Electronic Supporting Information

Unusual Triplet-Triplet Annihilation in a 3D Copper Chloride Coordination Polymer

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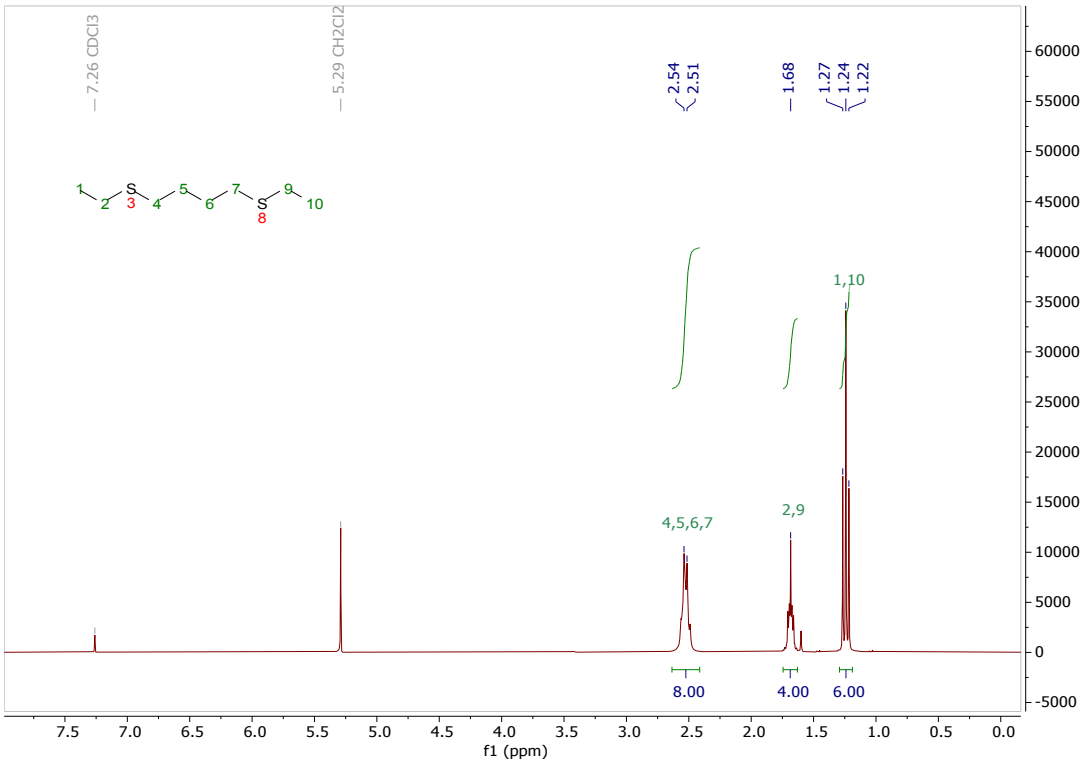

Figure S1. ^{1}H NMR spectrum of **L** recorded in $CDCl_3$.

