

Reversible luminescence detection of dihalogenomethanes in a 3D CuI coordination polymer assembled by a thioether-functionalized POSS ligand

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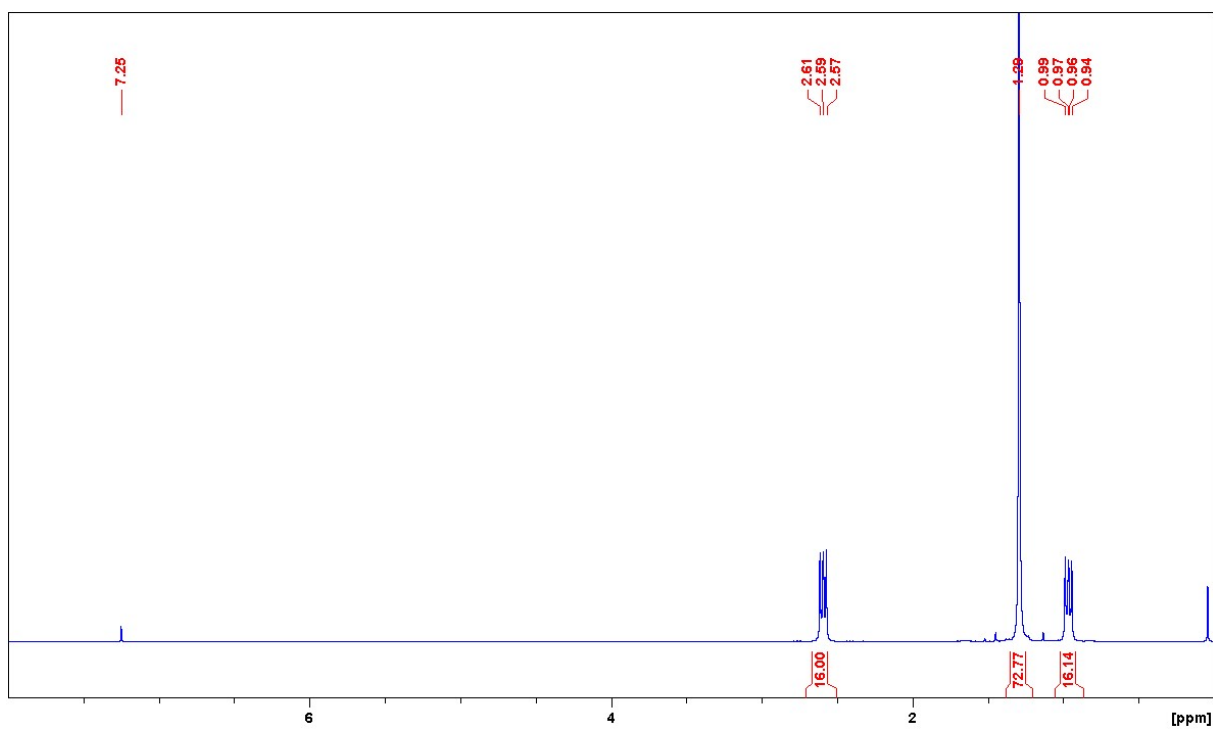


Figure S1. ^1H NMR spectrum of **L** in CDCl_3 .

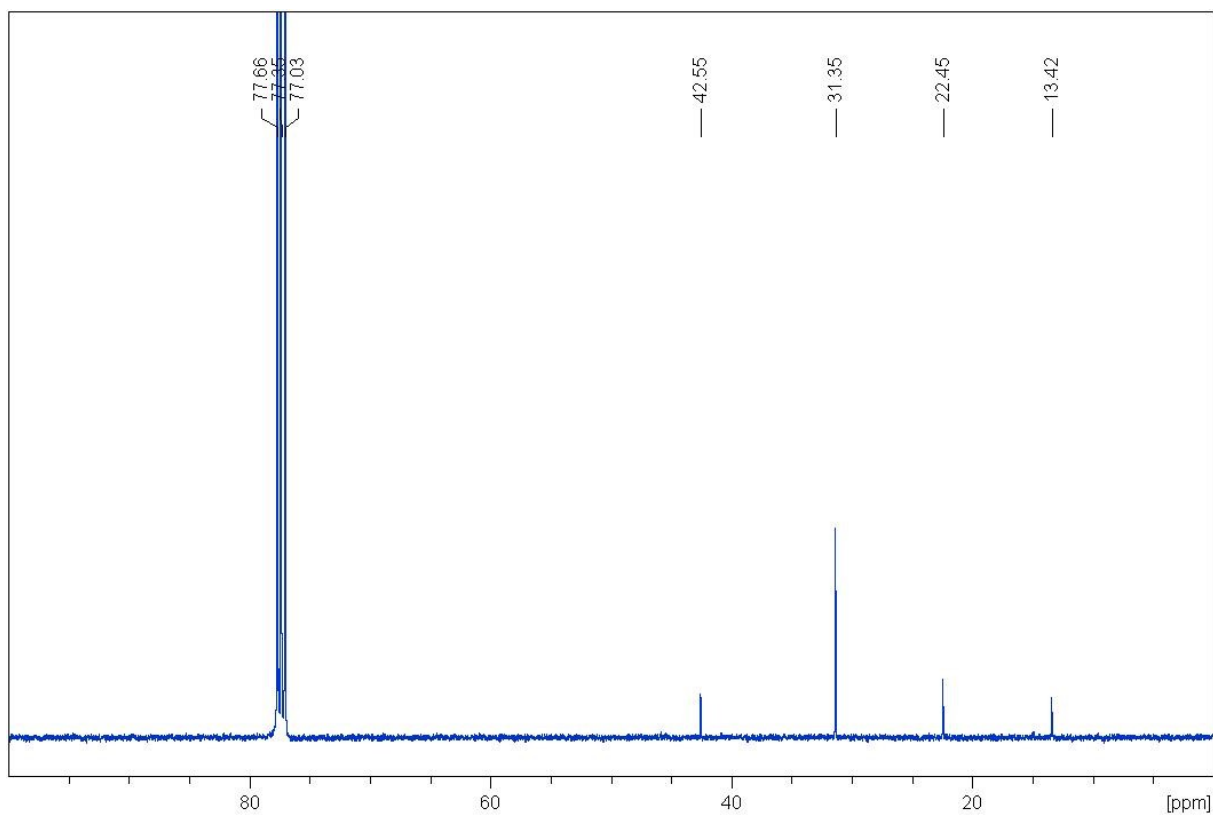


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **L** in CDCl_3 .

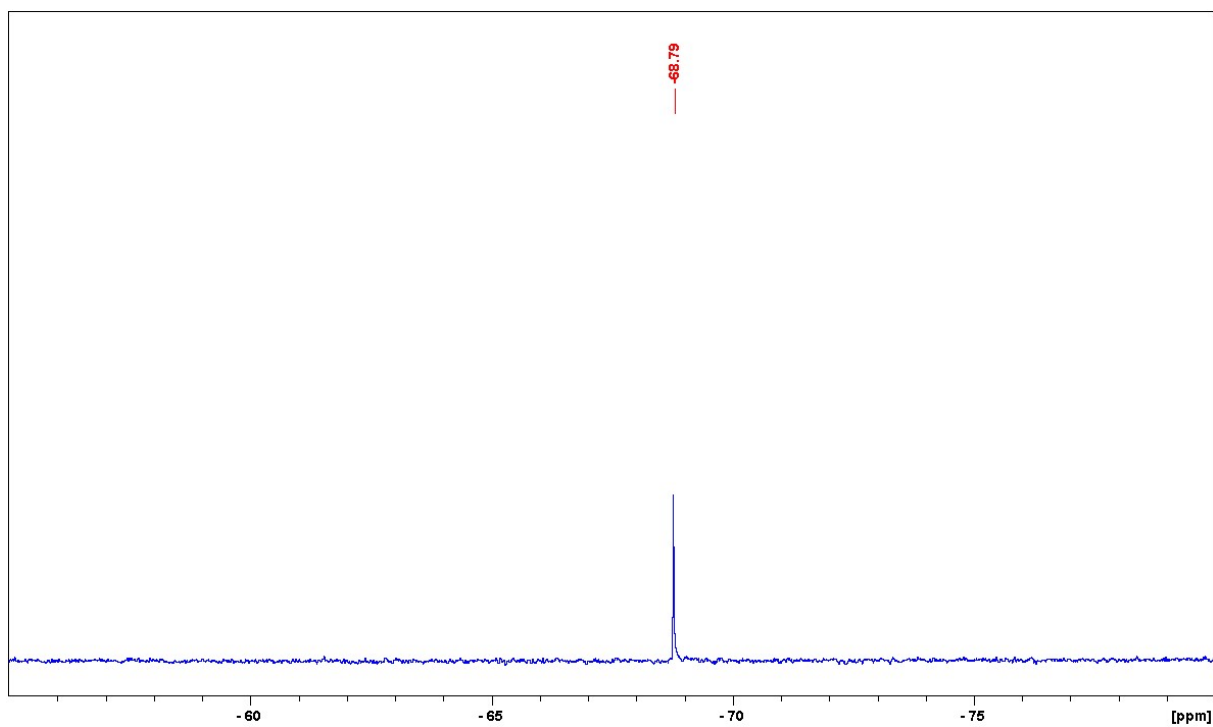


Figure S3. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **L** in CDCl_3 .

