 cm^{-1} attributed to ClO_4^- and the peak at 1337 cm^{-1} attributed to NO_3^-.

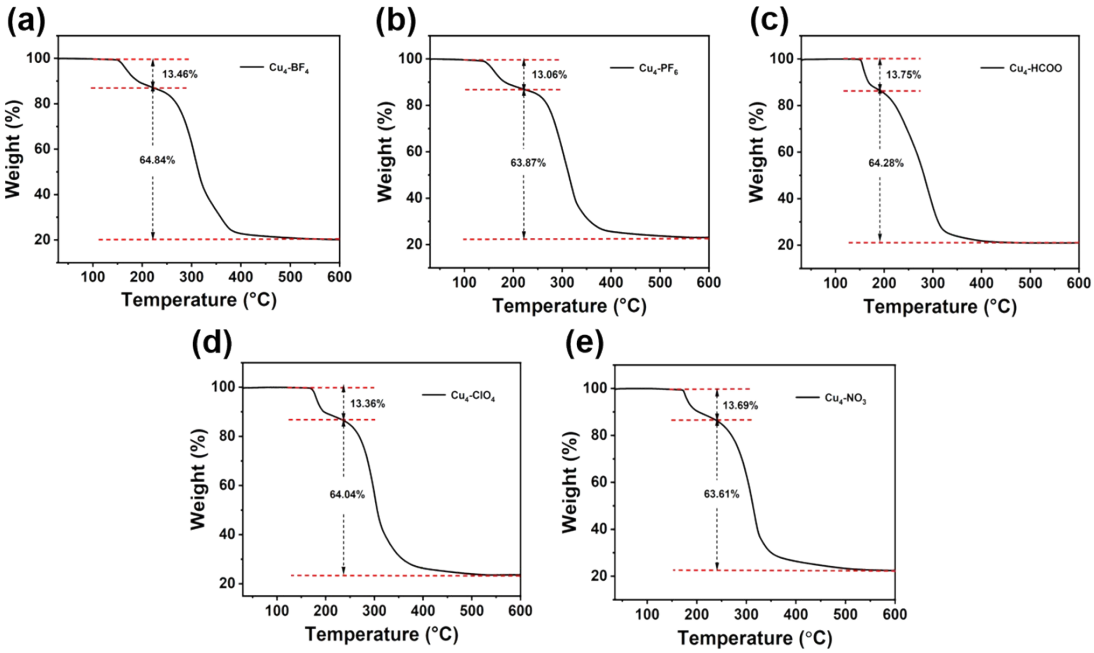

Figure S34. Thermogravimetric analysis profiles of **Cu_4-BF_4** (a), **Cu_4-PF_6** (b), **Cu_4-HCOO** (c), **Cu_4-ClO_4** (d), and **Cu_4-NO_3** (e).

Since the anions in the Cu_4 crystals are present in the interior of the Cu_4 structure and are connected by hydrogen bonds, to a certain extent the anions in the interior of Cu_4 are not easy to be detached first during the heating process. We calculate that at the

beginning of the weight loss one PPh_3 ligand is detached, and at the end of the weight loss all PPh_3 ligands, one anion, and two alkyne ligands are completely detached. All samples were vacuum-dried at 50 ℃ prior to testing to eliminate solvent interference. For example, for the weight loss of **Cu_4-NO_3**, it can be seen from Figure S29e that **Cu_4-NO_3** starts to show weight loss from heating to 170 ℃, and when the temperature continues to rise to 240 ℃, there is a significant loss of weight, which is due to the detachment of a PPh_3 above the Cu_4 clusters, and the actual loss of weight ratio is about 13.69% is close to the theoretical loss of weight ratio of 13.61%; when the temperature continues to rise to 550 ℃, the weight loss platform appears, and the molecular weight loss process ends, at this time, the weight loss can be attributed to the detachment of one NO_3^- and three PPh_3 as well as two **L**, and the actual weight loss ratio is about 63.61%, and the theoretical weight loss ratio is 63.59%.

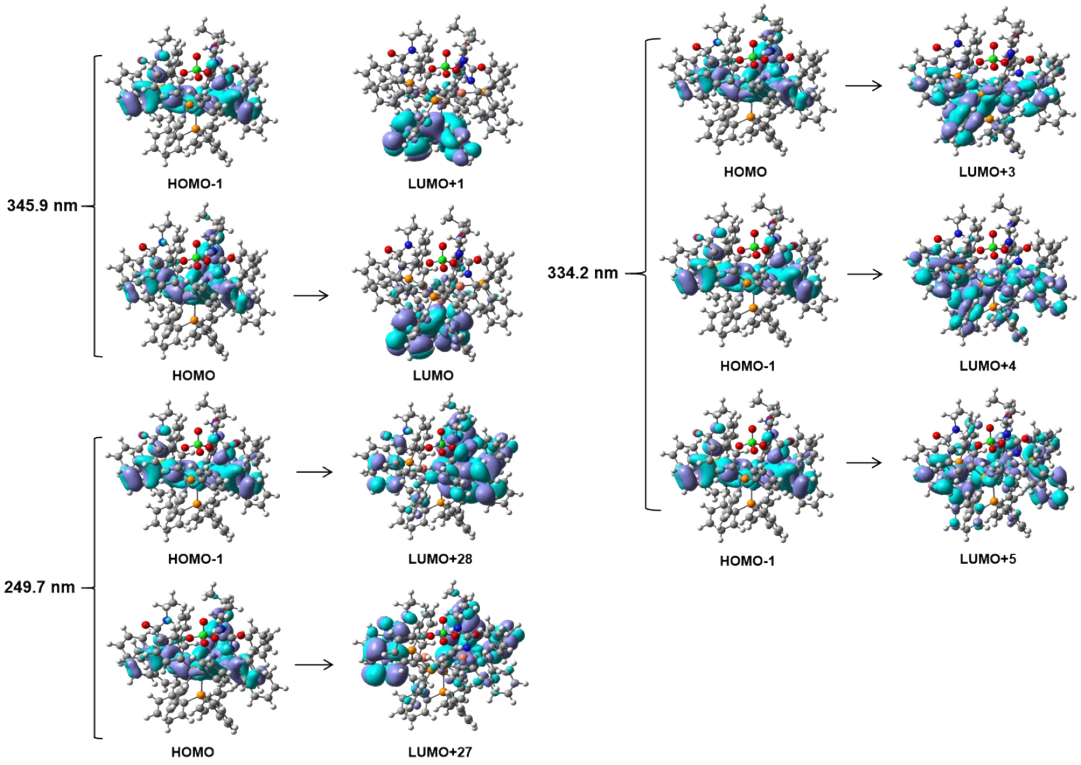

Figure S35. Partial Kohn-Sham orbital of **Cu_4-ClO_4**.

