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Electronic Supplementary Information (ESI):

Red Phosphorescent Cuprous Halide/Pseudohalide Coordination Polymers with Pyrimidine-2-thionates as Co-ligands

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Scheme S1. Coordination Modes of pymt

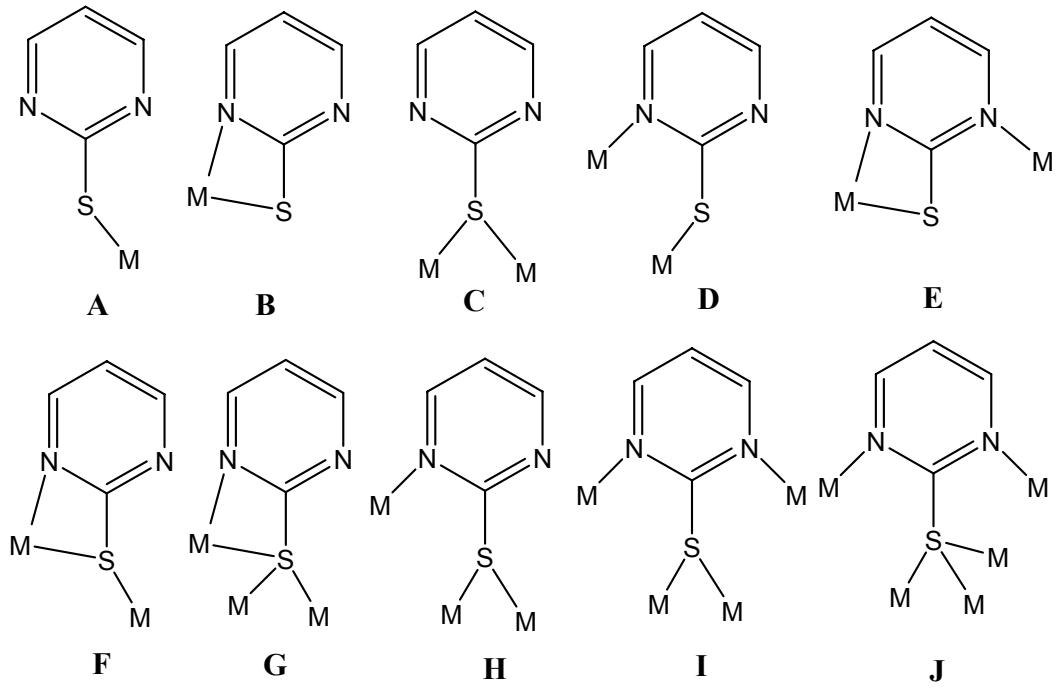

Table S1. Crystallographic data of **1-4**

	1	**2**	**3**	**4**
Formula	$C_4H_3ClCu_2N_2S$	$C_9H_6Cu_3N_5S_3$	$C_8H_6Cu_3IN_4S_2$	$C_{16}H_{12}Cu_{11}I_7N_8S_4$
Fwt	273.67	470.99	539.81	2031.82
T/K	298(2)	298(2)	298(2)	298(2)
Crystal system	triclinic	Monoclinic	monoclinic	orthorhombic
Space group	*P*-1	$P2_1/n$	$P2_1/n$	*P*nma
a/Å	3.8822(8)	10.764(3)	10.4687(16)	17.3499(12)
b/Å	8.0900(17)	7.732(2)	7.7318(12)	15.4640(10)
c/ Å	10.318(2)	16.538(4)	15.289(2)	13.2336(9)
α/°	96.751(4)	90	90	90
β/°	91.577(4)	101.929(5)	95.702(3)	90
γ/°	93.729(4)	90	90	90
V/ $Å^3$	320.93(11)	1346.6(6)	1231.4(3)	3550.6(4)
ρ/g cm^{-3}	2.832	2.323	2.912	3.801
μ/mm^{-1}	7.264	5.151	7.961	12.794

R_1[a][I>2σ(*I*)]	0.0527	0.0494	0.0572	0.0597
wR_2 [all data]	0.1475	0.1104	0.1147	0.1816
S	1.081	1.083	1.123	1.141