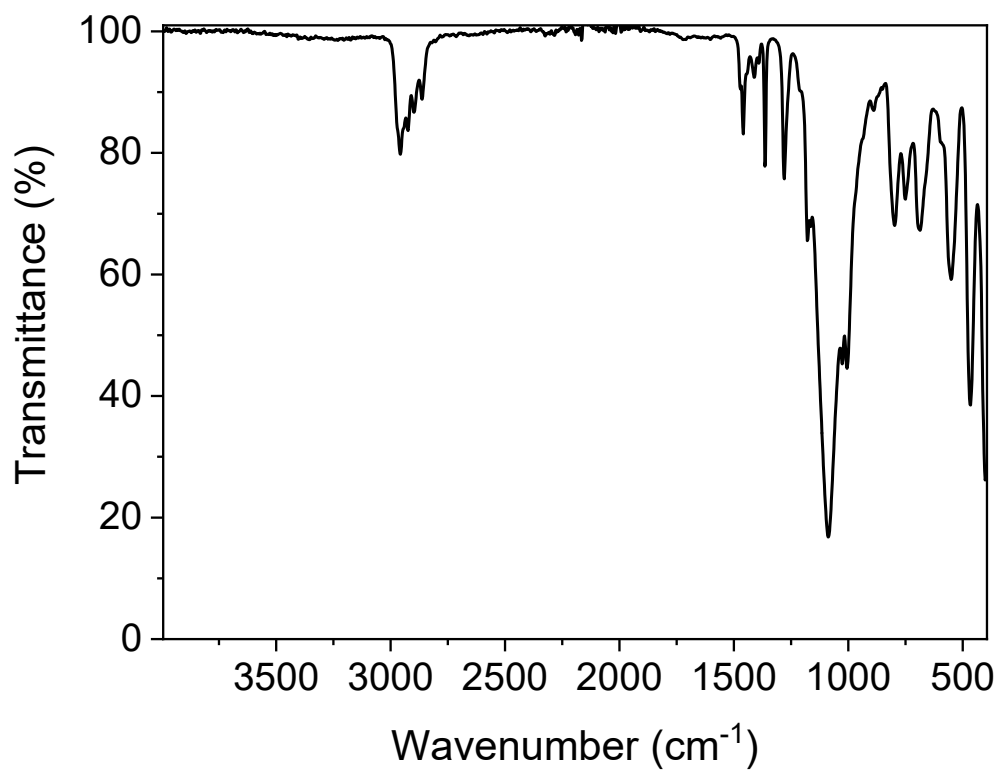


Figure S4. ATR-IR spectrum of **L**.

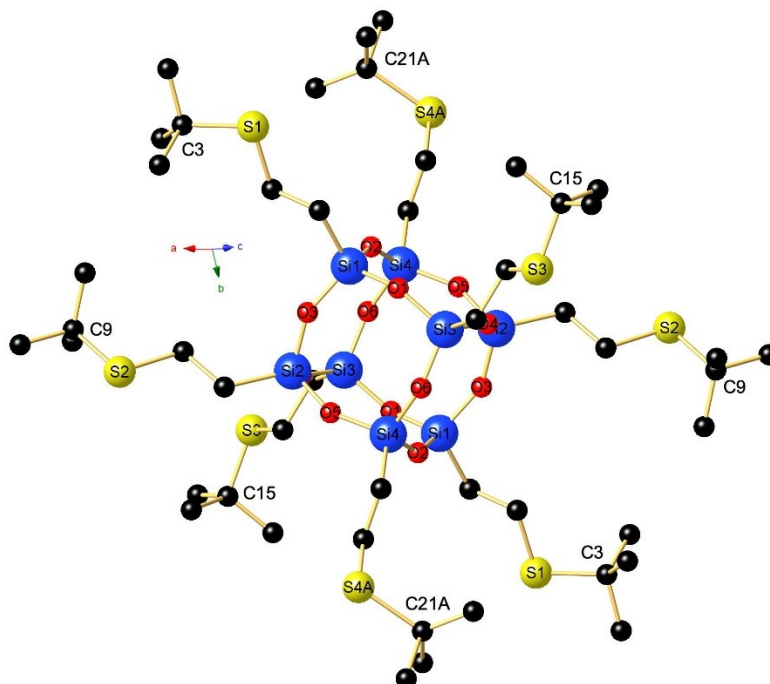


Figure S5. Molecular structure of **L**. The H atoms are omitted for clarity.

Selected bond lengths (Å) and angles (°): Si1–C1 1.841(3), Si2–C7 1.843(3), Si3–C13 1.845(3), Si4–C19 1.838(3), S1–C2 1.808(3), S2–C8 1.809(3), S3–C14 1.815(3), S4A–C20A 1.757(9), Si1–O1 1.6150(19), Si1–O2 1.6178(18), Si1–O3 1.6150(19), Si2–O3 1.6162(18), Si2–O4 1.6178(19), Si2–O5 1.614(2), Si3–O1¹ 1.6122(19), Si3–O4 1.6141(19); Si3–O6¹ 1.6121(19); Si1–O1–Si3¹ 151.47(13), Si1–O2–Si4¹ 143.97(12), Si2–O3–Si1 151.63(13), Si2–O4–Si3 143.92(12), Si2–O5–Si4 151.73(13), Si3¹–O6–Si4 151.70(13), C2–S1–C3 105.1(2), C8–S2–C9 104.24(14), C14–S3–C15 104.73(16), C20A–S4A–C21A 108.4(7). Symmetry transformations used to generate equivalent atoms: ¹-x, 1-y, 1-z.

Table S1. Selected bond distances (Å) and angles (°) for **L**.

Mean Si-O		Mean Si-O-Si		O-Si-O	
average value	range of values	average value	range of values	average value	range of values
1.6141	1.6076(19)- 1.6217(18)	149.07	143.92(12)- 151.73(13)	109.03	108.50(10)- 109.52(11)

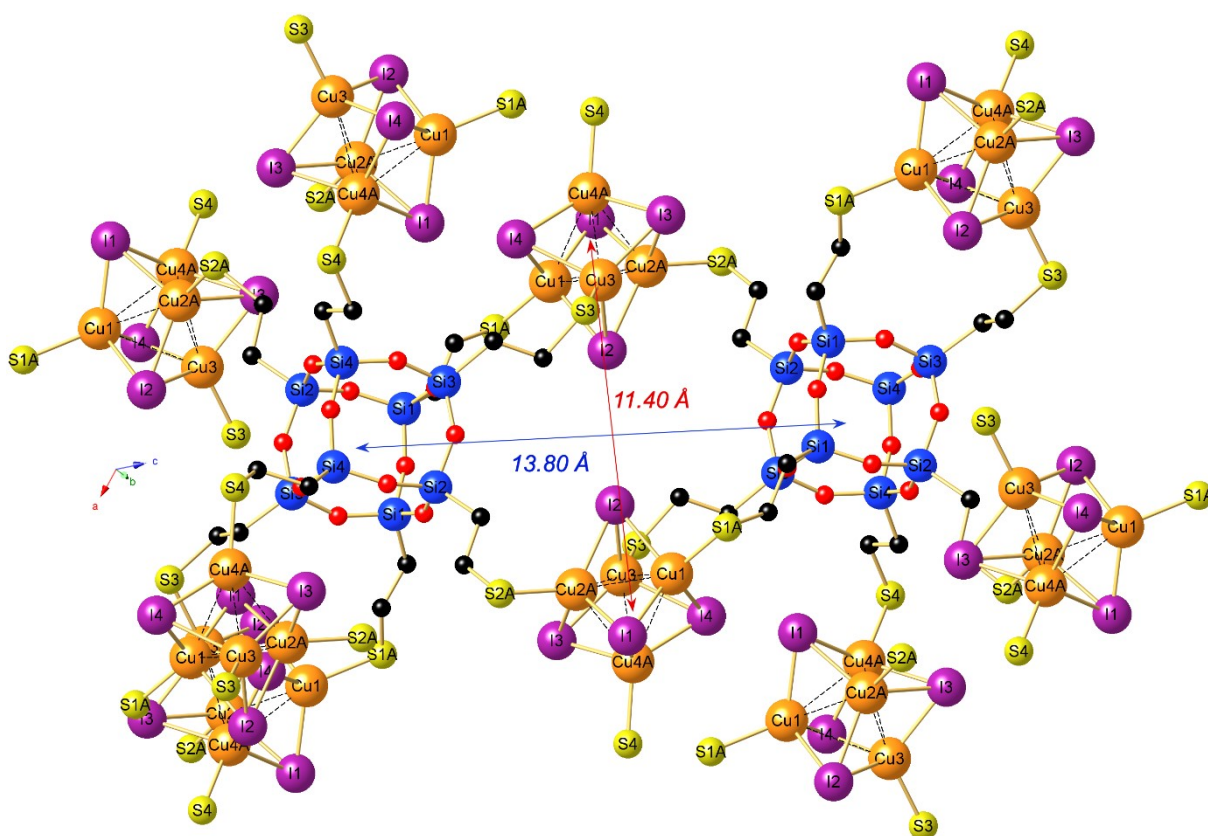


Figure S6. View of two interconnected POSS cores of **CP1** forming 22-membered macrocycles. All H atoms and *t*-Bu groups are omitted for clarity. Red and blue arrows indicate centroid-to-centroid separations.

Selected bond lengths (Å) and angles (°) at 100 K: Cu1–Cu2A¹ 2.7871(18), Cu1–Cu3³ 3.171(1), Cu1–Cu4A² 3.014(2), Cu2A–Cu3⁴ 2.747(2), Cu2A–Cu4A⁸ 2.750(3), Cu3–Cu4A⁵ 2.963(2), Cu1–S1A 2.3319(15), Cu2A–S2A 2.293(3), Cu3–S3 2.3357(15), Cu4A–S4A 2.315(4), Cu1–I1 2.6055(11), Cu1³–I2 2.7322(12), Cu1⁶–I4 2.7065(13), Cu2A¹–I1 2.708(2), Cu2A⁴–I2 2.693(2), Cu2A⁴–I3 2.733(2), Cu3–I2 2.7102(11), Cu3–I3 2.6177(10), Cu3⁷–I4 2.7372(13), Cu4A²–I1 2.768(3), Cu4A⁵–I3 2.684(2), Cu4A–I4 2.647(2); Cu1–I1–Cu2A¹ 63.24(5), Cu1–I1–Cu4A² 68.16(5), Cu1⁴–I2–Cu2A³ 61.82(4), Cu1⁴–I2–Cu3 71.28(3), Cu1⁷–I4–Cu3⁶ 71.26(3), Cu1⁷–I4–Cu4A 68.51(5), Cu2A¹–I1–Cu4A² 60.28(6), Cu2A³–I2–Cu3 61.12(5), Cu2A³–I3–Cu3 61.75(5), Cu3–I3–Cu2A³ 61.75(5), Cu3⁶–I4–Cu1⁷ 71.26(3), Cu4A⁵–I3–Cu2A³ 61.02(6), Cu4A⁵–I3–Cu3 67.941(5), Cu4A–I4–Cu1⁷ 65.0(5), S1A–Cu1–I1 116.96(4), S1A–Cu1–I2⁴ 99.68(5), S1A–Cu1–I4² 113.72(5), S2A–Cu2A–I1⁸ 105.27(13), S2A–Cu2A–I2³ 119.54(15), S2A–Cu2A–I3³ 92.59(10), S3–Cu3–I2 110.67(4), S3–Cu3–I3 116.37(4), S3–Cu3–I4⁵ 101.34(4), S4A–Cu4–I1⁷ 108.06(12), S4A–Cu4–I3⁶ 100.49(11), S4A–Cu4A–I4 120.29(11). Symmetry transformations used to generate equivalent atoms: ¹+x, 1–y, ½+z; ²–1/2+x, ½+y, +z; ³1–x, 1–y, 1–z; ⁴1–x, +y, 3/2–z; ⁵3/2–x, ½+y, 3/2–z; ⁶3/2–x, –1/2+y, 3/2–z; ⁷1/2+x, –1/2+y, +z; ⁸+x, 1–y, –1/2+z.

