

## **Electronic Supplementary Information**

**For**

### **Networking of macrocycles: 1D and 2D coordination polymers of dithia-18-crown-6 with copper(I) and copper(II)**

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**Table S1** Selected bond lengths (Å) and bond angles (°) for **1**

Cu1-O3	1.998(2)	Cu1-O7	2.006(2)
Cu1-O8#1	2.363(2)	Cu1-O1W	1.912(2)
Cu1-O2W	1.918(2)		
O3-Cu1-O7	158.20(9)	O3-Cu1-O1W	91.37(10)
O3-Cu1-O8#1	81.10(8)	O3-Cu1-O2W	93.41(10)
O7-Cu1-O8#1	120.69(8)	O7-Cu1-O1W	89.21(10)
O7-Cu1-O2W	87.95(11)	O8#1-Cu1-O1W	89.75(10)
O8#1-Cu1-O2W	86.77(11)	O1W-Cu1-O2W	173.58(11)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 x+1,y,z #3 -x+2,-y+2,-z+1 #4 -x+3,-y+3,-z

**Table S2** Selected bond lengths (Å) and bond angles (°) for **2**

Cu1-Cu2	2.6419(18)	Cu1-Cu3	2.7268(19)
Cu1-Cu4	2.762(2)	Cu2-Cu3	2.6668(18)
Cu2-Cu4	2.8489(19)	Cu3-Cu4	2.6557(18)
Cu1-I1	2.6574(14)	Cu1-I2	2.7276(14)
Cu1-I4	2.6804(16)	Cu1-S1	2.299(3)
Cu2-I1	2.7202(15)	Cu2-I2	2.6321(15)
Cu2-I3	2.6725(17)	Cu2-S3	2.305(3)
Cu3-I2	2.6815(16)	Cu3-I3	2.6604(15)
Cu3-I4	2.6915(15)	Cu3-S4#1	2.290(3)
Cu4-I1	2.6621(17)	Cu4-I3	2.7361(16)
Cu4-I4	2.6604(15)	Cu4-S2#2	2.302(3)
I1-Cu1-I2	116.36(5)	I1-Cu1-I4	110.22(6)
I1-Cu1-S1	109.46(9)	I1-Cu2-I2	117.49(5)
I1-Cu2-I3	107.78(5)	I1-Cu4-I3	107.62(5)
I1-Cu4-I4	110.69(6)	I1-Cu4-S2#2	106.55(9)
I2-Cu1-I4	110.03(5)	I2-Cu1-S1	104.02(9)
I2-Cu2-I3	112.29(5)	I2-Cu2-S3	111.92(9)
I2-Cu3-I4	111.10(5)	I3-Cu2-S3	103.70(9)
I3-Cu3-I4	117.37(5)	I3-Cu3-I2	111.11(5)
I3-Cu3-S4#1	110.59(9)	I3-Cu4-I4	115.82(5)
I3-Cu4-S2#2	104.78(9)	I4-Cu1-S1	106.13(9)
I4-Cu4-S2#2	110.85(9)	I4-Cu3-S4#1	105.57(9)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y-1,z-1 #2 x-1,y,z-1 #3 x+1,y,z+1 #4 x+1,y+1,z+1

**Table S3** Selected bond lengths (Å) and bond angles (°) for **3**

Cu1-S1	2.3324(5)	Cu1-S2#1	2.3459(5)
Cu1-I1	2.6942(3)	Cu1-I1#2	2.6120(3)
Co1-O1W	2.1009(15)	Co1-O2W	2.0378(13)
Co1-O3W	2.0932(16)		
S1-Cu1-S2#1	99.462(18)	S1-Cu1-I1#2	113.632(15)
S1-Cu1-I1	108.296(14)	S2#1-Cu1-I1#2	124.028(15)
S2#1-Cu1-I1	100.484(14)	I1-Cu1-I1#2	109.388(10)
Cu1-I1-Cu1#2	70.611(10)	O1W-Co1-O3W	84.48(6)
O2W-Co1-O3W	91.62(6)	O1W-Co1-O2W	89.28(6)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+1,-y,-z+1 #3 -x+1,-y+1,-z

### X-ray structure analysis

In all cases, all nonhydrogen atoms were refined anisotropically and all hydrogen atoms except coordinated water molecules were placed in idealised positions and refined isotropically in a riding manner along with the their respective parent atoms. In the cases of coordinated water molecules, the initial positions of the hydrogen atoms were obtained from difference electron density maps and refined with riding constraints.