2,2'-Ethylenebis(1,3-dithiane) as polydentate μ_2-, μ_4- and μ_5-assembling ligand for the construction of sulphur-rich Cu(I), Hg(II) and heterometallic Cu(I)/Hg(II) coordination polymers featuring uncommon network architectures

Lydie Viau,*[a] Michael Knorr,*[a] Lena Knauer,[b] Lukas Brieger,[b] and Carsten Strohmann*[b]

Table of contents

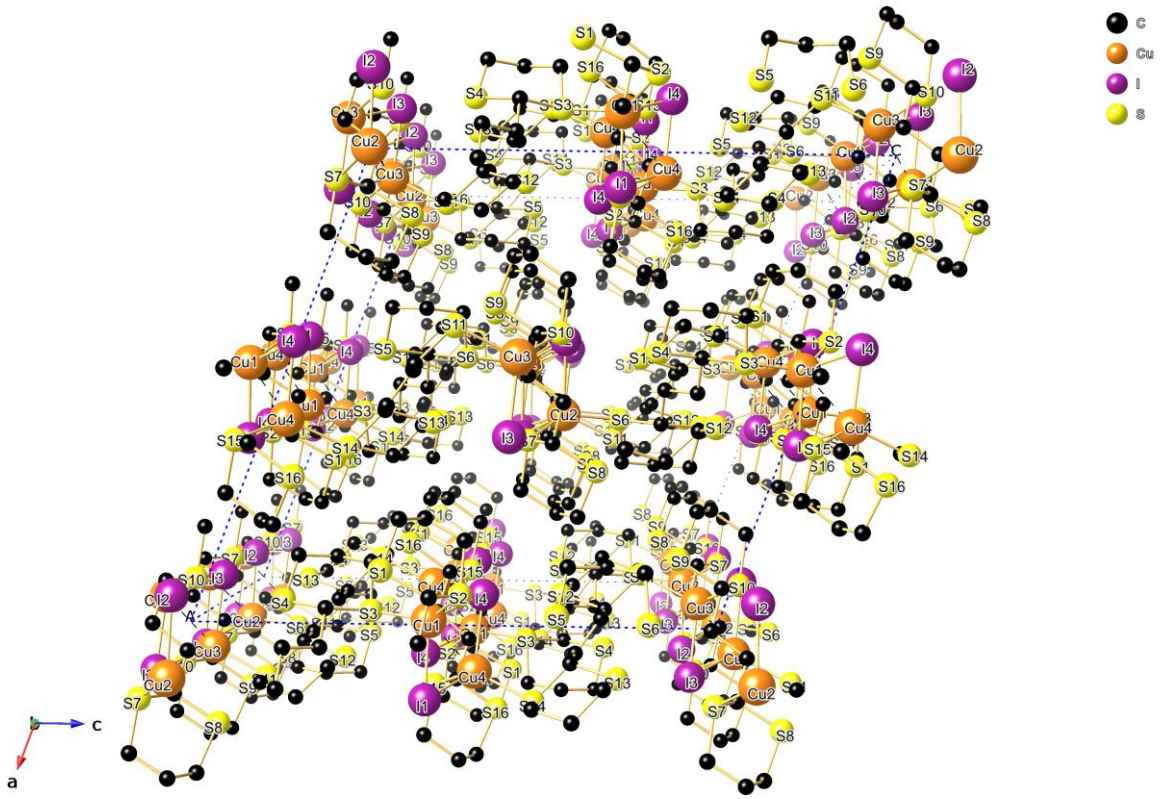

Figure S1. View down the *b* axis of three layers of the 2D network of $[\{Cu(\mu_2\text{-}I)_2Cu\}(\mu_2\text{-}\mathbf{L1})_2]_n$ **CP1**.

Selected angles (°) at 100 K: Cu1A-I1A-Cu4^1 65.144(10), Cu2-I2A-Cu2^2 64.360(9), Cu3-I3-Cu3^3 66.954(9), Cu4-I4-Cu1A^4 65.427(9), I1A-Cu1A-I4^1 114.236(11), I1A-Cu1A-Cu4^1 57.537(7), I4^1-Cu1A-Cu4^1 56.950(8), S2-Cu1A-I1A 108.639(15), S2-Cu1A-I4^1 94.816(15), S2-Cu1A-Cu4^1 116.447(17), S2-Cu1A-S3 136.45(2), S3-Cu1A-I1A 98.417(17), S3-Cu1A-I4^1 104.548(16), S3-Cu1A-Cu4^1 106.776(16), I2A-Cu2-I2A^2 115.641(9), I2A^2-Cu2-Cu2^2 57.281(8), I2A-Cu2-Cu2^2 58.361(8), S6-Cu2-I2A^2 97.718(14), S6-Cu2-I2A 99.428(14), S6-Cu2-Cu2^2 106.242(16), S7-Cu2-I2A 96.568(14), S7-Cu2-I2A^2 106.490(14), S7-Cu2-Cu2^2 112.012(16), S7-Cu2-S6 141.460(19), I3-Cu3-I3^3 113.046(8), I3^3-Cu3-Cu3^3 57.325(8), I3-Cu3-Cu3^3 57.325(8), S10-Cu3-I3^3 93.476(13), S10-Cu3-I3 108.460(14), S10-Cu3-Cu3^3 109.864(15), S10-Cu3-S11 121.608(18), S11-Cu3-I3 111.015(14), S11-Cu3-I3^3 108.138(14), S11-Cu3-Cu3^3 127.358(17), I1A^4-Cu4-Cu1A^4 57.318(9), I4-Cu4-I1A^4 114.687(10), I4-Cu4-Cu1A^4 57.624(8), S14-Cu4-I1A^4 103.824(15), S14-Cu4-I4 110.421(14), S14-Cu4-Cu1A^4 127.750(17), S15-Cu4-I1A^4 95.011(13), S15-Cu4-I4 105.353(13), S15-Cu4-Cu1A^4 104.282(14), S15-Cu4-S14 126.926(18). Symmetry transformations used to generate equivalent atoms: ^{1}+ *x*,+ *y*,1+*z*; ^{2}1-*x*, 2-*y*, 1-*z*; ^{3}1-*x*, 1-*y*,1-*z*; ^{4}+*x*,+*y*,-1+*z*.

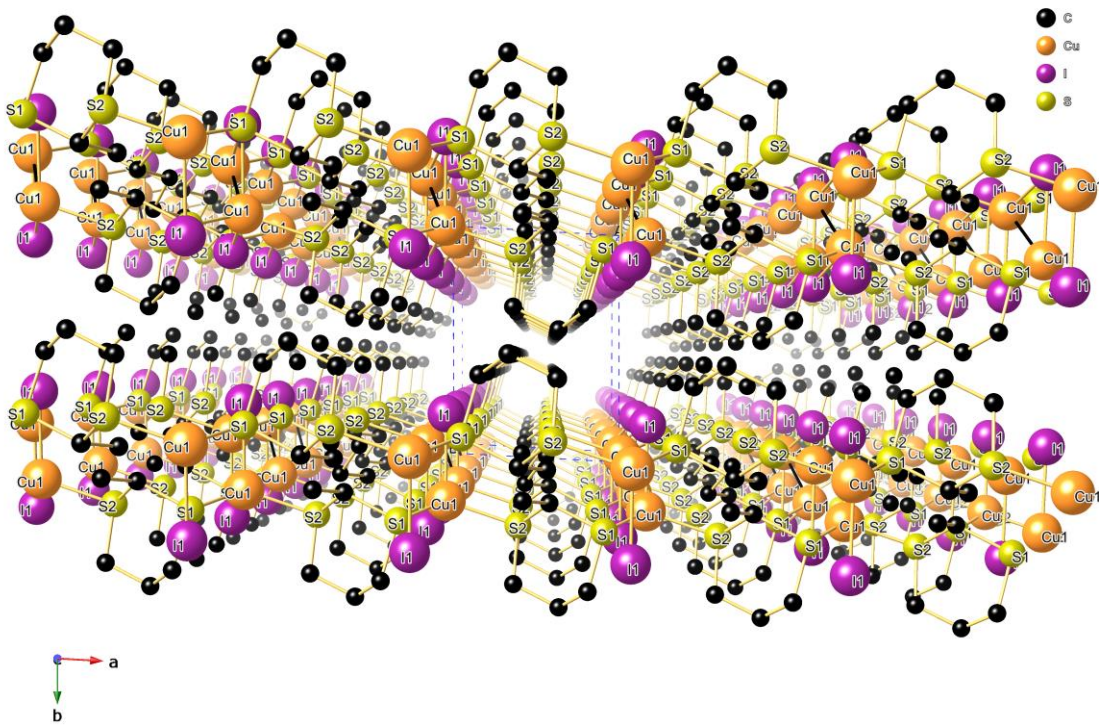

Figure S2. View down the *c* axis of two layers of the 2D network of $[\{Cu(\mu_2\text{-}I)_2Cu\}(\mu_4\text{-}L1)]_n$ **CP2**.