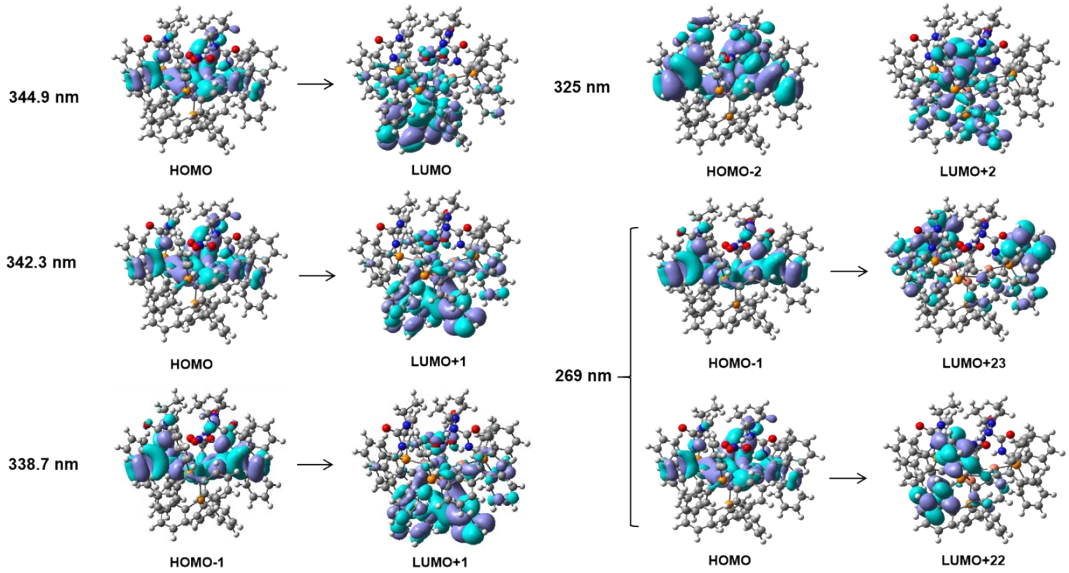

Figure S36. Partial Kohn-Sham orbital of Cu_4-NO_3.

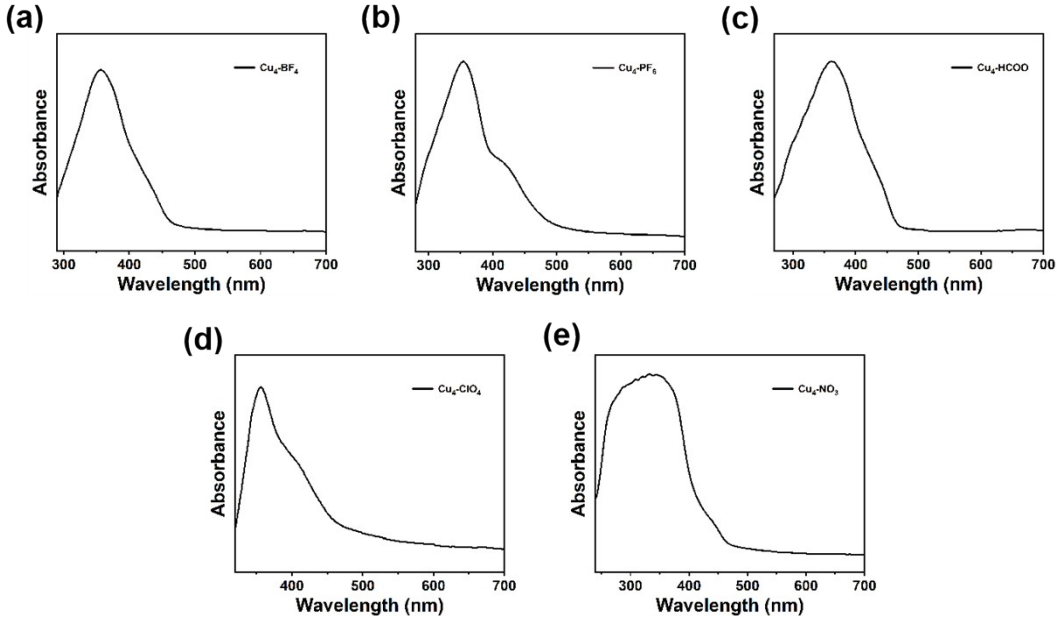

Figure S37. Solid diffuse reflectance UV-Vis spectra of Cu_4-BF_4 (a), Cu_4-PF_6 (b), Cu_4-HCOO (c), Cu_4-ClO_4 (d), and Cu_4-NO_3 (e) at room temperature.

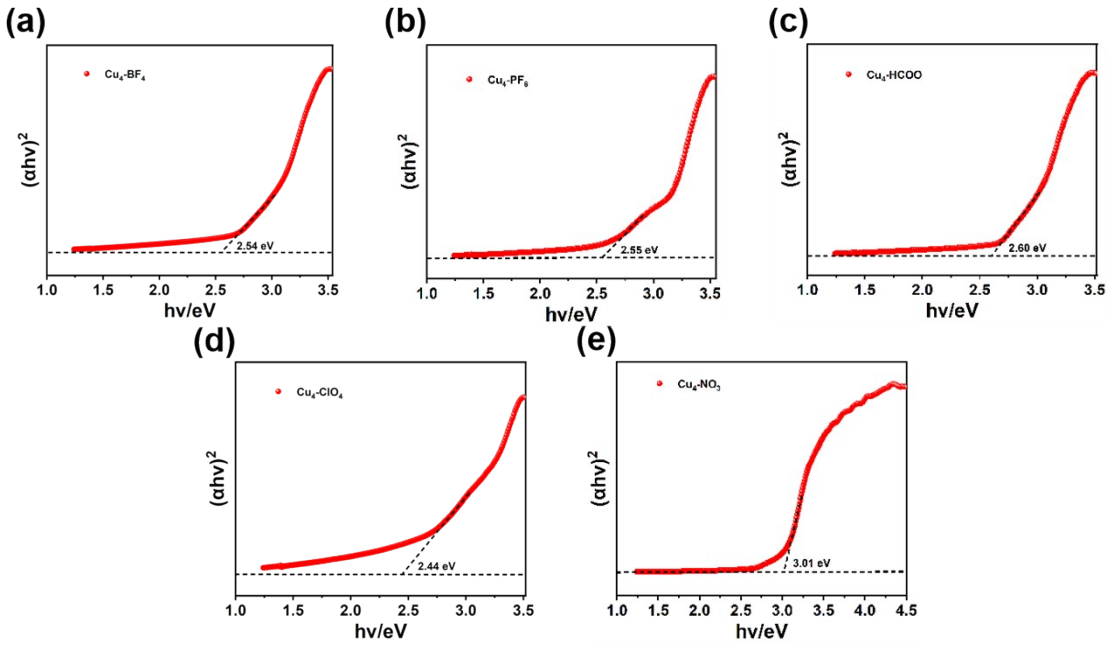

Figure S38. Band gap energy diagrams of **Cu_4-BF_4** (a), **Cu_4-PF_6** (b), **Cu_4-HCOO** (c), **Cu_4-ClO_4** (d), and **Cu_4-NO_3** (e) at room temperature.

