Structural Diversity of Copper(I) Alkynyl Cluster-Based Coordination Polymers Utilizing Bifunctional Pyridine Carboxylic Acid Ligands

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Experimental Section

Synthesis of CACPs

Synthesis of 1a. In a conical flask, Cu_2O (0.71 mg, 0.5 mmol) and INA (41 mg, 0.33 mmol) were combined in a 7.5 mL mixed solvent of methanol and acetonitrile (2:1). Subsequently, 100 μL of ^{t}BuC≡CH and 50 μL of Hhfac were added dropwise following sonication of the mixture for 30 minutes. The mixture was then stirred at room temperature for 12 hours before being subjected to a solvothermal reaction within a Teflon-lined vessel at 80°C, yielding yellow bulk crystals after 20 hours. The resulting yellow powdered product was collected following washing with methanol and acetone and subsequent drying in a vacuum oven, affording a yield of 53 mg.

Synthesis of 1b. In a conical flask, Cu_2O (0.71 mg, 0.5 mmol) and INA (33 mg, 0.29 mmol) were combined in a 7.5 mL mixed solvent of methanol and acetonitrile (2:1). Subsequently, 100 μL of ^{t}BuC≡CH and 100 μL of Hhfac were added dropwise following sonication of the mixture for 30 minutes. The mixture was then stirred at room temperature for 12 hours before being subjected to a solvothermal reaction within a Teflon-lined vessel at 80°C, yellow crystals of **1b** were produced as a by-product of **1a** after 20 hours.

Synthesis of 1c. In a conical flask, Cu_2O (0.71 mg, 0.5 mmol) and INA (20.5 mg, 0.17 mmol) were combined in a 7.5 mL mixed solvent of methanol and DMF (2:1). Subsequently, 100 μL of ^{t}BuC≡CH, 50 μL of Hhfac and 20μL of deionized water were added dropwise following sonication of the mixture for 30 minutes. The mixture was then stirred at room temperature for 12 hours before being subjected to a solvothermal reaction within a Teflon-lined vessel at 80°C, yielding yellow bulk crystals after 20 hours. The resulting yellow powdered product was collected following washing with methanol and acetone and subsequent drying in a vacuum oven, affording a yield of 26 mg.

Synthesis of 1d. In a conical flask, Cu_2O (0.71 mg, 0.5 mmol) and INA (20.5 mg, 0.17 mmol) were combined in a 7.5 mL mixed solvent of methanol and acetonitrile (2:1). Subsequently, 100 μL of ^{t}BuC≡CH, 50 μL of Hhfac and 20μL of deionized water were added dropwise following sonication of the mixture for 30 minutes. The mixture was then stirred at room temperature for 12 hours before being subjected to a solvothermal reaction within a Teflon-lined vessel at 80°C, yellow crystals of **1d** were produced as a by-product of **1c** after 20 hours.

Synthesis of 2a. In a conical flask, Cu_2O (0.71 mg, 0.5 mmol) and IQL (69.2 mg, 0.4 mmol) were combined in a 7.5 mL mixed solvent of methanol and DMF (2:1). Subsequently, 100 μL of ^{t}BuC≡CH, 50 μL of Hhfac and 20μL of deionized water were added dropwise following sonication of the mixture for 30 minutes. The mixture was then stirred at room temperature for 12 hours before being subjected to a solvothermal reaction within a Teflon-lined vessel at 80°C, yellow crystals of **2a** were produced as a by-product of **2c** after 20 hours.

Synthesis of 2b. In a conical flask, Cu_2O (0.71 mg, 0.5 mmol) and IQL (69.2 mg, 0.4 mmol) were combined in a 7.5 mL mixed solvent of methanol and DMF (2:1). Subsequently, 100 μL of ^{t}BuC≡CH and 50 μL of Hhfac were added dropwise following sonication of the mixture for 30 minutes. The mixture was then stirred at room temperature for 12 hours before being subjected to a solvothermal reaction within a Teflon-lined vessel at 80°C, yellow crystals of **2b** were produced as a by-product of **2c** after 20 hours.

Synthesis of 2c. In a conical flask, Cu_2O (0.71 mg, 0.5 mmol) and IQL (69.2 mg, 0.4 mmol) were combined in a 7.5 mL mixed solvent of methanol and DMF (2:1). Subsequently, 100 μL of ^{t}BuC≡CH, 50 μL of Hhfac and 20μL of deionized water were added dropwise following sonication of the mixture for 30 minutes. The mixture was then stirred at room temperature for 12 hours before being subjected to a solvothermal reaction within a Teflon-lined vessel at 80°C, yielding yellow bulk crystals after 20 hours. The resulting yellow powdered product was collected following washing with methanol and acetone and subsequent drying in a vacuum oven, affording a yield of 46 mg.

Synthesis of 3. In a conical flask, Cu_2O (0.71 mg, 0.5 mmol) and 4-PyBA (33.2 mg, 0.167 mmol) were combined in a 7.5 mL mixed solvent of methanol and DMF (2:1). Subsequently, 100 μL of ^{t}BuC≡CH, 50 μL of Hhfac were added dropwise following sonication of the mixture for 30 minutes. The mixture was then stirred at room temperature for 12 hours before being subjected to a solvothermal reaction within a Teflon-lined vessel at 80°C, yielding yellow bulk crystals after 20 hours. The resulting yellow powdered product was collected following washing with methanol and acetone and subsequent drying in a vacuum oven, affording a yield of 66 mg.

Synthesis of 4. In a conical flask, Cu_2O (0.71 mg, 0.5 mmol) and IQL (33.2 mg, 0.167 mmol) were combined in a 7.5 mL mixed solvent of methanol and DMF (2:1). Subsequently, 100 μL of ^{t}BuC≡CH, 50 μL of DMF and 20μL of deionized water were added dropwise following sonication of the mixture for 30 minutes. The mixture was then stirred at room temperature for 12 hours before being subjected to a solvothermal reaction within a Teflon-lined vessel at 80°C, yielding yellow bulk crystals after 20 hours. The resulting yellow powdered product was collected following washing with methanol and acetone and subsequent drying in a vacuum oven, affording a yield of 36 mg.

Instrumentation

All reagents and solvents utilized in the experiments were commercially available and deemed suitable for immediate use without requiring further purification. Vis-NIR experiments were conducted using a PE Lambda 750S UV-vis-NIR spectrophotometer. Fluorescent spectra and lifetime decay test of photoluminescence were captured employing a QuantaMaster 8000 fluorescence spectrometer. Powder X-ray diffraction (PXRD) data were collected on a x'pert3 powder X-ray diffractometer with Cu-Kα (λ = 1.5406 Å) radiation manufactured by PANalytical B.V.. X-ray photoelectron spectroscopy (XPS) was collected on a Thermo Scientific ESCALAB Xi+ spectrometer. Fourier transform infrared (FTIR) spectra were acquired from KBr pellets within the 4000-00 cm^{-1} range using a Bruker VERTEX 70 spectrometer.

Characterizations

Powder X-ray Diffraction Patterns

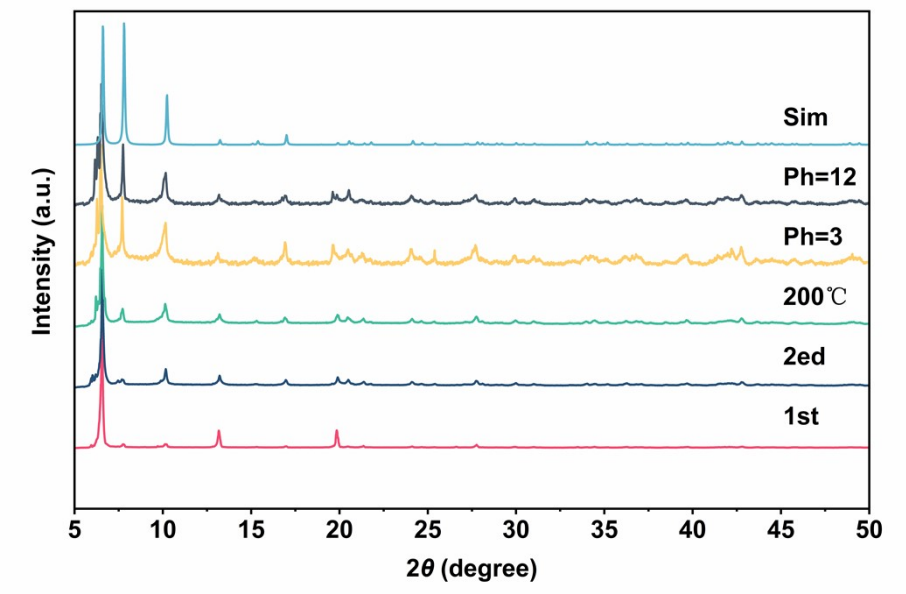

Figure S1. The PXRD patterns of **1a** with different treatments.

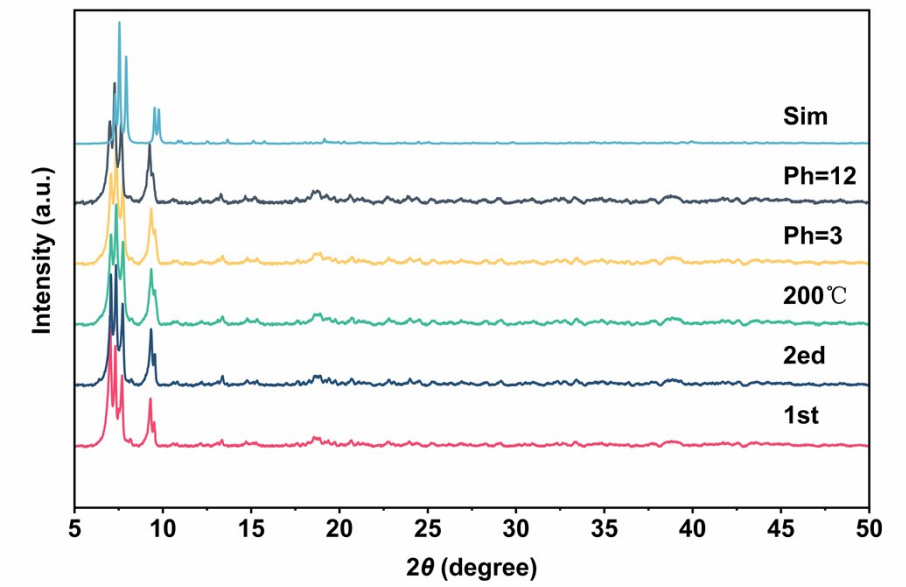

Figure S2. The PXRD patterns of **1c** with different treatments.

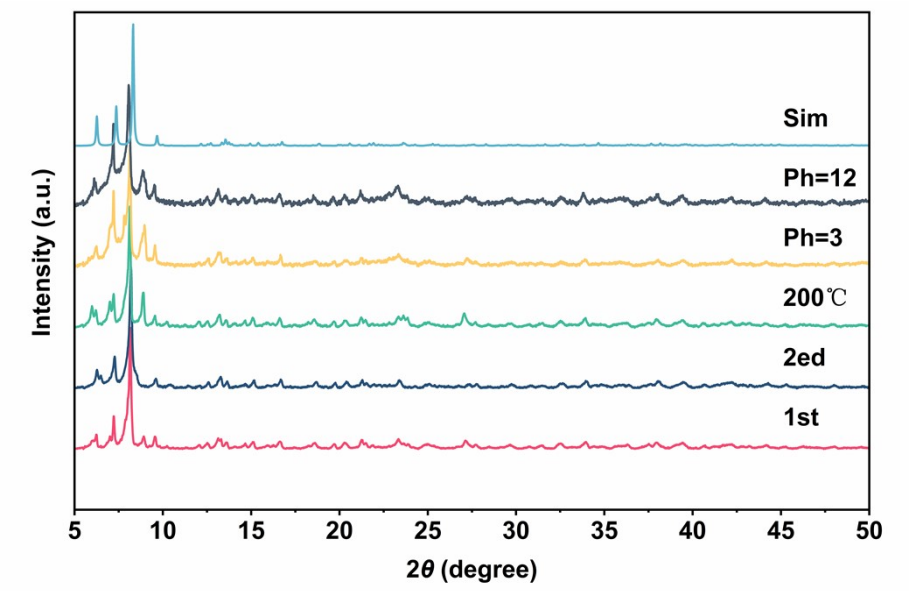

Figure S3. The PXRD patterns of **2c** with different treatments.