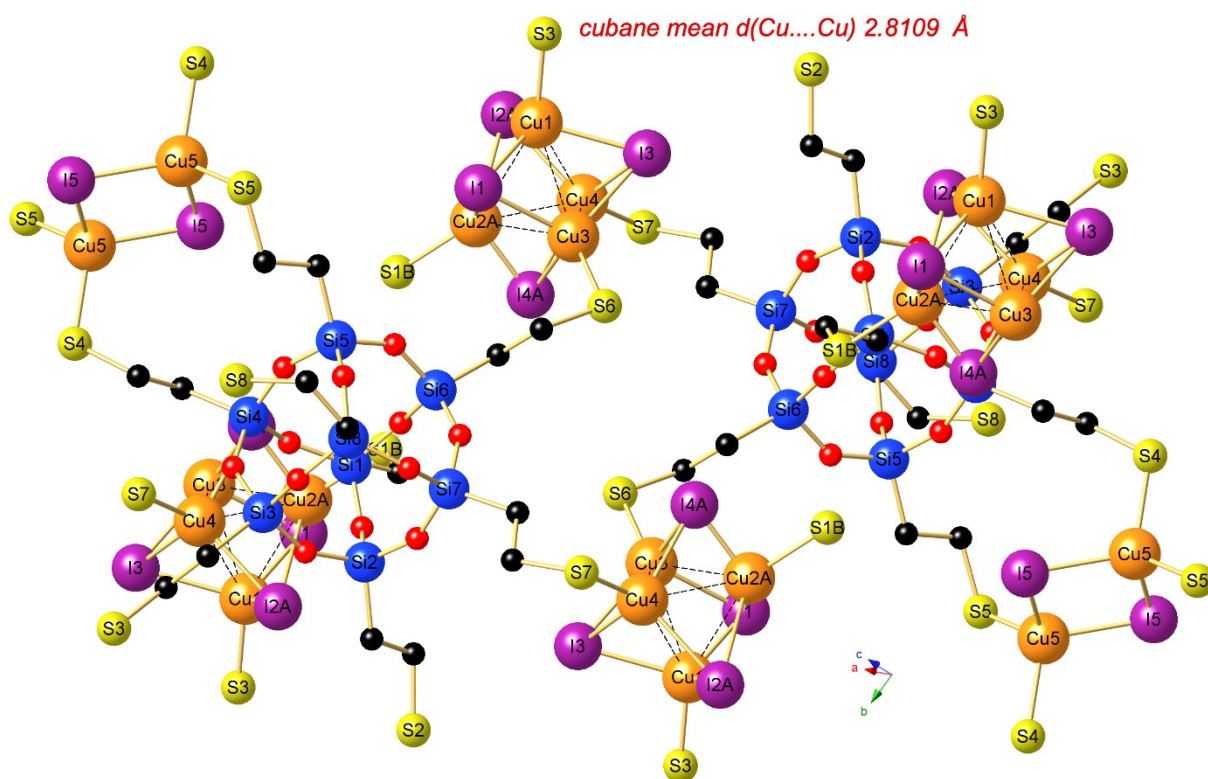


Figure S7. View of two interconnected POSS cores of CP2 forming 22-membered macrocycles. All H atoms and *t*-Bu groups are omitted for clarity.

Selected bond lengths (Å) and angles (°) at 100 K: Cu1–Cu2A⁴ 2.868(3), Cu1–Cu3³ 2.8652(12), Cu1–Cu4⁵ 2.8984(17), Cu2A⁷–Cu3 2.743(3), Cu2A–Cu4 2.755(3), Cu3–Cu4² 2.7161(12), Cu1–S3 2.3172(17), Cu2A–S1B 2.313(3), Cu3–S6 2.3236(16), Cu4–S7 2.3167(17), Cu5–S4 2.237(16), Cu5–S5⁶ 2.3322(17), Cu1–I1 2.6385(10), Cu1–I2A 2.507(16), Cu1¹–I3 2.6851(11), Cu2A⁴–I1 2.669(3), Cu3–I3 2.6792(10), Cu3³–I1 2.7102(10), Cu3–I4A 2.672(7), Cu3³–I1 2.7102(10), Cu4²–I3 2.7153(12), Cu4⁵–I2A 2.746(11), Cu4²–I4A 2.587(7), Cu5–I5 2.6322(10), Cu5⁶–I5 2.6384(13); Cu1–I1–Cu2A⁴ 65.42(7), Cu1–I1–Cu3³ 64.77(3), Cu1¹–I2A–Cu4⁵ 66.8(4), Cu1¹–I3–Cu4² 64.91(4), Cu3–I3–Cu1¹ 64.57(2), Cu3–I3–Cu4² 60.46(2), Cu4²–I4A–Cu3 62.17(6), Cu5–I5–Cu5⁶ 83.09(4), I5–Cu5–I5⁶ 96.91(4), S3–Cu1–I1 107.19(5), S3–Cu1–I2A 111.2(6), S3–Cu1–I3³ 99.84(5), S1B–Cu2A–I1⁴ 118.10(13), S1B–Cu2A–I2A⁴ 116.10(13), S6–Cu3–I3 116.67(4), S6–Cu3–I1¹ 107.74(4), S6–Cu3–I4A 104.3(5), S7–Cu4–I3² 107.68(4), S7–Cu4–I2A⁵ 120.21(6), S7–Cu4–I4A² 101.3(5), S4–Cu5–I5 109.09(5), S4–Cu5–I5⁶ 119.72(5), S5⁶–Cu5–I5 121.51(4), S5⁶–Cu5–I5⁶ 108.34(4), S4–Cu5–S5⁶ 102.50(5). Symmetry transformations used to generate equivalent atoms: ¹+x, +y, +z; ²1-x, 1-y, 1-z; ³+x, -1+y, +z; ⁴-x, -y, -z; ⁵1-x, -y, 1-z, ⁶-x, 1-y, -z, ⁷-x, 1-y, 1-z, ⁸1+x, +y, +z.

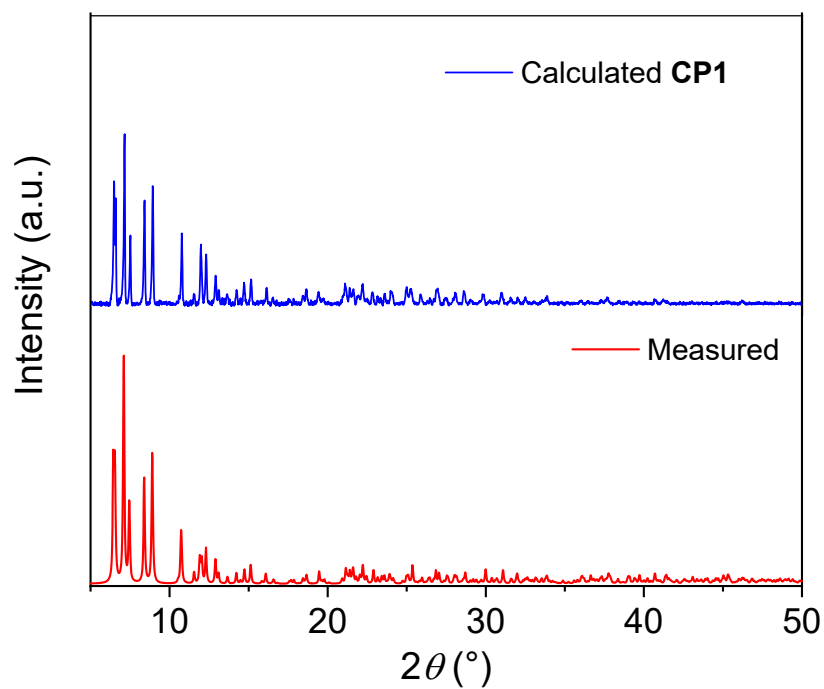


Figure S8. Experimental and simulated PXR D of CP1 [LCu_8I_8] $_n$.

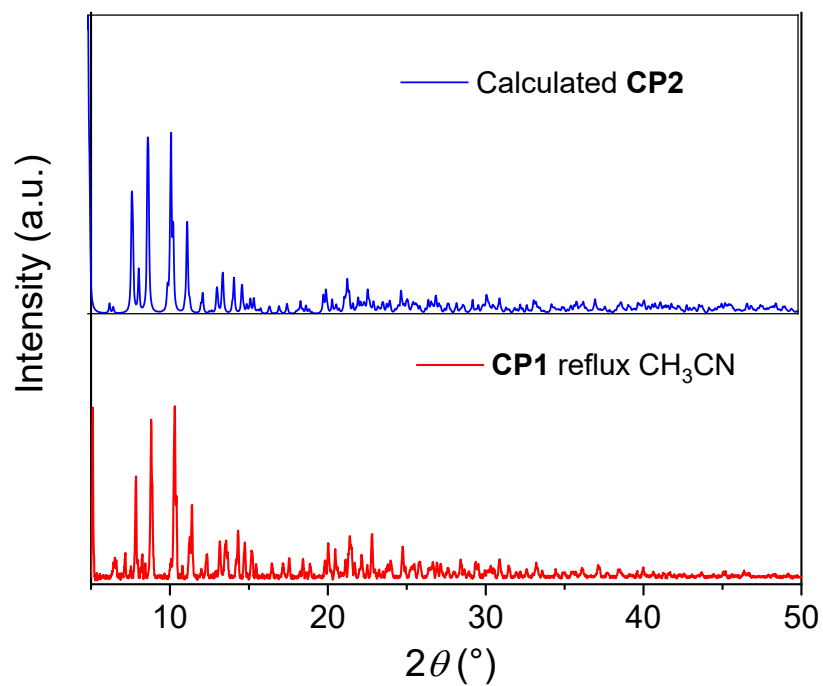


Figure S9. Simulated PXR D of CP2 [LCu_5I_5] $_n$ and experimental PXR D of CP1 after heating in refluxing acetonitrile.

Table S2. Porosity parameters calculated using the Pore Analyser Tool (in Mercury) for **CP1** and **CP1.CH₂Cl₂**.

