ELECTRONIC SUPPLEMETARY INFORMATION

Copper Dithiolene $[Cu(SC_6H_2Cl_2S)_2]^-$ Units Connected to Alkaline/Copper Complexes: From Ionic Assemblies to Discrete Molecular Entities and Coordination Polymers

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Table S1. Selected coordination bond distances (Å) for **1** (CCDC 1590257).

Cu1-S1	2.1718(5)	Na1-O1	2.345(2)
Cu1-S1^{i}	2.1719(5)	Na1-O1^{ii}	2.345(2)
Cu1-S2	2.1861(5)	Na1-O2	2.423(2)
Cu1-S2^{i}	2.1862(5)	Na1-O2ii	2.423(2)
		Na1-O3	2.339(3)
		Na1-O4	2.320(3)

Symmetry codes: i) -x+1/2, -y+1/2, -z; ii) -x, y, -z+1/2.

Table S2. Selected coordination bond distances (Å) for **2** (CCDC 1590258).

Cu1-S1	2.170(1)	K1-O1	2.715(4)
Cu1-S1^{i}	2.170(1)	K1-O1^{ii}	2.715(4)
Cu1-S2	2.173(1)	K1-O2	2.690(4)
Cu1-S2^{i}	2.173(1)	K1-O2^{ii}	2.690(4)
		K1-O3	2.694(7)
		K1-O3^{ii}	2.320(3)

Symmetry codes: i) –x+1, -y+1, -z+1; ii) –x+2, -y, -z+1.

Table S3. Selected coordination bond distances (Å) for **3** (CCDC 1590261).

Cu1-S1	2.177(1)	Rb1-O1	2.793(9)
Cu1-S1^{i}	2.177(1)	Rb1-O1^{ii}	3.04(1)
Cu1-S2	2.171(1)	Rb1-S1	3.364(2)
Cu1-S2^{i}	2.171(1)	Rb1-S2^{iii}	3.381(2)
		Rb1-S2^{iv}	3.442(2)
		Rb1-Cl1	3.270(2)
		Rb1-Cl2^{v}	3.458(2)

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

Table S4. Selected coordination bond distances (Å) for **4** (CCDC 1590262).

Cu1-S1	2.176(1)	Cs1-O1	2.898(7)
Cu1-S1^{i}	2.176(1)	Cs1-S1	3.653(1)
Cu1-S2	2.181(1)	Cs1-S1^{ii}	3.653(1)
Cu1-S2^{i}	2.181(1)	Cs1-S2^{iii}	3.632(1)
		Cs1-S2^{iv}	3.632(1)
		Cs1-Cl1	3.582(1)
		Cs1-Cl1^{ii}	3.582(1)
		Cs1-Cl2^{iii}	3.744(1)
		Cs1-Cl2^{iv}	3.744(1)

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

Table S5. Selected coordination bond distances (Å) for **5** (CCDC 1590259).

Cu1-S1	2.174(1)	Cu2-S5	2.171(2)
Cu1-S2	2.167(2)	Cu2-S6	2.186(1)
Cu1-S3	2.190(2)	Cu2-S7	2.188(1)
Cu1-S4	2.176(1)	Cu2-S8	2.195(2)
Cu3-N1	1.979(5)	Cu4-N4	1.988(5)
Cu3-N2	1.974(5)	Cu4-S6	2.470(2)
Cu3-N3	1.989(6)	Cu4-S7	2.267(1)
Cu3-S3	2.395(2)	Cu4-S8	2.378(1)
Cu2···Cu4^{i}	2.6895(9)		

Symmetry codes: i) –x+1, -y+1, -z+1.

Table S6. Selected coordination bond distances (Å) for **6** (CCDC 1590260).

Cu1-S1	2.178(1)	K1-S1	3.343(3)
Cu1-S1^{i}	2.178(1)	K1-S1^{ii}	3.689(3)
Cu1-S2	2.172(1)	K1-S2^{iii}	3.271(4)
Cu1-S2^{i}	2.172(1)	K1-S2^{iv}	2.195(2)
		K1-Cl1	3.218(3)
		K1-Cl2^{iv}	3.410(3)
		K1-O1^{v}	3.01(1)

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

Table S7. Crystallographic data and structure refinement details of compounds **1**-**6**.