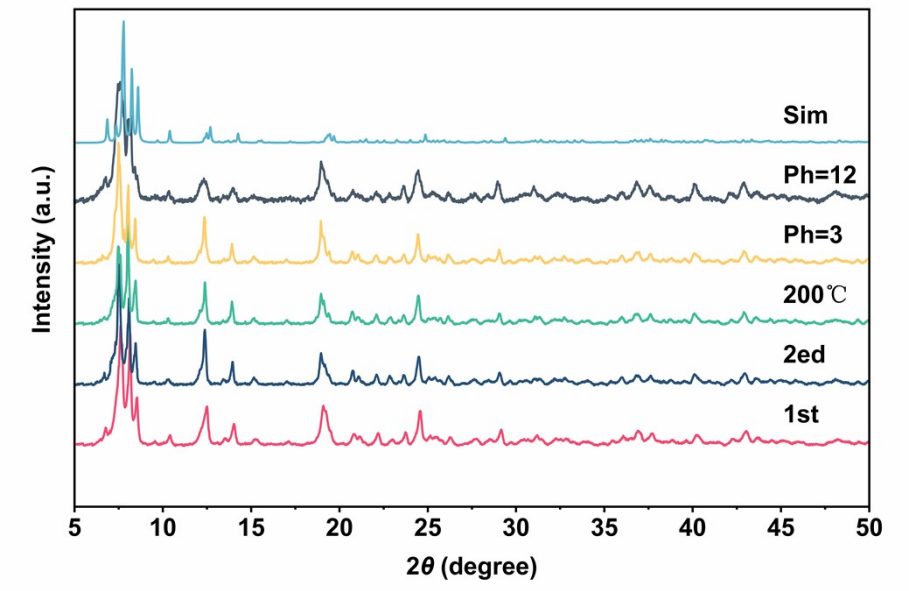

Figure S4. The PXRD patterns of **3** with different treatments.

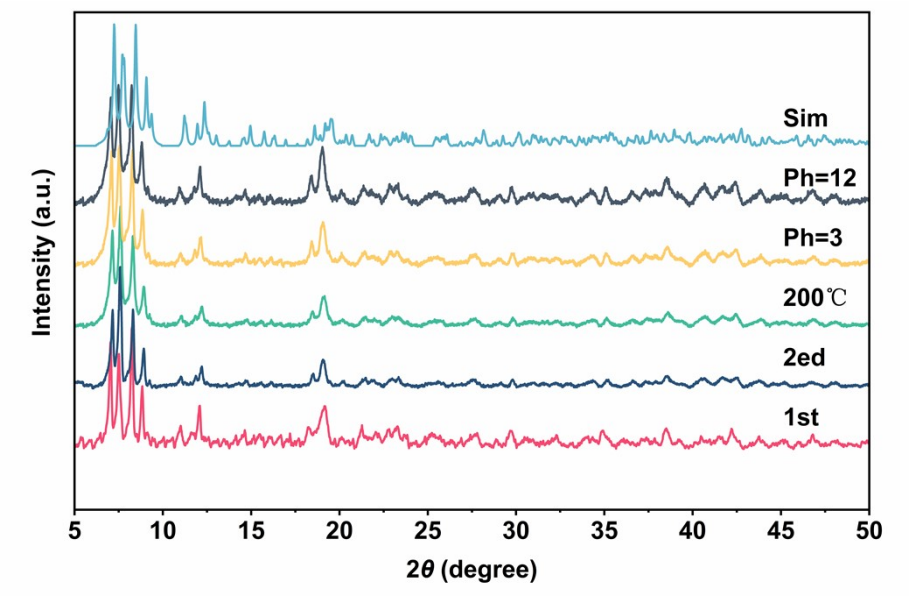

Figure S5. The PXRD patterns of **4** with different treatments.

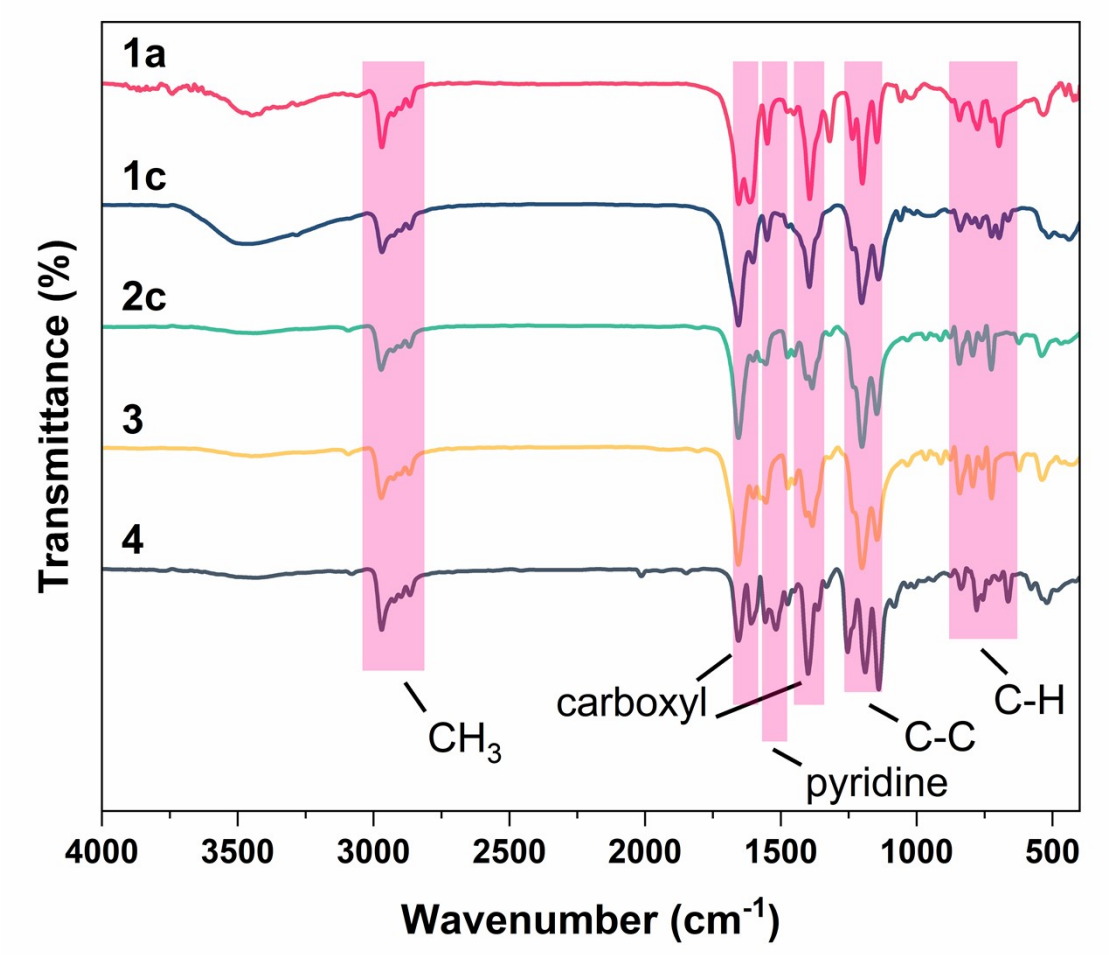

Figure S6. The FT-IR spectra of CACPs.

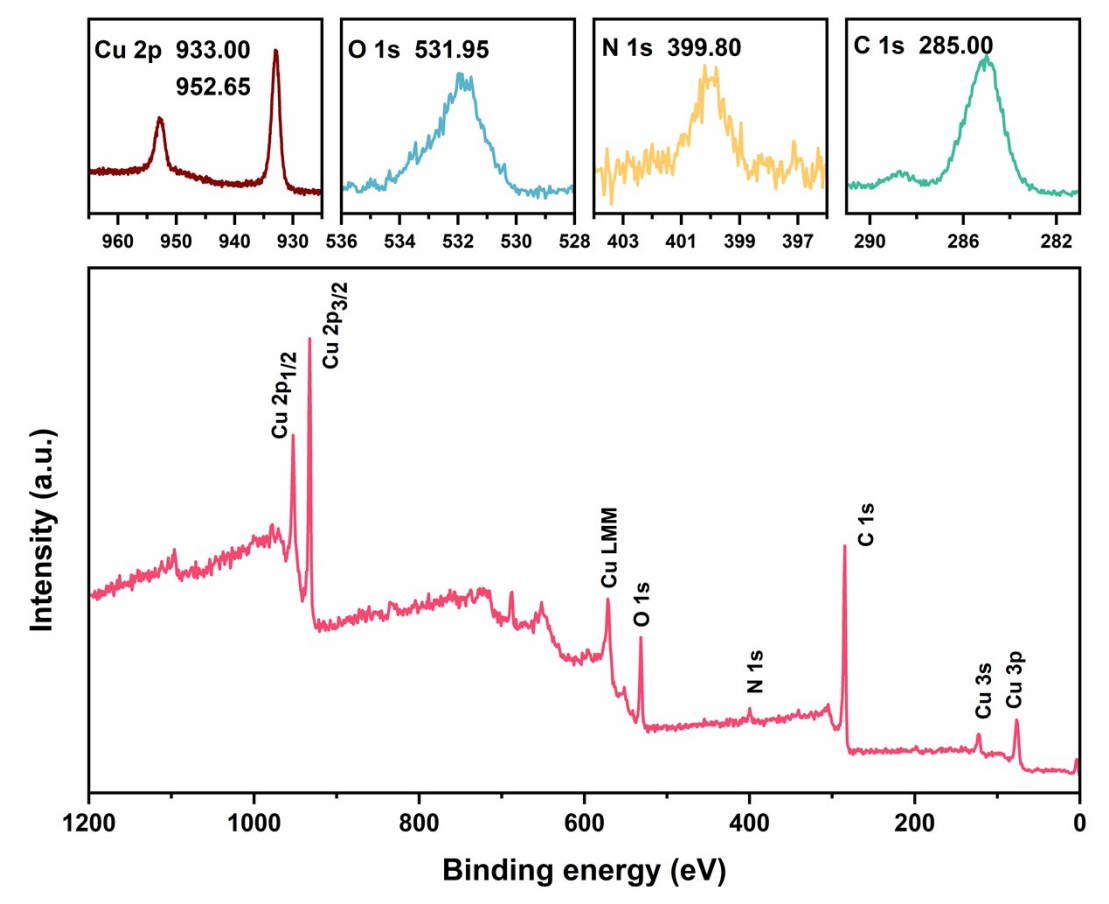

Figure S7. XPS spectra of the **1a**, Survey spectrum confirms the presence of all the expected elements (Cu, O, C, and N).

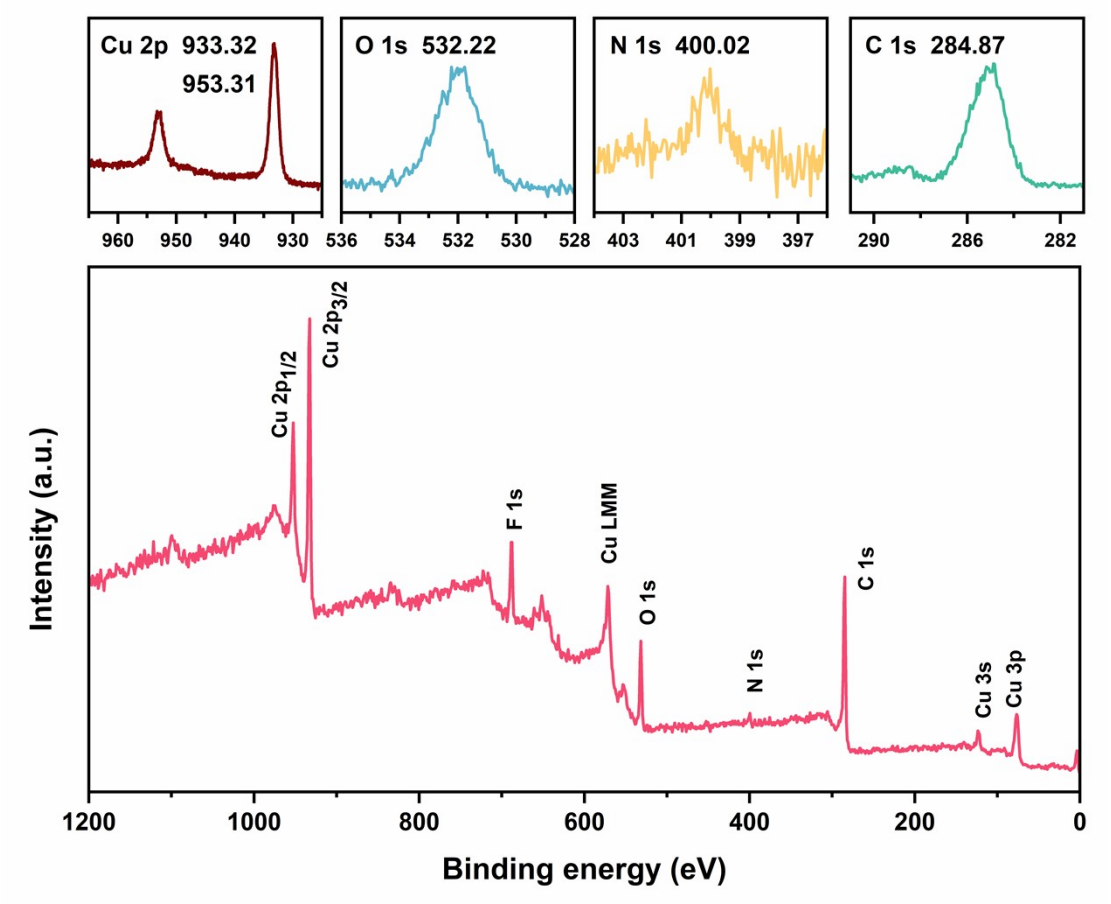

Figure S8. XPS spectra of the **2c** Survey spectrum confirms the presence of all the expected elements (Cu, O, C, and N).