Selected angles (°) at 100 K: S1–Cu–S2 118.02(3), S1–Cu–I 118.40(3), S1–Cu–I# 94.81(3), S2–Cu–I 97.77(3), S2–Cu–I# 107.86(3), I–Cu–I# 121.050(17), Cu–I–Cu# 58.950(17). Symmetry transformations used to generate equivalent atoms: ^{1}-*x*, 2-*y*, 1-*y*; ^{2}-1+*x*, +*y*, +*z*; ^{3}1-*x*, 2-*y*, 2-*z*.

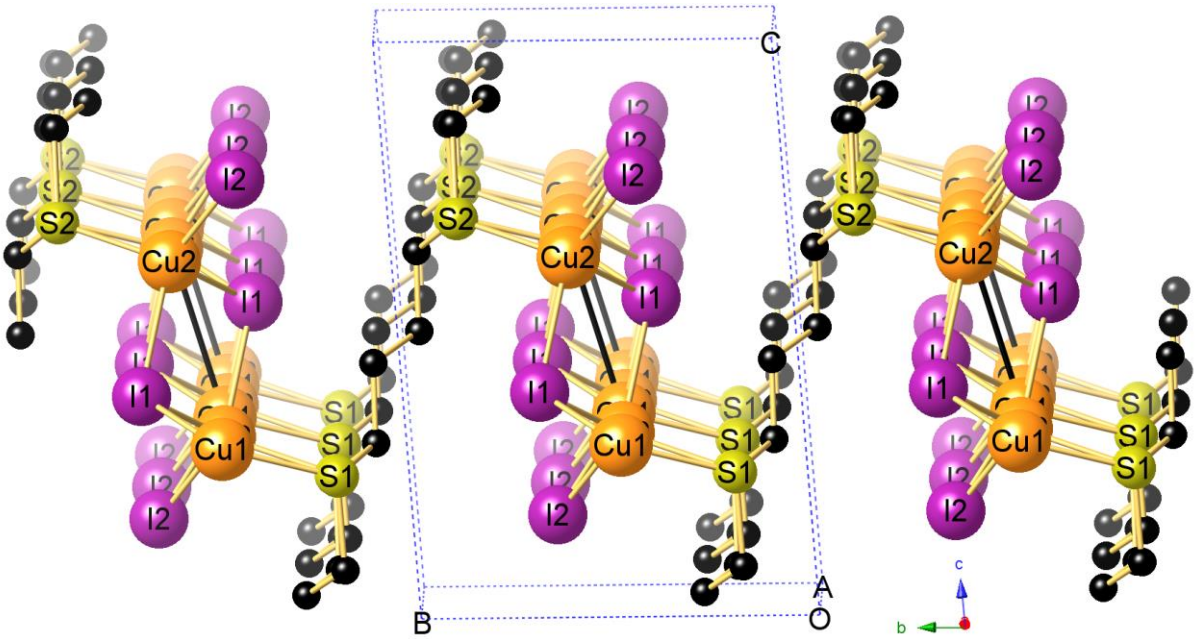

Figure S3. View down the *a* axis of the *bc* plane of **CP3**.

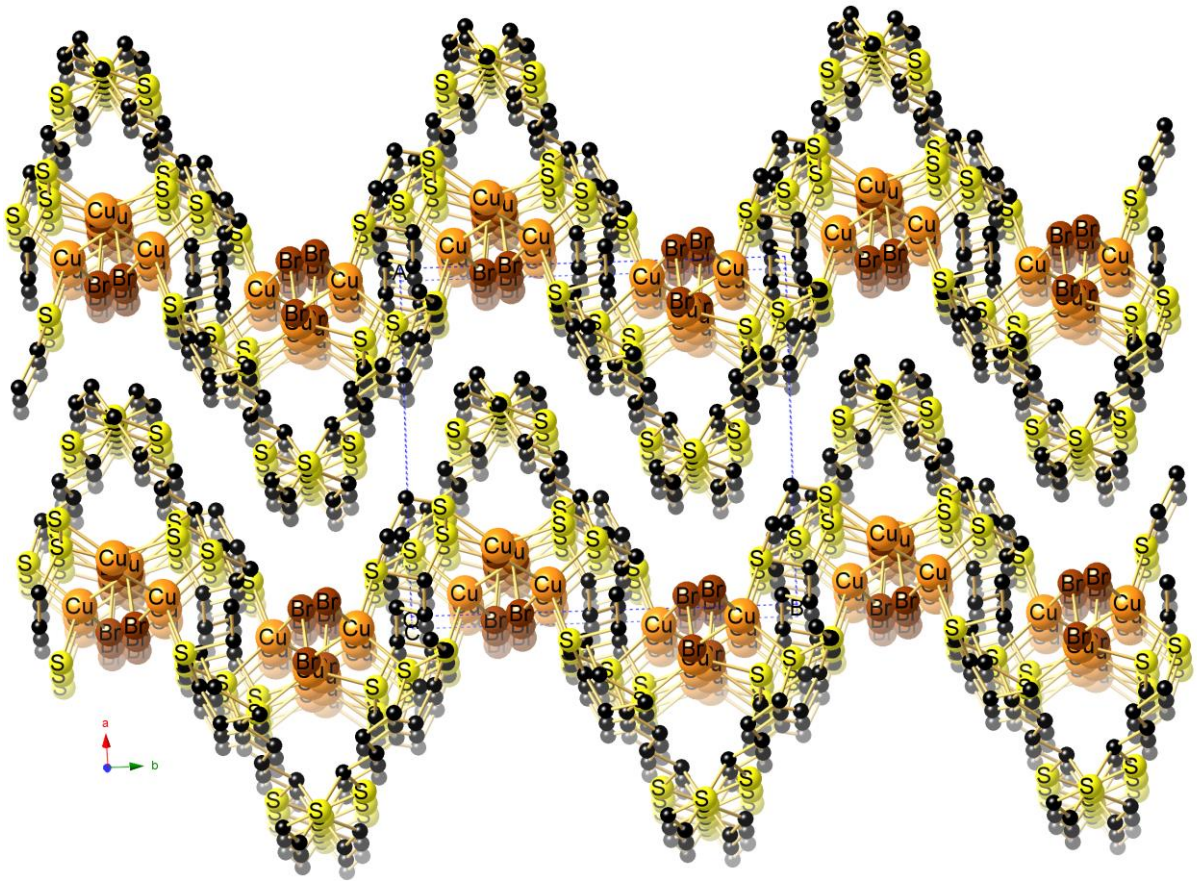

Figure S4. View down the *c* axis on the *ab* plane showing two layers of the 2D network of $[\{Cu(\mu_2\text{-}Br)\}_2(\mu_2\text{-}\mathbf{L1})(\mu_4\text{-}\mathbf{L1})_{0.5}]_n$ (**CP4**).

Selected bond angles [°] at 100 K: Cu2–Br1–Cu1 97.945(19), Cu2–Br2–Cu1^1 127.267(17), Br1-Cu1-Br2^2 113.937(19), S1-Cu1-Br1 105.47(2), S1-Cu1-Br2^2 100.66(2), S3-Cu1-Br1 112.49(2), S3-Cu1-Br2^2 98.30(2), S3-Cu1-S1 125.31(3), Br1-Cu2-Br2 111.701(18), Br1-Cu2-Br2 111.701(18), S2^3-Cu2-Br1 101.31(3), S2^3-Cu2-Br2 106.02(2), S4-Cu2-Br1 114.21(2), S4-Cu2-Br2 109.49(3), S4-Cu2-S2^3 113.64(3). Symmetry transformations used to generate equivalent atoms: ^{1}+*x*, ½-*y*, ½+*z*; ^{2}1-*x*, 1-*y*, 1-*z*; ^{3}+*x*, ½-*y*, +*z*, ^{4}1-*x*, -½+*y*, ½-*z*, ^{5}1-*x*, ½+*y*, ½-*z*.

