Electronic Supplementary Material

Ligand effects in photoluminescence of copper nanoclusters

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Figure S1. Digital photograph of single crystal of the **Cu_9-1** cluster.

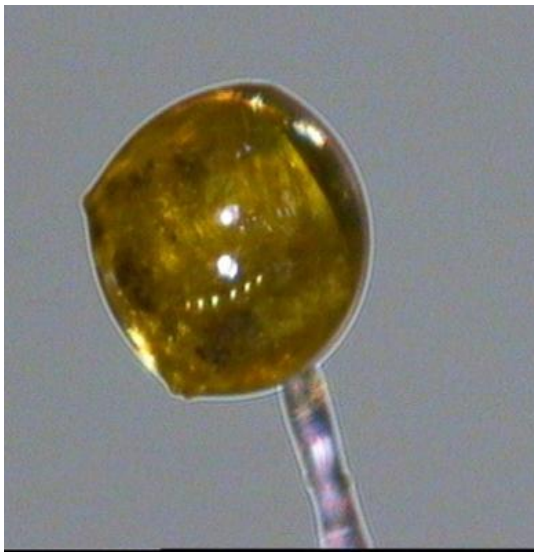

Figure S2. Digital photograph of single crystal of the **Cu_9-2** cluster.

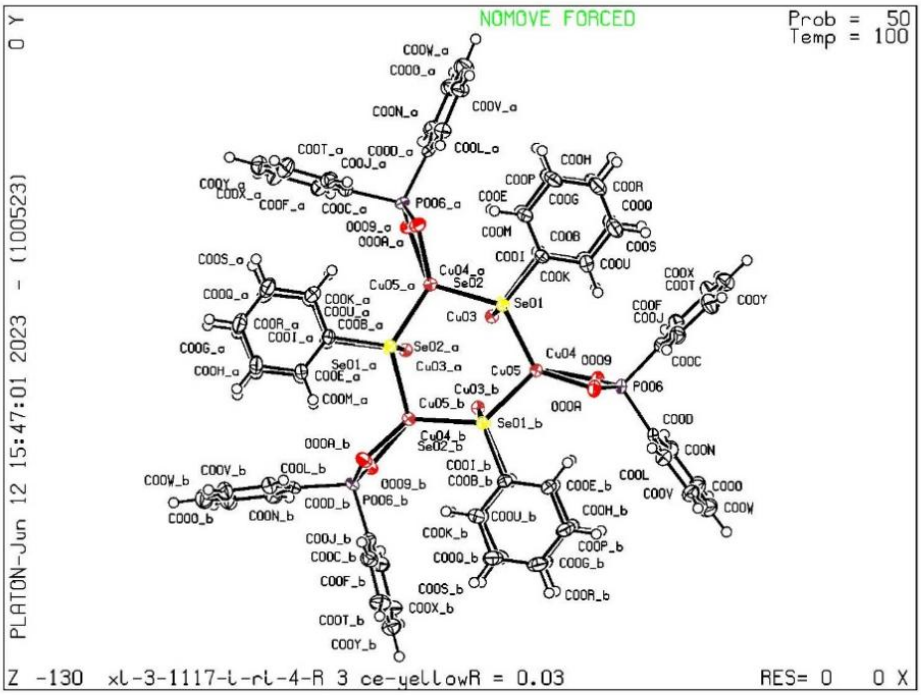

Figure S3. The thermal ellipsoids of the ORTEP diagram of the **Cu_9-1** cluster.

