Electronic supplementary information

A mixed-valence copper chloride coordination polymer composed of one-dimensional cationic and anionic substructures

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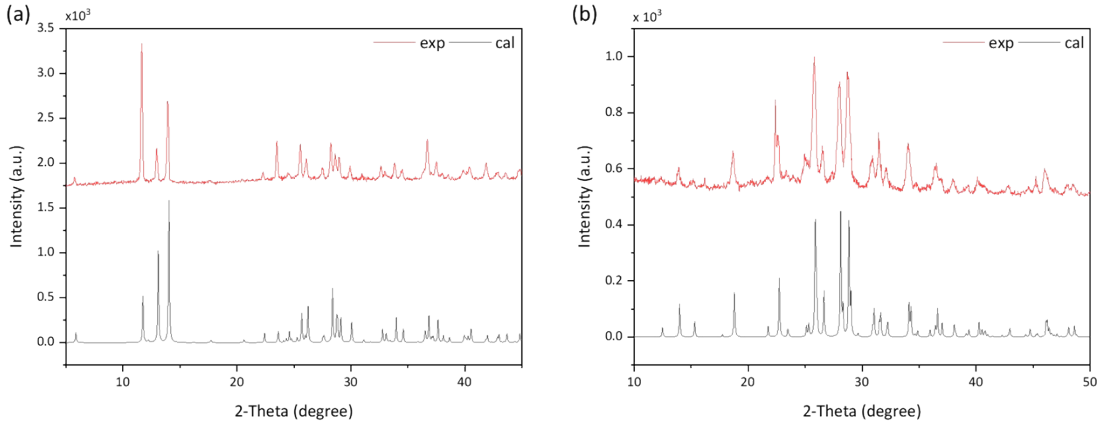

Figure S1 Powder X-ray diffraction patterns for (a) compound (**1**) and (b) compound (**2**) (red line). For comparison, calculated X-ray diffraction patterns (black line) were included.

Table S1 Detailed crystallographic information for (**1**) and (**2**).

Compound	(**1**)	(**2**)
Chemical formula	$C_4H_{12}Cl_6Cu_3N_{10}$	$C_2H_7Cl_2N_5$
CCDC number	2209556	2209557
M (g mol^{-1})	603.56	172.03
T (K)	296(2)	295(2)
Crystal system	Triclinic	Orthorhombic
Space group	*P*$\bar{1}$	*P*bca
a (Å)	3.71660(10)	14.0559(3)
b (Å)	7.2862(3)	7.0932(2)
c (Å)	15.1680(5)	14.1687(3)
α (deg)	84.5650(10)	90
β (deg)	84.9840(10)	90
γ (deg)	85.1940(10)	90
V (Å^3)	406.15(2)	1412.64(6)
Z	1	8
ρ (g cm^{-3})	2.468	1.618
μ (mm^{-1})	4.889	0.839
Reflections/unique	16905/2036	48171/1769
R(int)	0.0304	0.0433
GOF on F_2	1.101	1.15
R_1, wR_2 [I > 2σ(I)]	0.0435, 0.0954	0.0366, 0.0809
R_1, wR_2 (all data)	0.0475, 0.0973	0.0453, 0.0846

Table S2 Hydrogen bond geometry for (**1**).

D–H···A	H···A	D···A	D–H···A
N2–H2···Cl1[a]	2.67	3.191(3)	119.9
N4–H4A···Cl1[c]	2.59	3.260(4)	136.0
N4–H4B···Cl1[d]	2.85	3.254(3)	111.0
N4–H4B···Cl2	2.52	3.275(4)	147.3
N5–H5A···Cl2[b]	2.49	3.258(4)	149.5
N5–H5B···Cl3	2.50	3.285(4)	152.6

Symmetry codes: (a) -x, -y, 1-z; (b) -1+x, -1+y, z; (c) 1+x, y, z; (d) 1-x, 1-y, 1-z.

