Electronic Supplementary Information

A Novel Mixed Valent Cu^{II}-Cu^{I} 2D Framework Made of a Hydrazone and μ-SCN Bridged Metallacyclic Loops Cross-linked by μ_3-SCN Chains

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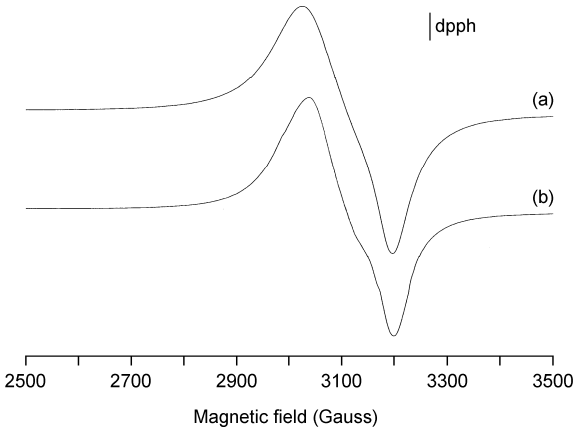

Figure F1. X-band EPR spectra of the polycrystalline complex: (a) at RT, (b) at 100 K. Diphenylpicrylhydrazyl (dpph) is the standard field marker (g = 2.0036).

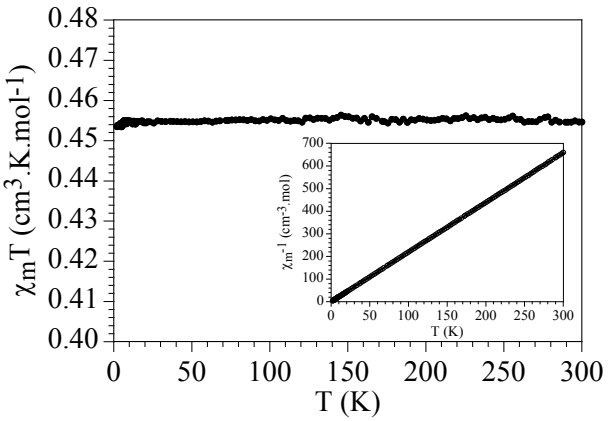

Figure F2. Thermal variation of the $\chi_m T$ product for the complex. Inset shows the Curie plot. Solid line is the best fit to the Curie-Weiss law