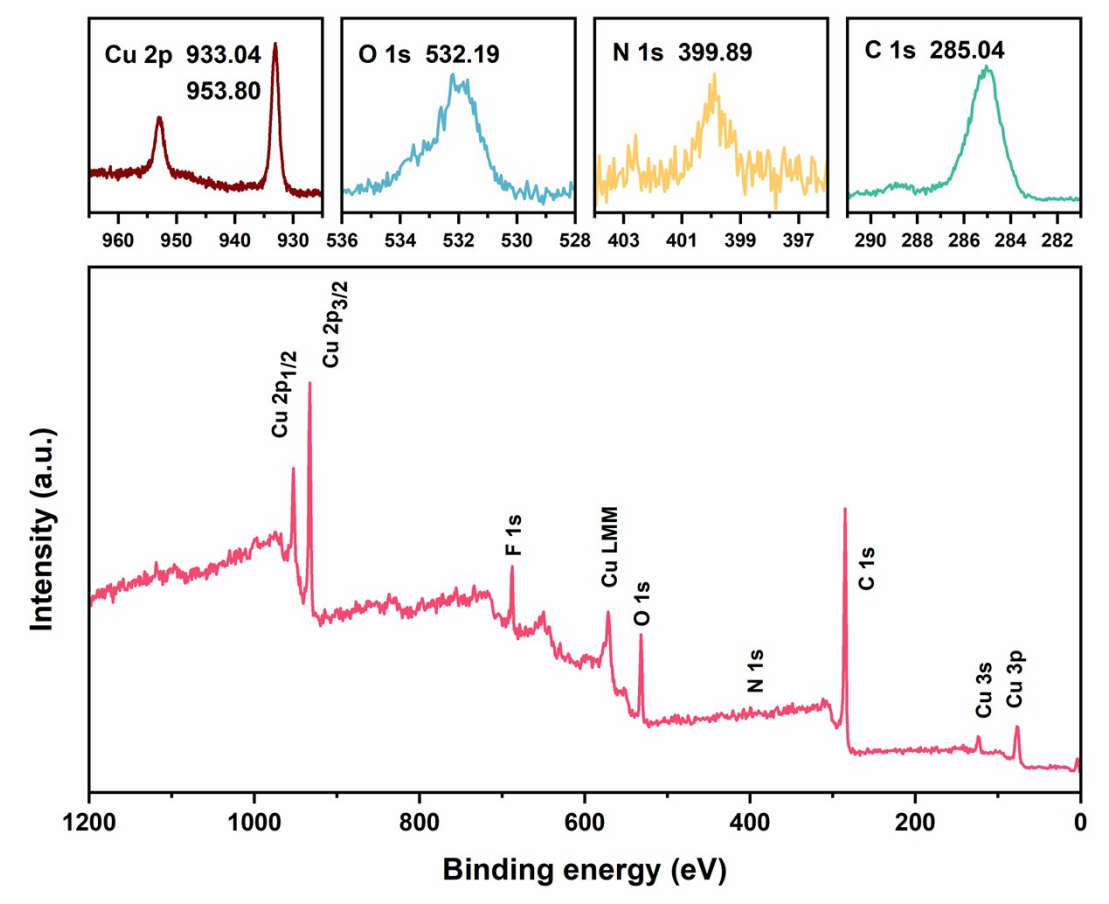

Figure S9. XPS spectra of the **4**, Survey spectrum confirms the presence of all the expected elements (Cu, O, C, and N).

Photophysical Properties

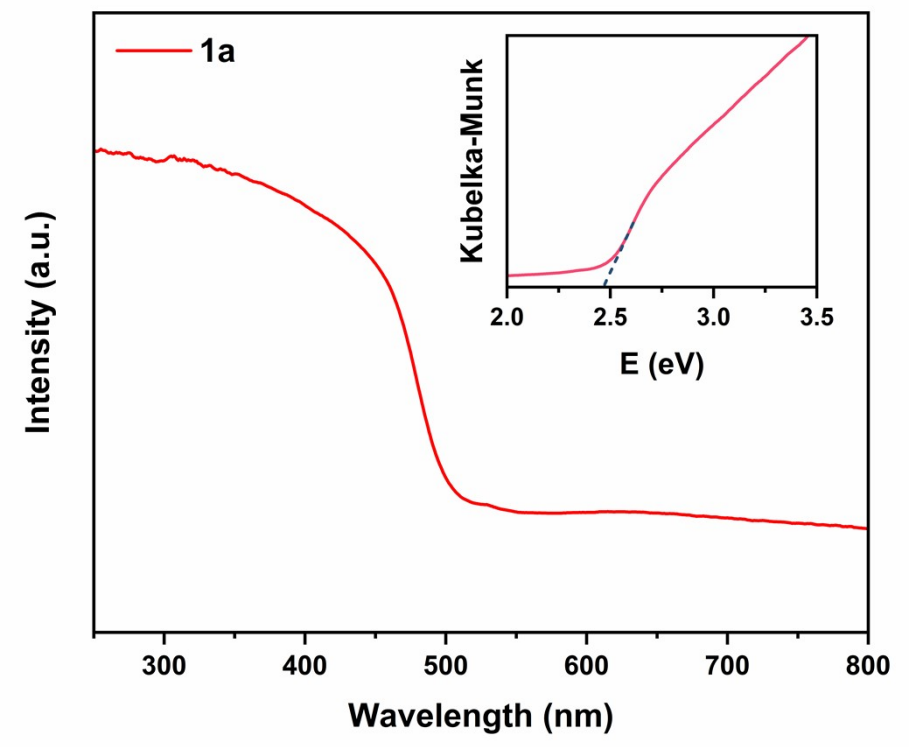

Figure S10. UV−vis absorption spectra of **1a** in the solid state at room temperature.

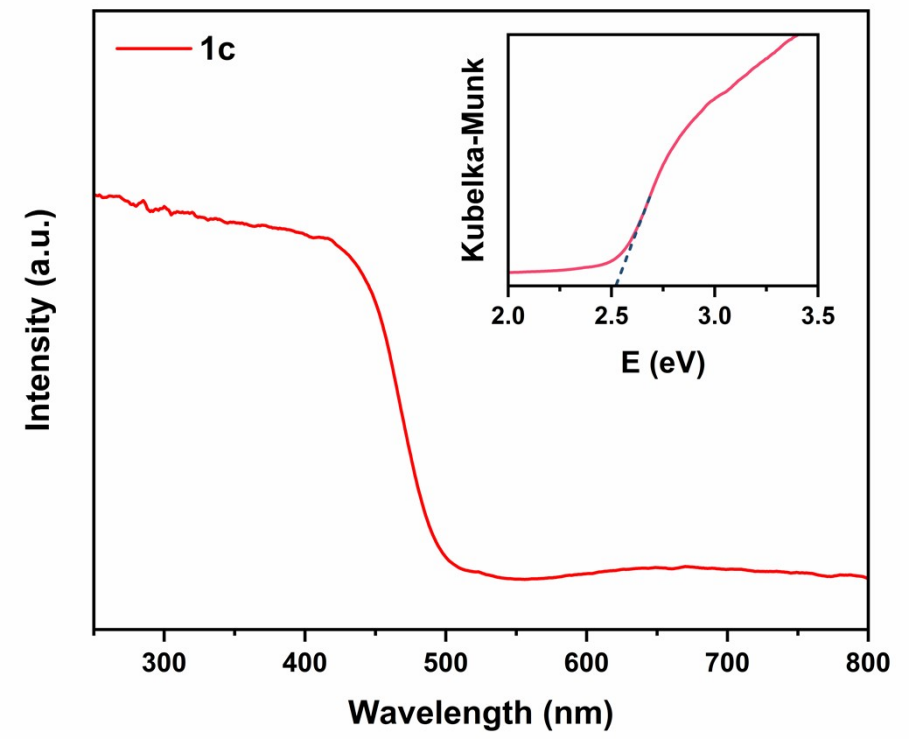

Figure S11. UV−vis absorption spectra of **1c** in the solid state at room temperature.

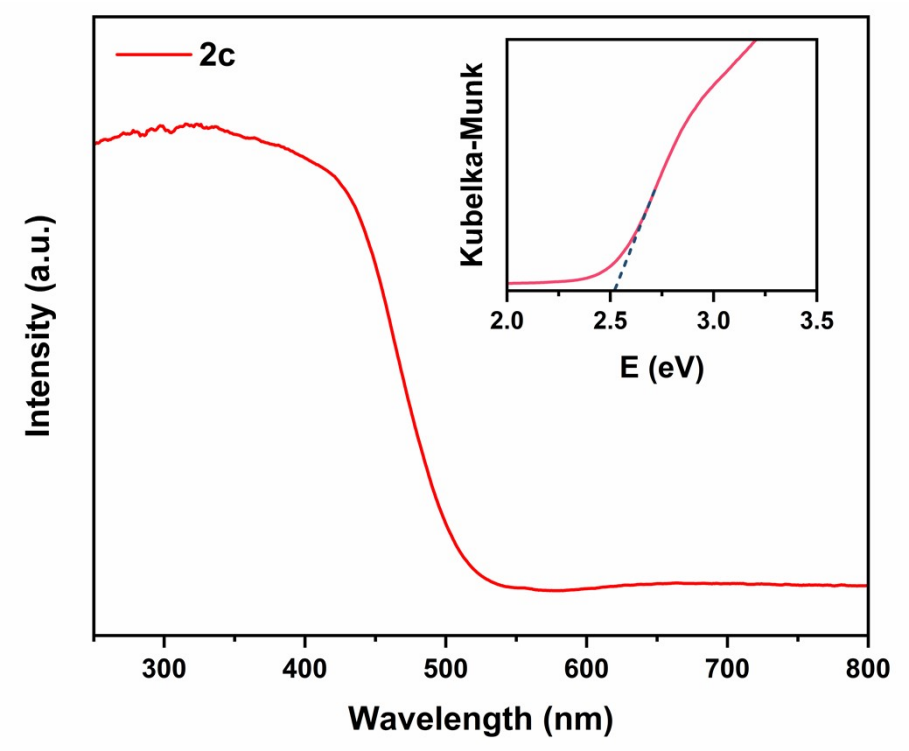

Figure S12. UV−vis absorption spectra of **2c** in the solid state at room temperature.