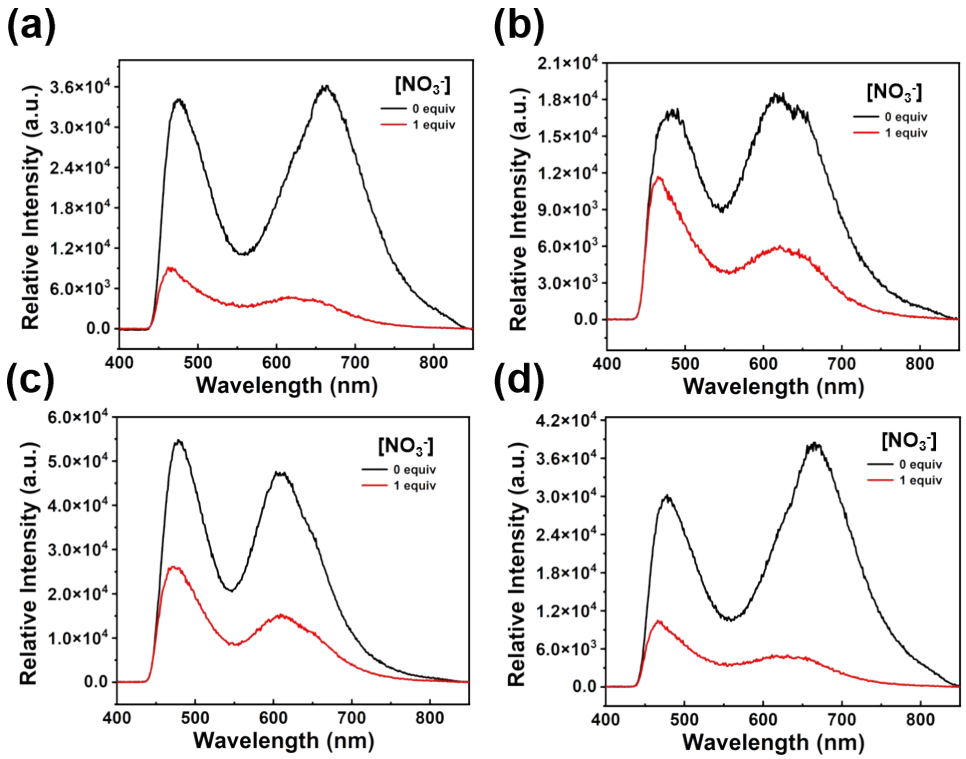

Figure S39. Liquid fluorescence spectra of **Cu_4-BF_4**, **Cu_4-PF_6**, **Cu_4-HCOO** and **Cu_4-ClO_4** before and after addition of 1 equal amount of NO_3^-.

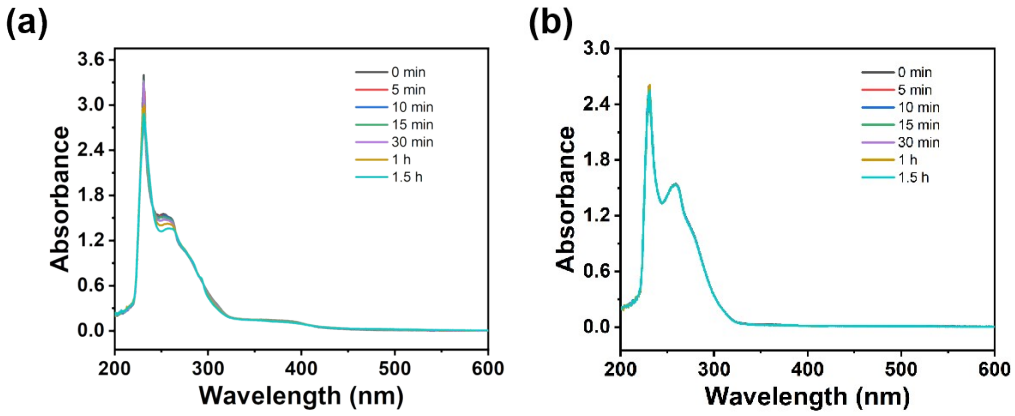

Figure S40. UV-Vis absorption spectra of **Cu_4-ClO_4** (a) and **Cu_4-ClO_4** + PPh_3 (b) in mixed solutions of CH_2Cl_2 and CH_3OH at different times.

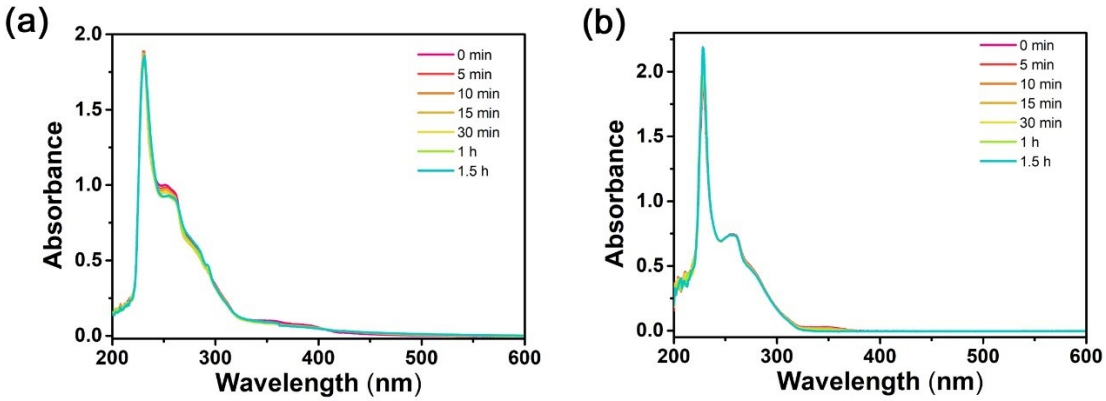

Figure S41. UV-Vis absorption spectra of **Cu_4-BF_4** (a) and **Cu_4-BF_4** + PPh_3 (b) in mixed solutions of CH_2Cl_2 and CH_3OH at different times.

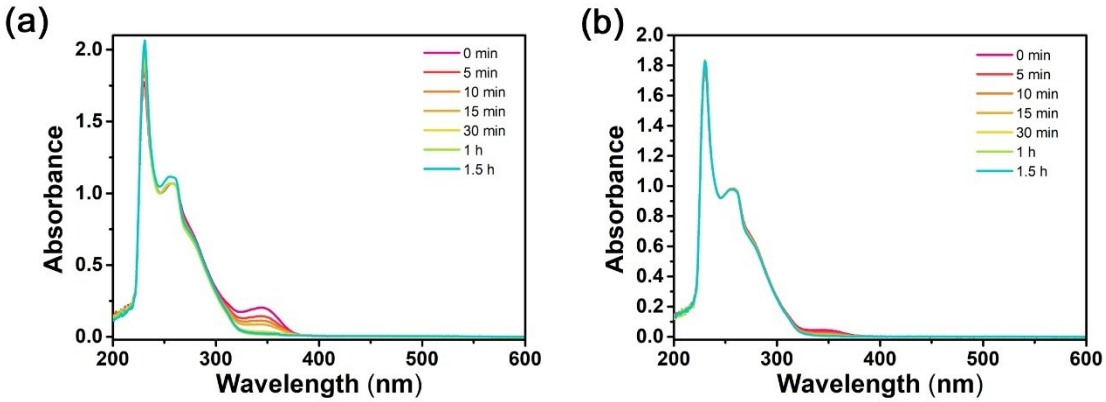

Figure S42. UV-Vis absorption spectra of **Cu_4-PF_6** (a) and **Cu_4-PF_6** + PPh_3 (b) in mixed solutions of CH_2Cl_2 and CH_3OH at different times.