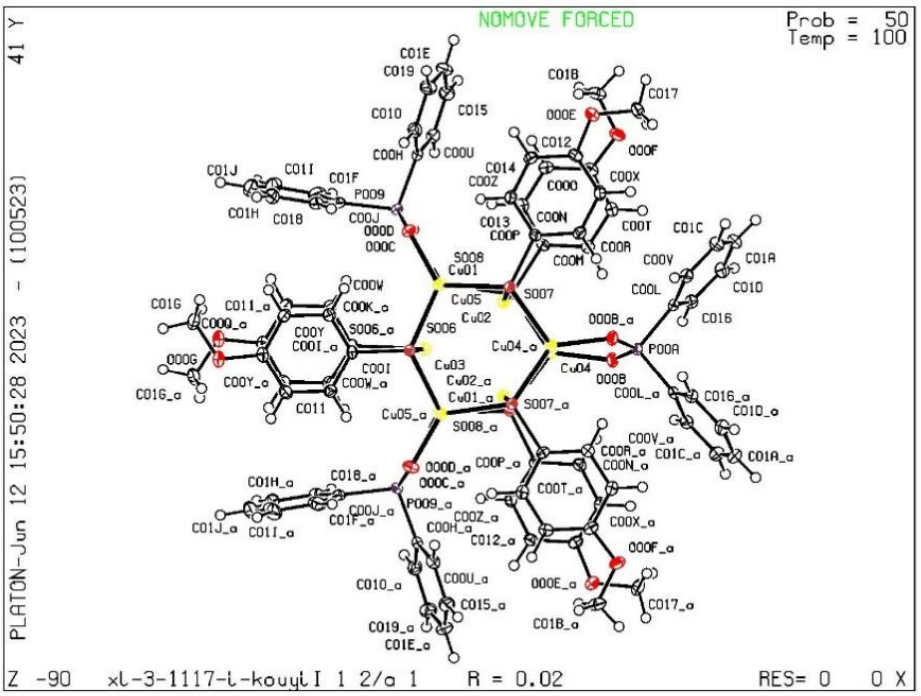

Figure S4. The thermal ellipsoids of the ORTEP diagram of the **Cu_9-2** cluster.

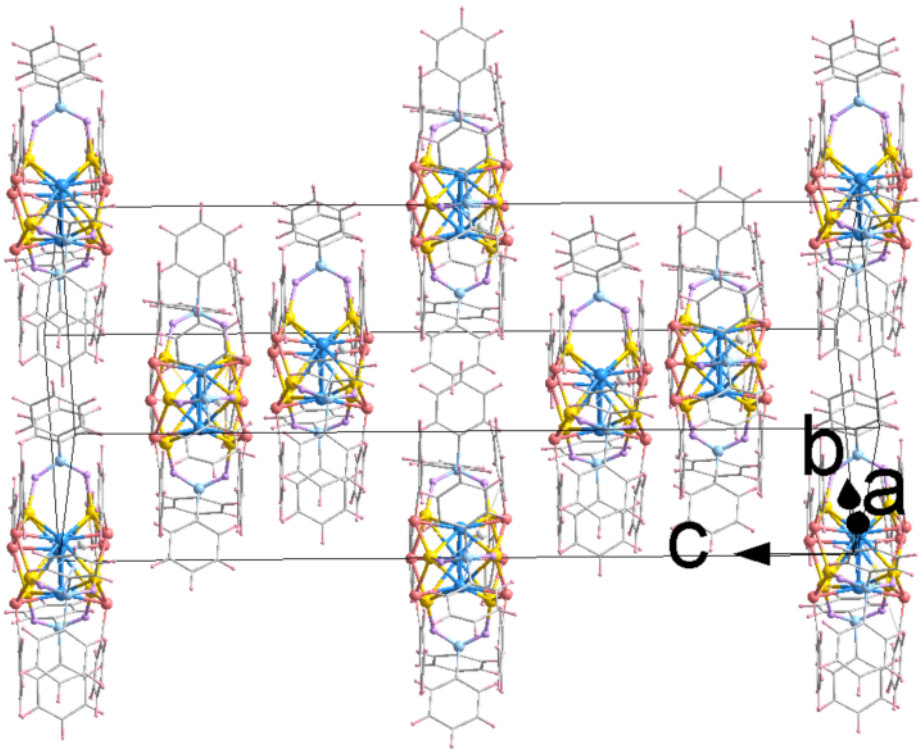

Figure S5. The packing structure of **Cu_9-1** in the unit cell. Color codes for atoms: blue, Cu (centre); yellow, Cu (side); brick red, Se; purple, O; light-blue, P; grey, C; pink, H.