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_{36}H_{52}Cl_4CuNaO_6S_4$	$C_{36}H_{52}Cl_4CuKO_6S_4$	$C_{12}H_6Cl_4CuORbS_4$	$C_{12}H_6Cl_4CsCuOS_4$	$C_{68}H_{46}Cl_{16}Cu_8N_{10}S_{16}$	$C_{12}H_6Cl_4CuKOS_4$
M	937.34 g/mol	953.50 g/mol	585.22 g/mol	632.66 g/mol	2591.63 g/mol	538.85 g/mol
Temperatur	100(2) K	200(2) K	200(2) K	200(2) K	200(2) K	200(2) K
Crystal	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*P*2$_1$/*n*	*C*2/*c*	*C*2/*c*	*P*2$_1$/*n*	*C*2/*c*
a/Å	21.8050(6)	12.2137(4)	26.295(4)	10.3169(7)	7.827(1)	26.271(1)
b/Å	12.6126(4	12.4992(5)	3.9413(7)	26.745(2)	13.197(1)	3.9461(2)
c/Å	16.2518(5)	15.7574(5)	17.479(3)	7.6185(5)	44.680(7)	17.3670(7)
β/°	107.833(1)	109.812(2)	102.299(6)	119.840(4)	92.759(5)	102.370(2)°
U/ Å^3	4254.8(2)	2263.2(1)	1769.9(5)	1823.4(2)	4609(1)	1758.6(1)
Z	4	2	4	4	2	4
D_c/Mgm^{-3}	1.463	1.399	2.196	2.305	1.867	2.035
μ/ mm^{-1}	1.013	1.035	5.038	4.206	2.682	2.557
F(000)	1952	992	112836	1208	2568	1064
Goodness of	1.104	1.043	0.990	1.031	1.011	1.120
Reflections	44431	72277	12869	14339	37393	13226
Independen t reflections	5279 [R(int) = 0.0284]	4129 [R(int) = 0.0778]	1600 [R(int) = 0.1101]	1655 [R(int) = 0.0467]	8452 [R(int) = 0.0948]	1612 [R(int) = 0.0708]
R indices [I>2σ(I)]	R_1=0.0344, *w*R_2= 0.0911	R_1=0.0536, *w*R_2= 0.1388	R_1=0.0407, *w*R_2= 0.0768	R_1=0.0298, *w*R_2= 0.0664	R_1=0.0491, *w*R_2= 0.0885	R_1=0.0396, *w*R_2= 0.0816
R indices (all data)	R_1=0.0437, *w*R_2 = 0.1085	R_1=0.0910, *w*R_2 = 0.1661	R_1=0.0938, *w*R_2 = 0.0922	R_1=0.0380, *w*R_2 = 0.0699	R_1=0.0913, *w*R_2 = 0.1558040	R_1=0.0564, *w*R_2 = 0.0898
Residual electron density (max, min) (eÅ^{-3})	0.956 and -0.772	0.782 and -0.348	0.516 and -0.558	2.021 and -0.687	0.940 and -0.807	0.294 and -0.388

Comparison of the 2D coordination polymers of compounds 3 and 4

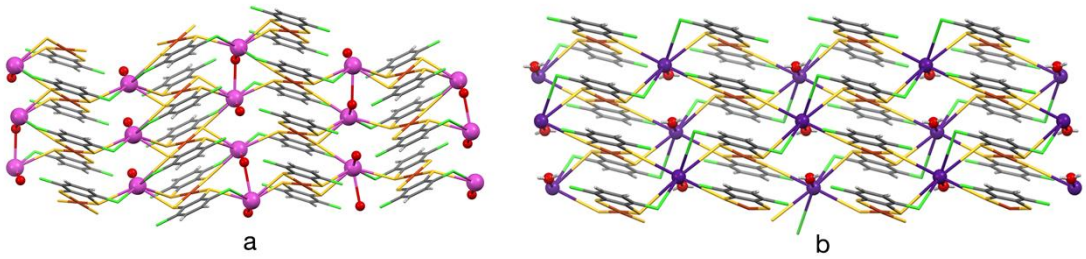

Figure S1. Comparative view of the polymeric layers $\{[M(OH_2)][Cu(SC_6H_2Cl_2S)_2]\}_n$ in compounds **3** (a) and **4** (b).