Compounds	CP1	CP1.CH ₂ Cl ₂ ^a	
Parameter			Unit
System Volume	10270.240	10444.792	Å ³
System Mass	11496.414	11512.541	g/mol
System Density	1.859	1.830	g/cm ³
Total surface area	2.79	20.30	Å ²
Total surface area per volume	2.72	19.44	m ² /cm ³
Total surface area per mass	1.46	10.62	m ² /g
Network-accessible surface area	0.00	0.00	Å ²
Network-accessible surface area per volume	0.00	0.00	m ² /cm ³
Network-accessible surface area per mass	0.00	0.00	m ² /g
Total helium volume	2112.671	2337.993	Å ³
Total helium volume	0.111	0.122	cm ³ /g
Total geometric volume	4061.295	4198.989	Å ³
Total geometric volume	0.213	0.220	cm ³ /g
Network-accessible helium volume	2112.381	2337.815	Å ³
Network-accessible helium volume	0.111	0.122	cm ³ /g
Network-accessible geometric volume	4057.420	4195.277	Å ³
Network-accessible geometric volume	0.213	0.219	cm ³ /g
Pore limiting diameter	3.13	3.30	Å
Maximum pore diameter	4.06	4.28	Å
Number of percolated dimensions	1	1	Dimension

^a DCM molecules were removed manually

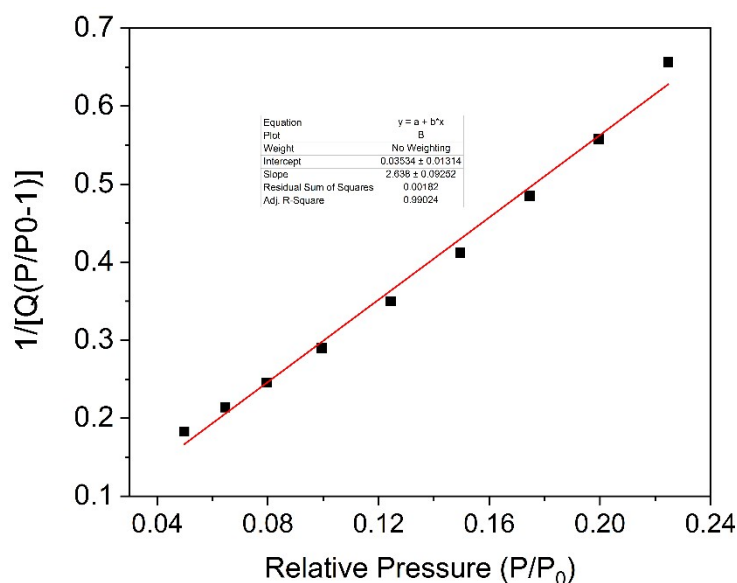


Figure S10. BET Surface Area Plot of **CP1**.

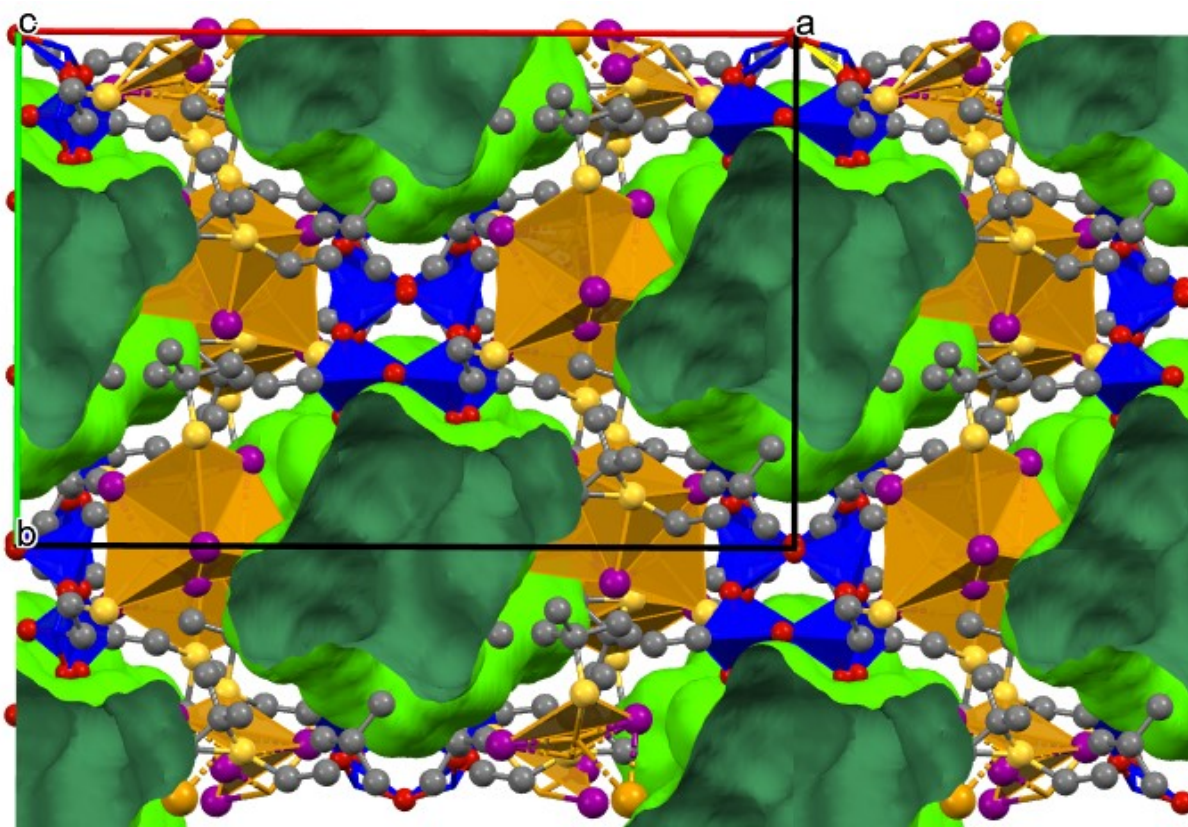


Figure S11. Structural voids visualized in CP1 in the *ab* plane. The green void contact surfaces were plotted at 1.6 Å probe radius with a grid spacing of 0.3 Å in Mercury.

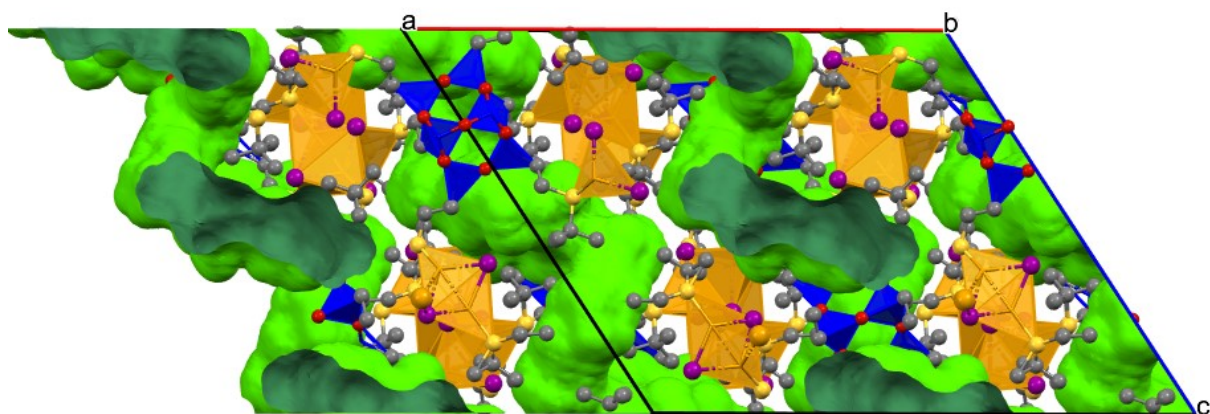


Figure S12. Structural voids visualized in CP1 in the *ac* plane. The green void contact surfaces were plotted at 1.6 Å probe radius with a grid spacing of 0.3 Å in Mercury.

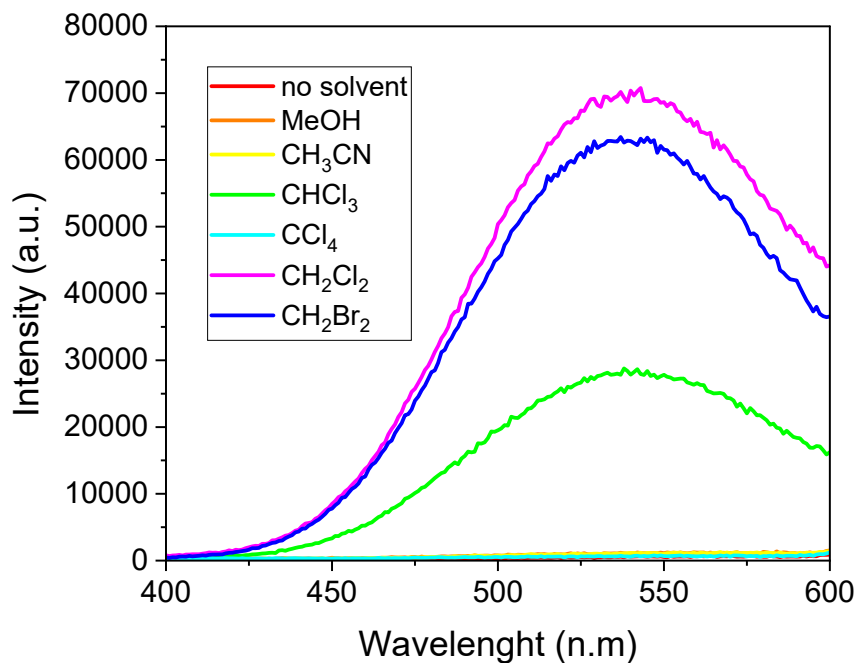


Figure S13. Solid-state emission of **CP1** after exposition to various solvent vapors for 20 min ($\lambda_{\text{ex}} = 330$ nm).