[a] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$. [b] $wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$

Table S2. Selected Bond Lengths (Å) and Angles (°) for **1-4**

1			
Cu(1)-N(2a)	2.016(6)	Cu(1)-S(1)	2.2506(18)
Cu(1)-Cl(1)	2.530(2)	Cu(1)-S(1b)	2.371(2)
Cu(2)-N(1)	1.955(6)	Cu(2)-S(1c)	2.182(2)
Cu(2)-Cl(1c)	2.669(2)		
S(1)-Cu(1)-S(1b)	114.25(8)	S(1b)-Cu(1)-Cl(1)	103.61(8)
N(2a)-Cu(1)-Cl(1)	100.56(16)	S(1)-Cu(1)-Cl(1)	84.66(7)
N(2a)-Cu(1)-S(1)	141.65(18)	N(1)-Cu(2)-Cl(1c)	100.34(17)
N(1)-Cu(2)-S(1c)	174.69(18)	S(1c)-Cu(2)-Cl(1c)	82.71(7)
N(2a)-Cu(1)-S(1b)	101.50(17)		

Symmetry code for **1**: a) –x, -y+1, -z+2; b) x+1, y, z; c) –x-1, -y+2, -z+2.

2			
Cu(1)-N(2)	1.979(4)	Cu(1)-S(2a)	2.2122(14)
Cu(1)-S(3)	2.2901(15)	Cu(2)-N(3)	2.067(4)
Cu(2)-N(5b)	2.032(5)	Cu(2)-S(1)	2.2731(16)
Cu(2)-S(3)	2.4955(17)	Cu(3)-S(1)	2.2320(15)
Cu(3)-S(2)	2.2803(14)	Cu(3)-N(4a)	2.024(4)
Cu(1)-Cu(2)	2.7124(10)	Cu(1)-Cu(3)	2.7240(11)
N(2)-Cu(1)-S(2a)	138.41(13)	N(2)-Cu(1)-S(3)	111.66(13)
S(2a)-Cu(1)-S(3)	109.09(5)	N(5b)-Cu(2)-N(3)	99.6(2)
N(5b)-Cu(2)-S(1)	103.35(16)	N(3)-Cu(2)-S(1)	128.14(12)
N(5b)-Cu(2)-S(3)	103.83(17)	N(3)-Cu(2)-S(3)	95.36(13)
S(1)-Cu(2)-S(3)	122.53(5)	N(4a)-Cu(3)-S(1)	130.12(11)
N(4a)-Cu(3)-S(2)	110.35(11)	S(1)-Cu(3)-S(2)	118.76(5)

Symmetry code for **2**: a) –x+3/2, y-1/2, -z+1/2; b) –x+3/2, y+1/2, -z+1/2.

3			
Cu(1)-I(1)	2.6139(12)	Cu(1)-S(2)	2.203(2)
Cu(2)-N(3)	2.025(6)	Cu(2)-S(2a)	2.290(2)
Cu(1)-N(1)	1.987(6)	Cu(2)-S(1)	2.248(2)
Cu(3)-I(1)	2.7066(12)	Cu(3)-N(4a)	2.016(6)
Cu(3)-S(1)	2.2363(19)		
N(1)-Cu(1)-S(2)	135.92(18)	N(1)-Cu(1)-I(1)	104.79(17)
S(2)-Cu(1)-I(1)	118.50(6)	N(3)-Cu(2)-S(1)	129.16(17)
S(1)-Cu(2)-S(2a)	121.58(8)	N(4a)-Cu(3)-S(1)	135.85(19)
N(4a)-Cu(3)-I(1)	98.91(18)	S(1)-Cu(3)-I(1)	121.89(6)

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N(3)-Cu(2)-S(2a)	109.17(17)

Symmetry code for **3**: a) –x+3/2, y-1/2, -z+1/2; b) –x+1/2, y+1/2,-z+1/2.