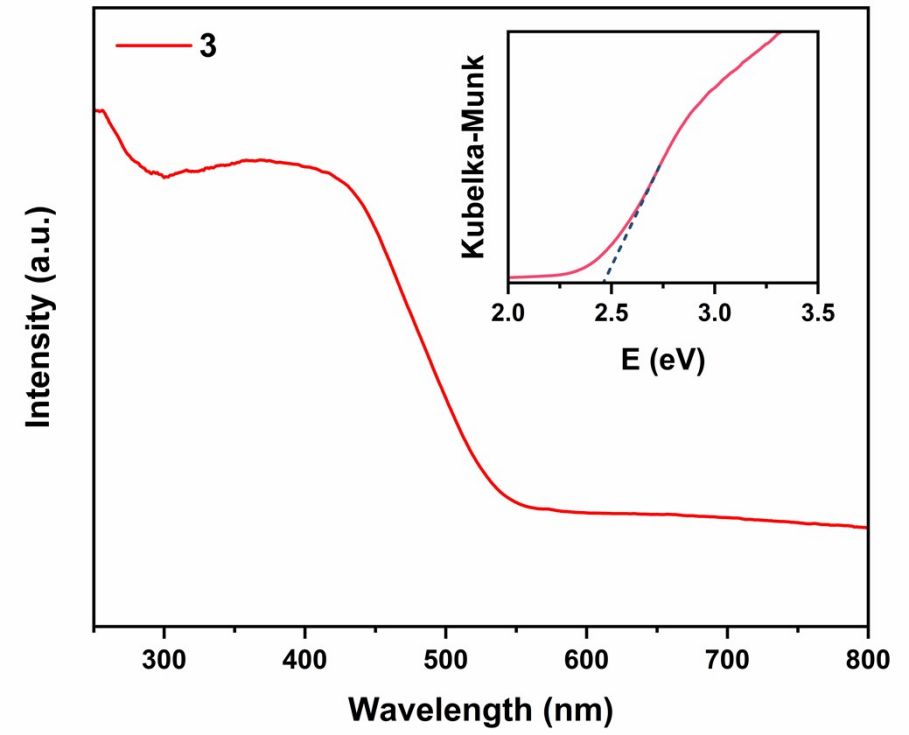

Figure S13. UV−vis absorption spectra of **3** in the solid state at room temperature.

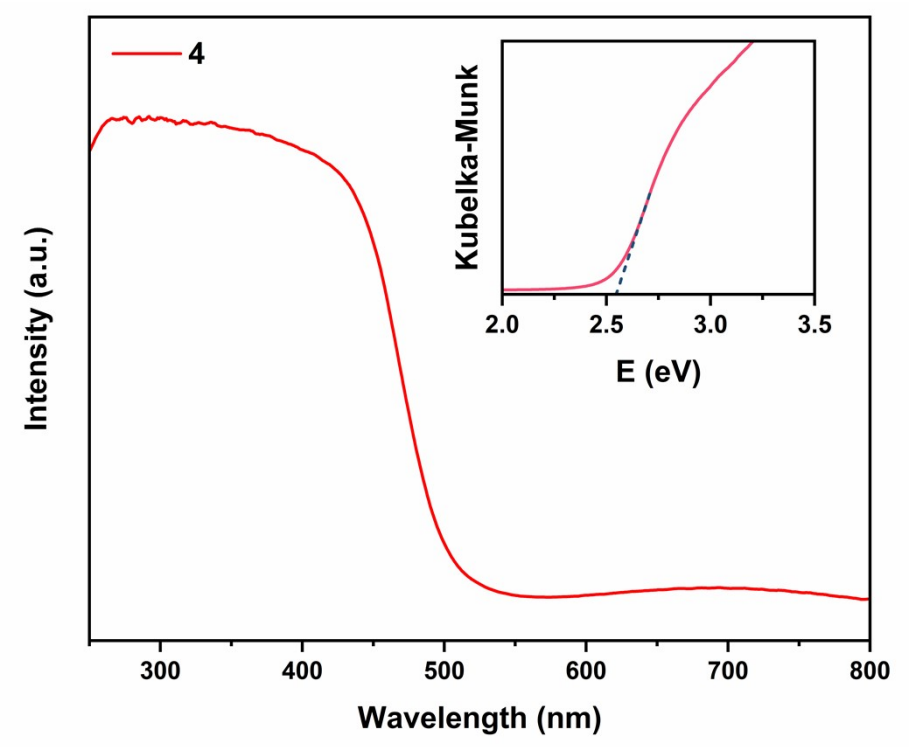

Figure S14. UV−vis absorption spectra of **4** in the solid state at room temperature.

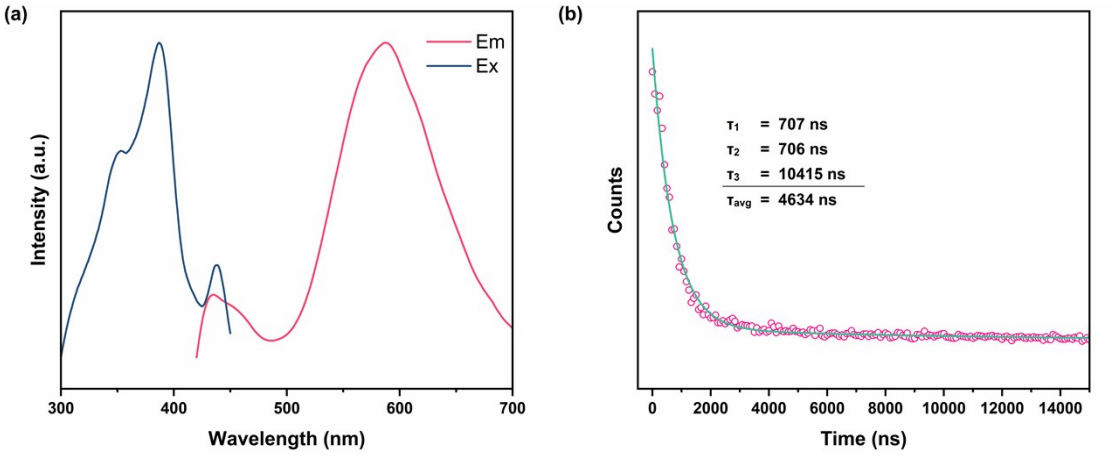

Figure S15. Excitation (blue) and emission (red) spectra of **1a** in the solid state; λ_{ex}= 387 nm, λ_{em}= 587 nm.

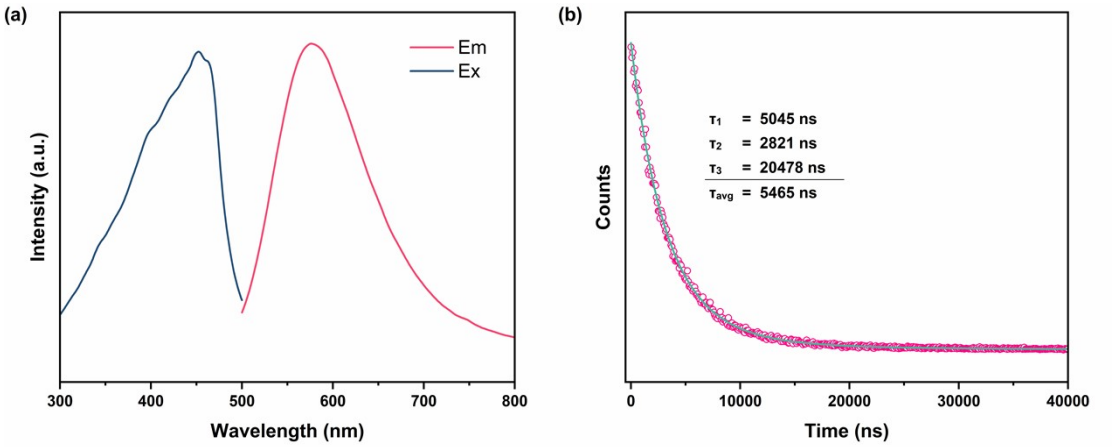

Figure S16. Excitation (blue) and emission (red) spectra of **1c** in the solid state; λ_{ex}=452 nm, λ_{em}=576 nm.

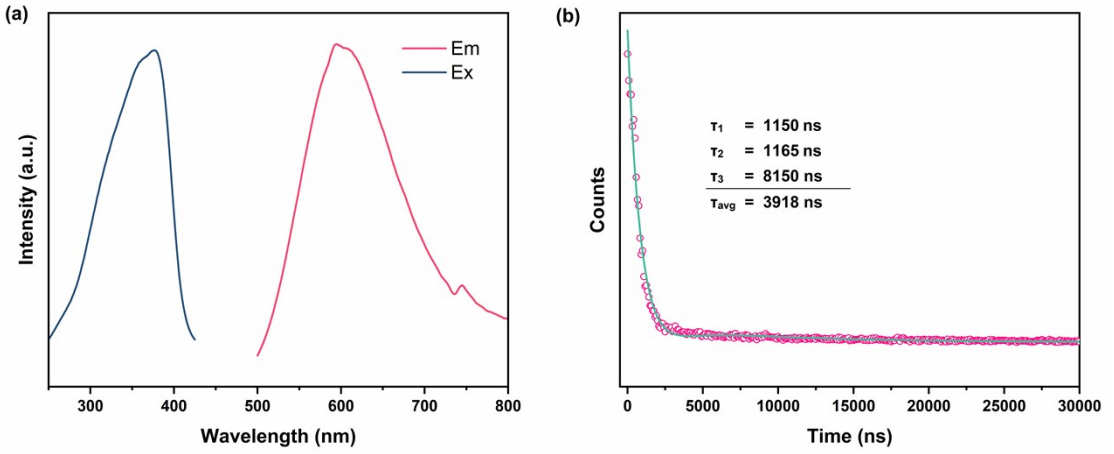

Figure S17. Excitation (blue) and emission (red) spectra of **2c** in the solid state; λ_{ex}=376 nm, λ_{em}=594 nm.

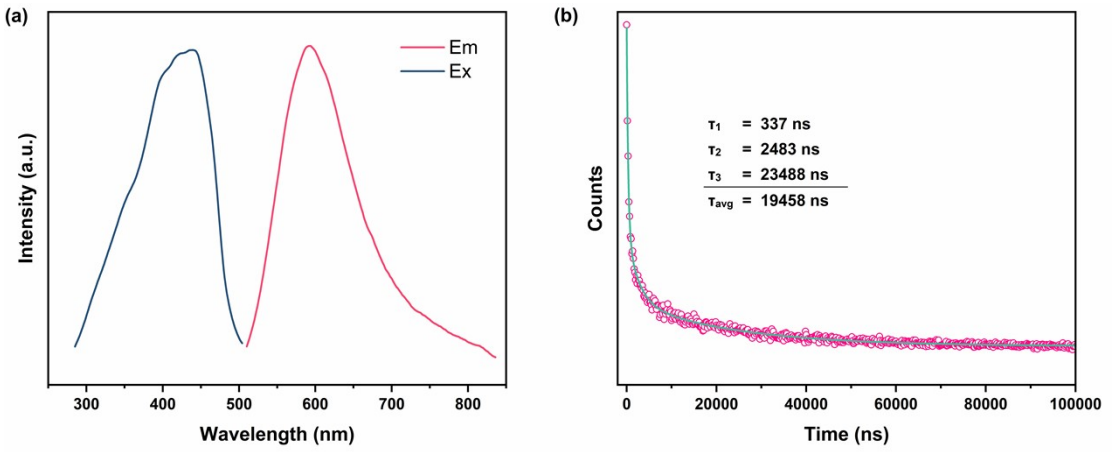

Figure S18. Excitation (blue) and emission (red) spectra of **3** in the solid state; λ_{ex}=439 nm, λ_{em}=592 nm.

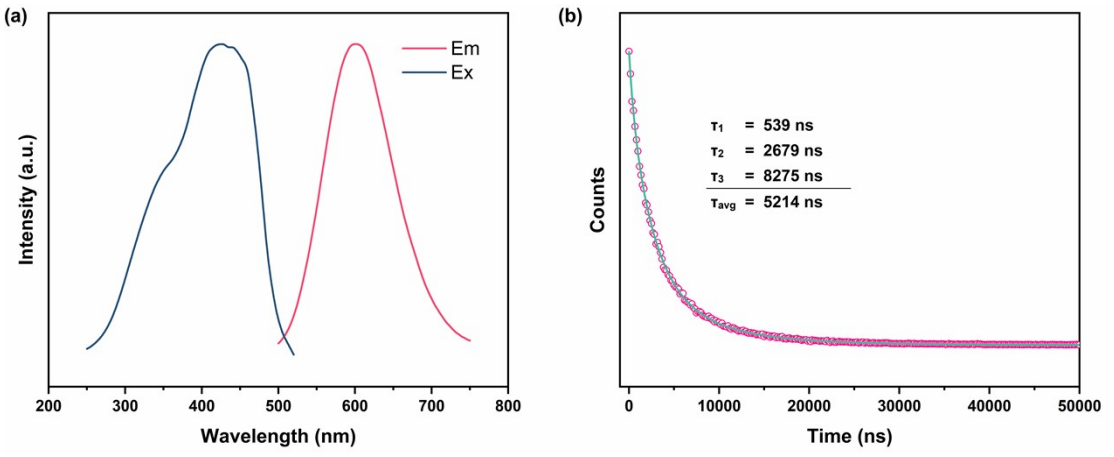

Figure S19. Excitation (blue) and emission (red) spectra of **4** in the solid state; λ_{ex}=426 nm, λ_{em}=601 nm.