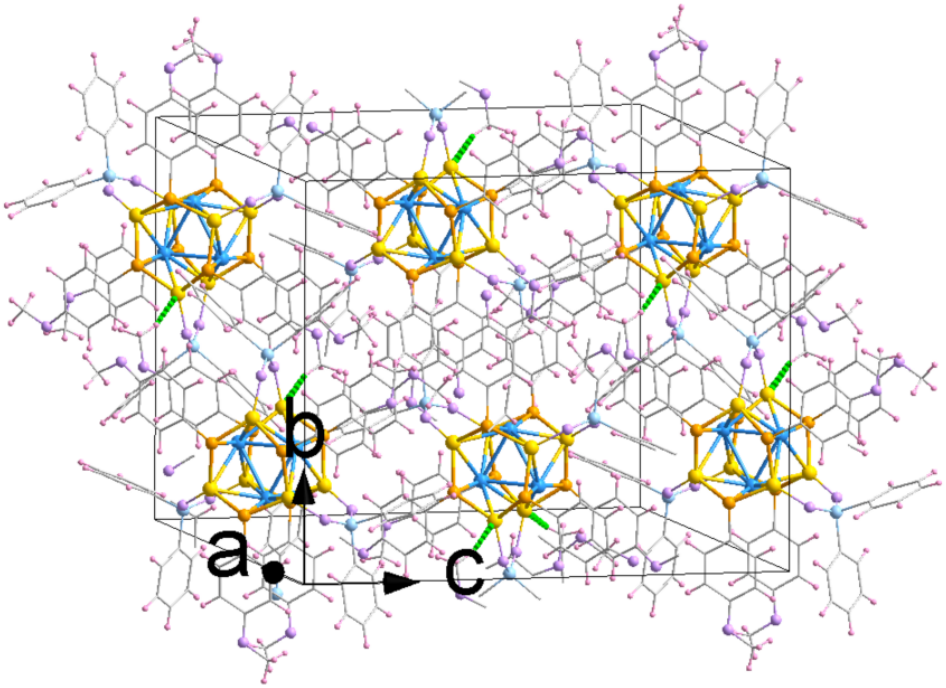

Figure S6. The packing structure of **Cu_9-2** in the unit cell. Color codes for atoms: blue, Cu (centre); yellow, Cu (side); orange, S; purple, O; light-blue, P; grey, C; pink, H. Hydrogen bonding between Cu and H: green.

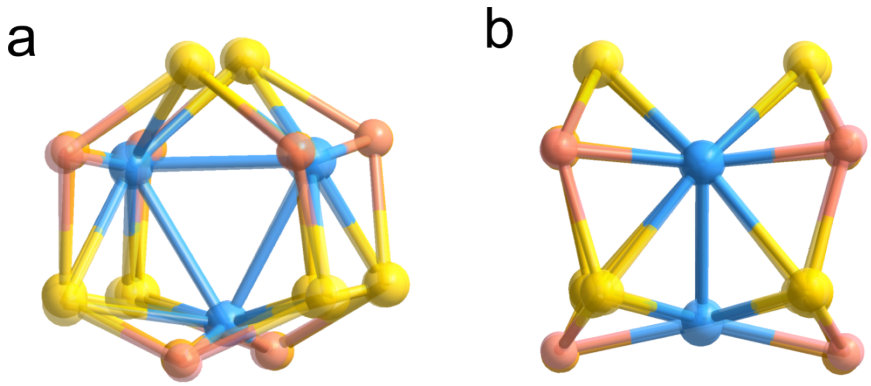

Figure S7. The overlay of the core of Cu_9-**1** and Cu_9-**2** clusters in front (a) and side (b) views.