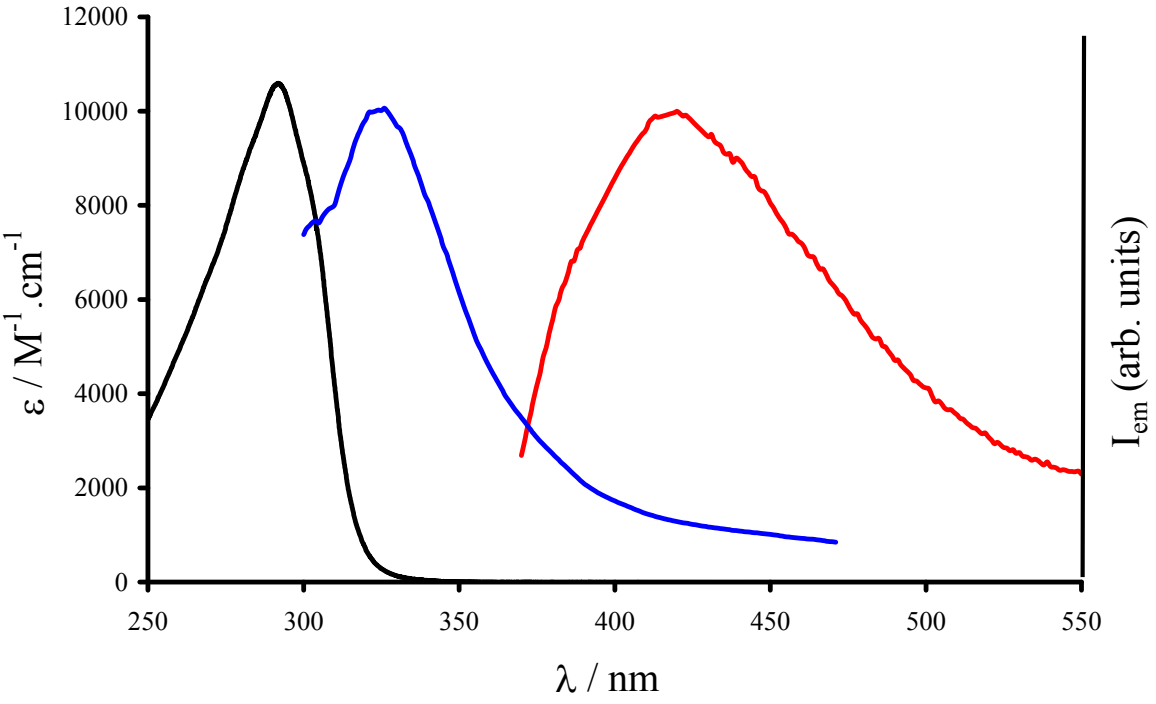

Figure F3. UV-Vis absorption spectrum of LH in ethanol (c = 1.18×10^{-4} M, black) and emission spectra of LH in ethanol (λ_{exc} = 270 nm, blue) and of the mixed valent copper complex in the solid state (λ_{exc} = 338 nm, red)

Table T1 Bond length (Å) and bond angles (º) for the complex

Bond lengths		Bond angles	
Cu1-N1	2.015(4)	N1-Cu1-N2	80.76(14)
Cu1-N2	1.925(3)	N1-Cu1-N4	102.58(16)
Cu1-N4	1.931(4)	N2-Cu1-N4	164.90(16)
Cu1-O1	1.983(3)	O1-Cu1-N1	158.00(14)
Cu1-S1	2.6444(17)	O1-Cu1-N2	78.62(13)
Cu2-N3^{ii}	2.033(3)	O1-Cu1-N4	95.47(15)
Cu2-N3^{iv}	2.033(3)	S1-Cu1-O1	93.41(11)
Cu2-S2	2.4249(14)	S1-Cu1-N1	96.39(12)
Cu2-S2^{v}	2.4249(14)	S1-Cu1-N2	96.20(11)
Cu3-N5^{i}	1.938(5)	S1-Cu1-N4	98.03(13)
Cu3-N5^{iii}	1.938(5)	N3^{ii}-Cu2-N3^{iv}	116.10(13)
Cu3-S2	2.4292(15)	S2-Cu2-S2^{v}	107.05(5)
Cu3-S2^{v}	2.4292(15)	S2-Cu2-N3^{ii}	101.51(11)
Cu1···Cu2	5.5938(6)	S2-Cu2-N3^{iv}	115.44(10)
Cu1···Cu3	5.8449(6)	S2^{v}-Cu2-N3^{ii}	115.44(10)
Cu2···Cu3	2.8903(12)	S2^{v}-Cu2-N3^{iv}	101.51(11)
		N5^{i}-Cu3-N5^{iii}	116.7(2)
		S2-Cu3-S2^{v}	106.77(6)
		S2-Cu3-N5^{i}	109.17(17)
		S2-Cu3-N5^{iii}	107.32(16)
		S2^{v}-Cu3-N5^{i}	107.32(16)
		S2v-Cu3-N5^{iii}	109.17(17)

Symmetry codes: (i) 1/2-x, 1/2-y, 1-z; (ii) 1/2-x, 3/2-y, 1-z; (iii) 1/2+x, 1/2-y, 1/2+z; (iv) 1/2+x, 3/2-y, 1/2+z; (v) 1-x, y, 3/2-z.

Table T2 Bond valence values for copper centers in the complex

Bond type	Bond distance (R_{ij}) (Å)	R_0 (Å)	b (Å)	Bond valence (S_{ij}) Cu1	Cu2	Cu3	BVS (N_i)
Cu1-N1	2.015(4)	1.713	0.37	0.4421			2.1597
Cu1-N2	1.925(3)	1.713	0.37	0.5638			
Cu1-N4	1.931(4)	1.713	0.37	0.5548			
Cu1-O1	1.983(3)	1.655	0.37	0.4121			
Cu1-S1	2.6444(17)	2.024	0.37	0.1869			
Cu2-N3^{ii}	2.033(3)	1.571	0.37		0.2869		0.9788
Cu2-N3^{iv}	2.033(3)	1.571	0.37		0.2869		
Cu2-S2	2.4249(14)	1.834	0.37		0.2025		
Cu2-S2^{v}	2.4249(14)	1.834	0.37		0.2025		
Cu3-N5^{i}	1.938(5)	1.571	0.37			0.3708	1.1418
Cu3-N5^{iii}	1.938(5)	1.571	0.37			0.3708	
Cu3-S2	2.4292(15)	1.834	0.37			0.2001	
Cu3-S2^{v}	2.4292(15)	1.834	0.37			0.2001	