Crystal Structure

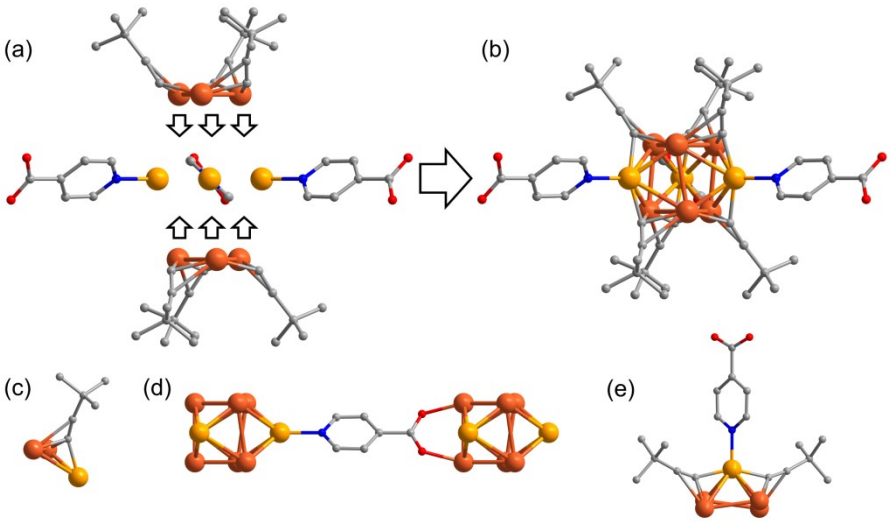

Figure S20. (a) and (b) Sandwich-like structures of node in **1a**; (c) Coordination modes of ^{t}BuC≡C^{-} in **1a**; (d) Coordination modes of INA in **1a**; (e) Spatial distribution of ^{t}BuC≡C^{-} in **1a**, atoms and INA. codes are as follows: rufous, Cu in external layer; yellow, Cu in internal layer; red, O; blue, N; gray, C; green, F. H atoms are omitted for clarity.

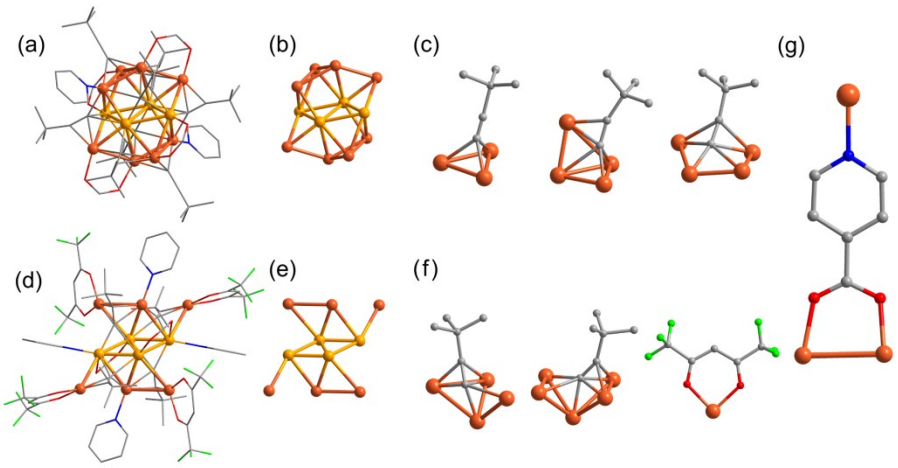

Figure S21. (a) Structures of Cu_{12} node in **1b**; (b) Core structures of Cu_{12} node in **1b**; (c) Coordination modes of $^{t}BuC{\equiv}C^{-}$ in Cu_{12} node; (d) Structures of Cu_{10} node in **1b**; (e) Core structures of Cu_{10} node in **1b**; (f) Coordination modes of hfac in Cu_{10} node; (g) Coordination modes of INA in **1b**. codes are as follows: rufous, Cu in external layer; yellow, Cu in internal layer; red, O; blue, N; gray, C; green, F. H atoms are omitted for clarity.

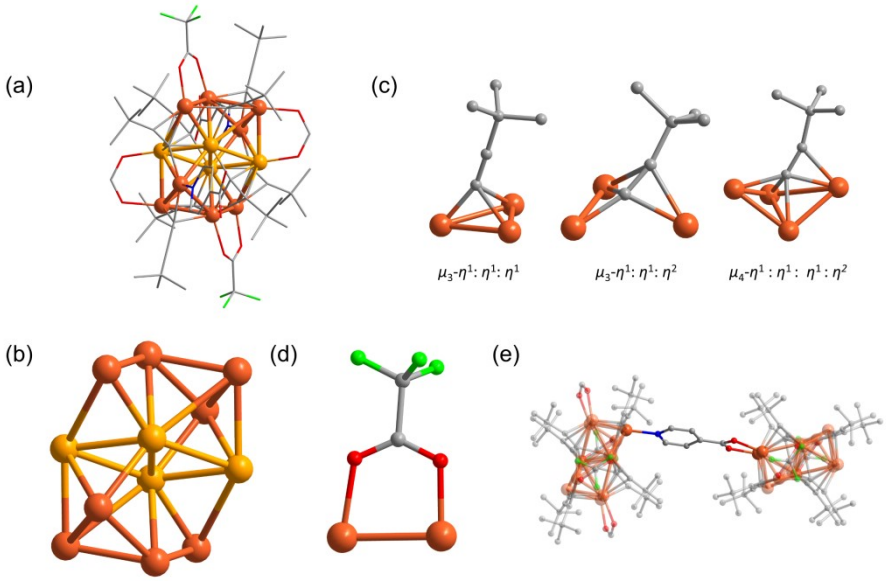

Figure S22. (a) Structures of node in **1c**; (b) Core structures of node in **1c**; Coordination modes of (c) $^{t}BuC{\equiv}C^{-}$; (d) $CF_3CO_2^{-}$ and (e) INA in **1c**. codes are as follows: rufous, Cu in external layer; yellow, Cu in internal layer; red, O; blue, N; gray, C; green, F. H atoms are omitted for clarity.

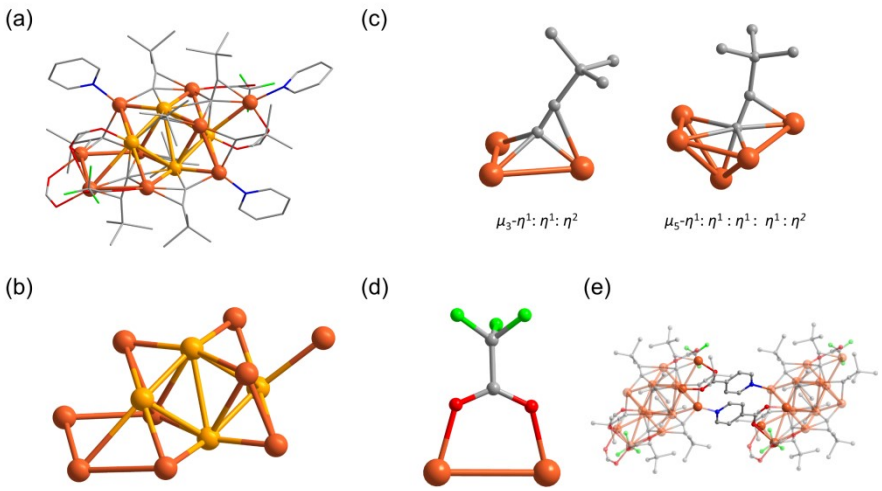

Figure S23. (a) Structures of node in **1d**; (b) Core structures of node in **1d**; Coordination modes of (c) ^{t}BuC≡C$^-$; (d) $CF_3CO_2^-$ and (e) INA in **1d**. codes are as follows: rufous, Cu in external layer; yellow, Cu in internal layer; red, O; blue, N; gray, C; green, F. H atoms are omitted for clarity.

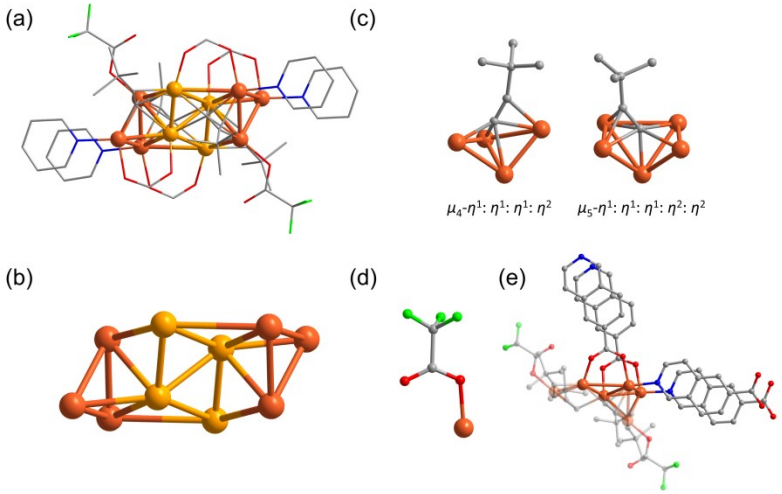

Figure S24. (a) Structures of node in **2a**; (b) Core structures of node in **2a**; Coordination modes of (c) ^{t}BuC≡C$^-$; (d) $CF_3CO_2^-$ and (e) IQL in **2a**. codes are as follows: rufous, Cu in external layer; yellow, Cu in internal layer; red, O; blue, N; gray, C; green, F. H atoms are omitted for clarity.

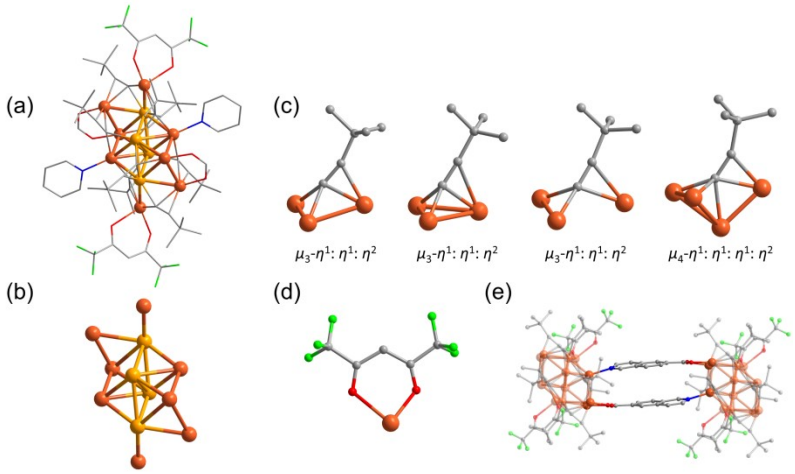

Figure S25. (a) Structures of node in **2b**; (b) Core structures of node in **2b**; Coordination modes of (c) ^{t}BuC≡C$^-$; (d) hfac and (e) IQL in **2b**. codes are as follows: rufous, Cu in external layer; yellow, Cu in internal layer; red, O; blue, N; gray, C; green, F. H atoms are omitted for clarity.

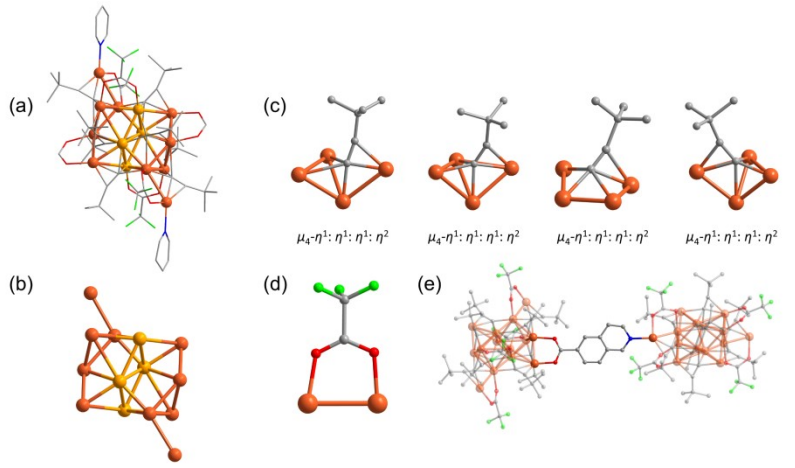

Figure S26. (a) Structures of node in **2c**; (b) Core structures of node in **2c**; Coordination modes of (c) ^{t}BuC≡C$^-$; (d) $CF_3CO_2^-$ and (e) IQL in **2c**. codes are as follows: rufous, Cu in external layer; yellow, Cu in internal layer; red, O; blue, N; gray, C; green, F. H atoms are omitted for clarity.