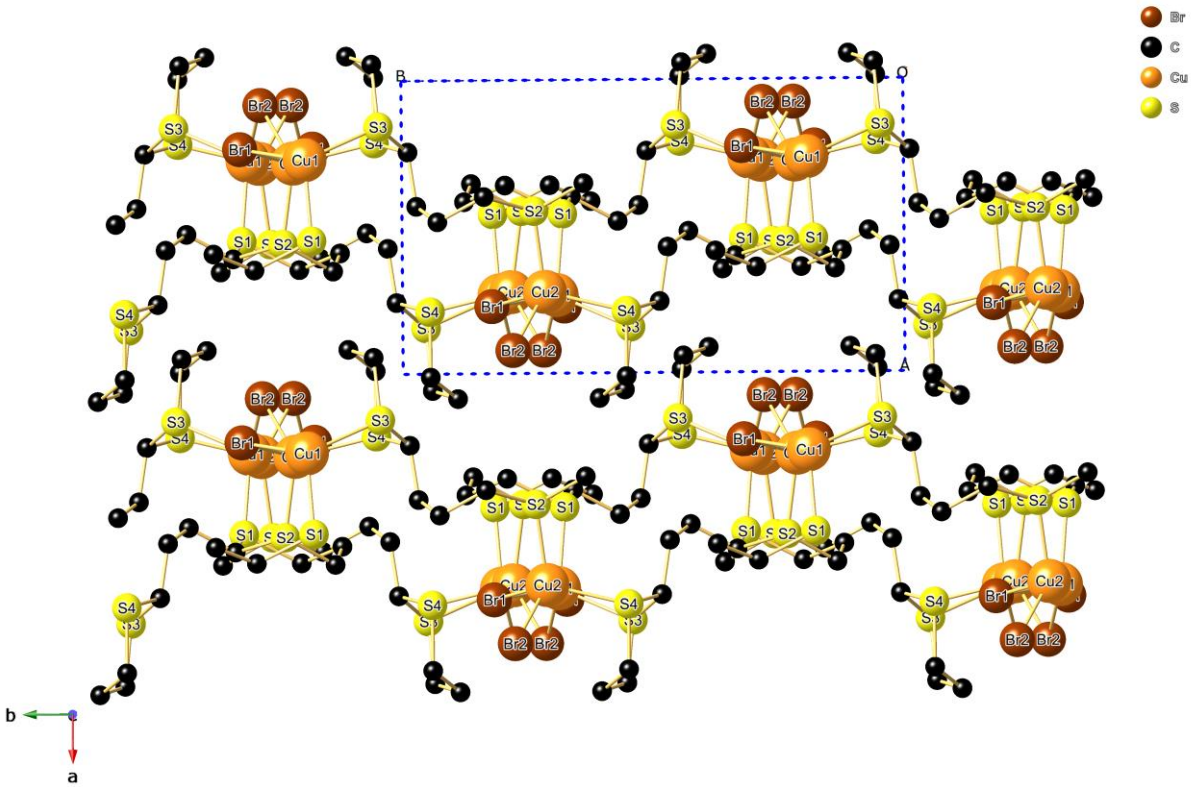

Figure S5. View down the *c* axis on the *ab* plane showing two layers of the 2D network of $[\{Cu(\mu_2\text{-}Br)\}_2(\mu_4\text{-}\mathbf{L1})]_n$ **CP5**.

Selected bond angles [°] at 100 K: S1–Cu1–S3^4 111.34(3), S2–Cu2–S4^3 110.63(3), Cu1-Br1-Cu2^1 95.446(17), Cu1-Br2-Cu2 100.585(17), Br1-Cu1-Br2 110.070(17), S1-Cu1-Br1 107.80(2), S1-Cu1-Br2 117.62(2), S3^4-Cu1-Br1 113.18(2), S3^4-Cu1-Br2 96.68(2), Br2-Cu2-Br1^2 103.363(17), S2-Cu2-Br1^2 101.45(2), S2-Cu2-Br2 118.97(2), S4^3-Cu2-Br1^2 122.25(2), S4^3-Cu2-Br2 101.16(2) Symmetry transformations used to generate equivalent atoms: ^1x, ½-y, ½+z; ^{2}+x, ½-y, ½+z; ^{3}1-x, -1/2+y, 1/2-z; ^{4}1-x,1-y,1-z.

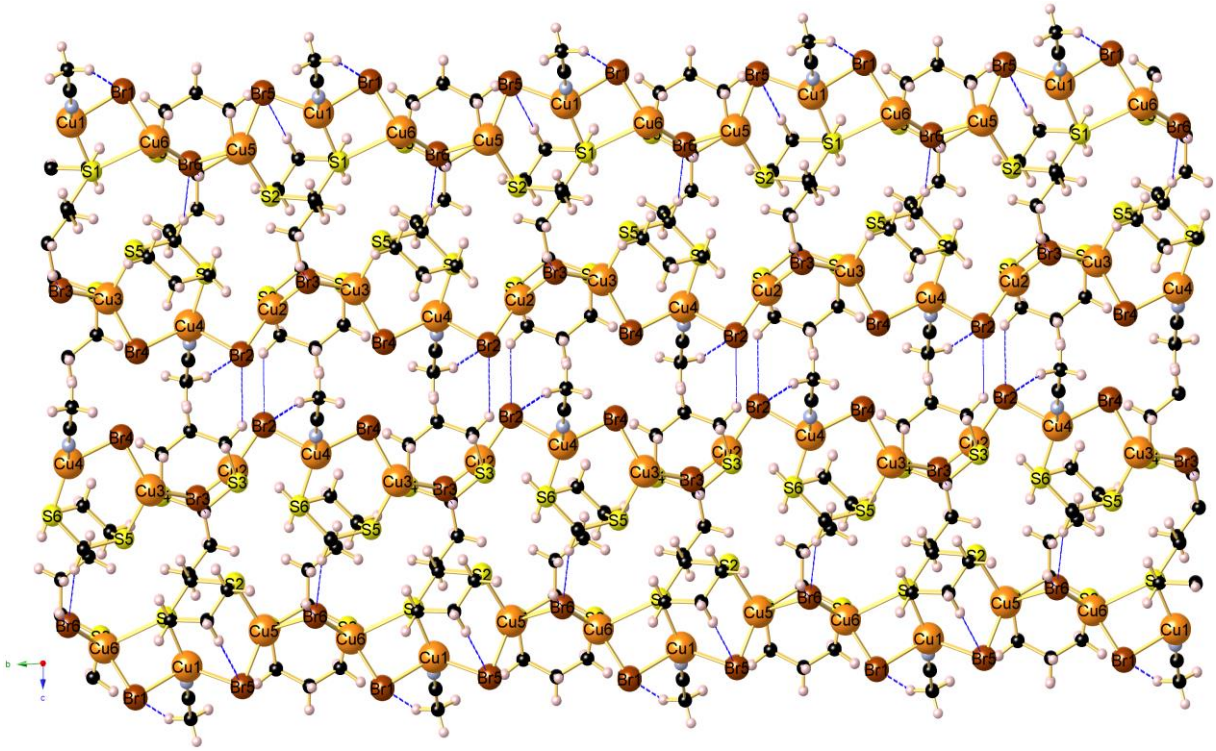

Figure S6. A view along the *b* axis of the crystal packing of **CP6**. The C—H···Br hydrogen bonds are shown as dashed lines.

Selected bond angles [°] at 100 K: Cu6-Br1-Cu1 86.095(11), Cu2-Br2-Cu4^{1} 85.690(10), Cu2-Br3-Cu3 86.593(10), Cu3-Br4-Cu4 88.610(10), Cu5-Br5-Cu1^{2} 87.092(10), Cu6-Br6-Cu5 90.168(10), Br5^{1}-Cu1-Br1 114.647(11), S1-Cu1-Br1 88.147(13), S1-Cu1-Br5^{1} 116.754(14), N1-Cu1-Br1 102.761(5), N1-Cu1-Br5^{1} 103.15(5), N1-Cu1-S1 129.55(5), Br3-Cu2-Br2 113.534(11), S3-Cu2-Br2 119.320(15), S3-Cu2-Br3 127.119(15), Br4-Cu3-Br3 110.546(11), S4-Cu3-Br3 119.028(143), S4-Cu3-Br4 110.145(14), S4-Cu3-S5 110.445(17), S5-Cu3-Br3 89.848(13), S5-Cu3-Br4 115.767(14), Br4-Cu4-Br2^{2} 110.040(10), S6-Cu4-Br2^{2} 92.521(14), S6-Cu4-Br4 119.944(14), N2-Cu4-Br2^{2} 101.94(5), N2-Cu4-Br4 100.99(5), N2-Cu4-S6 128.49(5), Br5-Cu5-Br6 111.723(10), S2^{2}-Cu5-Br5 118.267(14), S2^{2}-Cu5-Br6 91.616(13), S7-Cu5-Br5 108.229(143), S7-Cu5-Br6 116.736(13), S7-Cu5-S2^{2} 109.898(16), Br1-Cu6-S1 81.800(12), Br6-Cu6-Br1 118.119(12), Br6-Cu6-S1 105.731(14), S8-Cu6-Br1 114.194(15), S8-Cu6-Br6 125.243(15), S8-Cu6-S1 96.326(16), Cu1-S1-Cu6 84.189(15) Symmetry transformations used to generate equivalent atoms: ^{1}+*x*,-1+*y*,+*z*; ^{2}+*x*,1+*y*,+*z*.