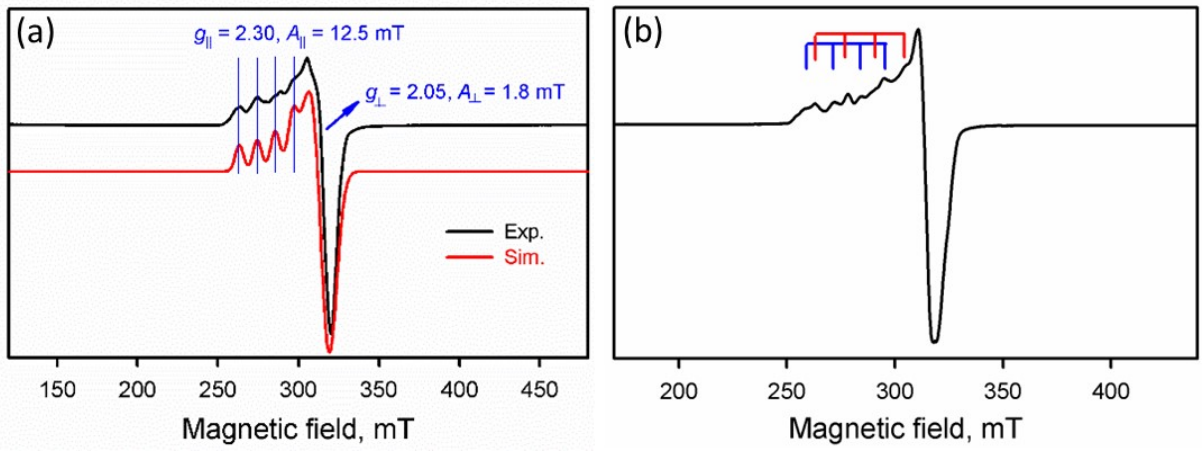

Figure S2 (a) X-band frozen EPR spectrum of (**1**) (black line) in Ar-saturated DMF at 80 K. Red line shows the simulated spectrum with the simulation parameters of g = [2.05, 2.05, 2.30] and A = [1.8, 1.8, 12.5] mT. (b) X-band frozen EPR spectrum of (**1**) in O_2-saturated DMF measured at 80 K. The EPR spectrum exhibits two different Cu^{II} species. One (blue) corresponds to $[Cu^{II}Cl_2(Hdatrz)_2]^{2+}$ and the other (red) is due to one-electron oxidized species of anionic $[Cu^{I}_2Cl_4]^{2-}$ subunit by O_2-activation.

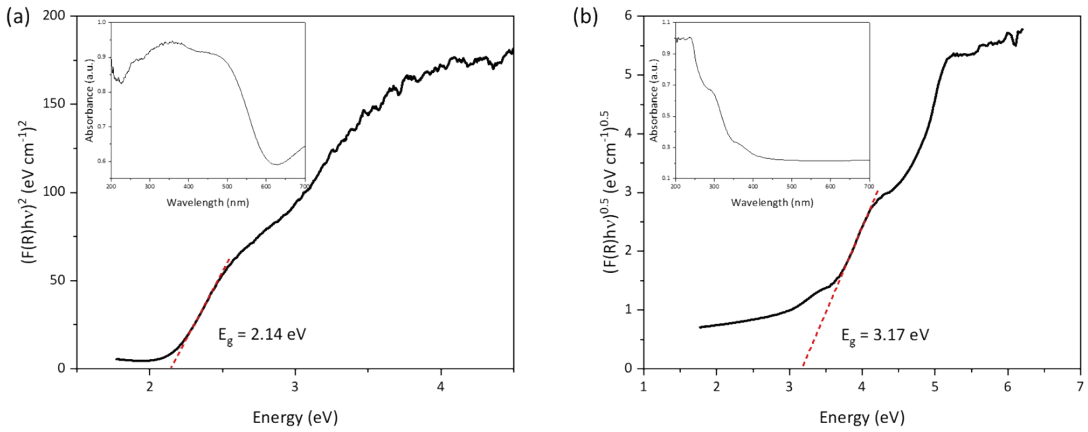

Figure S3 Kubelka-Munk function for (a) compound (**1**) and (b) compound (**2**). The determinations of E_g are shown as dotted red lines. The inset shows the corresponding measured spectrum.

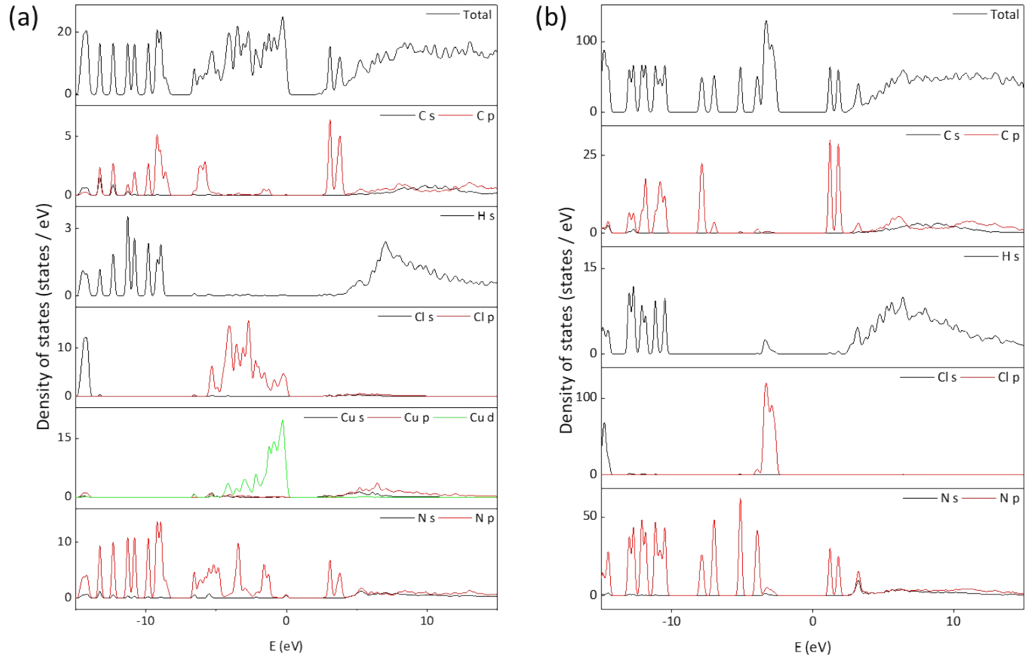

Figure S4 Total and projected density of states for (a) compound (**1**) and (b) compound (**2**).