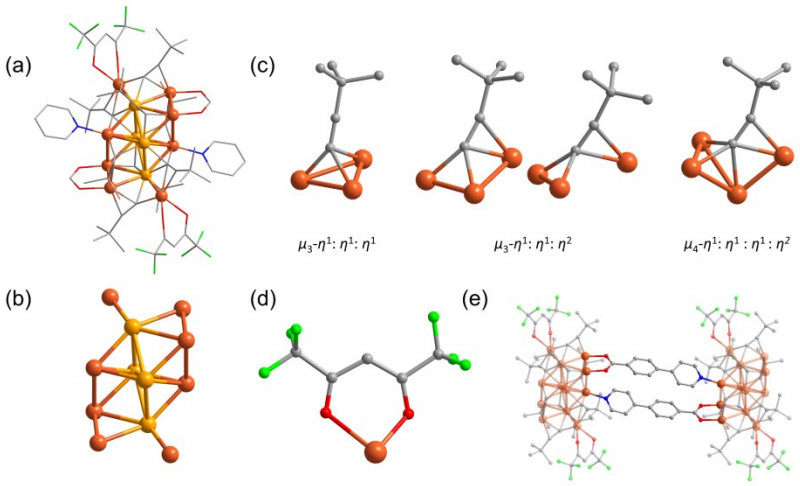

Figure S27. (a) Structures of node in **3**; (b) Core structures of node in **3**; Coordination modes of (c) ^{t}BuC≡C$^-$; (d) hfac and (e) 4-PyBA in **3**. codes are as follows: rufous, Cu in external layer; yellow, Cu in internal layer; red, O; blue, N; gray, C; green, F. H atoms are omitted for clarity.

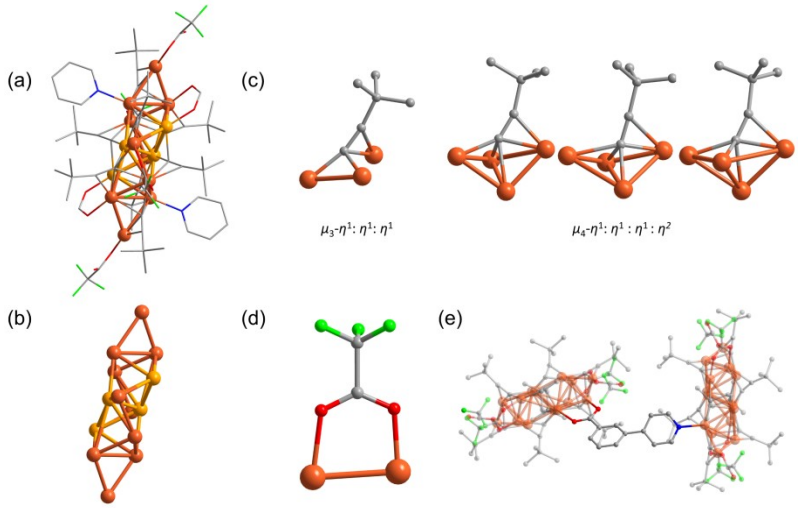

Figure S28. (a) Structures of node in **4**; (b) Core structures of node in **4**; Coordination modes of (c) ^{t}BuC≡C$^-$; (d) $CF_3CO_2^-$ and (e) 3-PyBA in **4**. codes are as follows: rufous, Cu in external layer; yellow, Cu in internal layer; red, O; blue, N; gray, C; green, F. H atoms are omitted for clarity.

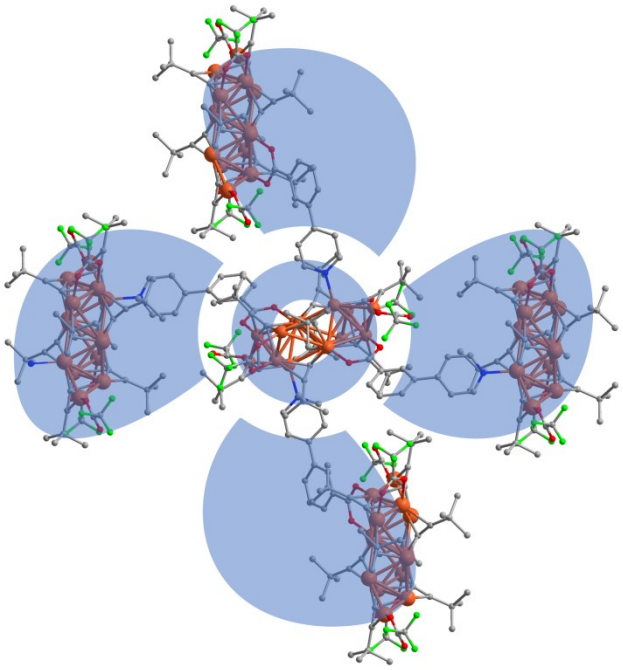

Figure S29. Propeller structure of **4**. codes are as follows: rufous, Cu in external layer; yellow, Cu in internal layer; red, O; blue, N; gray, C; green, F. H atoms are omitted for clarity.

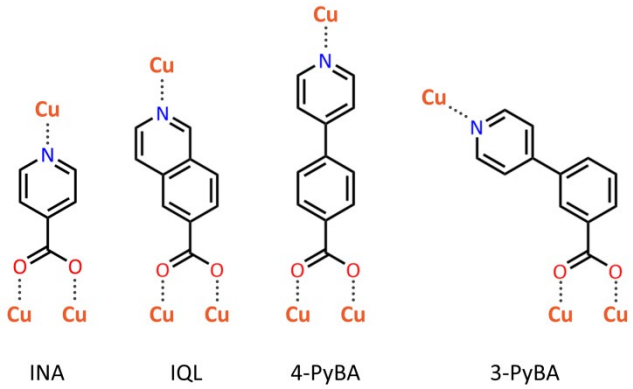

Figure S30. Coordination modes of pyridine carboxylic acids with copper.

Crystal Data

Table S1. Crystal data and structure refinement for **1a**.

Identification code	**1a**
Empirical formula	$C_{18.67}H_{24.67}Cu_3NO_{2.67}$
Formula weight	496.35
Temperature/K	291.15
Crystal system	trigonal
Space group	*P*321

a/Å	13.067(3)
b/Å	13.067(3)
c/Å	13.365(4)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	1976.3(11)
Z	3
ρ_{calc}g/cm^3	1.251
μ/mm^{-1}	2.410
F(000)	756.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	Synchrotron (λ = 0.6888)
2Θ range for data collection/°	6.096 to 50.05
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -15 ≤ l ≤ 6
Reflections collected	8221
Independent reflections	2324 [R_{int} = 0.0708, R_{sigma} = 0.0556]
Data/restraints/parameters	2324/201/162
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0570, wR_2 = 0.1457
Final R indexes [all data]	R_1 = 0.0879, wR_2 = 0.1768
Largest diff. peak/hole / e Å^{-3}	0.69/-0.59

Table S2. Crystal data and structure refinement for **1b**.

Identification code	**1b**
Empirical formula	$C_{64.42}H_{69.04}Cu_{11}F_{12}N_{3.12}O_{10.17}$
Formula weight	1976.64
Temperature/K	273.15
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	14.8797(9)
b/Å	15.9071(9)
c/Å	19.7103(13)
α/°	98.802(2)
β/°	109.142(2)
γ/°	108.741(2)
Volume/Å^3	3995.8(4)
Z	2
ρ_{calc}g/cm^3	1.643

μ/mm^{-1}	2.942
F(000)	1972.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	Synchrotron (λ = 0.6888)
2Θ range for data collection/°	5.182 to 56.864
Index ranges	-19 ≤ h ≤ 13, -21 ≤ k ≤ 21, -21 ≤ l ≤ 26
Reflections collected	33691
Independent reflections	19759 [R_{int} = 0.0218, R_{sigma} = 0.0433]
Data/restraints/parameters	19759/1199/1151
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0368, wR_2 = 0.0935
Final R indexes [all data]	R_1 = 0.0615, wR_2 = 0.1040
Largest diff. peak/hole / e Å^{-3}	0.48/-0.53

Table S3. Crystal data and structure refinement for **1c**.

Identification code	**1c**
Empirical formula	$C_{69.76}H_{90}Cu_{12}F_6N_2O_8$
Formula weight	1961.06
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	24.310(3)
b/Å	18.0920(19)
c/Å	18.612(2)
α/°	90
β/°	94.883(4)
γ/°	90
Volume/Å^3	8155.9(17)
Z	4
ρ_{calc}g/cm^3	1.597
μ/mm^{-1}	3.121
F(000)	3954.0
Crystal size/mm^3	0.3 × 0.1 × 0.1
Radiation	Synchrotron (λ = 0.6888)
2Θ range for data collection/°	1.682 to 50.724
Index ranges	-29 ≤ h ≤ 29, -19 ≤ k ≤ 20, -22 ≤ l ≤ 22
Reflections collected	95455
Independent reflections	14105 [R_{int} = 0.0635, R_{sigma} = 0.0420]
Data/restraints/parameters	14105/1013/1005

Goodness-of-fit on F^2	1.099
Final R indexes [I>=2σ (I)]	R_1 = 0.0672, wR_2 = 0.1812
Final R indexes [all data]	R_1 = 0.0751, wR_2 = 0.1952
Largest diff. peak/hole / e $Å^{-3}$	1.95/-1.93

Table S4. Crystal data and structure refinement for **1d**.

Identification code	**1d**
Empirical formula	$C_{70}H_{84}Cu_{13}F_6N_3O_{10}$
Formula weight	2067.42
Temperature/K	273.15
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	13.1388(12)
b/Å	13.5488(15)
c/Å	14.2759(13)
α/°	62.883(3)
β/°	80.888(3)
γ/°	70.396(3)
Volume/$Å^3$	2130.8(4)
Z	1
$\rho_{calc}g/cm^3$	1.611
μ/mm^{-1}	3.233
F(000)	1036.0
Crystal size/mm^3	0.3 × 0.2 × 0.2
Radiation	synchrotron (λ = 0.6888)
2Θ range for data collection/°	5.51 to 50.826
Index ranges	$-15 \le h \le 15$, $-16 \le k \le 9$, $-17 \le l \le 16$
Reflections collected	13533
Independent reflections	7409 [R_{int} = 0.0390, R_{sigma} = 0.0773]
Data/restraints/parameters	7409/819/649
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0772, wR_2 = 0.2312
Final R indexes [all data]	R_1 = 0.1227, wR_2 = 0.2662
Largest diff. peak/hole / e $Å^{-3}$	3.16/-0.93

Table S5. Crystal data and structure refinement for **2a**.

Identification code	**2a**
Empirical formula	$C_{78}H_{78}Cu_{10}F_6N_6O_{14}$

Formula weight	2072.86
Temperature/K	273.15
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	11.6633(7)
b/Å	18.9908(12)
c/Å	20.1994(13)
α/°	81.451(2)
β/°	89.413(2)
γ/°	74.577(2)
Volume/Å^3	4263.0(5)
Z	2
ρ_{calc}g/cm^3	1.615
μ/mm^{-1}	2.516
F(000)	2088.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	Synchrotron (λ = 0.6888)
2Θ range for data collection/°	3.258 to 50.742
Index ranges	-14 ≤ h ≤ 13, -22 ≤ k ≤ 22, -24 ≤ l ≤ 24
Reflections collected	50189
Independent reflections	13997 [R_{int} = 0.0513, R_{sigma} = 0.0503]
Data/restraints/parameters	13997/228/913
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0721, wR_2 = 0.1925
Final R indexes [all data]	R_1 = 0.0868, wR_2 = 0.2119
Largest diff. peak/hole / e Å^{-3}	1.27/-0.98

Table S6. Crystal data and structure refinement for **2b**.

Identification code	**2b**
Empirical formula	$C_{39}H_{43}Cu_6F_6NO_4$
Formula weight	1084.98
Temperature/K	273.15
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	12.6843(10)
b/Å	14.1427(9)
c/Å	14.7359(10)
α/°	115.220(3)
β/°	97.199(2)

γ/°	111.483(2)
Volume/Å^3	2097.4(3)
Z	2
ρ_{calc}g/cm^3	1.718
μ/mm^{-1}	3.053
F(000)	1088.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	Synchrotron (λ = 0.6888)
2Θ range for data collection/°	3.242 to 50.72
Index ranges	-15 ≤ h ≤ 15, -17 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	19018
Independent reflections	6855 [R_{int} = 0.0642, R_{sigma} = 0.0802]
Data/restraints/parameters	6855/187/545
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.1275, wR_2 = 0.3268
Final R indexes [all data]	R_1 = 0.1309, wR_2 = 0.3380
Largest diff. peak/hole / e Å^{-3}	2.62/-2.02

Table S7. Crystal data and structure refinement for **2c**.