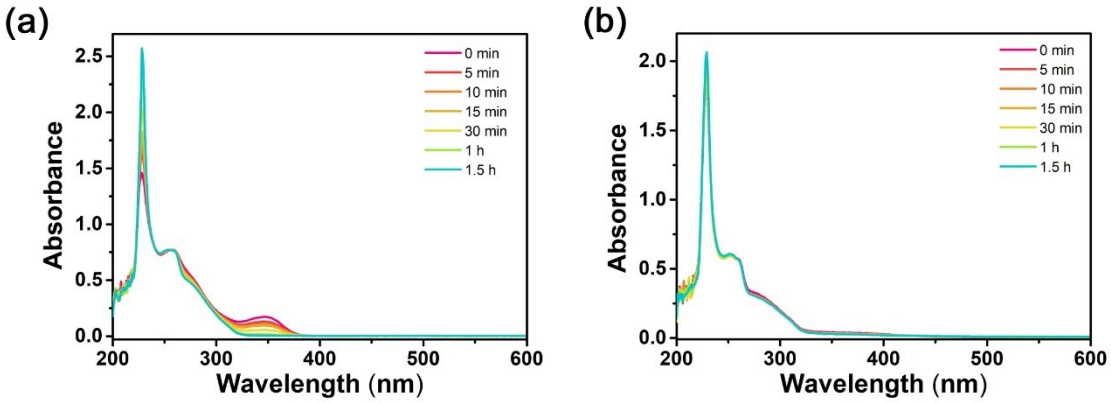

Figure S43. UV-Vis absorption spectra of **Cu_4-HCOO** (a) and **Cu_4- HCOO** + PPh_3 (b) in mixed solutions of CH_2Cl_2 and CH_3OH at different times.

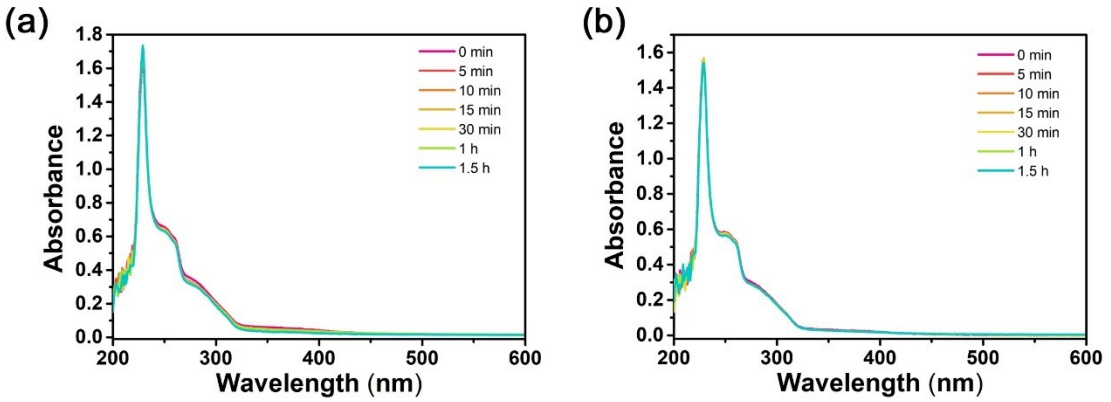

Figure S44. UV-Vis absorption spectra of **Cu_4-NO_3** (a) and **Cu_4-NO_3** + PPh_3 (b) in mixed solutions of CH_2Cl_2 and CH_3OH at different times.

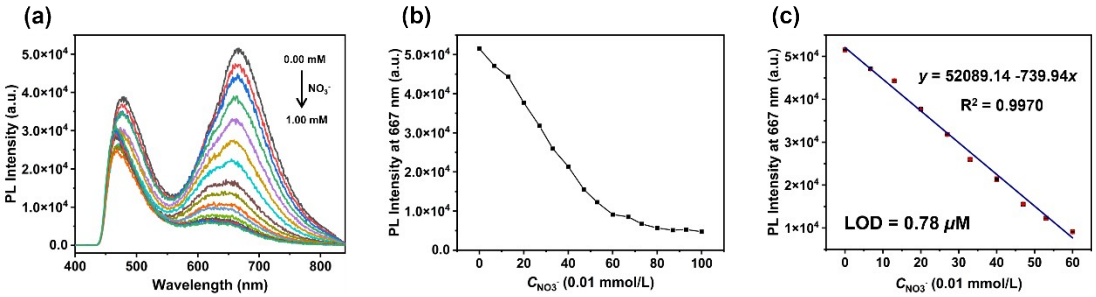

Figure S45. (a) Fluorescence titration curve of NO_3^- against **Cu_4-ClO_4**; (b) Function of NO_3^- concentration versus fluorescence intensity of **Cu_4-ClO_4** at 664 nm; (c) Linear fit of the relative fluorescence intensity of **Cu_4-ClO_4** at 664 nm versus NO_3^- concentration.