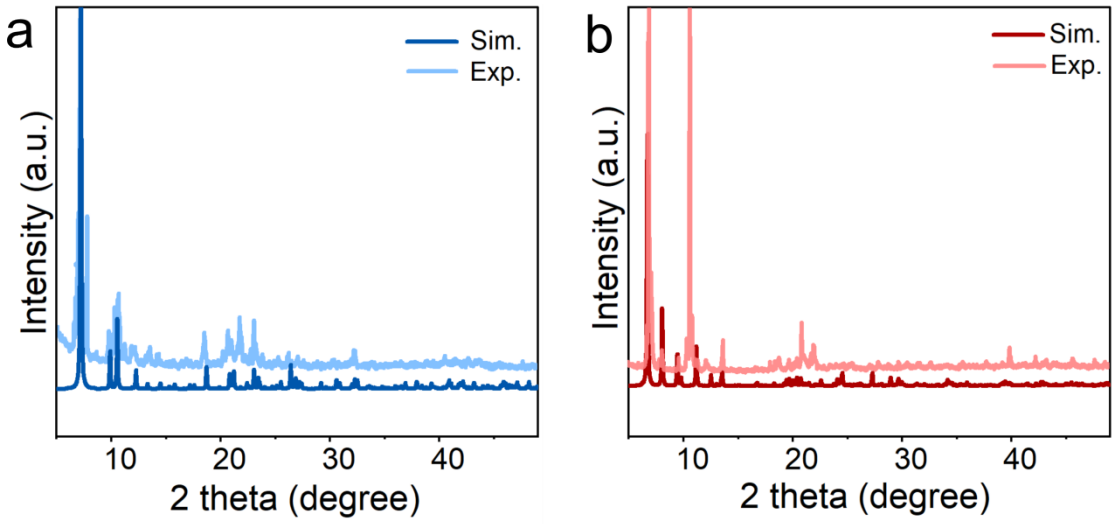

Figure S8. Powder X-ray diffraction (PXRD) patterns for **Cu_9-1** (a) and **Cu_9-2** (b) measured at room temperature. Simulated patterns were compared with the experimental ones to confirm purity of the sample.

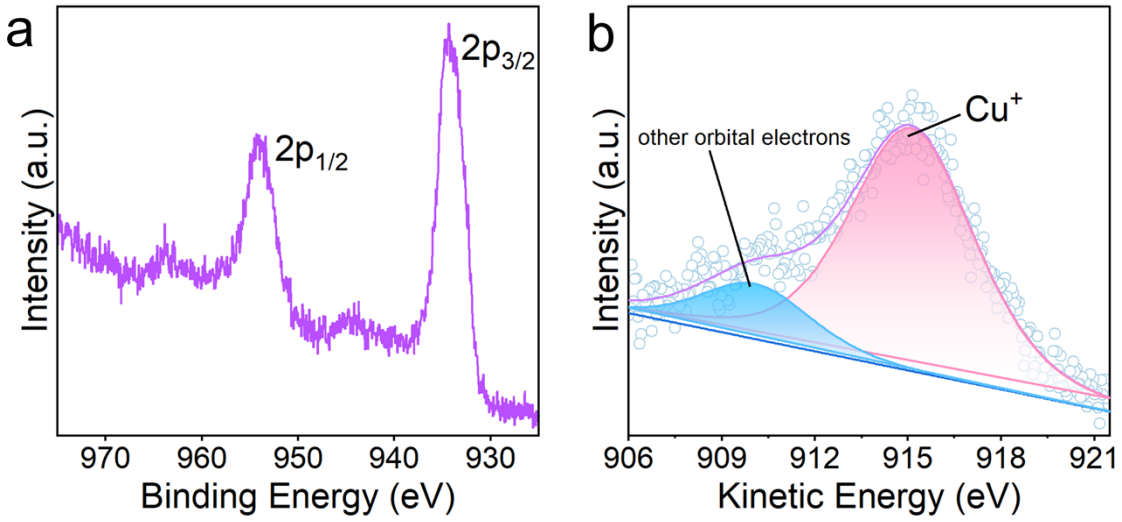

Figure S9. XPS spectra of **Cu_9-1**. (a) Cu 2p XPS spectrum. (b) Cu LMM Auger spectrum.