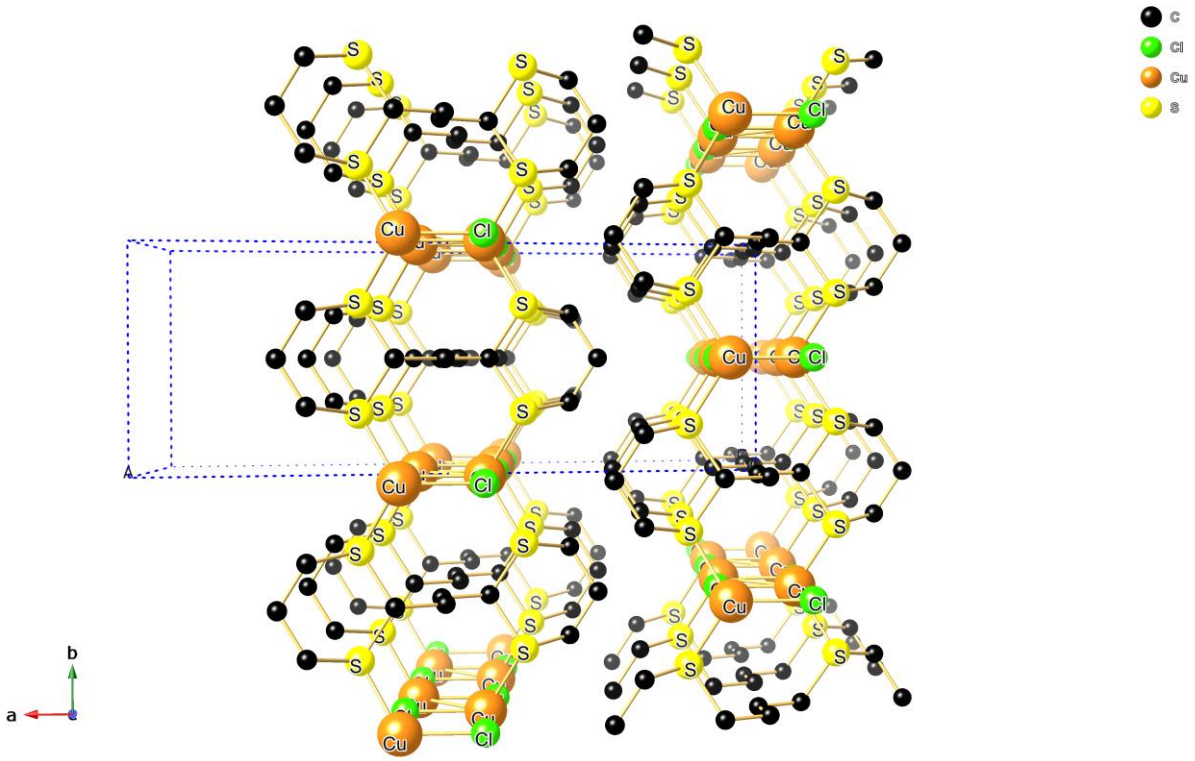

Figure S7. View down the *c* axis on the *ab* plane showing two layers of the 2D network of $[\{Cu(\mu_2\text{-}Cl)_2Cu\}(\mu_4\text{-}\mathbf{L1})]_n$ **CP7**.

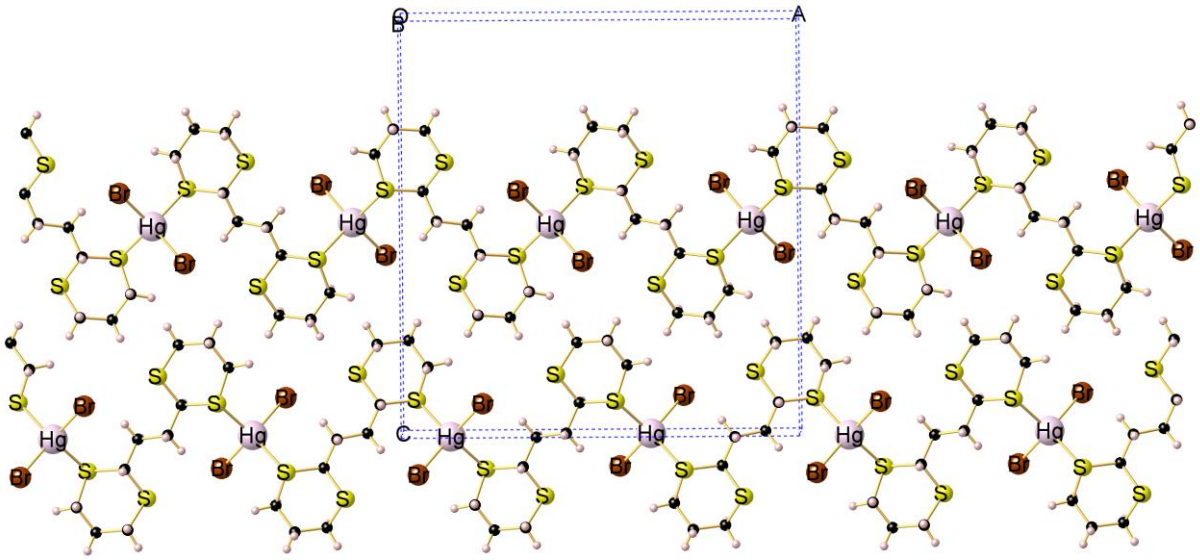

Figure S8. View of the unit cell of **CP9** containing two parallel running 1D ribbons.

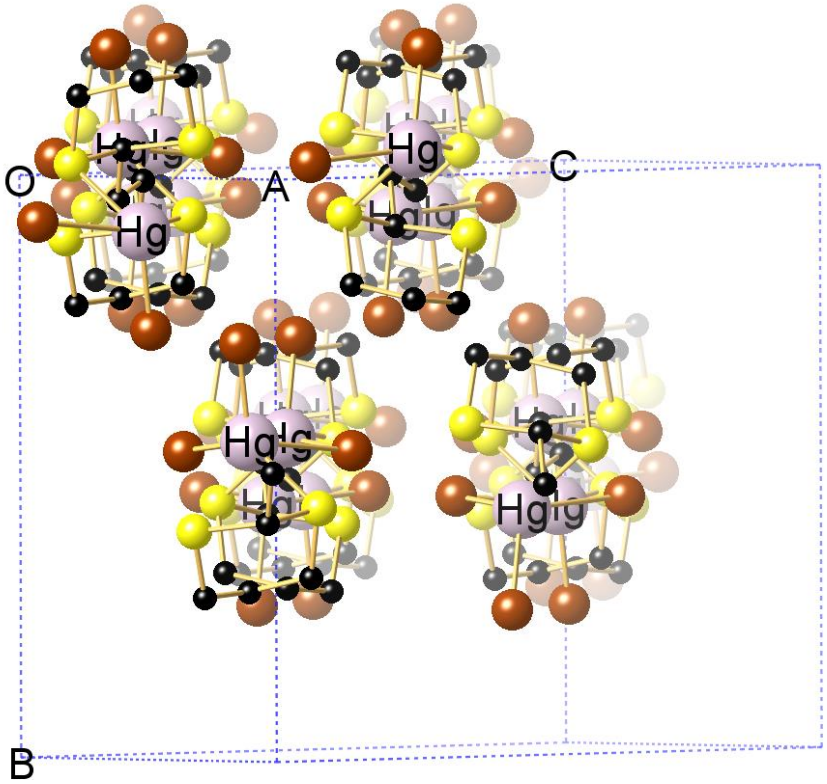

Figure S9. View of the packing of the ribbons of **CP10** within the unit cell.

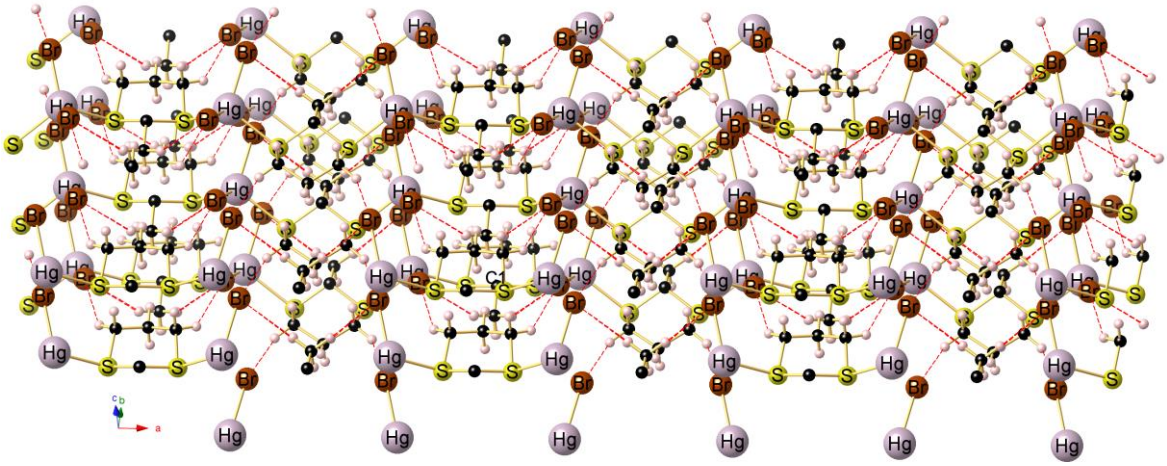

Figure S10. View of the association of parallel running 1D chains of $[(HgBr_2)(\mu_2\text{-}\mathbf{L2})]_n$ (**CP11**) through intermolecular H…Br bonding generating a 3D supramolecular network.