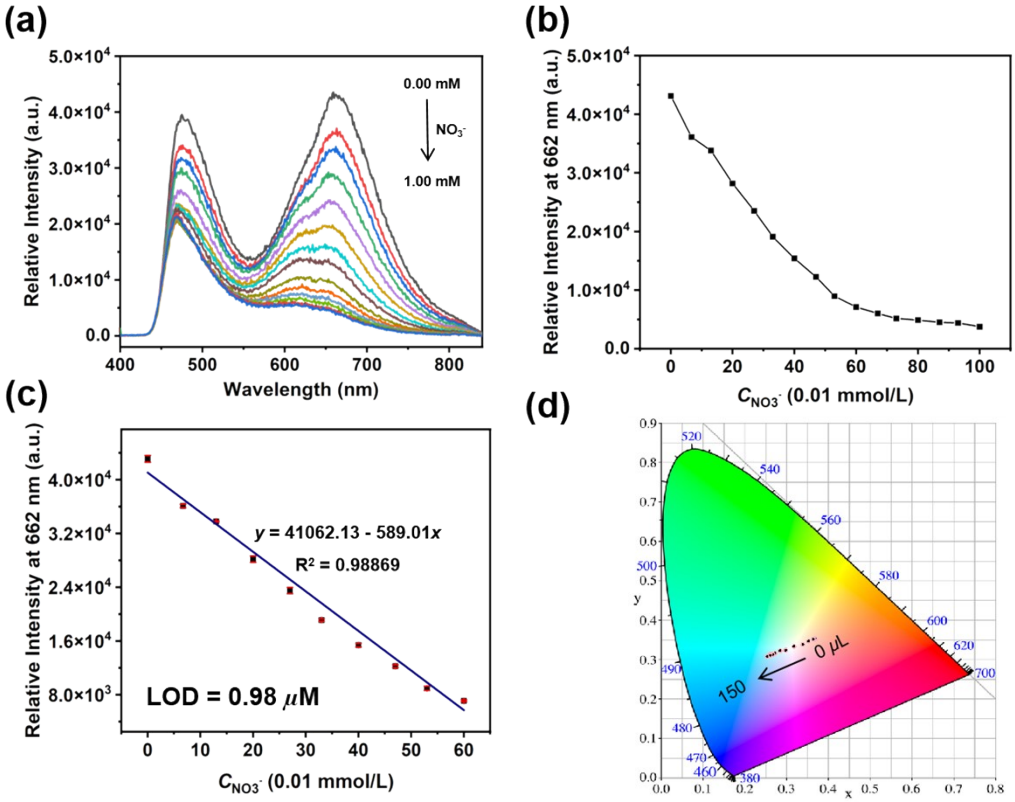

Figure S46. (a) Fluorescence titration curve of NO_3^- against **Cu_4-BF_4**; (b) Function of NO_3^- concentration versus fluorescence intensity of **Cu_4-BF_4** at 662 nm; (c) Linear fit of the relative fluorescence intensity of **Cu_4-BF_4** at 662 nm versus NO_3^- concentration; (d) CIE diagram corresponding to the fluorescence titration process of NO_3^- with **Cu_4-BF_4**.

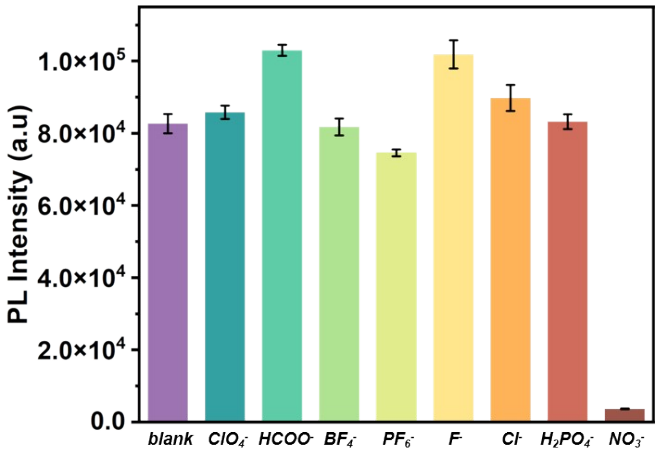

Figure S47. Luminescence intensity of the **Cu_4-BF_4** solution after adding different anions. .

Table S1. Crystal data and structure refinement for **Cu_4-BF_4**, **Cu_4-PF_6** and **Cu_4-HCOO**.

	Cu_4-BF_4	**Cu_4-PF_6**	**Cu_4-HCOO**
CCDC	2505115	2505114	2505116
Empirical formula	$C_{106}H_{97}BCu_4F_4N_6O_4P_4$	$C_{109}H_{107}ClCu_4F_6N_6O_{6.5}P_5$	$C_{215}H_{214}Cu_8N_{12}O_{17}P_8$
Molecular formula	$(BF_4)@[Cu_4(PPh_3)_4L_3]\cdot(CH_3OH)$	$(PF_6)@[Cu_4(PPh_3)_4L_3]\cdot(CH_3OH)_{3.5}\cdot(CH_2Cl_2)_{0.5}$	$[(HCOO)@[Cu_4(PPh_3)_4L_3]]_2\cdot(CH_3OH)_6\cdot(H_2O)$
Formula weight	1983.74	2163.46	4030.08
Temperature / K	200(2)	200	200(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	P-1
a / Å	12.814(10)	25.612(6)	14.802(2)
b / Å	14.460(10)	14.765(4)	20.940(3)
c / Å	50.890(4)	27.484(6)	31.980(4)
α / °	90	90	91.799(10)
β / °	95.348(10)	96.146(2)	90.084(10)
γ / °	90	90	94.367(10)
Volume / Å^3	9388.54(12)	10344.1(4)	9879.1(2)
Z	4	4	2
ρ_{calc}g / cm^3	1.403	1.389	1.355
μ /mm^{-1}	2.185	0.982	2.061
F (000)	4096.0	4468.0	41880.0
Crystal size / mm^3	0.15 × 0.15 × 0.05	0.11 × 0.04 × 0.03	0.15 × 0.05 × 0.05
Radiation	CuKα (λ = 1.54184 Å)	MoKα (λ = 0.71073 Å)	CuKα (λ = 1.54184 Å)
2θ range for data collection /°	6.356 to 150.914	4.244 to 57.588	4.234 to 156.768
Index ranges	$-14 \le h \le 16$, $-16 \le k \le 18$, $-63 \le l \le 63$	$-31 \le h \le 34$, $-18 \le k \le 20$, $-37 \le l \le 34$	$-18 \le h \le 18$, $-26 \le k \le 25$, $-40 \le l \le 37$
Reflections collected	111641	83076	136916
Independent reflections	19160 [R_{int} = 0.0623, R_{sigma} = 0.0341]	24134 [R_{int} = 0.0361, R_{sigma} = 0.0481]	40190 [R_{int} = 0.0554, R_{sigma} = 0.0462]
Data/restraints/parameters	19160/366/1253	24134/399/1467	40190/1739/2774
Goodness-of-fit on F^2	1.020	1.010	1.054
Final R indexes [$I >= 2\sigma$ (I)]	R_1 = 0.0393, wR_2 = 0.1068	R_1 = 0.0462, wR_2 = 0.1045	R_1 = 0.0591, wR_2 = 0.1496

Final *R* indexes [all data]	R_1 = 0.0429, wR_2 = 0.1097	R_1 = 0.0727, wR_2 = 0.1134	R_1 = 0.0725, wR_2 = 0.1585
Largest diff. peak/hole / e Å^{-3}	0.49/-0.64	0.53/-0.46	1.96/-0.79

$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$. $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S2. Crystal data and structure refinement for **Cu_4-ClO_4** and **Cu_4-NO_3**.