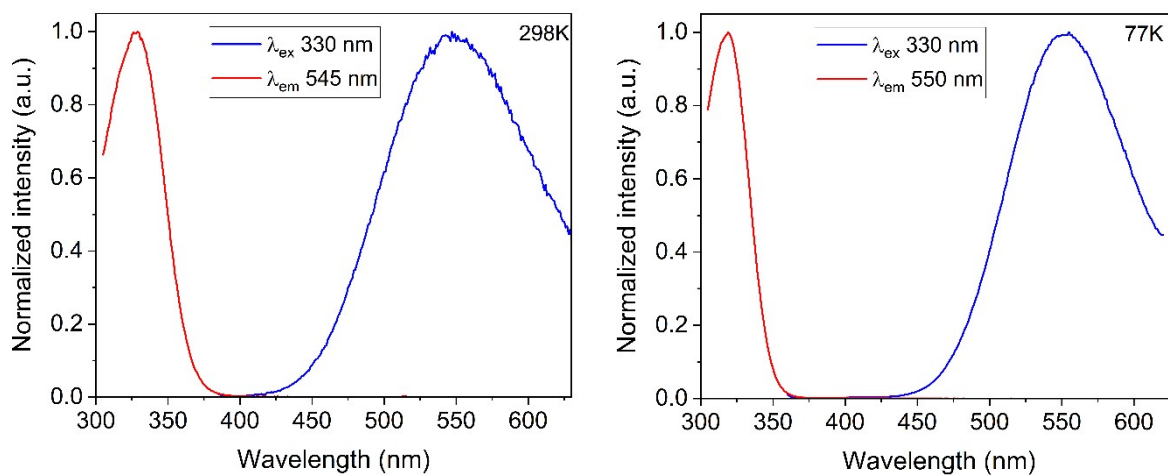


Figure S14. Solid-state emission (blue) and excitation (red) spectra of **CP1·CH₂Br₂** at 298 K and 77 K.

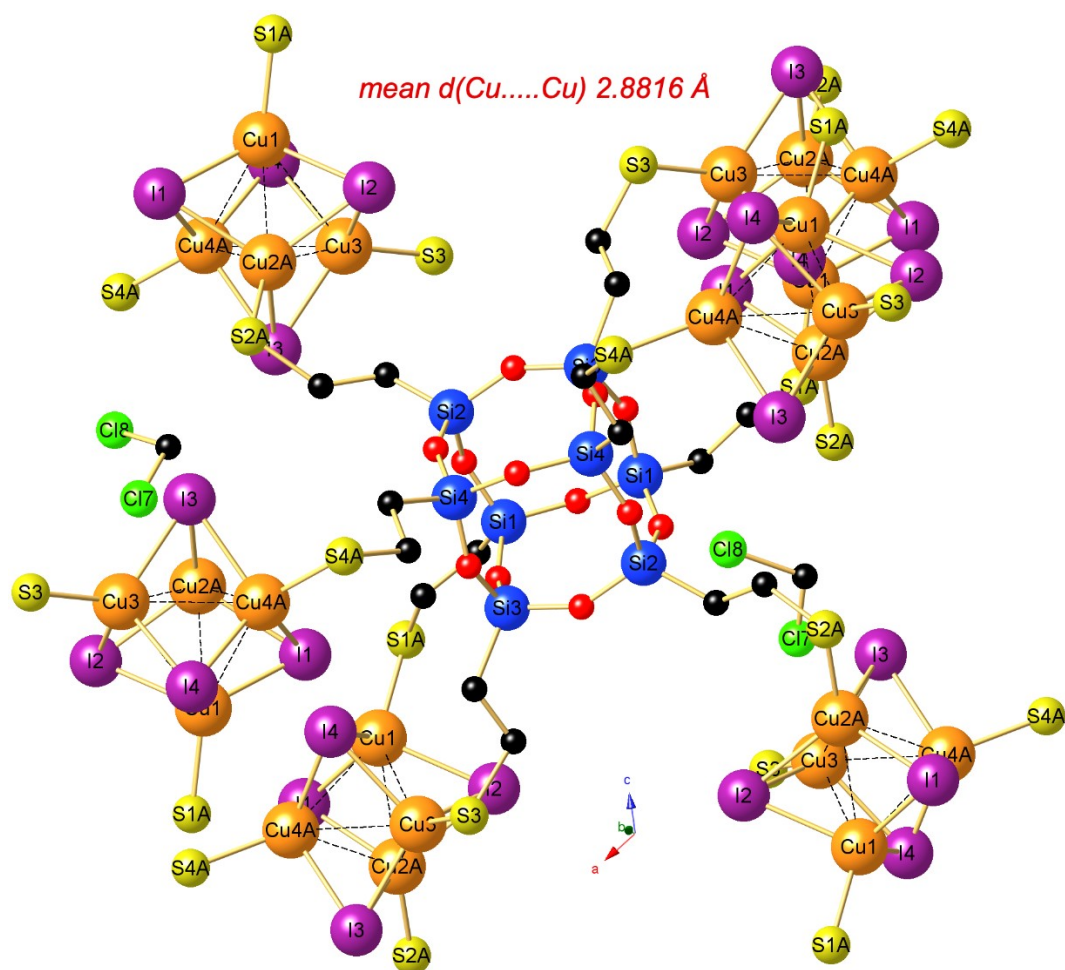


Figure S15. View of the POSS core of $\text{CP1}\cdot\text{CH}_2\text{Cl}_2$ surrounded by six cubane-shaped $\text{Cu}_4\text{I}_4\text{S}_4$ clusters.

The H atoms are omitted for clarity and only the disordered Cl7-C-Cl8 solvent molecules are shown. Selected bond lengths (Å) and angles ($^\circ$) at 100 K: Cu1–Cu2A¹ 2.760(2), Cu1–Cu3 3.1319(8), Cu1–Cu4A² 2.9275(13), Cu2A–Cu3⁴ 2.761(3), Cu2A–Cu4A⁸ 2.730(3), Cu3–Cu4A⁵ 2.9790(16), Cu1–S1A 2.3301(10), Cu2A–S2A 2.260(3), Cu3–S3 2.3378(10), Cu4–S4A 2.301(3), Cu1–I1 2.5954(7), Cu1³–I2 2.7087(8), Cu1⁶–I6 2.7022(9), Cu2A¹–I1 2.715(3), Cu2A²–I2 2.7026(12), Cu3–I2 2.7000(7), Cu2A⁴–I3 2.719(2), Cu3–I3 2.6281(7), Cu4A⁵–I3 2.6930(14), Cu1⁶–I4 2.7022(9), Cu3⁷–I4 2.7119(8), Cu4A–I4 2.636(13); Cu1–I1–Cu2A¹ 62.59(5), Cu1–I1–Cu4A² 67.05(3), Cu1⁴–I2–Cu2A³ 61.59(6), Cu1⁴–I2–Cu3 70.772(18), Cu2A³–I3–Cu3 62.15(6), Cu2A³–I3–Cu4A⁵ 60.59(7), Cu3–I3–Cu4A⁵ 68.08(3), Cu1⁷–I4–Cu3⁶ 70.689(19), Cu1⁷–I4–Cu4A 66.50(3), Cu3⁶–I4–Cu4A 67.68(8), S1A–Cu1–I1 115.54(3), S1A–Cu1–I2⁴ 100.26(3), S1A–Cu1–I4² 112.88(38), S2A–Cu2A–I1⁸ 104.35(13), S2A–Cu2A–I2³ 121.22(3), S2A–Cu2A–I3³ 92.64(9), S3–Cu3–I2 110.79(2), S3–Cu3–I3 115.64(2), S3–Cu3–I4⁵ 103.28(3), S4A–Cu4A–I1⁷ 108.39(8), S4A–Cu4A–I3⁶ 98.67(6), S4A–Cu4A–I4 119.69(9). Symmetry transformations used to generate equivalent atoms: ¹+x, 1–y, 1/2+z; ²–1/2+x, 1/2+y, +z; ³1–x, +y, 3/2–z; ⁴1–x, 1–y, 1–z; ⁵3/2–x, 1/2+y, 3/2–z; ⁶1/2+x, –1/2+y, +z; ⁷3/2–x, –1/2+y, 3/2–z; ⁸–1/2+x, 1/2–y, –1/2+z.

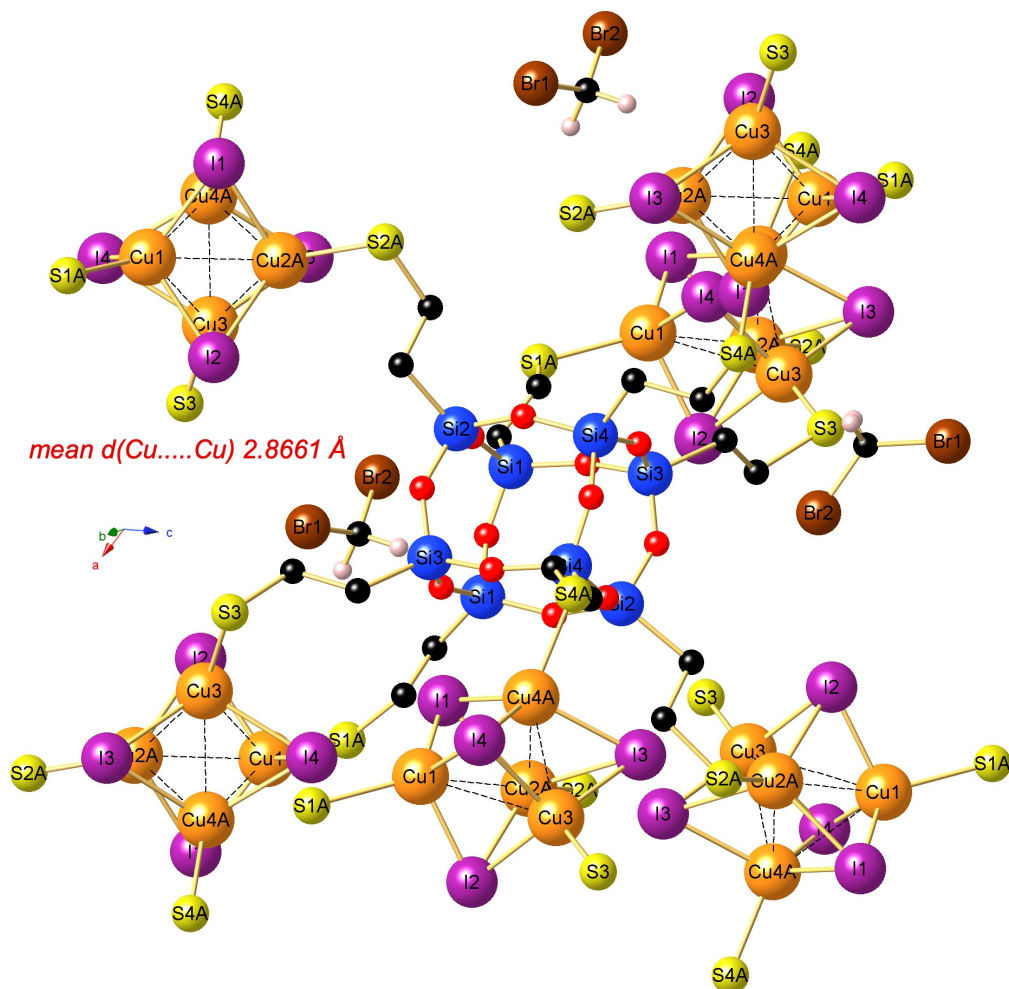


Figure S16. View of the POSS core of **CP1.CH₂Br₂** surrounded by six cubane-shaped Cu₄I₄S₄ clusters.