Disorder of compounds 3 and 6

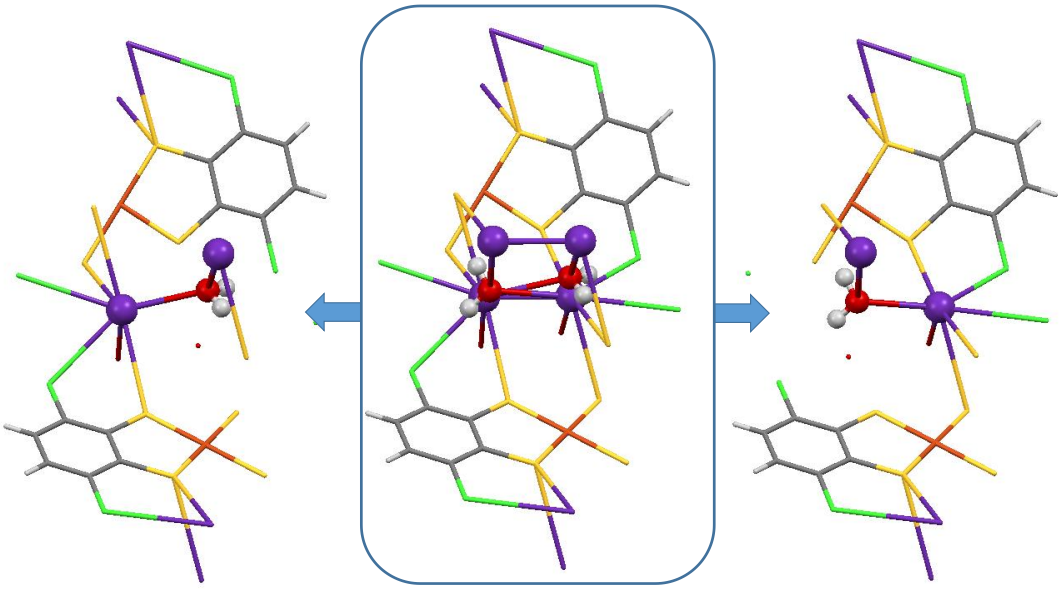

Figure S2. Detail of the disordered structure in the middle and two of the possibilities for the statistical occupation of the atom sites at the sides.

Topological analysis of compound 4

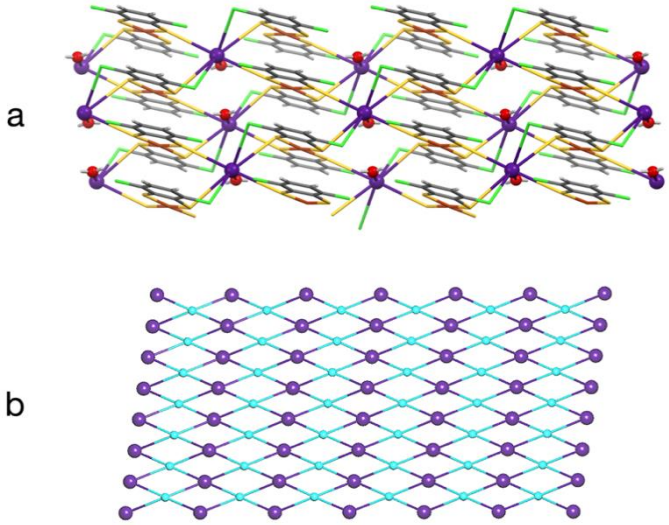

Figure S3. Topological simplification of the structure of compound **4**: (a) view of the polymeric layer $\{[Cs(OH_2)][Cu(SC_6H_2Cl_2S)_2]\}_n$ in compound **4**; (b) projection in the [010] direction of the underlying 2D net with the anionic $[Cu(SC_6H_2Cl_2S)_2]^-$ fragments depicted as cyan spheres and the Cs^+ cations as purple balls.

Electrical Characterization

Direct current (dc) electrical conductivity measurements were performed on different single crystals of compound **4** and pellets of compounds **3** and **4**. The compounds were electrically contacted, with two-contacts and graphite paste. The contacts were made with wolframium wires (25 μm diameter). Measurements were carried out at 300 K applying an electrical current with voltages ranging from +10 to -10 V. The samples were measured in a design equipment connected to an external voltage source (Keithley model 2400 source-meter) and amperometer (Keithley model 6514 electrometer). All the conductivity quoted values have been measured in the voltage range where the crystals are Ohmic conductors.