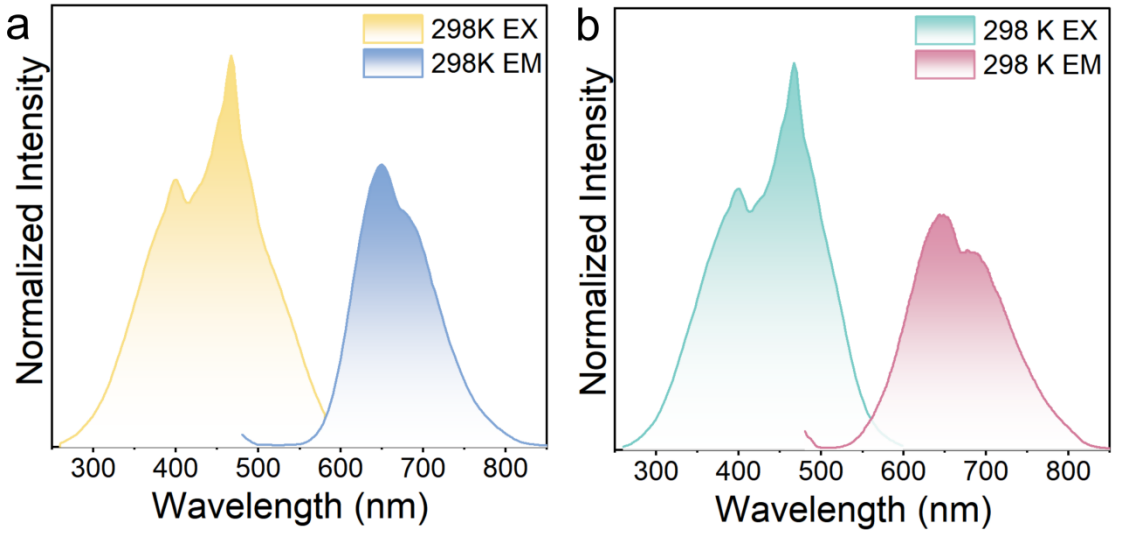

Figure S10. (a) Excitation (yellow, λ_{em} = 466 nm) and emission (blue) spectra of **Cu_9-1** at 298 K. (b) Excitation (green, λ_{em} = 467 nm) and emission (red) spectra of **Cu_9-2** at 298 K.