The H atoms are omitted for clarity and only the disordered Br1-C-Br2 solvent molecules are shown. Selected bond lengths (Å) and angles (°) at 100 K: Cu1–Cu2A¹ 2.927(6), Cu1–Cu3¹ 3.175(2), Cu1–Cu4A² 2.934(6), Cu2A–Cu3⁴ 2.748(7), Cu2A–Cu4A⁸ 2.632(10), Cu3–Cu4A⁵ 2.781(7), Cu1–S1A 2.459(3), Cu2A–S2A 2.346(8), Cu3–S3 2.2656(19), Cu4A–S4A 2.411(14), Cu1–I1 2.5519(13), Cu2A¹–I1 2.645(7), Cu4A²–I1 2.668(4), Cu1³–I2 2.5911(16); Cu2A⁴–I2 2.648(6), Cu3–I2 2.6873(14), Cu2A⁴–I3 2.763(5), Cu3–I3 2.6909(13), Cu4A⁵–I3 2.734(4), Cu1⁶–I4 2.6984(16), Cu3⁷–I4 2.7183(15), Cu4A–I4 2.655(4); Cu1–I1–Cu2A¹ 68.55(14), Cu1–I1–Cu4A² 68.06(13), Cu2A¹–I1–Cu4A² 59.1(2), Cu1⁴–I2–Cu2A³ 67.94(15), Cu1⁴–I2–Cu3 73.94(4), Cu2A³–I2–Cu3 60.00(15), Cu2A³–I3–Cu3 60.50(14), Cu2A³–I3–Cu4A⁵ 57.2(2), Cu4A⁵–I3–Cu3 61.47(14), Cu1⁷–I4–Cu4A 66.47(13), Cu1⁷–I4–Cu3⁶ 71.77(4), S1A–Cu1–I1 117.52(7), S1A–Cu1–I2⁴ 102.66(8), S1A–Cu1–I4³ 102.66(8), S2A–Cu2A–I1⁸ 106.6(3), S2A–Cu2A–I2³ 127.0(3), S2A–Cu2A–I3³ 88.2(2), S3–Cu3–I2 113.66(5), S3–Cu3–I3 113.28(5), S3–Cu3–I4⁵ 100.32(6), S4A–Cu4A–I1⁷ 106.1(4), S4A–Cu4A–I3⁶ 95.3(4), S4A–Cu4A–I4 119.6(4). Symmetry transformations used to generate equivalent atoms: ¹+x, 1–y, 1/2+z; ²1/2+x, 1/2+y, +z; ³1–x, +y, 3/2–z; ⁴1–x, 1–y, 1–z; ⁵3/2–x, 1/2+y, 3/2–z, ⁶1/2+–x, –1/2+y, +z, ⁷3/2–x, 1/2+y, 3/2–z, ⁸–1/2+x, 1/2–y, –1/2+z.

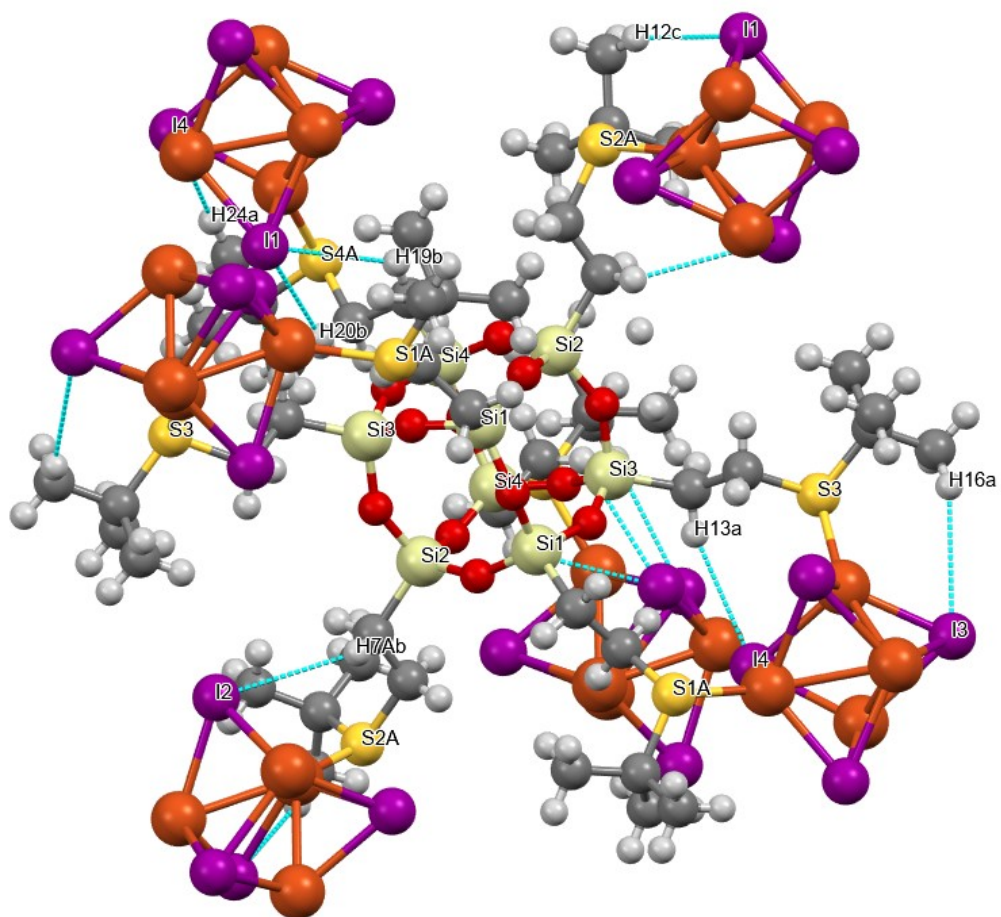


Figure S17. Hydrogen bonding in CP1.

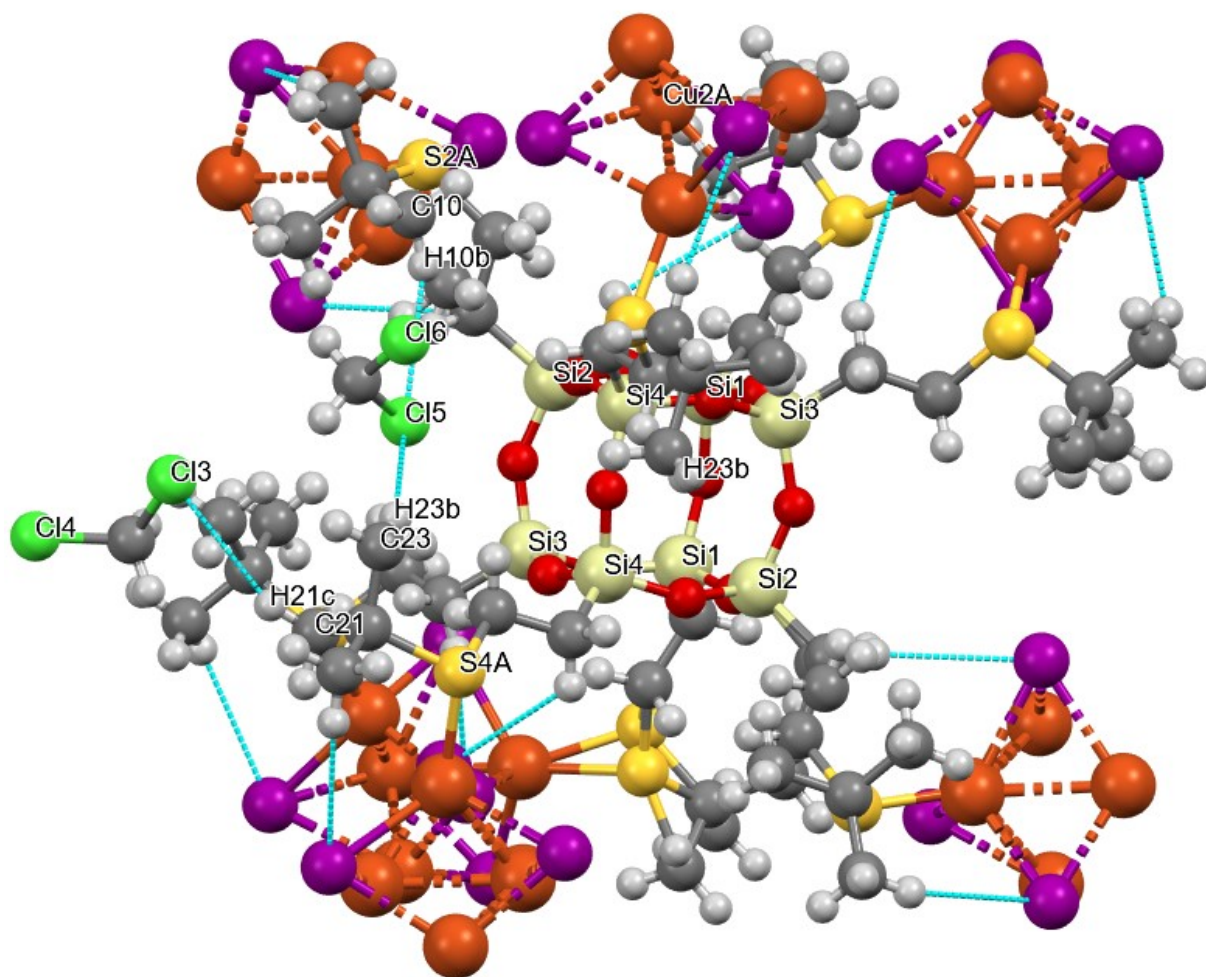


Figure S18. Hydrogen bonding in CP1.CH₂Cl₂.