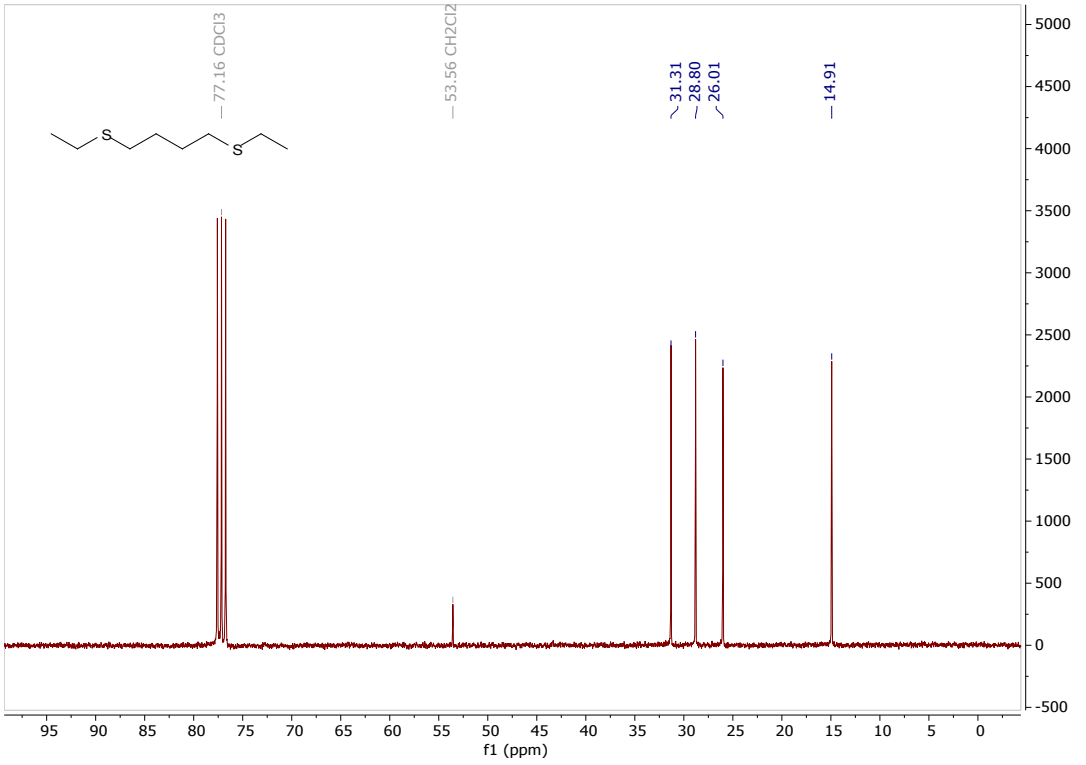

Figure S2. ^{13}C NMR spectrum of **L** recorded in $CDCl_3$.

Table S1. Crystal data, data collection, and structure refinement for **CP2**.

	100 K	**118 K**	**137 K**	**151 K**	**168 K**
Formula	C_4H_9ClCuS	C_4H_9ClCuS	C_4H_9ClCuS	C_4H_9ClCuS	C_4H_9ClCuS
Formula weight	188.16	188.16	188.16	188.16	188.16
Temperature/K	100(2)	118(2)	137(2)	151(2)	168(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\ 1\ 2_1/n\ 1$	$P\ 1\ 2_1/n\ 1$	$P\ 1\ 2_1/n\ 1$	$P\ 1\ 2_1/n\ 1$	$P\ 1\ 2_1/n\ 1$
a/Å	8.9309(9)	8.9363(13)	8.9369(12)	8.9360(9)	8.9415(9)
b/Å	6.7591(7)	6.7653(10)	6.7675(9)	6.7693(7)	6.7764(7)
c/Å	10.8963(11)	10.9019(16)	10.9024(15)	10.9057(11)	10.9128(11)
α/°	90	90	90	90	90
β/°	109.028(2)	109.053(3)	109.052(3)	109.008(2)	109.007(2)
γ/°	90	90	90	90	90
Volume/ Å^3	621.81(11)	622.99(16)	623.26(15)	623.72(11)	625.17(11)
Z	4	4	4	4	4
Density (calc.) g/cm^3	2.010	2.006	2.005	2.004	1.999
Absorption coefficient/mm^{-1}	4.144	4.136	4.134	4.131	4.122
F(000)	380	380	380	380	380
Crystal size/mm	0.040 × 0.100 × 0.330	0.040 × 0.100 × 0.330	0.040 × 0.100 × 0.330	0.040 × 0.100 × 0.330	0.040 × 0.100 × 0.330
2θ range for data collection/°	5.14 to 52.92	5.14 to 52.80	5.14 to 52.78	5.14 to 52.82	5.14 to 52.94
Index ranges	$-11 \le h \le 11$ $-8 \le k \le 8$ $-13 \le l \le 13$	$-11 \le h \le 11$ $-8 \le k \le 8$ $-13 \le l \le 13$	$-11 \le h \le 11$ $-8 \le k \le 8$ $-13 \le l \le 13$	$-11 \le h \le 11$ $-8 \le k \le 8$ $-13 \le l \le 13$	$-11 \le h \le 11$ $-8 \le k \le 8$ $-13 \le l \le 13$
Reflections collected	10329	10274	10293	10303	10361
Independent reflections	9261	9173	9160	9122	9118
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	10329 / 0 / 66	10274 / 0 / 66	10293 / 0 / 66	10303 / 0 / 66	10361 / 0 / 66
Goodness-of-fit on F^2	1.089	1.064	1.085	1.062	1.001
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0332$, $wR_2 = 0.0839$	$R_1 = 0.0326$, $wR_2 = 0.0798$	$R_1 = 0.0314$, $wR_2 = 0.0759$	$R_1 = 0.0334$, $wR_2 = 0.0792$	$R_1 = 0.0326$, $wR_2 = 0.0761$
R indices (all data)	$R_1 = 0.0390$, $wR_2 = 0.0863$	$R_1 = 0.0388$, $wR_2 = 0.0822$	$R_1 = 0.0374$, $wR_2 = 0.0780$	$R_1 = 0.0400$, $wR_2 = 0.0817$	$R_1 = 0.0396$, $wR_2 = 0.0788$
Largest diff. peak and hole/e. Å^{-3}	0.868 and -1.368	0.794 and -1.281	0.654 and -1.095	0.825 and -1.169	0.765 and -1.038