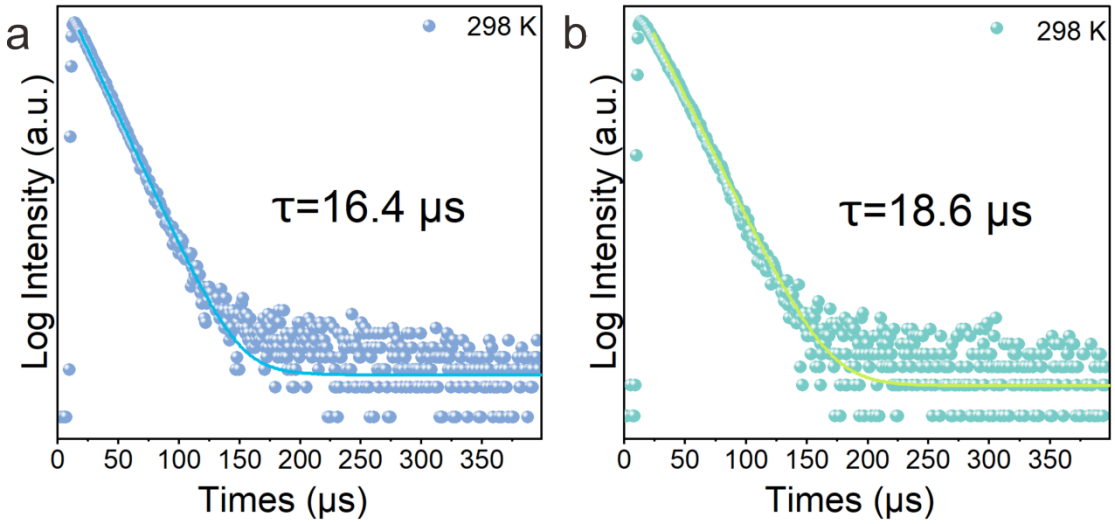

Figure S11. Plots of emission decay lifetime of **Cu_9-1** (a) and **Cu_9-2** (b) at 298 K.

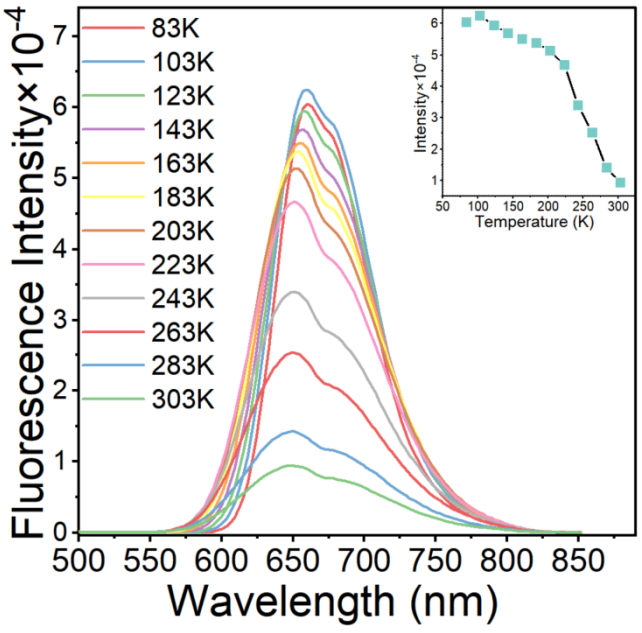

Figure S12. Temperature dependence in the range of 83 ~ 303 K of **Cu_9-1**. Insert: maximum photoluminescence intensity at each temperature.