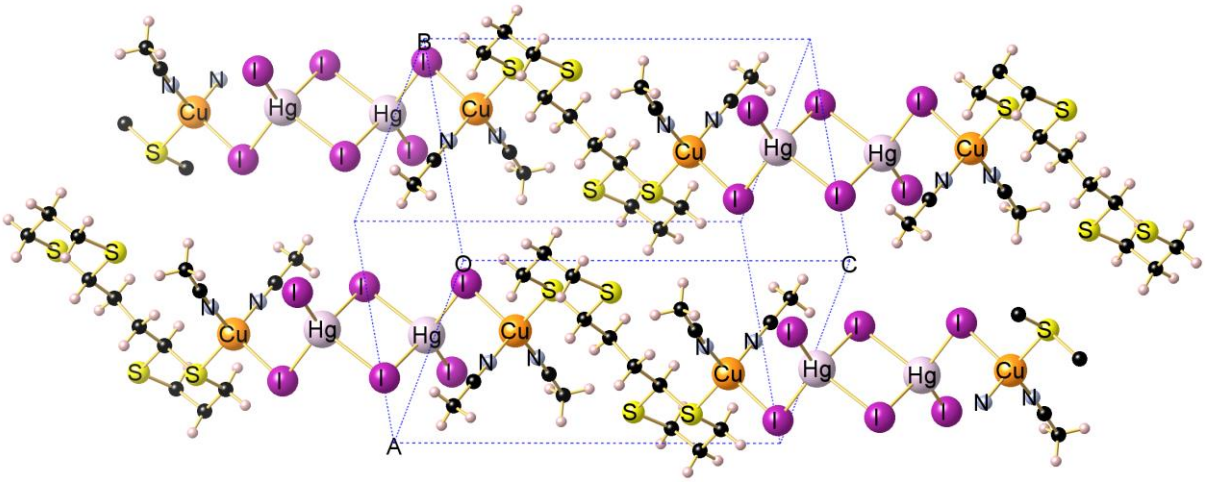

Figure S11. Parallel arrangement of the ribbons of **CP13** in the packing.

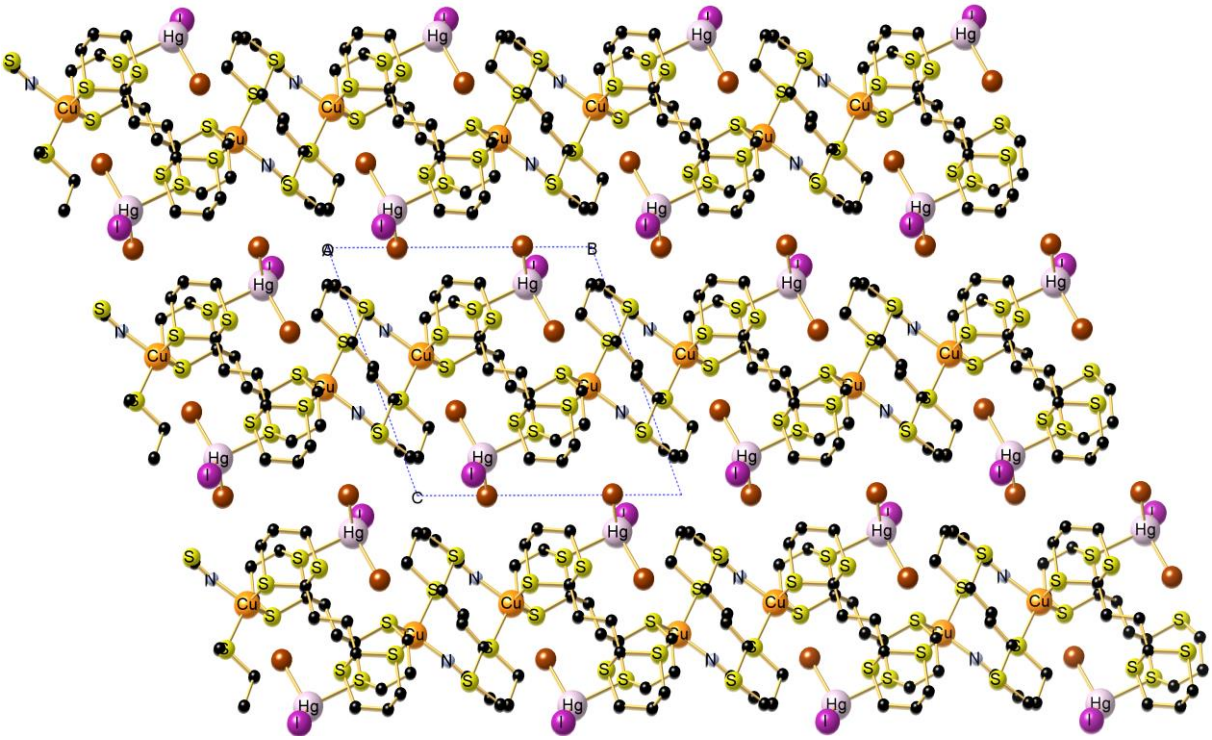

Figure S12. View of the packing of three layers of the 2D network of $[\{Cu(MeCN)\}(HgIBr_2)(\mu_2\text{-}\mathbf{L1})_{1.5}]_n$ (**CP15**).

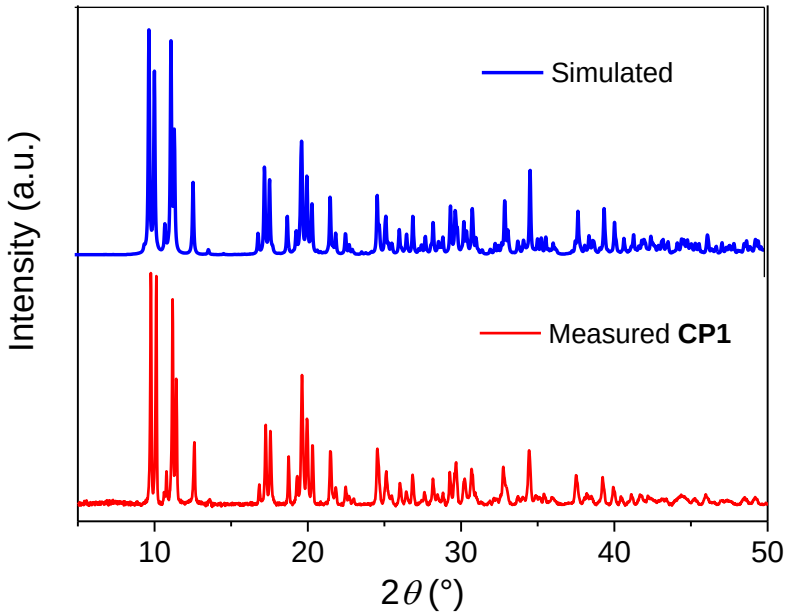

Figure S13. Simulated and experimental PXRD patterns of **CP1**.

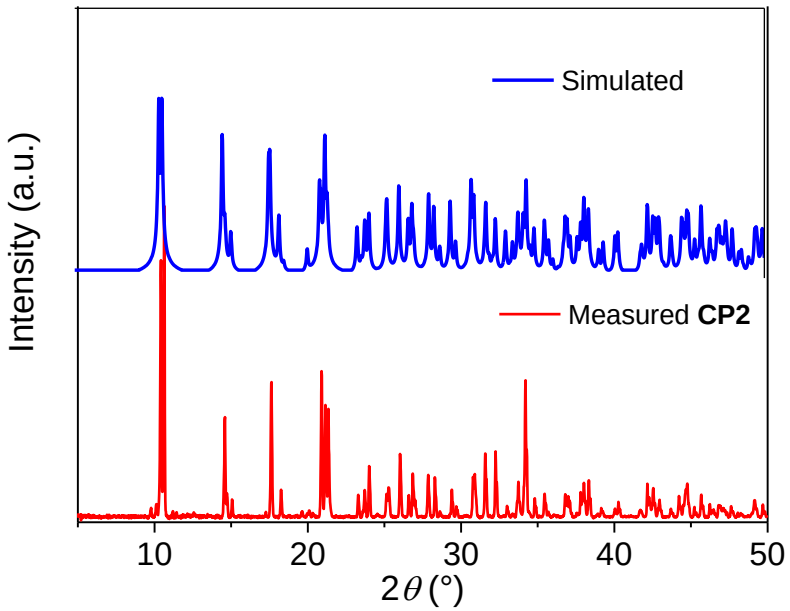

Figure S14. Simulated and experimental PXRD patterns of **CP2**.

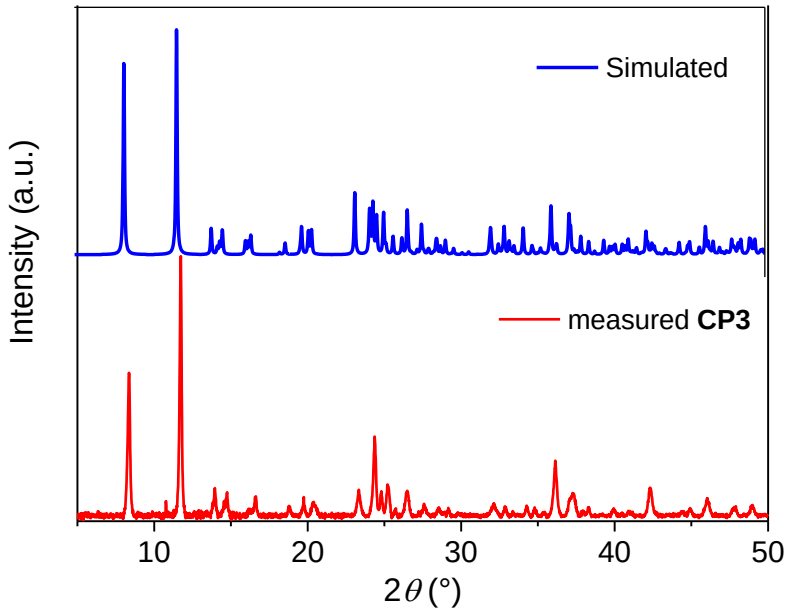

Figure S15. Simulated and experimental PXRD patterns of **CP3**.