Table S2. Crystal data, data collection, and structure refinement for **CP2**.

	184 K	**217 K**	**250 K**	**298 K**
Formula	C_4H_9ClCuS	C_4H_9ClCuS	C_4H_9ClCuS	C_4H_9ClCuS
Formula weight	188.16	188.16	188.16	188.16
Temperature/K	184(2)	217(2)	250(2)	298(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\ 1\ 2_1/n\ 1$	$P\ 1\ 2_1/n\ 1$	$P\ 1\ 2_1/n\ 1$	$P\ 1\ 2_1/n\ 1$
a/Å	8.9401(9)	8.9459(9)	8.9479(8)	8.9566(10)
b/Å	6.7780(7)	6.7880(7)	6.7968(6)	6.8133(8)
c/Å	10.9123(11)	10.9215(10)	10.9255(10)	10.9391(12)
α/°	90	90	90	90
β/°	108.995(2)	108.982(2)	108.967(2)	108.913(2)
γ/°	90	90	90	90
Volume/ Å^3	625.24(11)	627.14(11)	628.38(10)	631.51(12)
Z	4	4	4	4
Density (calc.) g/cm^3	1.999	1.993	1.989	1.979
Absorption coefficient/mm^{-1}	4.121	4.109	4.100	4.080
F(000)	380	380	380	380
Crystal size/mm	0.040 × 0.100 × 0.330	0.040 × 0.100 × 0.330	0.040 × 0.100 × 0.330	0.040 × 0.100 × 0.330
2θ range for data collection/°	5.14 to 52.82	5.14 to 52.92	5.14 to 52.88	5.14 to 52.94
Index ranges	$-11 \le h \le 11$ $-8 \le k \le 8$ $-13 \le l \le 13$	$-11 \le h \le 11$ $-8 \le k \le 8$ $-13 \le l \le 13$	$-11 \le h \le 11$ $-8 \le k \le 8$ $-13 \le l \le 13$	$-11 \le h \le 11$ $-8 \le k \le 8$ $-13 \le l \le 13$
Reflections collected	10342	10385	10401	10449
Independent reflections	9057	9052	9129	9024
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	10342 / 0 / 66	10385 / 0 / 66	10401 / 0 / 66	10449 / 0 / 66
Goodness-of-fit on F^2	1.016	0.737	1.076	1.037
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0326$, $wR_2 = 0.0762$	$R_1 = 0.0333$, $wR_2 = 0.0848$	$R_1 = 0.0324$, $wR_2 = 0.0745$	$R_1 = 0.0334$, $wR_2 = 0.0760$
R indices (all data)	$R_1 = 0.0400$, $wR_2 = 0.0789$	$R_1 = 0.0415$, $wR_2 = 0.0905$	$R_1 = 0.0396$, $wR_2 = 0.0772$	$R_1 = 0.0421$, $wR_2 = 0.0794$
Largest diff. peak and hole/e. Å^{-3}	0.760 and -1.099	0.754 and -0.986	0.550 and -0.873	0.574 and -0.830

Table S3. Selected bond distance as a function of temperature for **CP2**.