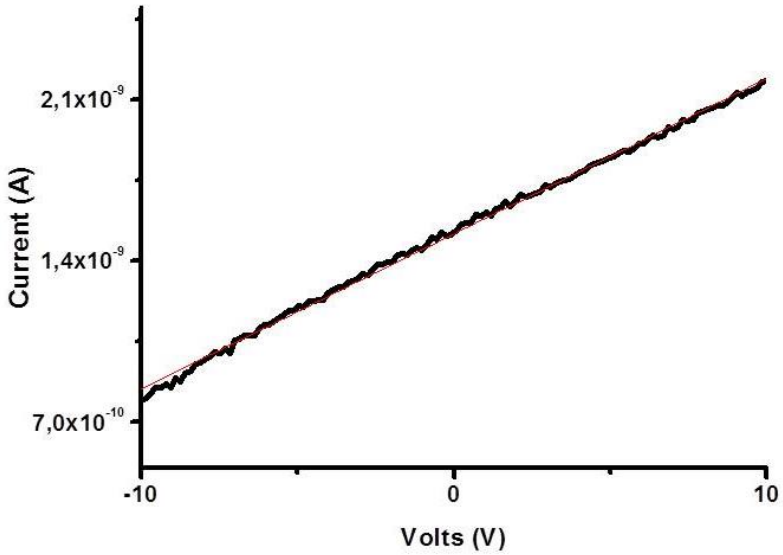

Figure S4. Current *versus* voltage measurements on a crystal of compound **4** at 300 K.

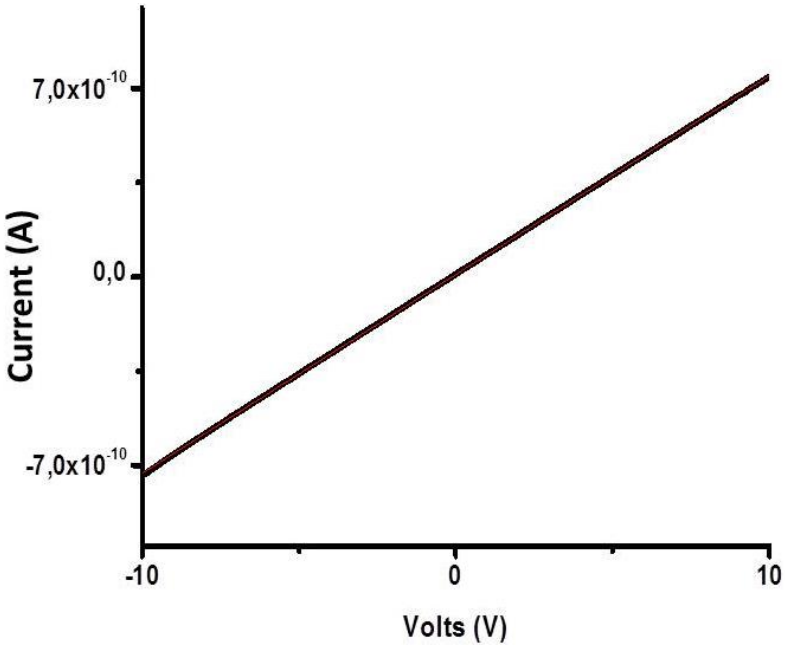

Figure S5. Current *versus* voltage measurements on a pellet of compound **4** at 300 K.

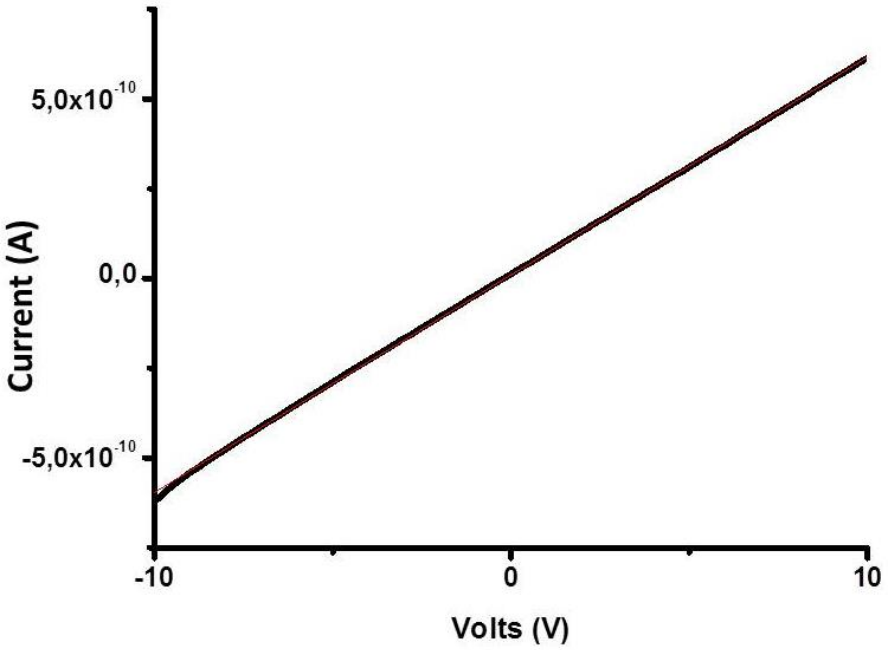

Figure S6. Current *versus* voltage measurements on a pellet of compound **3** at 300 K.