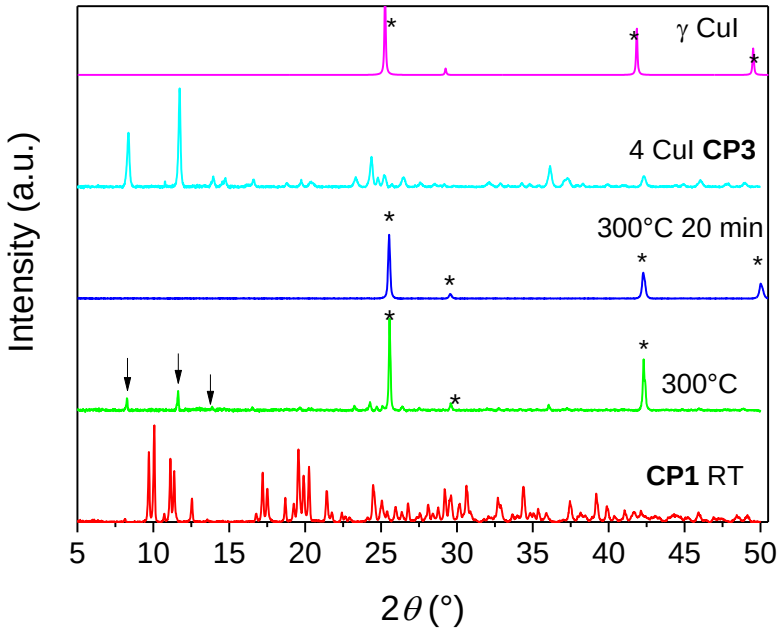

Figure S16. PXRD pattern of **CP1** before and after heating at 300°C. Arrows and asterisk are assigned to **CP3** and γ-CuI respectively.

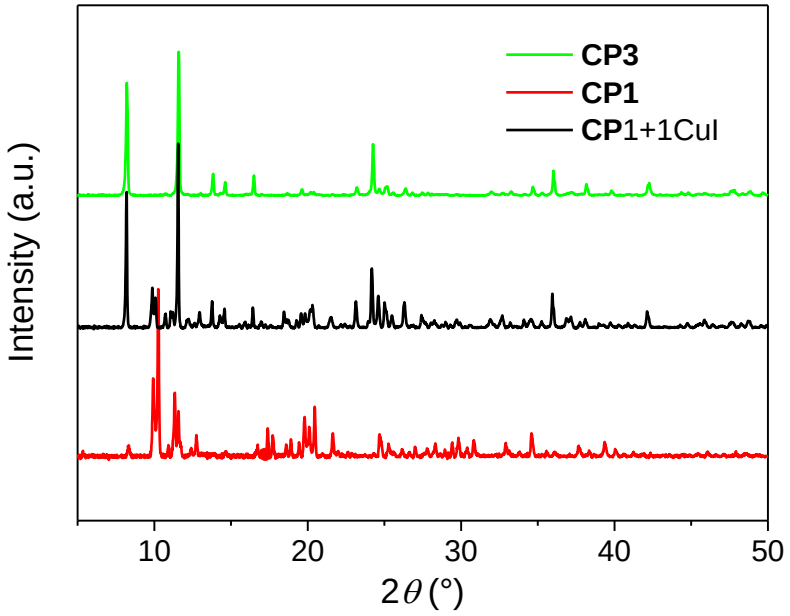

Figure S17. PXRD pattern of **CP1** before and after addition of 1 equivalent CuI. Comparison with the PXRD of **CP3**.

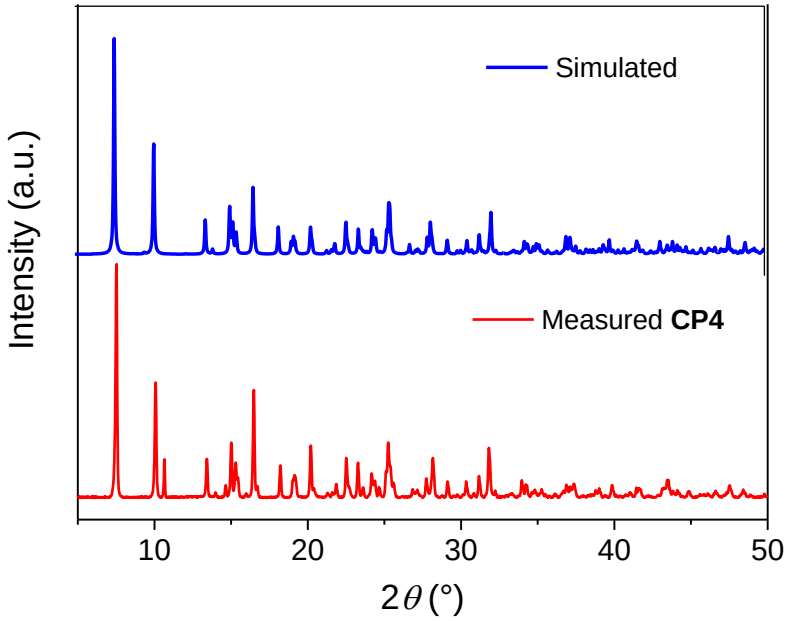

Figure S18. Simulated and experimental PXRD patterns of **CP4**.

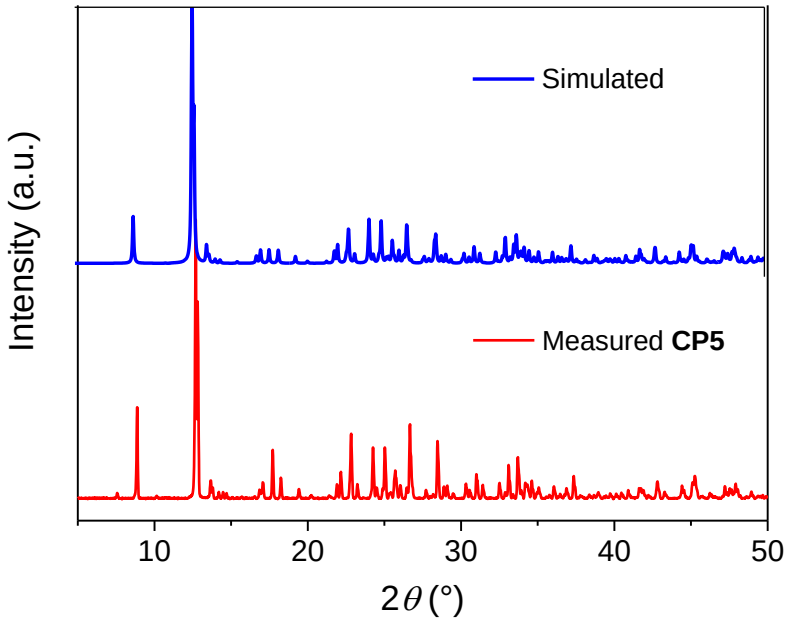

Figure S19. Simulated and experimental PXRD patterns of **CP5**.

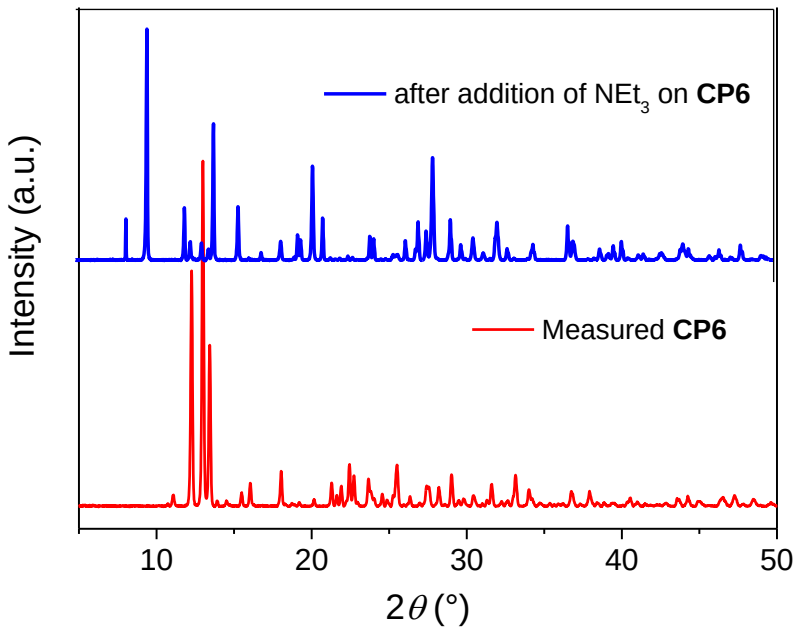

Figure S20. PXRD patterns of **CP6** before and after exposure to NEt_3.