Table S3. Comparison of geometrical parameters for the hydrogen-bonding interactions in CP1, CP1.CH₂Cl₂.

	interaction	distance/Å			angle/deg
		D-H	H···A	D···A	D-H···A
CP1	C12–H12C···I1	0.980	3.173	4.106	159.63
	C7–H7A···I2	0.989	3.206	3.868	125.73
	C16–H16a···I3	0.979	3.231	4.100	148.85
	C13–H13a···I4	0.990	3.156	4.047	150.43
	C19–H19b···I1	0.990	3.200	3.877	127.00
	C24–H24a···I4	0.981	3.177	4.114	160.46
	C20–H20b···I1	0.991	3.184	3.790	120.91
CP1.CH₂Cl₂	C12–H12C···I1	0.980	3.057	4.001	162.13
	C7A–H7A···I2	0.989	3.128	3.873	133.22
	C16–H16a···I3	0.980	3.193	3.999	140.56
	C13–H13a···I4	0.990	3.062	3.995	148.56
	C19–H19b···I1	0.990	3.142	3.834	128.17
	C24–H24a···I4	0.978	3.129	4.067	161.04
	C20–H20b···I1	-	-	-	-
	C10–H10b···Cl5	0.972	2.909	3.788	150.17
	C23–H23b···Cl5	0.980	2.854	3.817	167.59
	C21–H21c···Cl3	0.982	2.943	3.876	159.05

Table S4. Crystal data, data collection, and structure refinement for **L** and **CP2** at 100K.

Compound	L	CP2
CCDC number	2540788	2540789
Formula	$C_{48}H_{104}O_{12}S_8Si_8$	$C_{48}H_{104}Cu_5I_5O_{12}S_8Si_8$
Formula weight	1354.51	2306.71
Temperature [K]	290.0	100.00
Crystal system	0.71073	0.71073
Space group	Triclinic	Triclinic
a [Å]	$P\bar{1}$	$P\bar{1}$
b [Å]	12.4593(8)	13.633(6)
c [Å]	13.1453(8)	17.896(5)
α [°]	13.2020(9)	18.226(9)
β [°]	94.590(2)	76.982(15)
γ [°]	106.477(2)	81.072(16)
Volume/ Å ³	109.748(2)	81.091(11)
Z	1914.1(2)	4246(3)
$\rho_{\text{calc.}}$ [g/cm ³]	1.175	1.804
μ [mm ⁻¹]	0.405	3.405
$F(000)$	728.0	2276.0
Crystal size [mm]	0.494×0.356×0.074	0.147× 0.1×0.082
Radiation	Mo $K\alpha_1$ ($\lambda=0.71073$ Å)	Mo $K\alpha_1$ ($\lambda=0.71073$ Å)
2θ range [°]	4.748 to 52.878	3.612 to 52
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -16 ≤ l ≤ 16	-16 ≤ h ≤ 16, -22 ≤ k ≤ 21, -22 ≤ l ≤ 22
Reflections collected	41798	80941
Independent reflections	7809 $R_{\text{int}} = 0.0233$ $R_{\text{sigma}} = 0.0165$	16684 $R_{\text{int}} = 0.0526$ $R_{\text{sigma}} = 0.0397$
Data / restraints / parameters	7809/78/388	16684/0/843
Goodness-of-fit on F^2	1.074	1.049
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0558$, $wR_2 = 0.1562$	$R_1 = 0.0375$ $wR_2 = 0.0839$
R indices (all data)	$R_1 = 0.0642$, $wR_2 = 0.1641$	$R_1 = 0.0501$ $wR_2 = 0.0921$
Largest peak/hole [e. Å ⁻³]	0.56/-0.53	1.51/-1.33

Table S5. Crystal data, data collection, and structure refinement for **CP1** at 100–300K.

CCDC number	2540066	2540067	2540068	2540069	2540070	2539835	2540071	2540072
Formula	C ₂₄ H _{51.79} Cu ₄ I ₄ O ₆ S ₄ Si ₄	C ₂₄ H _{51.77} Cu ₄ I ₄ O ₆ S ₄ Si ₄	C ₂₄ H _{51.75} Cu ₄ I ₄ O ₆ S ₄ Si ₄	C ₂₄ H _{51.72} Cu ₄ I ₄ O ₆ S ₄ Si ₄	C ₂₄ H _{51.74} Cu ₄ I ₄ O ₆ S ₄ Si ₄	C ₂₄ H _{51.73} Cu ₄ I ₄ O ₆ S ₄ Si ₄	C ₂₄ H _{51.73} Cu ₄ I ₄ O ₆ S ₄ Si ₄	C ₂₄ H _{51.75} Cu ₄ I ₄ O ₆ S ₄ Si ₄
Formula weight	1438.872	1438.888	1438.834	1438.800	1438.821	1438.815	1438.807	1438.833
Temperature [K]	100.00	130.00	160.00	190.00	220.00	250.00	280.00	300.00
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C2/c	C2/c	C2/c	C2/c	C2/c	C2/c	C2/c	C2/c
<i>a</i> [Å]	29.882(7)	29.821(8)	29.833(8)	29.847(8)	29.822(8)	29.824(9)	29.814(9)	29.930(9)
<i>b</i> [Å]	16.568(4)	16.572(4)	16.591(5)	16.600(4)	16.626(5)	16.629(5)	16.647(5)	16.683(5)
<i>c</i> [Å]	25.270(6)	25.239(7)	25.271(7)	25.280(7)	25.285(7)	25.274(8)	25.292(8)	25.314(8)
α [°]	90	90	90	90	90	90	90	90
β [°]	123.198(8)	123.039(8)	123.032(9)	122.980(9)	122.897(9)	122.823(9)	122.761(9)	122.716(9)
γ [°]	90	90	90	90	90	90	90	90
Volume/ Å ³	10469(4)	10456(5)	10487(5)	10507(5)	10526(5)	10533(5)	10556(6)	10634(6)
<i>Z</i>	8	8	8	8	8	8	8	8
ρ calc. [g/cm ³]	1.826	1.828	1.823	1.819	1.816	1.815	1.811	1.797
μ [mm ⁻¹]	4.243	4.249	4.236	4.228	4.220	4.217	4.208	4.177
<i>F</i> (000)	5541.8	5541.9	5541.5	5541.2	5541.4	5541.4	5541.3	5541.5
Crystal size [mm]	0.245×0.156×0.134	0.245×0.156×0.134	0.245×0.156×0.134	0.245×0.156×0.134	0.245×0.156×0.134	0.245×0.156×0.134	0.245×0.156×0.134	0.245×0.156×0.134
Radiation	$\lambda=0.71073$ Å	$\lambda=0.71073$ Å	$\lambda=0.71073$ Å	($\lambda=0.71073$ Å	$\lambda=0.71073$ Å	$\lambda=0.71073$ Å	$\lambda=0.71073$ Å	$\lambda=0.71073$ Å
2 θ range [°]	3.98 to 58.96	3.98 to 59.12	3.84 to 59.12	3.96 to 59.16	3.96 to 55.86	3.96 to 55.14	3.96 to 54.24	3.94 to 52.86
Index ranges	-41 ≤ <i>h</i> ≤ 37 -22 ≤ <i>k</i> ≤ 22 -25 ≤ <i>l</i> ≤ 34	-41 ≤ <i>h</i> ≤ 38 -22 ≤ <i>k</i> ≤ 22 -33 ≤ <i>l</i> ≤ 34	-41 ≤ <i>h</i> ≤ 38 -22 ≤ <i>k</i> ≤ 22 -33 ≤ <i>l</i> ≤ 35	-41 ≤ <i>h</i> ≤ 38 -22 ≤ <i>k</i> ≤ 22 -31 ≤ <i>l</i> ≤ 35	-39 ≤ <i>h</i> ≤ 37 -21 ≤ <i>k</i> ≤ 21 -32 ≤ <i>l</i> ≤ 33	-38 ≤ <i>h</i> ≤ 37 -21 ≤ <i>k</i> ≤ 21 -32 ≤ <i>l</i> ≤ 32	-38 ≤ <i>h</i> ≤ 36 -21 ≤ <i>k</i> ≤ 21 -31 ≤ <i>l</i> ≤ 32	-37 ≤ <i>h</i> ≤ 36 -20 ≤ <i>k</i> ≤ 20 -23 ≤ <i>l</i> ≤ 31
Reflections collected	97756	111571	109763	88874	86308	84374	81302	45784
Independent reflections	14493 <i>R</i> _{int} = 0.0674 <i>R</i> _{sigma} = 0.0408	14547 <i>R</i> _{int} = 0.0673 <i>R</i> _{sigma} = 0.0369	14585 <i>R</i> _{int} = 0.0644 <i>R</i> _{sigma} = 0.0354	14609 <i>R</i> _{int} = 0.0664 <i>R</i> _{sigma} = 0.0434	12475 <i>R</i> _{int} = 0.0668 <i>R</i> _{sigma} = 0.0381	12052 <i>R</i> _{int} = 0.0691 <i>R</i> _{sigma} = 0.0398	11583 <i>R</i> _{int} = 0.0783 <i>R</i> _{sigma} = 0.0441	10824 <i>R</i> _{int} = 0.0887 <i>R</i> _{sigma} = 0.0704
Data / restraints / parameters	14493/18/584	14547/18/590	14585/18/577	14609/24/577	12475/18/529	12052/18/58	11583/18/578	10824/18/576
Goodness-of-fit on <i>F</i> ²	1.039	1.040	1.054	1.043	1.049	1.057	1.057	1.051
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0423 <i>wR</i> ₂ = 0.0964	<i>R</i> ₁ = 0.0419 <i>wR</i> ₂ = 0.1004	<i>R</i> ₁ = 0.0430 <i>wR</i> ₂ = 0.1113	<i>R</i> ₁ = 0.0468 <i>wR</i> ₂ = 0.1096	<i>R</i> ₁ = 0.0490 <i>wR</i> ₂ = 0.1261	<i>R</i> ₁ = 0.0470 <i>wR</i> ₂ = 0.1176	<i>R</i> ₁ = 0.0511 <i>wR</i> ₂ = 0.1314	<i>R</i> ₁ = 0.0635 <i>wR</i> ₂ = 0.1593
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0599 <i>wR</i> ₂ = 0.1062	<i>R</i> ₁ = 0.0605 <i>wR</i> ₂ = 0.1115	<i>R</i> ₁ = 0.0645 <i>wR</i> ₂ = 0.1276	<i>R</i> ₁ = 0.0768 <i>wR</i> ₂ = 0.1264	<i>R</i> ₁ = 0.0760 <i>wR</i> ₂ = 0.1454	<i>R</i> ₁ = 0.0778 <i>wR</i> ₂ = 0.1376	<i>R</i> ₁ = 0.0890 <i>wR</i> ₂ = 0.1568	<i>R</i> ₁ = 0.1286 <i>wR</i> ₂ = 0.2018
Largest peak/hole [e. Å ⁻³]	2.21/-1.18	1.82/-1.13	1.93/-1.17	1.62/-1.16	1.41/-1.16	1.26/-1.07	1.26/-0.97	1.28/-1.21