4

Cu(1)-S(1a)	2.347(4)	Cu(1)-S(1b)	2.347(4)
Cu(1)-I(2)	2.617(3)	Cu(2)-S(2)	2.358(3)
Cu(1)-I(1)	2.606(3)	Cu(2)-S(2c)	2.358(3)
Cu(2)-I(5)	2.593(3)	Cu(2)-I(6)	2.715(3)
Cu(3)-N(1)	2.038(9)	Cu(3)-I(6)	2.912(2)
Cu(3)-S(2)	2.300(4)	Cu(3)-I(4)	2.655(2)
Cu(4)-N(3c)	1.953(10)	Cu(4)-N(3)	1.953(10)
Cu(4)-I(1)	2.958(3)	Cu(5)-N(2b)	1.931(10)
Cu(5)-N(2a)	1.931(10)	Cu(6)-S(2c)	2.417(4)
Cu(6)-S(2)	2.417(4)	Cu(6)-I(1)	2.630(3)
Cu(6)-I(2)	2.632(3)	Cu(7)-I(4)	2.789(5)
Cu(7)-N(4)	1.973(12)	Cu(7)-S(1)	2.203(5)
Cu(8)-I(5a)	2.685(4)	Cu(8)-I(4a)	2.617(4)
Cu(8)-S(1)	2.406(6)	Cu(8)-I(3)	2.632(4)
Cu(7')-N(4)	1.953(13)	Cu(7')-S(1)	2.075(6)
Cu(8')-I(3)	2.632(6)	Cu(8')-I(4a)	2.606(5)
Cu(8')-I(5a)	2.735(5)	Cu(8')-I(6a)	2.824(6)
S(1a)-Cu(1)-S(1b)	100.07(18)	S(1a)-Cu(1)-I(1)	114.14(10)
S(1b)-Cu(1)-I(1)	114.14(10)	S(1a)-Cu(1)-I(2)	109.64(11)
S(1b)-Cu(1)-I(2)	109.64(11)	I(1)-Cu(1)-I(2)	108.90(10)
S(2)-Cu(2)-S(2c)	104.79(18)	S(2)-Cu(2)-I(5)	116.79(10)
S(2c)-Cu(2)-I(5)	116.79(10)	S(2)-Cu(2)-I(6)	96.70(10)
S(2c)-Cu(2)-I(6)	96.70(10)	I(5)-Cu(2)-I(6)	121.37(11)
N(1)-Cu(3)-S(2)	134.0(3)	N(1)-Cu(3)-I(4)	105.3(3)
S(2)-Cu(3)-I(4)	113.36(11)	N(1)-Cu(3)-I(6)	100.8(3)
S(2)-Cu(3)-I(6)	92.77(10)	N(3c)-Cu(4)-N(3)	159.7(6)
N(3c)-Cu(4)-I(1)	99.8(3)	N(3)-Cu(4)-I(1)	99.8(3)
N(2b)-Cu(5)-N(2a)	170.9(6)	S(2c)-Cu(6)-S(2)	101.23(19)
S(2c)-Cu(6)-I(1)	113.73(11)	S(2)-Cu(6)-I(1)	113.73(11)
S(2c)-Cu(6)-I(2)	110.19(11)	S(2)-Cu(6)-I(2)	110.19(11)
I(1)-Cu(6)-I(2)	107.70(12)	N(4)-Cu(7)-S(1)	143.1(5)
N(4)-Cu(7)-I(4)	108.9(4)	S(1)-Cu(7)-I(4)	107.81(18)
S(1)-Cu(8)-I(4a)	113.86(16)	S(1)-Cu(8)-I(3)	94.91(16)
I(4a)-Cu(8)-I(3)	113.17(13)	S(1)-Cu(8)-I(5a)	109.55(16)
I(4a)-Cu(8)-I(5a)	108.55(15)	I(5a)-Cu(8')-I(6a)	112.7(2)
I(3)-Cu(8)-I(5a)	116.37(13)	N(4)-Cu(7')-S(1)	159.0(6)
I(4a)-Cu(8')-I(3)	113.5(2)	I(4a)-Cu(8')-I(5a)	107.37(18)
I(3)-Cu(8')-I(5a)	114.6(2)	I(4a)-Cu(8')-I(6a)	108.7(2)
I(3)-Cu(8')-I(6a)	99.77(17)		

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Symmetry code for **4**: a) –x+1/2, -y, z+1/2; b) –x+1/2, y-1/2, z+1/2; c) x, -y-1/2, z.