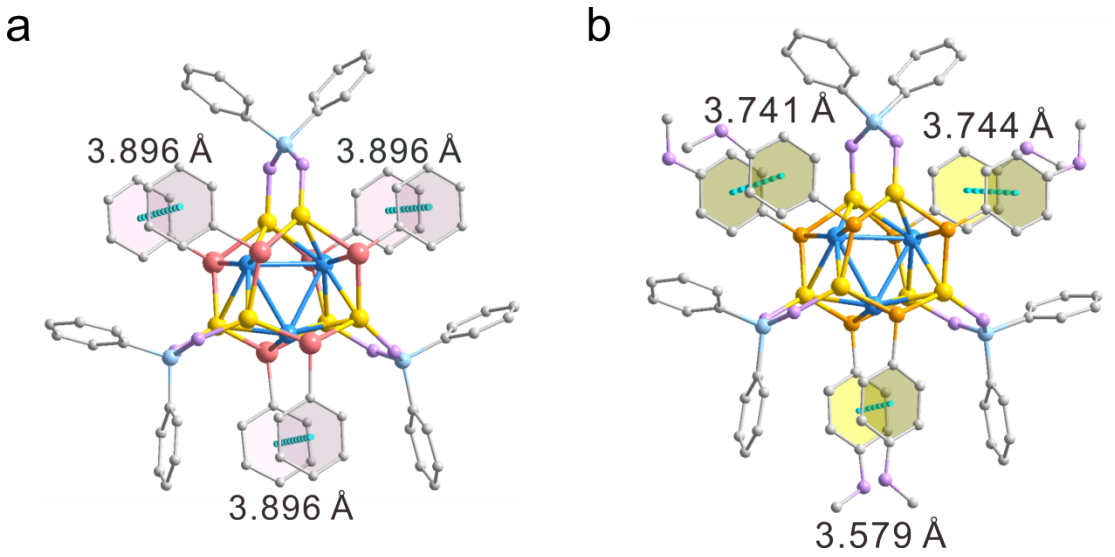

Figure S13. Distances between adjacent benzene rings in **Cu_9-1** (a) and **Cu_9-2** (b). Colour legend: blue, Cu (centre); yellow, Cu (side); brick red, Se; orange, S; Purple, O; light-blue, P; grey, C. All hydrogen atoms are omitted for clarity.

Table S1. Crystallographic data of **Cu_9-1**.

identification code	**Cu_9-1**
formula	$C_{72}H_{60}Cu_9O_6P_3Se_6$
formula weight	2159.73
Temperature/K	100.00(10)
crystal system	trigonal
space group	*R3c*
a (Å)	17.8552(3)
b (Å)	17.8552(3)
c (Å)	39.8409(10)
α (˚)	90
β (˚)	90
γ (˚)	120
V (Å^3)	10999.9(5)
Z	6
$\rho_{calc}g/cm^3$	1.956
Radiation	Cu Kα (λ= 1.54184 Å)
Theta (˚) range	7.238 to 129.628
Index ranges	-20 ≤ h ≤ 20, -20≤ k ≤ 20, -42 ≤ l ≤ 46
Refls. Total	23097
restraints	323
parameters	289
R_1/wR_2 [I>2σ(I)]	0.0348/ 0.0778
R_1/wR_2 (all data)	0.0441/0.0828
completeness	0.997
GooF	1.042

Table S2. Crystallographic data of **Cu_9-2**.

identification code	**Cu_9-2**
formula	$C_{78}H_{72}Cu_9O_{12}P_3S_6$
formula weight	2058.48
Temperature/K	100.00(10)
crystal system	monoclinic
space group	*I2/a*
a (Å)	19.04350(10)
b (Å)	18.48760(10)
c (Å)	22.3002(2)
α (˚)	90
β (˚)	100.8800(10)
γ (˚)	90
V (Å^3)	7710.07(9)
Z	4
D_c / (g·cm^{-3})	1.773
Radiation	Cu Kα (λ= 1.54184 Å)
Theta (˚) range	6.256 to 146.232
Index ranges	-21 ≤ h ≤ 22, -22≤ k ≤ 21, -27 ≤ l ≤ 25
Refls. Total	24413
restraints	72
parameters	492
R_1/wR_2 [I>2σ(I)]	0.0218/0.0572
R_1/wR_2 (all data)	0.0232/0.0581
completeness	0.993
GooF	1.046

Table S3. Selected bond lengths (Å) for cluster **Cu_9-1**.

Parameter	value	Parameter	value
Se01-Cu03	2.3258(17)	C00C-C00F	1.374(14)
Se01-Cu041	2.3944(15)	C00C-C00J	1.398(14)
Se01-Cu04	2.3835(15)	C00D-C00L	1.397(14)
Se01-C00B	1.948(8)	C00D-C00N	1.410(14)
Se02-Cu03	2.3282(18)	C00E-C00H	1.413(14)
Se02-Cu05	2.3628(15)	C00F-C00X	1.391(15)
Se02-Cu051	2.4278(15)	C00G-C00H	1.384(15)
Se02-C00I	1.931(8)	C00G-C00Q	1.378(14)
Cu03-Cu032	2.869(2)	C00I-C00M	1.369(13)
Cu03-Cu031	2.869(2)	C00I-C00U	1.394(14)
Cu03-Cu041	2.7169(18)	C00J-C00T	1.395(15)
Cu03-Cu04	2.6675(18)	C00K-C00Q	1.406(14)
Cu03-Cu051	2.6732(18)	C00L-C00V	1.384(15)
Cu03-Cu05	2.6822(18)	C00M-C00P	1.410(14)
Cu04-O009	1.943(6)	C00N-C00O	1.383(16)
Cu05-O00A	1.921(7)	C00O-C00W	1.391(17)
P006-O009	1.510(7)	C00P-C00R	1.376(15)
P006-O00A	1.510(7)	C00R-C00S	1.397(16)
P006-C00C	1.802(10)	C00S-C00U	1.395(14)
P006-C00D	1.800(9)	C00T-C00Y	1.387(16)
C00B-C00E	1.359(13)	C00V-C00W	1.370(16)
C00B-C00K	1.389(13)	C00X-C00Y	1.388(15)