Identification code	**2c**
Empirical formula	$C_{76}H_{84}Cu_{14}F_{12}N_2O_{12}$
Formula weight	2335.01
Temperature/K	273.15
Crystal system	orthorhombic
Space group	*P*ca2$_1$
a/Å	13.0606(8)
b/Å	23.9965(14)
c/Å	28.2045(16)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	8839.5(9)
Z	4
ρ_{calc}g/cm^3	1.755
μ/mm^{-1}	3.371
F(000)	4656.0
Crystal size/mm^3	0.3 × 0.2 × 0.2
Radiation	Synchrotron (λ = 0.6888)
2Θ range for data collection/°	3.35 to 50.73

Index ranges	$-15 \le h \le 15$, $-28 \le k \le 28$, $-33 \le l \le 34$
Reflections collected	105319
Independent reflections	16064 [R_{int} = 0.0771, R_{sigma} = 0.0521]
Data/restraints/parameters	16064/986/1073
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0689, wR_2 = 0.1647
Final R indexes [all data]	R_1 = 0.0841, wR_2 = 0.1770
Largest diff. peak/hole / e Å^{-3}	1.12/-1.51

Table S8. Crystal data and structure refinement for **3**.

Identification code	**3**
Empirical formula	$C_{41}H_{45}Cu_6F_6NO_4$
Formula weight	1111.02
Temperature/K	273.15
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	13.3217(5)
b/Å	14.0632(5)
c/Å	14.6193(6)
α/°	62.3950(10)
β/°	81.8880(10)
γ/°	64.9420(10)
Volume/Å^3	2193.45(15)
Z	2
ρ_{calc}g/cm^3	1.682
μ/mm^{-1}	2.921
F(000)	1116.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	Synchrotron (λ = 0.6888)
2Θ range for data collection/°	3.152 to 50.734
Index ranges	$-13 \le h \le 12$, $-16 \le k \le 16$, $-16 \le l \le 16$
Reflections collected	20313
Independent reflections	6083 [R_{int} = 0.0387, R_{sigma} = 0.0362]
Data/restraints/parameters	6083/206/552
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0425, wR_2 = 0.1447
Final R indexes [all data]	R_1 = 0.0435, wR_2 = 0.1462
Largest diff. peak/hole / e Å^{-3}	1.00/-0.78

Table S9. Crystal data and structure refinement for **4**.

Identification code	**4**
Empirical formula	$C_{78.19}H_{88}Cu_{12.5}F_{7.66}N_2O_{9.91}$
Formula weight	2154.24
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	*C*2/c
a/Å	23.8539(2)
b/Å	15.62430(10)
c/Å	24.1728(2)
α/°	90
β/°	108.4950(10)
γ/°	90
Volume/Å^3	8543.90(12)
Z	4
ρ_{calc}g/cm^3	1.675
μ/mm^{-1}	3.869
F(000)	4328.0
Crystal size/mm^3	0.35 × 0.3 × 0.15
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.876 to 149.034
Index ranges	-28 ≤ h ≤ 29, -19 ≤ k ≤ 13, -30 ≤ l ≤ 28
Reflections collected	48339
Independent reflections	8599 [R_{int} = 0.0527, R_{sigma} = 0.0235]
Data/restraints/parameters	8599/279/639
Goodness-of-fit on F^2	1.099
Final R indexes [I>=2σ (I)]	R_1 = 0.0484, wR_2 = 0.1385
Final R indexes [all data]	R_1 = 0.0497, wR_2 = 0.1395
Largest diff. peak/hole / e Å^{-3}	1.02/-0.55

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

Table S10. Bond lengths (Å) of **1a**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Cu1	Cu1^1	2.668(3)	Cu3	Cu1^3	2.883(2)
Cu1	Cu1^2	2.668(3)	Cu3	Cu11	2.883(2)
Cu1	Cu1^3	2.898(4)	Cu3	N4	2.040(15)
Cu1	Cu3^2	2.883(2)	Cu3	C2	2.000(12)
Cu1	Cu3	2.4932(19)	Cu3	C25	2.000(12)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	O9[4]	2.136(8)	O9	Cu16	2.136(8)
Cu1	C2	2.009(11)	C8	O95	1.274(12)
Cu1	C2[2]	2.036(10)	C2	Cu1[1]	2.036(10)
Cu1	C10[2]	2.482(14)	C10	Cu1[1]	2.482(14)
Cu3	Cu1[5]	2.4932(19)	C1	O3	1.41(3)

[1]+Y-X,-X,+Z; [2]-Y,+X-Y,+Z; [3]-X,-X+Y,-Z; [4]-Y+X,1-Y,-Z; [5]+Y,+X,-Z; [6]1-Y+X,1-Y,-Z

Table S11. Bond lengths (Å) of **1b**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu3	Cu2	2.6497(5)	Cu58	C59	2.111(3)
Cu3	Cu2[1]	2.5373(5)	Cu58	C66	2.036(3)
Cu3	Cu4	2.7830(5)	Cu58	O57	1.948(2)
Cu3	C5	2.071(3)	Cu58	C65	2.050(3)
Cu3	Cu6	2.9204(6)	Cu41	Cu41[3]	2.5748(8)
Cu3	O92	2.183(2)	Cu41	Cu39	2.7763(5)
Cu3	C83	2.058(3)	Cu41	Cu39[3]	2.8225(6)
Cu3	N54[2]	2.055(2)	Cu41	C59	1.974(3)
Cu2	Cu3[1]	2.5373(5)	Cu41	C42	1.949(3)
Cu2	Cu2[1]	2.5826(7)	Cu41	C66	2.469(3)
Cu2	Cu4[1]	2.4958(5)	Cu41	Cu71[3]	2.8271(6)
Cu2	Cu1	2.9151(6)	Cu39	Cu41[3]	2.8224(6)
Cu2	C5[1]	2.289(3)	Cu39	C42[3]	2.091(3)
Cu2	O94	1.9762(19)	Cu39	C66	2.030(3)
Cu2	C83	2.023(3)	Cu39	Cu71	2.7652(7)
Cu2	C83[1]	2.536(3)	Cu39	O38	2.006(2)
Cu48	Cu40[3]	2.6553(5)	Cu39	C43[3]	2.435(3)
Cu48	Cu58	2.7656(6)	C59	Cu71[3]	2.098(3)
Cu48	Cu41	2.6918(6)	Cu1	Cu4[1]	2.7640(6)
Cu48	C59	2.415(3)	Cu1	O101	1.993(2)
Cu48	C42[3]	2.158(3)	Cu1	O105	1.986(3)
Cu48	C72[3]	2.194(3)	Cu1	C83	2.021(3)
Cu48	Cu71[3]	2.5700(6)	Cu1	C84	2.041(3)
Cu48	O49	2.019(2)	C42	Cu48[3]	2.158(3)
Cu48	C43[3]	2.246(3)	C42	Cu39[3]	2.091(3)
Cu40	Cu48[3]	2.6554(5)	C72	Cu48[3]	2.194(3)
Cu40	Cu41	2.5612(5)	C72	Cu71	2.058(3)
Cu40	Cu39	2.6930(6)	C5	Cu2[1]	2.289(3)
Cu40	C42	2.515(3)	C5	Cu6	2.035(3)
Cu40	C66	1.976(3)	O11	Cu6	2.008(3)

Cu40	C72	2.005(3)	Cu71	Cu48[3]	2.5701(6)
Cu40	Cu71	2.8747(6)	Cu71	Cu41[3]	2.8271(6)
Cu40	N98[4]	2.096(2)	Cu71	C59[3]	2.098(3)
Cu4	Cu2[1]	2.4958(5)	Cu71	O82	1.963(2)
Cu4	Cu1[1]	2.7640(6)	Cu71	C60[3]	2.472(4)
Cu4	C5	2.096(3)	Cu6	O7	2.026(3)
Cu4	N31	1.991(2)	Cu6	C26	2.03(3)
Cu4	C83[1]	2.148(3)	Cu6	C2	1.988(17)
Cu4	C84[1]	2.113(3)	C84	Cu4[1]	2.113(3)
Cu58	Cu41	2.5371(5)	C60	Cu71[3]	2.472(4)
Cu58	Cu39	2.9837(6)			

[1]2-X,1-Y,2-Z; [2]1-X,1-Y,1-Z; [3]-X,-Y,1-Z; [4]1-X,-Y,1-Z

Table S12. Bond lengths (Å) of **1c**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Cu5	Cu5[1]	2.5247(12)	Cu57	Cu68	2.6430(9)
Cu5	Cu7[1]	2.6813(8)	Cu57	Cu50[3]	2.7156(10)
Cu5	Cu1[1]	2.5338(8)	Cu57	N64[4]	2.086(5)
Cu5	Cu11[1]	2.4371(9)	Cu57	C75	1.925(5)
Cu5	Cu4	2.7853(9)	Cu57	C56	1.952(6)
Cu5	Cu4[1]	2.6361(9)	Cu58	Cu47	2.9670(9)
Cu5	C12[1]	2.227(5)	Cu58	Cu68	2.6963(11)
Cu5	C27	2.050(5)	Cu58	Cu50[3]	2.5658(9)
Cu5	C6	1.931(5)	Cu58	O59	1.945(4)
Cu7	Cu1[1]	2.7409(9)	Cu58	C75	2.056(5)
Cu7	Cu3[1]	2.5619(9)	Cu58	C70	2.053(5)
Cu7	Cu11	2.6057(8)	Cu58	C69	2.126(6)
Cu7	O8	2.078(4)	Cu47	Cu47[3]	2.5561(13)
Cu7	C27[1]	2.165(5)	Cu47	Cu68	2.9466(10)
Cu7	C2[1]	2.245(5)	Cu47	Cu68[3]	2.6554(8)
Cu7	C6	2.128(5)	Cu47	Cu50[3]	2.6352(9)
Cu7	C22	2.184(5)	Cu47	Cu54[3]	2.4755(10)
Cu1	Cu3	2.6881(9)	Cu47	C56[3]	2.234(6)
Cu1	Cu4	2.6698(9)	Cu47	C70	2.037(5)
Cu1	N39[2]	2.069(4)	Cu47	C48[3]	2.548(5)
Cu1	C12	1.980(5)	Cu47	C48	1.917(5)
Cu1	C2	1.936(5)	Cu68	Cu54	3.0579(10)
Cu3	Cu4	2.6897(10)	Cu68	O67	1.976(4)
Cu3	O35	1.950(4)	Cu68	C56	2.069(6)
Cu3	C27	2.043(5)	Cu68	C48	2.059(5)
Cu3	C2	2.058(5)	Cu68	C49	2.322(6)

Cu3	C28	2.086(5)	Cu50	Cu54	2.6299(11)
Cu11	O10	1.937(4)	Cu50	O51	2.058(5)
Cu11	C12	2.048(5)	Cu50	C75[3]	2.196(6)
Cu11	C27[1]	2.054(5)	Cu50	C70[3]	2.202(5)
Cu11	C13	2.012(5)	Cu50	C48	2.136(5)
Cu4	O33	1.962(4)	Cu50	C49	2.268(6)
Cu4	C12	2.040(5)	Cu54	O53	1.949(5)
Cu4	C6	2.047(5)	Cu54	C56	2.041(6)
Cu4	C22	2.417(5)	Cu54	C70[3]	2.021(5)
Cu57	Cu58	2.7866(9)	Cu54	C55	2.010(6)
Cu57	Cu47[3]	2.5046(9)			