Temperature (K)	Bond length (Å)				
	Cu•••Cu	Cu-Cl1	Cu-Cl2	Cu-S1	Cu-S2
100	3.2922(10)	2.3440(12)	2.4210(12)	2.3058(11)	2.3418(12)
118	3.2935(10)	2.3443(12)	2.4227(12)	2.3074(10)	2.3441(12)
137	3.2922(10)	2.3436(11)	2.4225(11)	2.3081(11)	2.3453(11)
151	3.2936(10)	2.3435(12)	2.4231(12)	2.3088(11)	2.347(11)
168	3.2943(10)	2.3442(12)	2.4243(12)	2.3111(11)	2.3498(11)
184	3.2934(10)	2.3434(12)	2.4244(12)	2.3110(11)	2.3513(11)
217	3.2929(12)	2.3433(13)	2.4254(13)	2.3138(12)	2.3567(12)
250	3.2903(10)	2.3419(12)	2.4259(11)	2.3165(11)	2.3615(11)
298	3.2903(10)	2.3434(12)	2.4278(12)	2.3208(11)	2.3706(11)

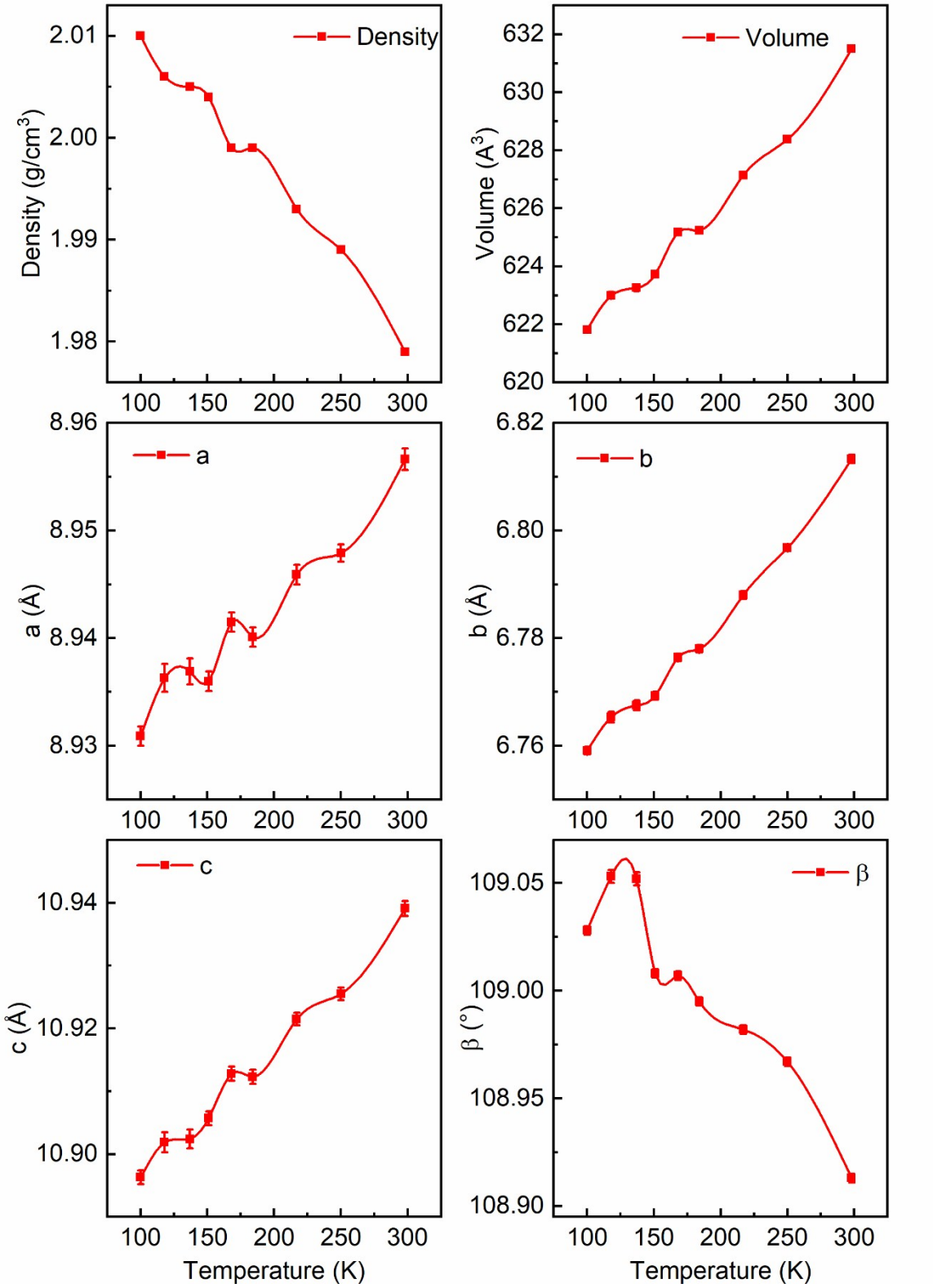

Figure S3. Evolution of the crystal volume and density, *β*, *a*, *b*, and *c* as a function of temperature for **CP2**.