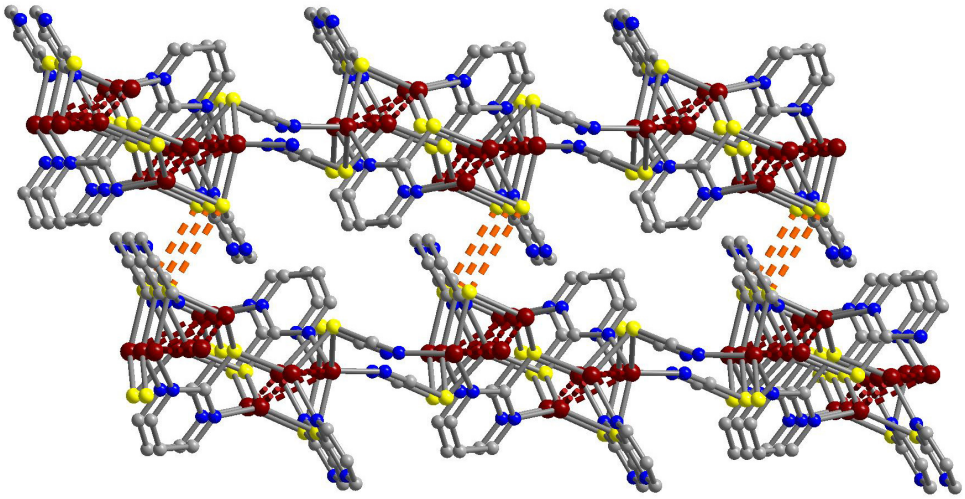

Figure S1. Three-dimensional supramolecular array showing S···S interactions in **2**

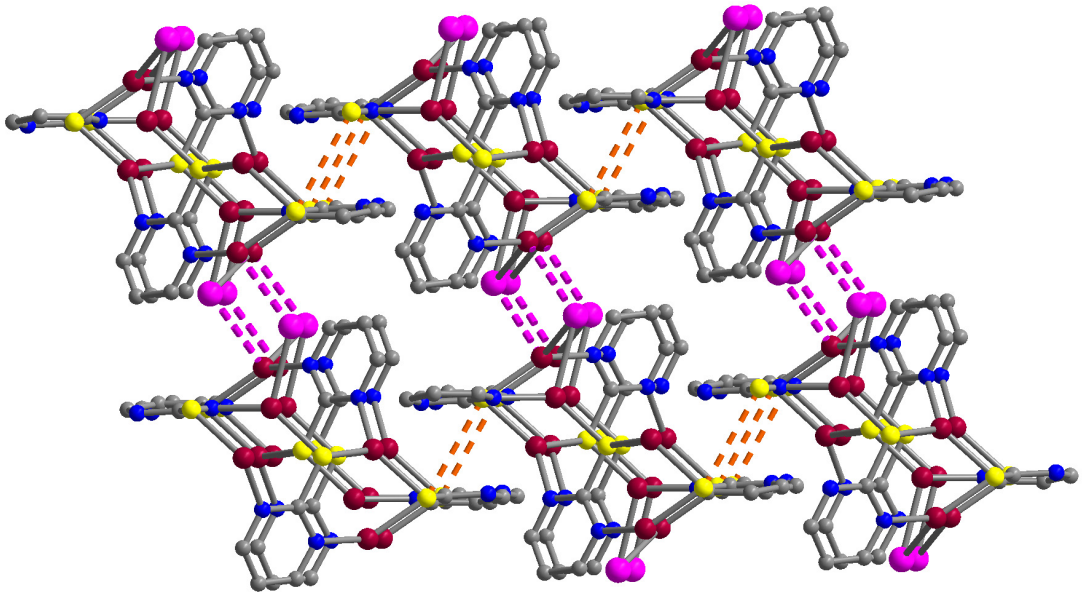

Figure S2. Supramolecular array constructed by helical chains via weak Cu–I and S…S interactions in **3**.