Table S6. Crystal data, data collection, and structure refinement for **CP1.CH₂Cl₂** at 100-250K and **CP1.CH₂Br₂** at 100K

Internal reference	CP1.CH ₂ Cl ₂	CP1.CH ₂ Cl ₂	CP1.CH ₂ Cl ₂	CP1.CH ₂ Cl ₂	CP1.CH ₂ Cl ₂	CP1.CH ₂ Cl ₂	CP1.CH ₂ Br ₂
CCDC number	2540793	2539831	2539832	2539833	2539834	2539836	2540790
Formula	C _{25.12} H _{54.04} Cl _{2.3} Cu ₄ I ₄ O ₆ S ₄ Si ₄	C _{25.12} H _{53.99} Cl _{2.27} Cu I ₄ O ₆ S ₄ Si ₄	C _{25.12} H _{53.97} Cl _{2.3} Cu ₄ I ₄ O ₆ S ₄ Si ₄	C _{25.12} H _{54.05} Cl _{2.31} Cu ₄ I ₄ O ₆ S ₄ Si ₄	C _{25.12} H _{54.06} Cl _{2.47} Cu ₄ I ₄ O ₆ S ₄ Si ₄	C _{25.12} H _{52.97} Cl _{2.2} Cu ₄ I ₄ O ₆ S ₄ Si ₄	C _{25.08} H _{50.26} Br _{2.17} Cu ₄ I I ₄ O ₆ S ₄ Si ₄
Formula weight	1536.056	1535.060	1535.874	1536.493	1542.358	1531.420	1623.433
Temperature [K]	100.00	130.00	160.00	190.00	220.00	250.00	100.00
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C2/c	C2/c	C2/c	C2/c	C2/c	C2/c	C2/c
<i>a</i> [Å]	29.802(6)	29.761(5)	29.786(5)	29.831(5)	29.830(6)	29.765(7)	29.6754(14)
<i>b</i> [Å]	16.488(3)	16.521(3)	16.563(3)	16.623(3)	16.640(3)	16.565(4)	16.4757(8)
<i>c</i> [Å]	25.250(5)	25.196(4)	25.217(4)	25.247(4)	25.230(5)	25.135(6)	26.5322(13)
α [°]	90	90	90	90	90	90	90
β [°]	122.666(5)	122.669(5)	122.619(5)	122.561(6)	122.587(7)	122.948(7)	127.2890(15)
γ [°]	90	90	90	90	90	90	90
Volume [Å ³]	10445(4)	10429(3)	10478(3)	10552(3)	10552(4)	10399(4)	10320.6(9)
<i>Z</i>	8	8	8	8	8	8	8
$\rho_{\text{calc.}}$ [g/cm ³]	1.954	1.955	1.947	1.934	1.942	1.956	2.090
μ [mm ⁻¹]	4.373	4.379	4.359	4.330	4.338	4.387	5.990
<i>F</i> (000)	5928.9	5924.8	5928.0	5930.6	5953.3	5906.5	6184.9
Crystal size [mm]	0.269×0.147×0.104	0.269×0.147×0.104	0.269×0.147×0.104	0.269×0.147×0.104	0.269×0.147×0.104	0.269×0.147×0.104	0.107×0.105×0.073
Radiation	Mo <i>K</i> α_1 ($\lambda=0.71073$ Å)	Mo <i>K</i> α_1 ($\lambda=0.71073$ Å)	Mo <i>K</i> α_1 ($\lambda=0.71073$ Å)	Mo <i>K</i> α_1 ($\lambda=0.71073$ Å)	Mo <i>K</i> α_1 ($\lambda=0.71073$ Å)	Mo <i>K</i> α_1 ($\lambda=0.71073$ Å)	Mo <i>K</i> α_1 ($\lambda=0.71073$ Å)
2 θ range [°]	3.98 to 74.04	3.98 to 61.26	3.96 to 61.3	3.96 to 61.28	3.96 to 59.56	3.98 to 56.3	2.96 to 60.12
Index ranges	-50 ≤ <i>h</i> ≤ 50 -27 ≤ <i>k</i> ≤ 27 -42 ≤ <i>l</i> ≤ 42	-42 ≤ <i>h</i> ≤ 42 -23 ≤ <i>k</i> ≤ 23 -35 ≤ <i>l</i> ≤ 36	-42 ≤ <i>h</i> ≤ 42 -23 ≤ <i>k</i> ≤ 23 -35 ≤ <i>l</i> ≤ 36	-42 ≤ <i>h</i> ≤ 42 -23 ≤ <i>k</i> ≤ 23 -35 ≤ <i>l</i> ≤ 36	-41 ≤ <i>h</i> ≤ 41 -21 ≤ <i>k</i> ≤ 23 -35 ≤ <i>l</i> ≤ 35	-39 ≤ <i>h</i> ≤ 39 -21 ≤ <i>k</i> ≤ 21 -33 ≤ <i>l</i> ≤ 33	-37 ≤ <i>h</i> ≤ 39 -20 ≤ <i>k</i> ≤ 21 -33 ≤ <i>l</i> ≤ 31
Reflections collected	483228	158479	159027	159963	102807	132259	212461
Independent reflections	26512 <i>R</i> _{int} = 0.0713 <i>R</i> _{sigma} = 0.0246	15995 <i>R</i> _{int} = 0.0608 <i>R</i> _{sigma} = 0.0284	16081 <i>R</i> _{int} = 0.0610 <i>R</i> _{sigma} = 0.0279	16166 <i>R</i> _{int} = 0.0628 <i>R</i> _{sigma} = 0.0290	14880 <i>R</i> _{int} = 0.0628 <i>R</i> _{sigma} = 0.0333	12556 <i>R</i> _{int} = 0.0734 <i>R</i> _{sigma} = 0.0322	12202 <i>R</i> _{int} = 0.0613 <i>R</i> _{sigma} = 0.0251
Data/restraints/parameters	26512/125/702	15995/125/702	16081/125/701	16166/137/690	14880/125/702	12556/125/708	12202/417/613
Goodness-of-fit on <i>F</i> ²	1.011	1.041	1.037	1.043	1.025	1.035	1.030
Final <i>R</i> indices [<i>I</i> >2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0401 <i>wR</i> ₂ = 0.1096	<i>R</i> ₁ = 0.0441 <i>wR</i> ₂ = 0.1194	<i>R</i> ₁ = 0.0444 <i>wR</i> ₂ = 0.1245	<i>R</i> ₁ = 0.0464 <i>wR</i> ₂ = 0.1298	<i>R</i> ₁ = 0.0481 <i>wR</i> ₂ = 0.1419	<i>R</i> ₁ = 0.0483 <i>wR</i> ₂ = 0.1424	<i>R</i> ₁ = 0.0558 <i>wR</i> ₂ = 0.1691
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0595 <i>wR</i> ₂ = 0.1217	<i>R</i> ₁ = 0.0621 <i>wR</i> ₂ = 0.1323	<i>R</i> ₁ = 0.0644 <i>wR</i> ₂ = 0.1396	<i>R</i> ₁ = 0.0704 <i>wR</i> ₂ = 0.1477	<i>R</i> ₁ = 0.0729 <i>wR</i> ₂ = 0.1618	<i>R</i> ₁ = 0.0746 <i>wR</i> ₂ = 0.1639	<i>R</i> ₁ = 0.0702 <i>wR</i> ₂ = 0.1807
Largest peak/hole [e. Å ⁻³]	2.19/-2.04	1.76/-1.98	1.41/-1.64	1.65/-1.72	2.35/-1.14	1.10/-0.96	4.22/-1.16

Table S7. Evolution of the Cu–Cu distances (Å), volumes of Cu4 tetrahedra (Å³) and volumes of the unit cells (Å³) with temperature (K) for **CP1**.

T(K)	100	130	160	190	220	250	280	300
Cu1–Cu2A	2.7871(18)	2.7920(19)	2.805(2)	2.826(3)	2.831(3)	2.845(2)	2.857(2)	2.875(3)
Cu1–Cu3	3.171(1)	3.173(1)	3.178(1)	3.181(1)	3.189(2)	3.193(2)	3.203(2)	3.204(3)
Cu1–Cu4A	3.014(2)	3.016(3)	3.019(3)	3.026(3)	3.043(6)	3.032(3)	3.041(3)	3.048(3)
Cu2A–Cu3	2.747(2)	2.755(3)	2.766(3)	2.788(3)	2.793(5)	2.821(3)	2.837(3)	2.857(4)
Cu2A–Cu4A	2.750(3)	2.758(3)	2.768(4)	2.793(4)	2.805(7)	2.820(4)	2.837(4)	2.852(6)
Cu3–Cu4A	2.963(2)	2.965(3)	2.973(3)	2.980(3)	2.965(7)	3.005(3)	3.012(4)	3.031(5)
Mean(1-4)	2.9053	2.9098	2.9182	2.9323	2.9383	2.9507	2.9645	2.9778
V_(unit cell)	10456(5)	10456(5)	10487(5)	10507(5)	10526(5)	10533(5)	10556(6)	10634(6)

Table S8. Evolution of the Cu–Cu distances (Å), volumes of Cu4 tetrahedra (Å³) and volumes of the unit cells (Å³) with temperature (K) for **CP1.CH₂Cl₂**.

T(K)	100	130	160	190	220	250
Cu1–Cu2A	2.760(2)	2.768(3)	2.786(3)	2.789(4)	2.792(9)	2.812(7)
Cu1–Cu3	3.1319(8)	3.127(1)	3.130(1)	3.134(1)	3.134(1)	3.153(2)
Cu1–Cu4A	2.9275(13)	2.9409(14)	2.9570(14)	2.9657(17)	2.969(3)	2.985(3)
Cu2A–Cu3	2.761(3)	2.775(4)	2.792(4)	2.786(6)	2.729(16)	2.765(11)
Cu2A–Cu4A	2.730(3)	2.742(4)	2.765(4)	2.754(6)	2.704(15)	2.731(12)
Cu3–Cu4A	2.9790(16)	2.9836(15)	2.9851(12)	2.9840(17)	2.973(5)	2.973(4)
Mean(1-4)	2.8816	2.8894	2.9025	2.9021	2.885	2.9031
V_(unit cell)	10445(4)	10429(3)	10478(3)	10552(3)	10552(4)	10399(4)