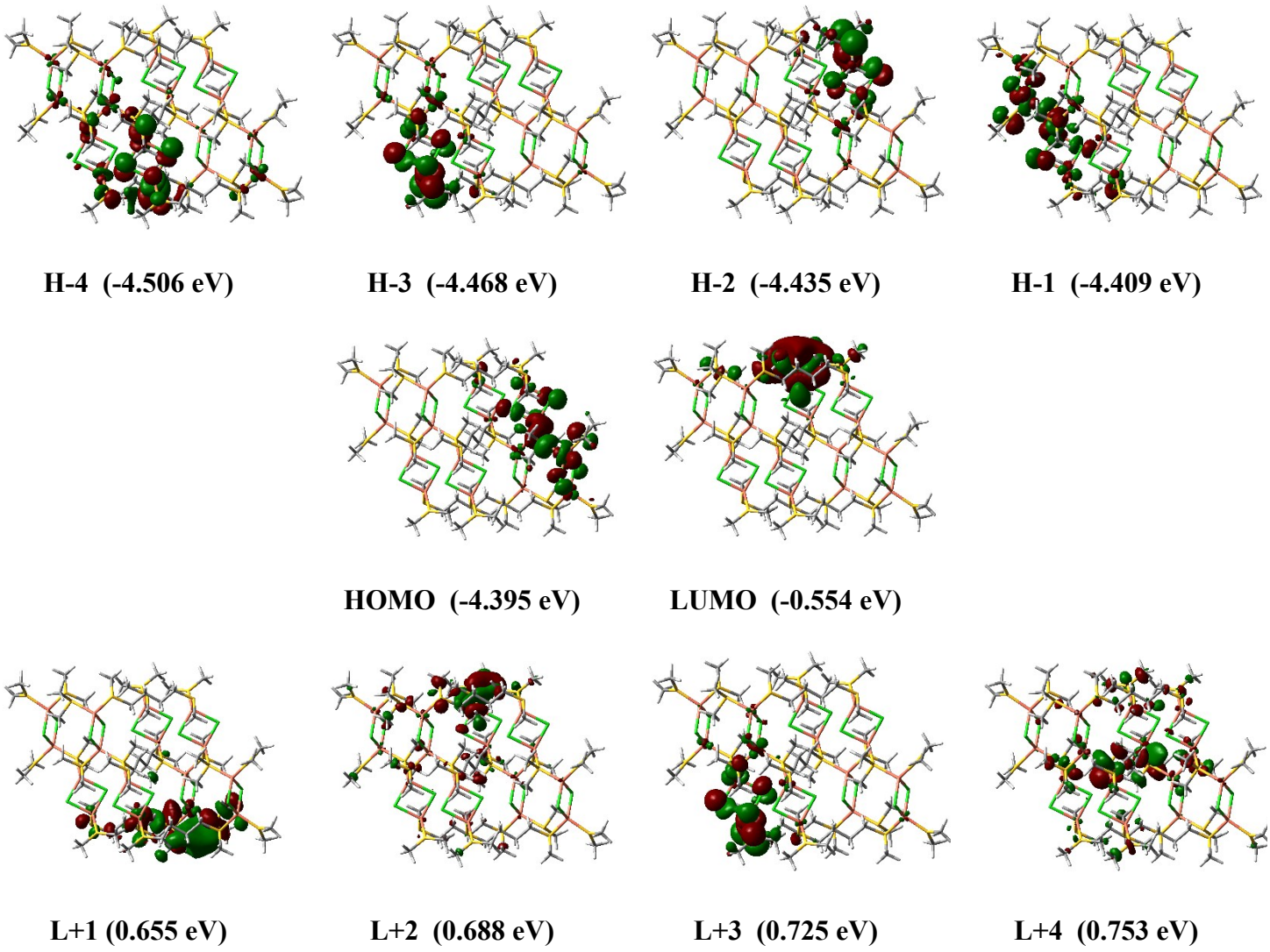

Figure S4. Molecular orbitals of the geometry of **CP2**.