	Cu_4-ClO_4	**Cu_4-NO_3**
CCDC	2505113	2505112
Empirical formula	$C_{106}H_{97}ClCu_4N_6O_8P_4$	$C_{112}H_{115}Cu_4N_7O_{11}P_4$
Molecular formula	$(ClO_4)@[Cu_4(PPh_3)_4L_3]\cdot(CH_3OH)$	$(NO_3)@[Cu_4(PPh_3)_4L_3]\cdot(CH_3OH)_4\cdot((CH_3)_2CO)$
Formula weight	1996.38	2116.19
Temperature / K	200(2)	200(2)
Crystal system	monoclinic	trigonal
Space group	$P2_1/c$	$P31c$
a / Å	12.840(3)	16.596(4)
b / Å	14.482(3)	16.596(4)
c / Å	50.985(8)	21.986(5)
α / °	90	90
β / °	95.340(2)	90
γ / °	90	120
Volume / Å^3	9439.4(3)	5244.5(3)
Z	4	2
ρ_{calc}g / cm^3	1.405	1.340
μ /mm^{-1}	1.046	0.923
F (000)	4128.0	2206.0
Crystal size / mm^3	0.10 × 0.10 × 0.01	0.15 × 0.15 × 0.05
Radiation	MoKα (λ = 0.71073 Å)	MoKα (λ = 0.71073 Å)
2θ range for data collection /°	4.268 to 57.686	5.964 to 57.554
Index ranges	$-15 \le h \le 17$, $-19 \le k \le 19$, $-64 \le l \le 68$	$-21 \le h \le 16$, $-17 \le k \le 20$, $-27 \le l \le 28$
Reflections collected	76735	42982
Independent reflections	21306 [R_{int} = 0.0495, R_{sigma} = 0.0648]	8277 [R_{int} = 0.0769, R_{sigma} = 0.0482]
Data/restraints/parameters	21306/439/1253	8277/65/444
Goodness-of-fit on F^2	1.034	1.040
Final R indexes [$I >= 2\sigma$ (I)]	R_1 = 0.0459, wR_2 = 0.0871	R_1 = 0.0430, wR_2 = 0.1021
Final *R* indexes [all data]	R_1 = 0.0748, wR_2 = 0.0947	R_1 = 0.0512, wR_2 = 0.1067

Largest diff. peak/hole / e Å^{-3}	0.51/-0.59	0.80/-0.60

$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$. $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S3. Optical information of unanionized Cu_4 clusters.

Cu_4 crystals	**Cu_4-BF_4**	**Cu_4-PF_6**	**Cu_4-HCOO**	**Cu_4-ClO_4**	**Cu_4-NO_3**
Daylight Photographs					
Photographs under UV light					
Crystal State	Colorless stick with blue light	Colorless stick with blue light	Colorless rod-shaped glowing blue	Colorless flakes with blue light	Colorless rods without luminescence
Lifetime/μs	39.20	22.65	14.76	43.50	\
Quantum Yield	34.41%	18.26%	8.55%	32.84%	\

Table S4. Atomic coordinates of **Cu_4-ClO_4** after crystal structure optimization.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	4.487048	-3.344975	-3.970442
2	6	0	3.702387	-2.531189	-3.514347
3	7	0	3.329076	-2.469857	-2.177498
4	7	0	3.109641	-1.563429	-4.273872
5	1	0	2.588739	-1.813473	-1.937715
6	6	0	3.782494	-3.257138	-1.133979
7	1	0	2.401339	-0.973663	-3.850343
8	6	0	3.275679	-1.525684	-5.706046
9	29	0	2.190844	0.069493	0.25395
10	6	0	3.17681	-3.08437	0.140882
11	6	0	4.804566	-4.210531	-1.27398
12	1	0	3.307225	-0.469736	-6.022222
13	1	0	4.25975	-1.963733	-5.927127
14	6	0	2.188631	-2.267846	-6.470237
15	29	0	0.00218	0.000525	1.439943
16	15	0	4.27818	1.014105	0.024783
17	6	0	0.988987	-1.63123	0.601544
18	6	0	0.922143	1.67178	0.601014
19	6	0	2.099046	-2.157706	0.337604
20	6	0	3.61466	-3.86727	1.223497
21	1	0	5.256456	-4.33687	-2.25547
22	6	0	5.213108	-4.971136	-0.18466
23	1	0	2.202287	-3.338128	-6.213897
24	1	0	1.192676	-1.863997	-6.229592
25	1	0	2.342446	-2.176783	-7.556891
26	29	0	-1.034705	-1.928214	0.252778
27	29	0	-1.15261	1.861757	0.253382
28	15	0	0.005708	0.002678	3.761754
29	6	0	-1.906585	-0.037736	0.60712
30	6	0	4.245097	2.31834	-1.258146
31	6	0	4.800464	1.880172	1.559266
32	6	0	5.766042	0.017621	-0.372629
33	6	0	0.822336	2.896562	0.338606
34	1	0	3.134396	-3.72178	2.193024
35	6	0	4.625462	-4.807868	1.071539
36	1	0	6.009569	-5.707126	-0.324628
37	15	0	-1.258322	-4.209417	0.031935
38	8	0	-0.773711	-1.169288	-2.263458
39	6	0	-2.918416	-0.735852	0.34677
40	15	0	-3.016771	3.195469	0.027349
41	8	0	-0.630843	1.24402	-2.270119
42	6	0	0.276317	1.639904	4.550214
43	6	0	1.288707	-1.047999	4.552421

44	6	0	-1.544895	-0.581094	4.555137
45	6	0	3.92012	1.944083	-2.570904
46	6	0	4.463376	3.668508	-0.965181
47	6	0	3.829278	2.255055	2.496046
48	6	0	6.146785	2.17773	1.813538
49	6	0	6.670246	0.358284	-1.385387
50	6	0	6.015273	-1.115085	0.413916
51	6	0	1.086116	4.29294	0.140338
52	1	0	4.94596	-5.412677	1.922871
53	6	0	-2.865505	-5.000315	-0.362949
54	6	0	-0.112797	-4.83737	-1.249227
55	6	0	-0.770428	-5.090216	1.569342
56	17	0	-0.009059	-0.004933	-2.763726
57	6	0	-4.260951	-1.204261	0.153919
58	6	0	-4.024575	3.216205	1.56413
59	6	0	-4.13275	2.514032	-1.252683
60	6	0	-2.90066	4.982239	-0.371143
61	6	0	1.031823	1.817327	5.71643
62	6	0	-0.331861	2.754001	3.955541
63	6	0	2.556987	-1.081318	3.956598
64	6	0	1.06521	-1.786896	5.721327
65	6	0	-2.207781	-1.664648	3.962554
66	6	0	-2.071686	-0.015991	5.723666
67	1	0	3.738269	0.894979	-2.816207
68	6	0	3.823081	2.908071	-3.570208
69	1	0	4.70493	3.977127	0.053994
70	6	0	4.352876	4.630761	-1.968893
71	1	0	2.776801	2.028379	2.30494
72	6	0	4.196411	2.923862	3.663903
73	1	0	6.915857	1.880058	1.096528
74	6	0	6.510055	2.845523	2.98079
75	1	0	6.489141	1.237577	-2.007406
76	6	0	7.806113	-0.421828	-1.602721
77	1	0	5.306606	-1.405486	1.194121
78	6	0	7.156108	-1.883752	0.202525
79	6	0	1.546408	5.064325	1.221969
80	6	0	0.93145	4.902877	-1.134713
81	6	0	-3.971309	-4.645401	0.421274
82	6	0	-3.022295	-5.958743	-1.370954
83	6	0	-0.276164	-4.374139	-2.563788
84	6	0	0.948267	-5.699475	-0.953915
85	6	0	0.040629	-4.434993	2.504336
86	6	0	-1.187904	-6.403542	1.827818
87	8	0	1.387312	-0.085482	-2.281232
88	8	0	-0.019741	-0.008333	-4.233883
89	6	0	-4.717086	-1.644669	-1.118795