[1]-X,2-Y,1-Z; [2]-X,1/2+Y,3/2-Z; [3]1-X,1-Y,1-Z; [4]+X,3/2-Y,1/2+Z

Table S13. Bond lengths (Å) of **1d**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Cu3	Cu4	2.6726(17)	Cu2	C17[1]	2.30(4)
Cu3	Cu4[1]	2.7350(15)	Cu2	C20	2.161(6)
Cu3	Cu2	2.6926(17)	Cu7	Cu3[1]	2.6778(18)
Cu3	Cu7[1]	2.6779(18)	Cu7	C6	2.043(10)
Cu3	O37	2.014(6)	Cu7	O8	1.932(9)
Cu3	C26	2.039(9)	Cu7	C32[1]	2.174(10)
Cu3	C32	1.936(10)	Cu7	C5	2.04(6)
Cu4	Cu3[1]	2.7350(15)	Cu7	C1C	2.14(2)
Cu4	Cu5	2.5329(17)	Cu1	O35	2.218(9)
Cu4	Cu2[1]	2.6728(17)	Cu1	Cu34	2.679(7)
Cu4	Cu2	2.8853(18)	Cu1	O46	2.02(2)
Cu4	Cu7	2.6293(18)	Cu1	C20	1.928(6)
Cu4	C6	1.955(11)	Cu1	C1I	2.065(17)
Cu4	C26	1.913(9)	O35	Cu34	2.358(8)
Cu4	C32[1]	2.471(9)	N41	Cu5[2]	2.005(8)
Cu5	Cu2	2.6166(19)	C26	Cu2[1]	2.051(9)
Cu5	C6	1.987(11)	C32	Cu4[1]	2.471(9)
Cu5	N41[2]	2.005(8)	C32	Cu7[1]	2.174(10)
Cu5	C20	2.062(6)	C32	Cu34	2.106(9)
Cu2	Cu4[1]	2.6728(17)	C33	Cu34	2.019(11)
Cu2	Cu1	3.041(3)	Cu34	O44	2.024(19)
Cu2	C26[1]	2.051(9)	Cu51	N50	2.02(2)
Cu2	C32	2.320(10)	C10	Cu2[1]	2.172(18)
Cu2	C10[1]	2.172(18)	C17	Cu2[1]	2.30(4)

[1]1-X,1-Y,1-Z; [2]-X,1-Y,1-Z

Table S14. Bond lengths (Å) of **2a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu01	Cu01[1]	2.5174(16)	Cu05	Cu09	2.6822(14)
Cu01	Cu02	2.9092(11)	Cu05	O00M	1.977(7)
Cu01	Cu03	2.8235(11)	Cu05	C00Z	2.154(7)
Cu01	Cu03[1]	2.5434(12)	Cu05	C01D	2.054(7)
Cu01	Cu04	2.5441(11)	Cu05	C01M	2.045(7)
Cu01	Cu0A	2.5625(12)	Cu06	Cu07[4]	2.8511(11)
Cu01	O00C	1.983(5)	Cu06	Cu09[4]	3.0233(12)
Cu01	C00R	2.050(6)	Cu06	O00E[4]	2.042(5)
Cu01	C00R[1]	2.279(7)	Cu06	N00J	1.983(6)
Cu01	C019	2.368(7)	Cu06	C00Z[4]	2.042(8)
Cu02	Cu04	2.6813(12)	Cu06	C01M[4]	2.130(8)
Cu02	Cu0A	3.0065(11)	Cu07	Cu07[3]	2.5040(19)
Cu02	O00B	2.042(5)	Cu07	Cu08	2.8400(13)
Cu02	N00I	1.994(6)	Cu07	Cu08[3]	2.5448(12)
Cu02	C00R	2.039(7)	Cu07	Cu09	2.6302(14)
Cu02	C013	2.137(7)	Cu07	O00F	1.979(6)
Cu03	Cu04[1]	3.0318(12)	Cu07	C00Z	2.060(7)
Cu03	O00D	1.947(5)	Cu07	C00Z[3]	2.260(7)
Cu03	C00R	2.040(7)	Cu07	C01D	2.457(7)
Cu03	C019[1]	2.083(8)	Cu08	O00G	1.958(5)
Cu03	C01P[1]	2.091(7)	Cu08	C00Z	2.042(7)
Cu04	Cu0A	2.6729(13)	Cu08	C01D[3]	2.102(8)
Cu04	O00H	1.941(6)	Cu08	C01I[3]	2.140(7)
Cu04	C00R	2.134(7)	Cu09	O00L	1.950(6)
Cu04	C013	2.053(6)	Cu09	N00Q[2]	2.077(8)
Cu04	C019	2.060(7)	Cu09	C01D	1.933(8)
Cu05	Cu06[2]	2.6979(12)	Cu0A	O00K	1.945(6)
Cu05	Cu07	2.5224(11)	Cu0A	N012	2.017(7)
Cu05	Cu08[3]	2.9828(12)	Cu0A	C019	1.939(8)

[1]1-X,1-Y,1-Z; [2]+X,1+Y,+Z; [3]-X,2-Y,2-Z; [4]+X,-1+Y,+Z

Table S15. Bond lengths (Å) of **2b**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu01	Cu02	2.6972(11)	Cu03	Cu06[1]	2.7405(12)
Cu01	Cu02[1]	2.6551(11)	Cu03	N00D[2]	2.076(6)
Cu01	Cu03	2.5497(11)	Cu03	C00J	1.970(7)
Cu01	Cu04	2.4320(11)	Cu03	C00N	2.017(8)
Cu01	Cu05	2.6863(12)	Cu04	O008	1.995(5)

Cu01	Cu06	2.8629(12)	Cu04	O00A	2.305(6)
Cu01	C00F	2.098(7)	Cu04	C00I	2.010(7)
Cu01	C00I	2.065(7)	Cu04	C00K	2.051(7)
Cu01	C00N	2.140(7)	Cu04	C00N	2.086(7)
Cu01	C015	2.500(7)	Cu05	Cu06	2.7280(13)
Cu02	Cu02[1]	2.7648(16)	Cu05	O007	2.028(6)
Cu02	Cu03[1]	2.6153(12)	Cu05	C00I	2.070(7)
Cu02	Cu03	2.5791(11)	Cu05	C00J[1]	2.209(6)
Cu02	Cu06	2.5953(11)	Cu05	C00S[1]	2.280(7)
Cu02	C00F	2.053(7)	Cu05	C00X	2.109(7)
Cu02	C00J	2.080(7)	Cu06	O00B	1.881(6)
Cu02	C00N[1]	2.082(7)	Cu06	C00F	1.888(8)

[1]1-X,1-Y,1-Z; [2]-1+X,-1+Y,+Z

Table S16. Bond lengths (Å) of **2c**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Cu18	Cu20	2.711(3)	Cu39	C70	2.12(2)
Cu18	Cu3	2.776(3)	Cu36	Cu1	2.537(3)
Cu18	Cu17	2.516(3)	Cu36	Cu37	2.588(3)
Cu18	Cu40	2.537(4)	Cu36	O77	1.970(14)
Cu18	Cu1	2.679(2)	Cu36	C35	2.12(2)
Cu18	Cu56	2.679(3)	Cu36	C111	1.97(3)
Cu18	C22	2.03(2)	Cu36	C38	2.102(19)
Cu18	C55	2.157(18)	Cu17	C22	2.12(2)
Cu18	C19	1.944(19)	Cu17	C64	2.07(2)
Cu20	Cu87	2.807(3)	Cu17	C55	2.00(2)
Cu20	Cu1	2.677(3)	Cu17	O16	1.912(18)
Cu20	Cu21	2.763(4)	Cu40	Cu56	2.776(4)
Cu20	O30	2.018(14)	Cu40	Cu37	2.692(3)
Cu20	C35	2.07(2)	Cu40	Cu42	2.784(4)
Cu20	C19	2.04(2)	Cu40	O69	2.168(15)
Cu86	Cu87	2.819(4)	Cu40	C41	1.95(2)
Cu86	N85[1]	1.973(15)	Cu40	C55	2.060(19)
Cu86	O99	2.110(17)	Cu40	C19	2.51(2)
Cu86	C88	2.03(2)	Cu1	Cu56	2.700(3)
Cu86	C89	2.091(17)	Cu1	Cu37	2.770(4)
Cu3	Cu87	2.718(3)	Cu1	C2	1.966(19)
Cu3	Cu17	2.571(4)	Cu1	C35	2.223(19)
Cu3	Cu21	2.715(3)	Cu1	C38	2.08(2)
Cu3	C22	2.09(2)	Cu56	O57	2.024(15)
Cu3	O4	2.056(16)	Cu56	C2	2.02(2)

Cu3	C2	2.15(2)	Cu56	C55	2.092(17)
Cu3	C116	2.13(2)	Cu37	O75	2.040(14)
Cu3	C88	2.54(2)	Cu37	C41	2.53(2)
Cu87	Cu1	2.502(3)	Cu37	C19	2.16(2)
Cu87	Cu21	2.768(4)	Cu37	C106	2.15(2)
Cu87	O97	2.128(14)	Cu37	C38	2.04(2)
Cu87	C2	2.527(18)	Cu21	C22	2.04(2)
Cu87	C35	1.99(2)	Cu21	O28	1.973(15)
Cu87	C88	1.94(2)	Cu21	C88	2.12(2)
Cu39	Cu40	2.809(4)	Cu21	C23	2.15(2)
Cu39	Cu56	2.742(4)	Cu42	O43	2.022(18)
Cu39	Cu37	2.697(4)	Cu42	C50	2.11(2)
Cu39	C41	2.20(2)	Cu42	C41	1.96(2)
Cu39	O59	2.016(15)	Cu42	N13[2]	2.16(3)
Cu39	C38	2.019(19)			

[1]1-X,1-Y,1/2+Z; [2]1-X,-Y,-1/2+Z

Table S17. Bond lengths (Å) of **3**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Cu15	Cu15[1]	2.8137(10)	Cu2	Cu14[1]	2.7686(7)
Cu15	Cu2	2.6329(7)	Cu2	N3[2]	2.063(4)
Cu15	Cu2[1]	2.5665(7)	Cu2	C56	1.972(4)
Cu15	Cu1	2.6591(7)	Cu2	C27	2.015(4)
Cu15	Cu1[1]	2.6880(7)	Cu1	Cu29	2.4448(7)
Cu15	Cu14[1]	2.6178(7)	Cu1	Cu14	2.7750(7)
Cu15	C56[1]	2.087(4)	Cu1	C27	2.150(5)
Cu15	C27	2.084(4)	Cu1	C46	2.075(5)
Cu15	C16[1]	2.069(4)	Cu1	C16	2.097(4)
Cu13	Cu1	2.6988(7)	Cu29	O30	2.368(3)
Cu13	Cu14	2.7262(7)	Cu29	O34	1.993(3)
Cu13	O12	2.010(3)	Cu29	C27	2.103(4)
Cu13	C56[1]	2.238(4)	Cu29	C46	2.022(5)
Cu13	C47	2.110(4)	Cu29	C2	2.043(4)
Cu13	C46	2.052(4)	Cu14	O22	1.883(3)
Cu13	C57[1]	2.298(4)	Cu14	C16	1.912(4)
Cu2	Cu1	2.5671(7)			

[1]1-X,-Y,2-Z; [2]-1+X,1+Y,-1+Z

Table S18. Bond lengths (Å) of **4**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu01	Cu03	2.6443(7)	Cu03	C00I	1.962(4)
Cu01	Cu04	2.6376(7)	Cu03	Cu1	2.698(2)
Cu01	Cu04[1]	2.7651(8)	Cu04	Cu04[1]	2.5772(11)
Cu01	Cu05	2.7105(8)	Cu04	Cu06	2.4699(8)
Cu01	O00A	1.963(3)	Cu04	C00F	2.048(4)
Cu01	C00G	2.057(4)	Cu04	C00G	2.284(4)
Cu01	C00K[1]	2.072(4)	Cu04	C00K	1.944(4)
Cu02	Cu03[1]	2.7474(8)	Cu05	O009	1.983(3)
Cu02	Cu04	2.7327(8)	Cu05	C00F[1]	2.065(4)
Cu02	Cu05[1]	2.5921(7)	Cu05	C00I	2.079(4)
Cu02	Cu06	2.6421(8)	Cu05	C00P[1]	2.23(3)
Cu02	O008	2.091(3)	Cu05	Cu1	2.638(2)
Cu02	C00F	2.173(4)	Cu05	C4[1]	2.093(8)
Cu02	C00I[1]	2.274(4)	Cu06	O00B	1.955(3)
Cu02	C00K[1]	2.139(4)	Cu06	C00F	2.074(4)
Cu02	C00S[1]	2.202(4)	Cu06	C00G	2.050(4)
Cu03	Cu04	2.5715(7)	Cu06	C00O	2.034(4)
Cu03	Cu05	2.7871(7)	C00I	Cu1	1.956(4)
Cu03	N00C[2]	2.079(3)	C00J	Cu1	2.171(4)
Cu03	C00G	1.978(4)	Cu1	O4	1.865(10)

[1]1/2-X,1/2-Y,1-Z; [2]+X,1-Y,1/2+Z