Table S4. Atomic contributions as a function of various fragments to the frontier MOs of **CP2**.

	H-4	H-3	H-2	H-1	HOMO	LUMO	L+1	L+2	L+3	L+4
ligands	46.0	38.9	40.9	33.7	32.0	61.5	47.9	47.4	64.1	57.5
Cu atoms	41.6	48.6	47.6	50.6	51.7	37.6	51.3	51.2	30.0	41.6
Cl atoms	12.5	12.5	11.5	15.7	16.3	0.9	0.9	1.4	5.9	0.9

Table S5. Calculated positions, oscillator strengths (f) and major contributions of the first 50 electronic transitions of **CP2**.

Transition No.	λ (nm)	Osc. Str.	Major contribs (%; -- means no major contribution)
1	297.3	0.0058	H-7→LUMO (33), H-6→LUMO (15)
2	286.7	0.0063	H-4→L+4 (48)
3	283.8	0.0102	H-2→LUMO (46), H-2→L+5 (12)
4	280.9	0.0022	H-17→LUMO (10), H-10→LUMO (13), H-9→LUMO (26)
5	280.7	0.0451	H-1→L+3 (17), H-1→L+11 (18)
6	280.2	0.0431	HOMO→L+5 (19), HOMO→L+8 (19), HOMO→L+17 (16)
7	279.3	0.0086	H-23→L+1 (17), H-22→L+1 (32)
8	278.5	0.0195	H-3→L+5 (13)
9	278.2	0.0088	H-23→L+2 (24), H-22→L+2 (13)
10	276.1	0.0109	H-7→L+3 (14), H-7→L+6 (10)
11	275.4	0.0312	--
12	275.1	0.0033	--
13	274.3	0.004	--
14	274.2	0.0052	H-21→L+1 (20), H-15→L+1 (26)
15	274	0.0258	H-4→L+6 (11), H-4→L+7 (16)
16	273.3	0.0072	H-19→L+2 (16)
17	273.1	0.0124	--
18	273	0.0153	--
19	272.3	0.0041	H-13→LUMO (12), H-5→LUMO (10)
20	272	0.003	H-2→LUMO (13), HOMO→LUMO (28)
21	271.9	0.0008	H-9→L+4 (11), H-8→L+4 (25)
22	271.6	0.0028	H-2→LUMO (12), H-2→L+3 (11), H-2→L+5 (14)
23	269.6	0.0081	H-6→L+8 (19), H-6→L+12 (14)
24	269.2	0.0032	H-3→L+1 (10), H-1→LUMO (14)
25	268.9	0.0151	--
26	268.6	0.0019	--
27	268.6	0.0014	--
28	268.3	0.0036	--
29	267.9	0.0025	--
30	267.6	0.0059	H-17→LUMO (10)
31	267.4	0.0044	H-29→L+2 (14)
32	267.4	0.005	--
33	267.1	0.0198	H-5→L+11 (11)
34	267	0.0092	--
35	266.6	0.0083	HOMO→LUMO (19)
36	266.4	0.0088	H-5→L+11 (13)
37	266.3	0.0258	--
38	266	0.0074	--
39	265.3	0.0247	--
40	265.1	0.0042	--
41	265	0.0094	--
42	264.6	0.0112	H-13→L+11 (32)
43	264.4	0.0258	--
44	264.2	0.0251	H-11→L+12 (12)
45	263.7	0.0196	--
46	263.6	0.022	H-3→L+4 (34)
47	263.3	0.0108	HOMO→L+10 (10)
48	263.2	0.0092	H-1→LUMO (10), H-1→L+3 (13)
49	263	0.0138	--
50	262.9	0.0021	H-1→LUMO (14)