90	6	0	-5.155541	-1.187691	1.238516
91	6	0	-4.956963	4.232273	1.817349
92	6	0	-3.859339	2.19122	2.5039
93	6	0	-5.409875	2.026487	-0.95639
94	6	0	-3.650366	2.422284	-2.567146
95	6	0	-3.655786	5.594995	-1.37795
96	6	0	-2.03858	5.764406	0.408998
97	1	0	1.523873	0.960968	6.183748
98	6	0	1.160903	3.084847	6.285109
99	1	0	-0.895598	2.631021	3.027023
100	6	0	-0.21168	4.016659	4.532254
101	1	0	2.732169	-0.534198	3.026473
102	6	0	3.59021	-1.816078	4.53447
103	1	0	0.078138	-1.782234	6.189834
104	6	0	2.098249	-2.531561	6.29139
105	1	0	-1.822674	-2.091242	3.032565
106	6	0	-3.359366	-2.191845	4.543369
107	1	0	-1.573879	0.837795	6.189609
108	6	0	-3.231877	-0.537965	6.296472
109	1	0	3.565807	2.605548	-4.588149
110	6	0	4.030239	4.255304	-3.270579
111	1	0	4.50333	5.684118	-1.723033
112	1	0	3.425842	3.204916	4.386095
113	6	0	5.536093	3.22	3.907282
114	1	0	7.562455	3.072567	3.168798
115	6	0	8.053213	-1.539525	-0.808483
116	1	0	8.502374	-0.150191	-2.399973
117	1	0	7.331076	-2.768216	0.81884
118	1	0	1.661565	4.576328	2.191696
119	6	0	1.855189	6.409954	1.068795
120	7	0	0.474332	4.115739	-2.176851
121	6	0	1.245776	6.264694	-1.275952
122	1	0	-3.868673	-3.882069	1.197059
123	6	0	-5.207498	-5.249835	0.212342
124	1	0	-2.170019	-6.245023	-1.990985
125	6	0	-4.26585	-6.553214	-1.58577
126	1	0	-1.094531	-3.693563	-2.810765
127	6	0	0.60613	-4.775814	-3.562454
128	1	0	1.096464	-6.058325	0.066691
129	6	0	1.835994	-6.08841	-1.957071
130	1	0	0.372162	-3.411349	2.310239
131	6	0	0.434702	-5.084151	3.674491
132	1	0	-1.830632	-6.922163	1.112229
133	6	0	-0.792521	-7.048999	2.997195
134	7	0	-3.810932	-1.65012	-2.164442
135	6	0	-6.054888	-2.050839	-1.254926

136	1	0	-4.786759	-0.842699	2.206372
137	6	0	-6.476541	-1.590819	1.090448
138	1	0	-5.087156	5.044432	1.097876
139	6	0	-5.713954	4.215462	2.98652
140	1	0	-3.136211	1.39354	2.313449
141	6	0	-4.618908	2.177322	3.673903
142	1	0	-5.794546	2.078569	0.064201
143	6	0	-6.190866	1.45093	-1.958583
144	1	0	-2.651893	2.790397	-2.815017
145	6	0	-4.439572	1.857516	-3.564856
146	1	0	-4.331173	4.998441	-1.995089
147	6	0	-3.550465	6.968873	-1.595468
148	6	0	-1.945581	7.13689	0.197503
149	1	0	-1.425856	5.295502	1.183571
150	1	0	1.752038	3.21118	7.195758
151	6	0	0.535793	4.184725	5.698155
152	1	0	-0.69913	4.874022	4.061939
153	1	0	4.575929	-1.825155	4.063117
154	6	0	3.362617	-2.543484	5.702975
155	1	0	1.912471	-3.103355	7.204196
156	6	0	-3.874244	-1.628856	5.71136
157	1	0	-3.86014	-3.042342	4.074578
158	1	0	-3.633324	-0.089626	7.208891
159	1	0	3.916856	5.014177	-4.04791
160	1	0	5.824941	3.740595	4.823916
161	1	0	8.942517	-2.149995	-0.983323
162	1	0	2.219373	6.990521	1.919432
163	6	0	1.701353	6.999622	-0.187665
164	1	0	0.276717	3.146546	-1.935972
165	6	0	0.339333	4.468621	-3.513799
166	1	0	1.127439	6.718689	-2.257482
167	6	0	-5.35766	-6.204108	-0.793759
168	1	0	-6.06108	-4.95558	0.826711
169	1	0	-4.37857	-7.295889	-2.379391
170	1	0	0.471173	-4.40643	-4.581909
171	6	0	1.670237	-5.626929	-3.260503
172	1	0	2.673675	-6.743836	-1.709417
173	6	0	0.019327	-6.39103	3.921923
174	1	0	1.06368	-4.555905	4.395363
175	1	0	-1.123662	-8.072856	3.188254
176	1	0	-2.870997	-1.338852	-1.927625
177	6	0	-4.053338	-1.950228	-3.499033
178	1	0	-6.392937	-2.380823	-2.234895
179	6	0	-6.915436	-2.0201	-0.163823
180	1	0	-7.158644	-1.562571	1.943208
181	1	0	-6.437952	5.012505	3.173583

182	6	0	-5.546647	3.18837	3.916238
183	1	0	-4.473583	1.372092	4.398353
184	1	0	-7.177144	1.053273	-1.710095
185	6	0	-5.70869	1.362133	-3.262056
186	1	0	-4.052228	1.788165	-4.584212
187	6	0	-2.700357	7.741801	-0.807382
188	1	0	-4.140108	7.436078	-2.388074
189	1	0	-1.262518	7.730614	0.808784
190	1	0	0.634387	5.175939	6.147747
191	1	0	4.171627	-3.124011	6.153354
192	1	0	-4.780393	-2.03908	6.164097
193	1	0	1.939916	8.057376	-0.328581
194	7	0	-0.202353	3.470701	-4.272493
195	8	0	0.650666	5.55494	-3.970959
196	1	0	-6.33099	-6.669727	-0.966666
197	1	0	2.383413	-5.910768	-4.037548
198	1	0	0.324549	-6.898944	4.840359
199	8	0	-5.150798	-2.228057	-3.951102
200	7	0	-2.92069	-1.923332	-4.261664
201	1	0	-7.951969	-2.340234	-0.300723
202	1	0	-6.139563	3.180147	4.834417
203	1	0	-6.311504	0.88574	-4.038355
204	1	0	-2.618174	8.817316	-0.982376
205	1	0	-0.357455	2.561754	-3.850125
206	6	0	-0.322797	3.596683	-5.704234
207	1	0	-2.056412	-1.595351	-3.84445
208	6	0	-2.975206	-2.093963	-5.69285
209	1	0	-1.254729	3.097649	-6.017771
210	1	0	-0.434523	4.668316	-5.923844
211	6	0	0.860125	3.025164	-6.472591
212	1	0	-2.074997	-2.646544	-6.009044
213	1	0	-3.844282	-2.732671	-5.907099
214	6	0	-3.083735	-0.786218	-6.463908
215	1	0	1.00821	1.960631	-6.23222
216	1	0	0.700241	3.112314	-7.558693
217	1	0	1.781604	3.57139	-6.219957
218	1	0	-3.084004	-0.970917	-7.549557
219	1	0	-4.019295	-0.266369	-6.207542
220	1	0	-2.238531	-0.120084	-6.229686