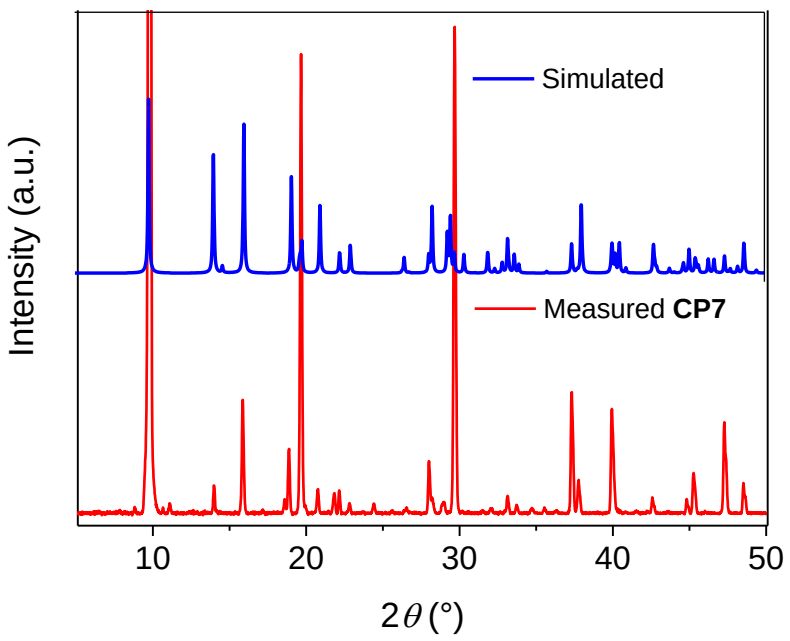

Figure S21. Simulated and experimental PXRD patterns of **CP7**.

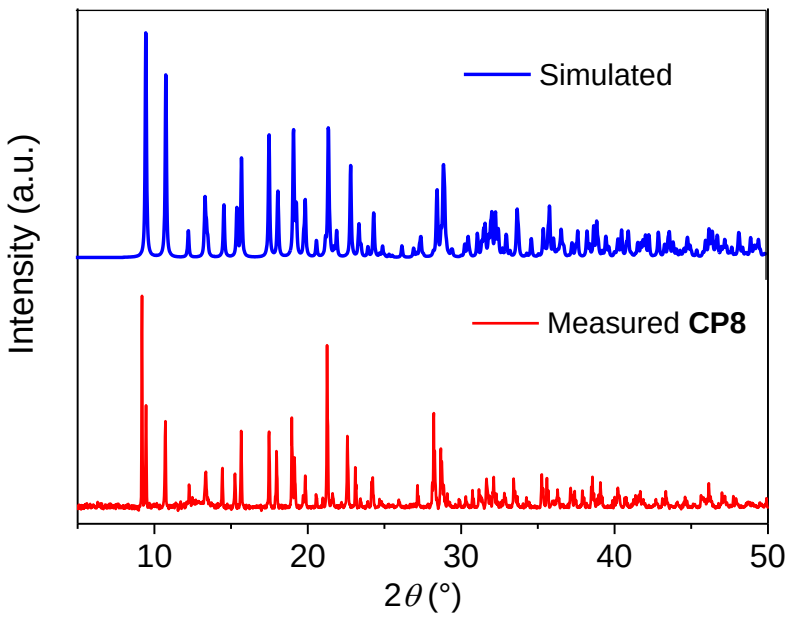

Figure S22. Simulated and experimental PXRD patterns of **CP8**.

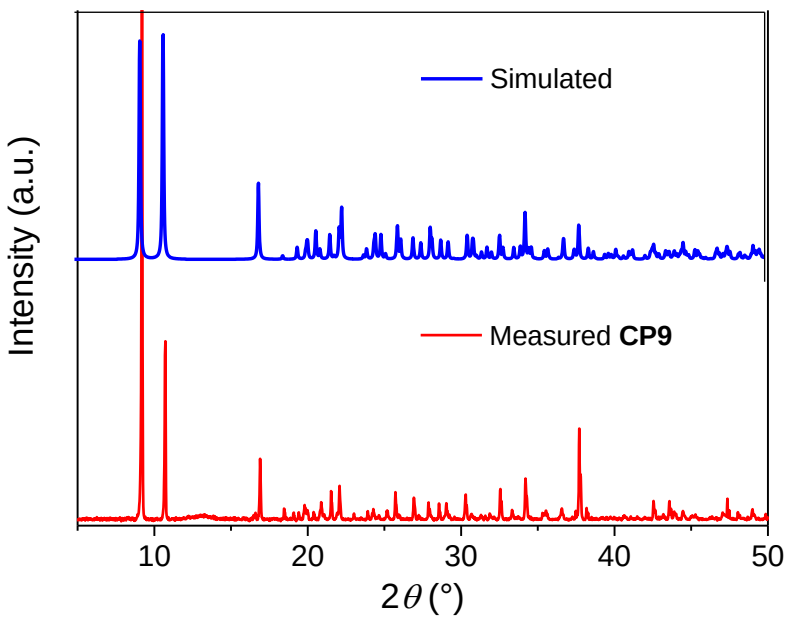

Figure S23. Simulated and experimental PXRD patterns of **CP9**.

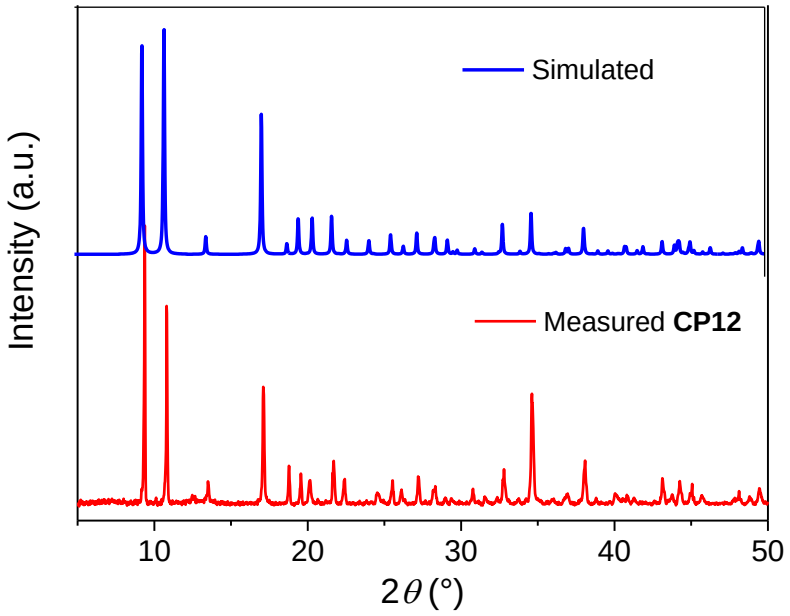

Figure S24. Simulated and experimental PXRD patterns of **CP12**.

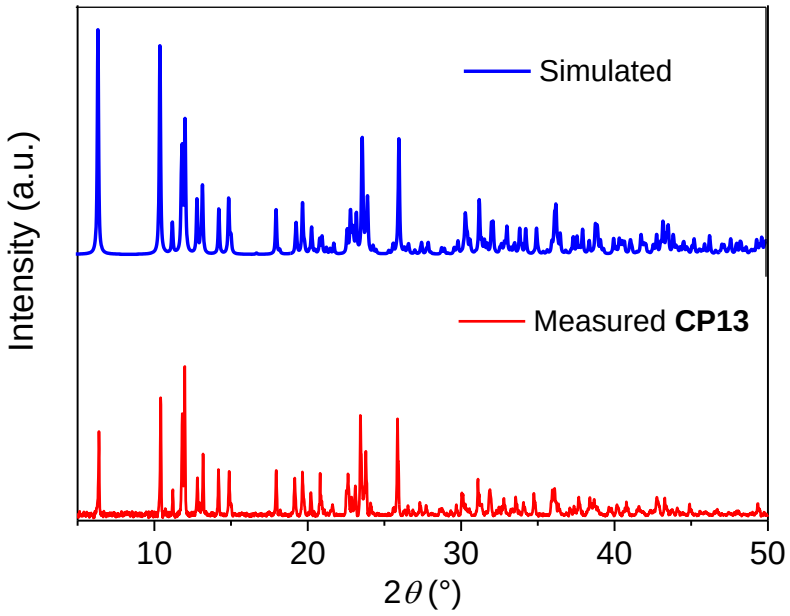

Figure S25. Simulated and experimental PXRD patterns of **CP13**.

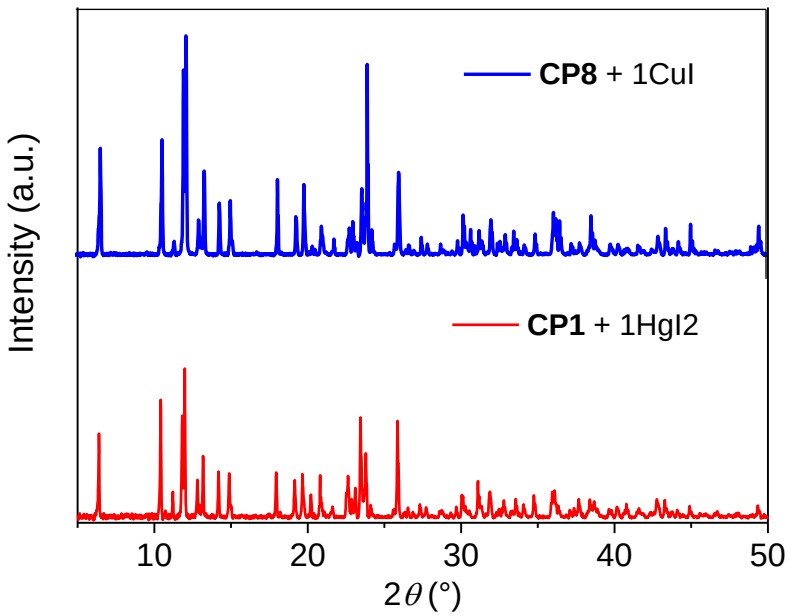

Figure S26. Experimental PXRD patterns of **CP13** obtained by addition of 1CuI to **CP8** and of 1HgI2 to **CP1**.