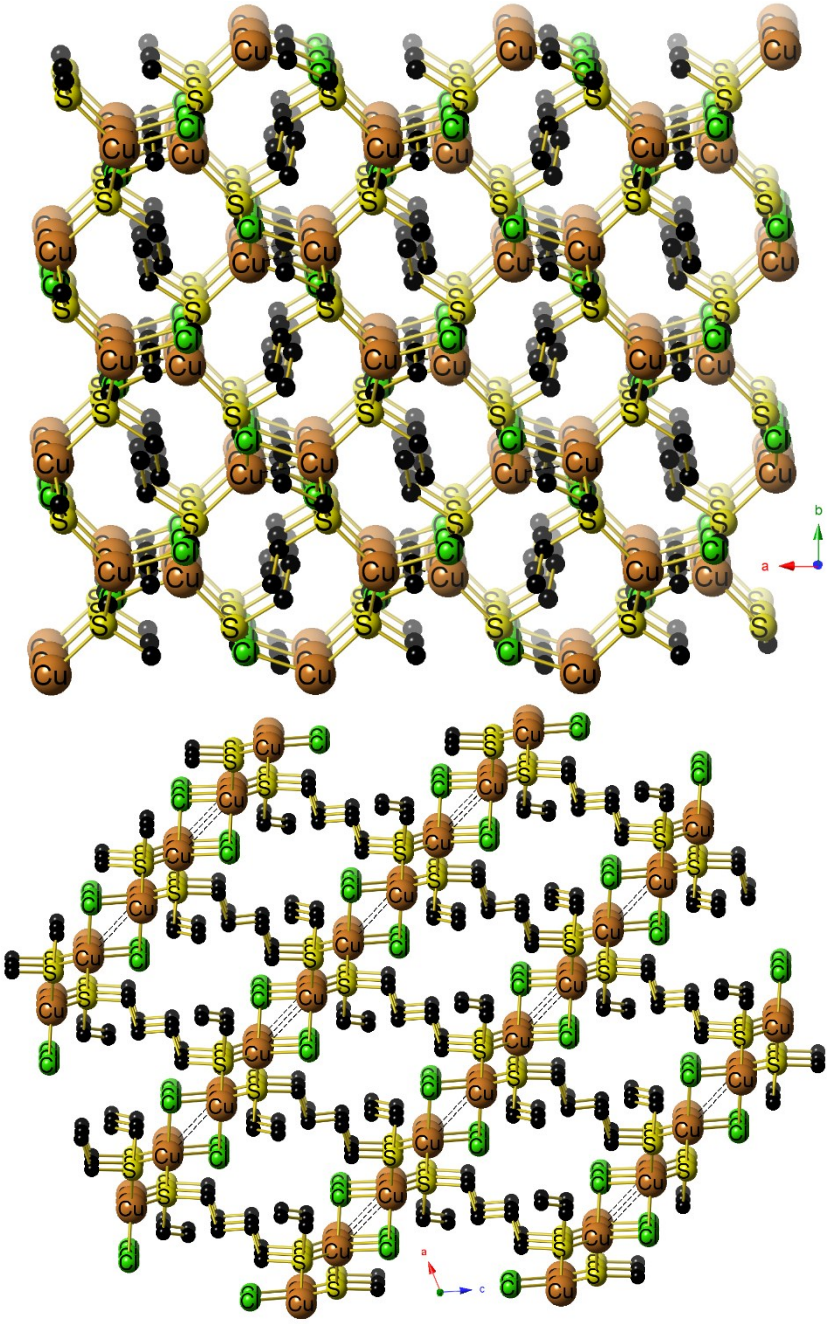

Figure S5. (Top) Perspective view down the *c* axis of the 3D network of **CP2** at 100 K**.** (Bottom) Perspective view down the *c* axis of the 3D network of **CP2**.

Selected bond lengths [Å] and angles [°] at 100 K: Cu–Cl 2.4210(12), Cu–Cl# 2.3440(12), Cu–S 2.3418(12), Cu–S# 2.3058(11); Cu–Cl–Cu# 87.43(4), S–Cu–S 112.94(3), Cl–Cu–Cl# 92.57(4), C1–S–C3 102.6(2) Symmetry transformations used to generate equivalent atoms: #1 x, y, z #2 -x+1/2, y+1/2, -z+1/2 #3 -x, -y, -z #4 x-1/2, -y-1/2, z-1/2. Using the CrystalMaker Software (version 9.1.3), the porosity (corrected for first-nearest-neighbor sphere overlap and site visibility) of **CP2** has been determined: at 100 K, the filled space is 148.829 Å³ (23.93%) per unit cell, the void space amounts for 472.984 Å³ (76.07%) per unit cell. At 298 K, the filled space has been calculated to be 148.991 Å³ (23.59%) per unit cell, and the void space lowers to 482. 517 Å³ (71.57%). The unit cell volume increases from 619.899 Å³ to 631.508 Å³.