Table S5. Atomic coordinates of **Cu_4-NO_3** after crystal structure optimization.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	29	0	-0.213874	-0.051552	1.359519
2	29	0	-2.214611	-0.442056	-0.03654
3	29	0	1.378905	-1.632813	0.29334
4	29	0	0.665103	2.011056	0.282196
5	15	0	-0.644074	-0.118647	3.640017
6	6	0	-0.661316	-1.847823	0.349811
7	6	0	-1.386064	1.388125	0.382773
8	6	0	1.767433	0.387814	0.882353
9	15	0	-4.481889	-0.375235	-0.420015
10	6	0	-1.582491	-2.58013	-0.089556
11	15	0	2.554837	-3.599788	0.125713
12	8	0	1.22673	-0.83192	-2.158587
13	1	0	2.543939	-2.312185	2.717101
14	6	0	2.929703	-0.08337	0.84653
15	15	0	1.844847	3.984602	0.228712
16	8	0	0.815696	1.279959	-2.136124
17	6	0	-1.487586	2.610149	0.116686
18	1	0	0.028341	3.618746	2.448583
19	6	0	-1.674034	1.262692	4.27748
20	6	0	0.838892	-0.066569	4.723023
21	6	0	-1.533812	-1.610284	4.237112
22	6	0	-5.395643	-1.651729	0.525437
23	6	0	-5.334349	1.177458	0.060334
24	6	0	-4.983004	-0.60003	-2.164958
25	6	0	-2.351255	-3.657698	-0.647473
26	6	0	1.695405	-5.042898	-0.613591
27	6	0	2.979927	-4.218857	1.798408
28	6	0	4.127911	-3.520076	-0.806979
29	7	0	0.417441	0.10827	-2.267349
30	6	0	2.87562	-3.341562	2.884281
31	6	0	4.34512	-0.296909	0.759636
32	6	0	3.662933	3.871317	0.008294
33	6	0	1.340593	5.199551	-1.04551
34	6	0	1.705443	4.840201	1.844714
35	6	0	-1.916821	3.918171	-0.286144
36	6	0	0.702378	4.432884	2.732332
37	6	0	-1.440211	1.885123	5.510854
38	6	0	-2.748981	1.695385	3.487438
39	6	0	0.977777	-0.851763	5.874762
40	6	0	1.870643	0.81461	4.368649
41	6	0	-1.162925	-2.848818	3.69428
42	6	0	-2.537088	-1.565774	5.213731

43	6	0	-5.038778	-1.843697	1.867891
44	6	0	-6.41922	-2.428176	-0.026695
45	6	0	-6.362494	1.232074	1.008929
46	6	0	-4.906628	2.361693	-0.554798
47	6	0	-4.101136	-1.259482	-3.029089
48	6	0	-6.211693	-0.136355	-2.65637
49	6	0	-3.287096	-4.365948	0.121884
50	6	0	-2.108204	-4.055727	-1.992515
51	6	0	0.486392	-5.444387	-0.02859
52	6	0	2.176689	-5.73544	-1.73025
53	6	0	3.371606	-5.545898	2.025962
54	6	0	5.34109	-4.029933	-0.332465
55	6	0	4.084838	-2.920096	-2.073981
56	8	0	-0.775914	-0.122786	-2.498668
57	6	0	3.177464	-3.774564	4.175507
58	6	0	4.999185	-0.041796	-0.478395
59	6	0	5.10326	-0.685999	1.87462
60	6	0	4.387124	3.13195	0.953843
61	6	0	4.342312	4.458345	-1.064877
62	6	0	1.155674	6.562612	-0.790524
63	6	0	1.154825	4.714764	-2.348612
64	6	0	2.589721	5.857095	2.232541
65	6	0	-2.218541	4.912417	0.656551
66	6	0	-2.098746	4.187084	-1.672379
67	6	0	0.567533	5.045482	3.978304
68	1	0	-0.600295	1.566124	6.132795
69	6	0	-2.275952	2.912833	5.948988
70	6	0	-3.586846	2.717229	3.930798
71	1	0	-2.918472	1.247044	2.505482
72	1	0	0.186023	-1.54902	6.158949
73	6	0	2.124558	-0.74817	6.662919
74	6	0	3.010471	0.921789	5.162784
75	1	0	1.784055	1.410214	3.456461
76	6	0	-1.766735	-4.022903	4.139327
77	1	0	-0.403763	-2.889966	2.909101
78	1	0	-2.842595	-0.60664	5.638766
79	6	0	-3.14565	-2.742845	5.651025
80	1	0	-4.219014	-1.267304	2.307398
81	6	0	-5.712976	-2.777614	2.650897
82	1	0	-6.693534	-2.304068	-1.076561
83	6	0	-7.083798	-3.372237	0.755796
84	1	0	-6.709966	0.318224	1.495502
85	6	0	-6.951488	2.455178	1.333354
86	1	0	-4.100818	2.333354	-1.29222
87	6	0	-5.499299	3.579561	-0.233417
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89	6	0	-4.452777	-1.477089	-4.360649
90	1	0	-6.896692	0.401142	-1.995614
91	6	0	-6.55584	-0.348242	-3.98937
92	1	0	-3.452252	-4.056255	1.155085
93	6	0	-3.990113	-5.438714	-0.413362
94	7	0	-1.151979	-3.354345	-2.706823
95	6	0	-2.836232	-5.130217	-2.525972
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97	6	0	-0.221791	-6.524951	-0.544502
98	1	0	3.116356	-5.435482	-2.198832
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105	6	0	5.229217	-2.860949	-2.865103
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124	7	0	-1.818234	3.162476	-2.560091
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141	6	0	-6.522841	3.628141	0.714003
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170	1	0	3.144803	7.263039	3.768662
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175	1	0	-2.718181	5.639219	-3.122873
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214	1	0	2.642843	1.05974	-6.016971
215	1	0	2.772022	2.779847	-6.468903
216	1	0	1.638137	2.277191	-5.196197
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218	1	0	-1.480114	0.321851	-7.467252
219	1	0	-1.120892	-0.34506	-5.859481

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