Table S4. Selected bond lengths (Å) for cluster **Cu_9-2**.

Parameter	value	Parameter	value
Cu01-Cu02	2.6717(4)	O00G-C01G	1.430(2)
Cu01-Cu03	2.6373(3)	C00H-C00U	1.391(3)
Cu01-S006	2.2616(5)	C00H-C010	1.396(3)
Cu01-S008	2.2619(5)	C00I-C00K	1.396(2)
Cu01-O00C	1.9515(12)	C00I-C00W	1.381(2)
Cu02-Cu021	2.9390(5)	C00J-C018	1.395(3)
Cu02-Cu03	2.8637(4)	C00J-C01F	1.394(3)
Cu02-Cu04	2.7261(4)	C00K-C011	1.383(3)
Cu02-Cu041	2.5841(3)	C00L-C00V	1.397(3)
Cu02-Cu05	2.6369(4)	C00L-C016	1.397(3)
Cu02-S007	2.2015(5)	C00M-C00R	1.393(2)
Cu02-S008	2.2144(5)	C00M-C013	1.379(3)
Cu03-Cu051	2.6778(3)	C00N-C00P	1.385(2)
Cu03-Cu05	2.6778(3)	C00N-C00X	1.390(3)
Cu03-S006	2.2053(4)	C00O-C00T	1.397(3)
Cu03-S0061	2.2052(4)	C00O-C014	1.389(3)
Cu04-S007	2.2507(5)	C00P-C00Z	1.396(2)
Cu04-S0081	2.2974(5)	C00Q-C00Y	1.388(3)
Cu04-O00B	1.9497(12)	C00Q-C011	1.394(3)
Cu05-S0061	2.2704(5)	C00R-C00T	1.383(3)
Cu05-S007	2.2746(5)	C00S-C00X	1.392(3)
Cu05-O00D	1.9393(12)	C00S-C012	1.396(3)
S006-C00I	1.7993(18)	C00U-C015	1.390(3)
S007-C00M	1.7982(17)	C00V-C01C	1.394(3)
S008-C00P	1.7988(17)	C00W-C00Y	1.394(3)
P009-O00C	1.5143(13)	C00Z-C012	1.380(3)
P009-O00D	1.5079(13)	C010-C019	1.386(3)
P009-C00H	1.8089(18)	C013-C014	1.390(3)
P009-C00J	1.8107(19)	C015-C01E	1.381(3)
P00A-O00B1	1.5124(13)	C016-C01D	1.389(3)
P00A-O00B	1.5125(13)	C018-C01H	1.390(3)
P00A-C00L	1.8094(18)	C019-C01E	1.389(3)
P00A-C00L1	1.8094(18)	C01A-C01C	1.384(3)
O00E-C00S	1.368(2)	C01A-C01D	1.388(3)
O00E-C017	1.428(2)	C01F-C01I	1.404(3)
O00F-C00O	1.365(2)	C01H-C01J	1.372(4)
O00F-C01B	1.430(2)	C01I-C01J	1.382(4)
O00G-C00Q	1.370(2)		