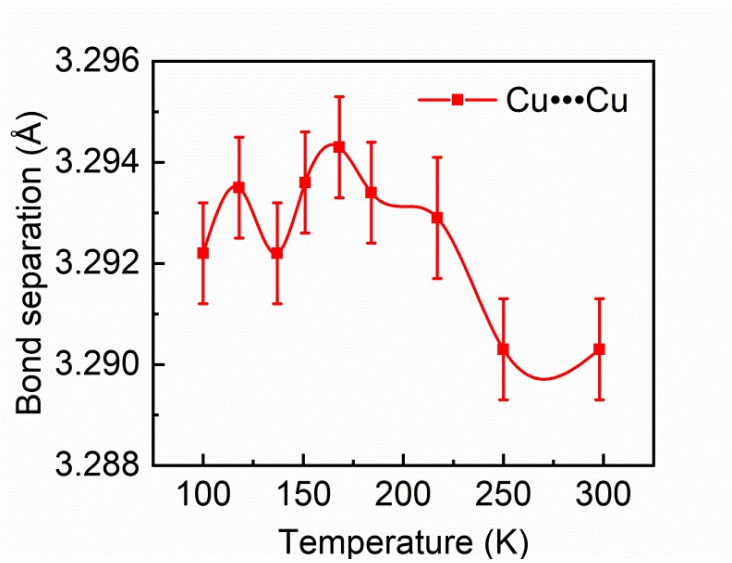

Figure S6. Graph of the Cu•••Cu separation *vs.* temperature in the Cu_2Cl_2 rhomboid. The error bars are the uncertainties.

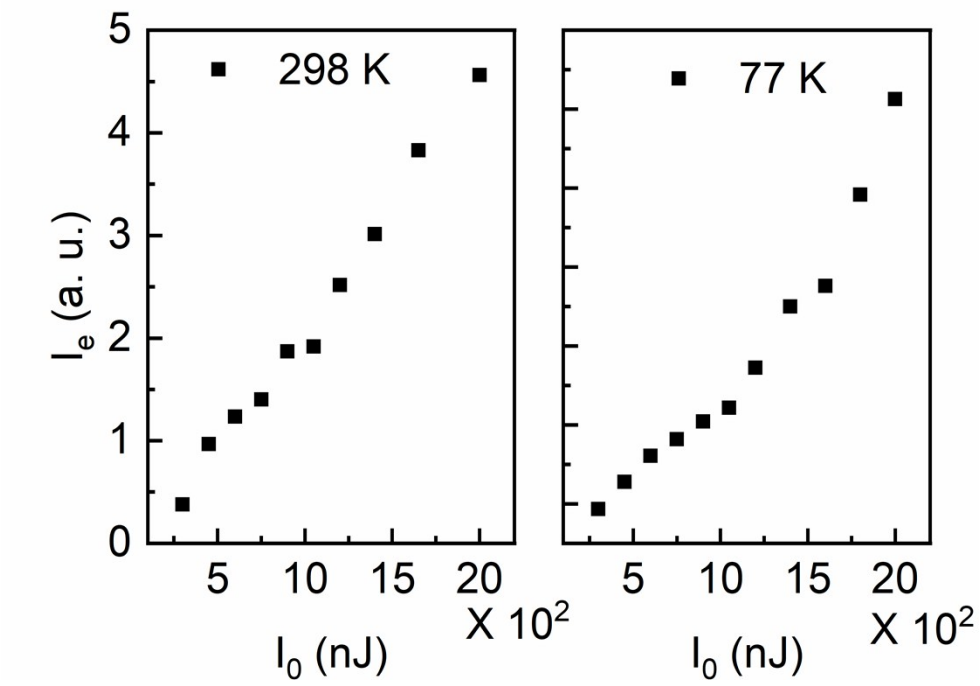

Figure S7. Graph of I_e *vs*. I_o (laser power). Note that the linear portion of the graph in the high-power region.