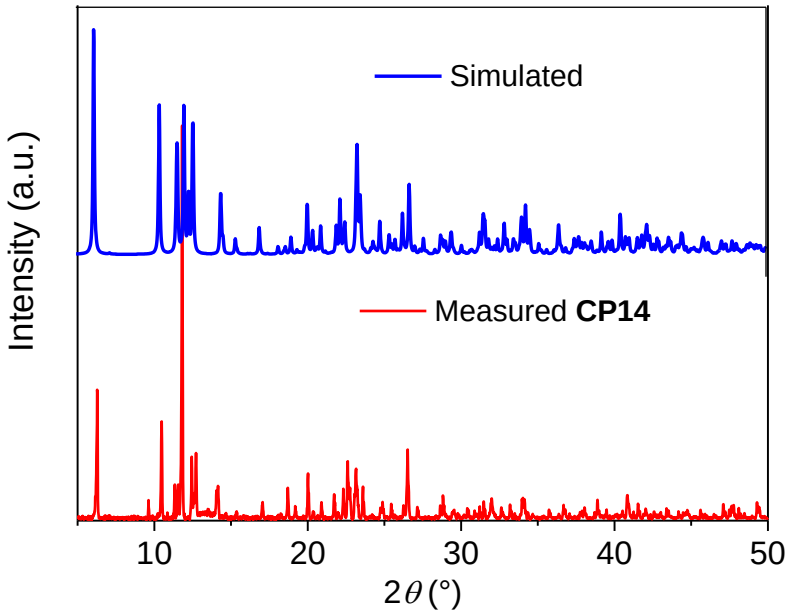

Figure S27. Simulated and experimental PXRD patterns of **CP14**.

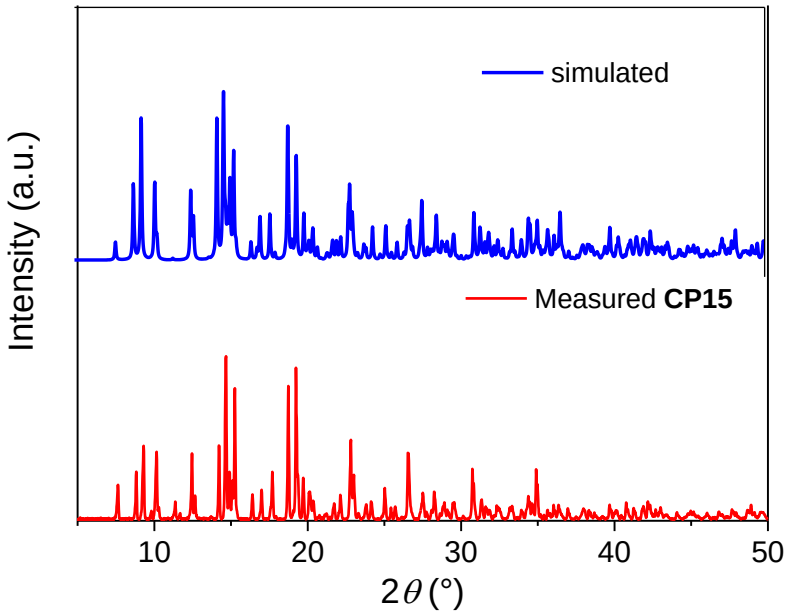

Figure S28. Simulated and experimental PXRD patterns of **CP15**.

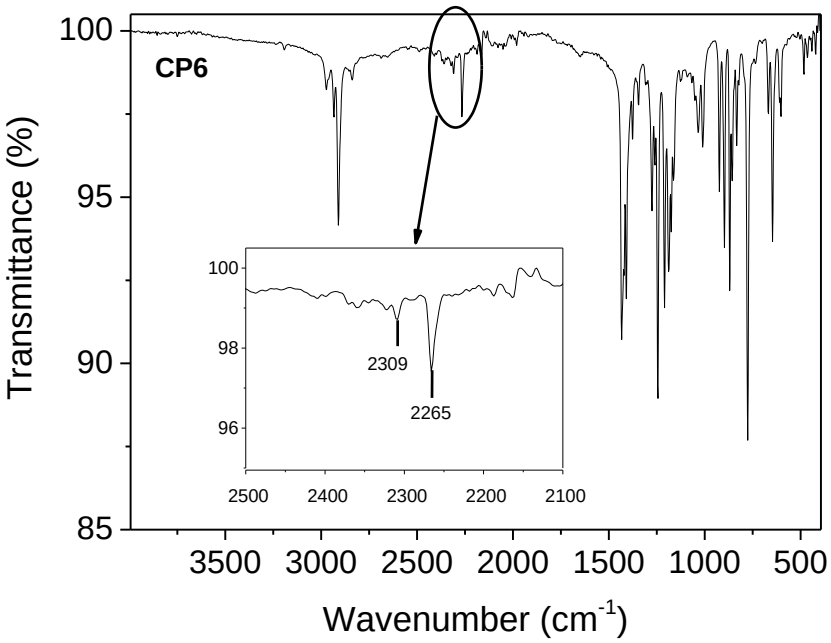

Figure S29. ATR-IR spectrum of **CP6**.

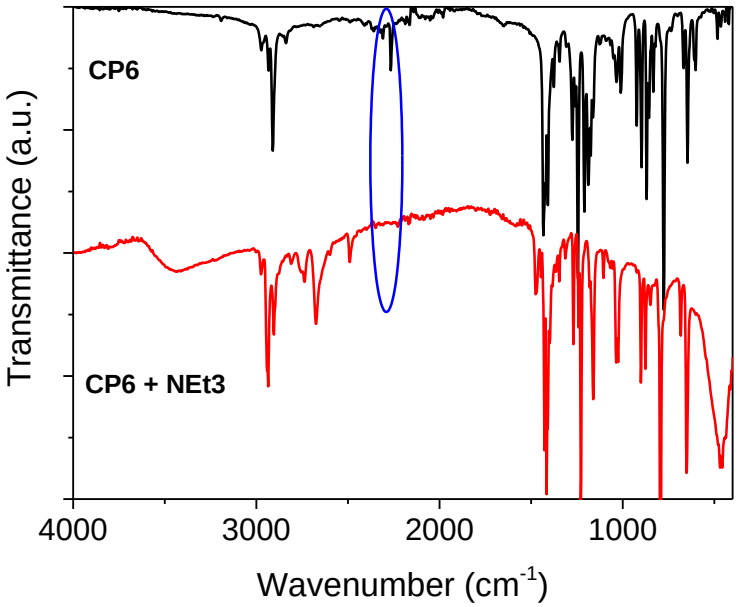

Figure S30. IR spectra of **CP6** before and after exposure to NEt_3.

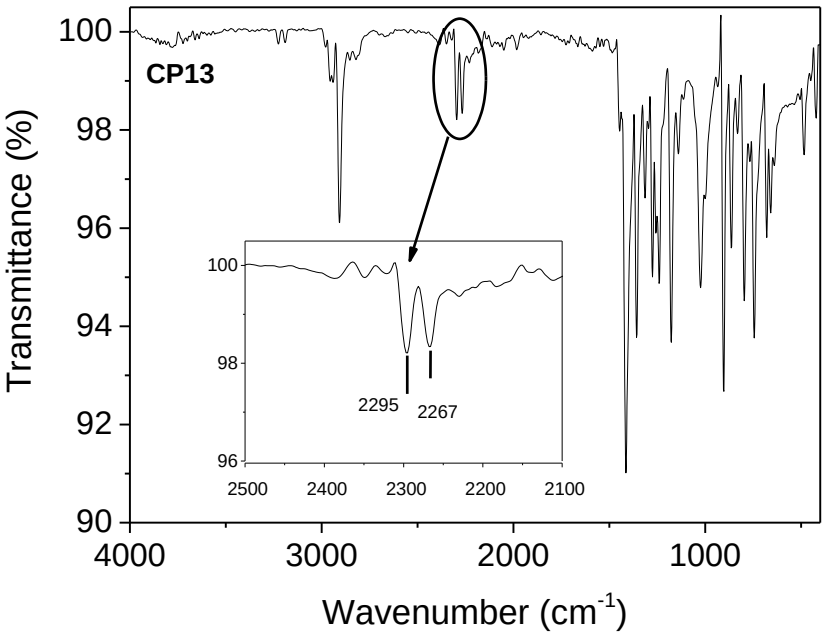

Figure S31. ATR-IR spectrum of **CP13**.

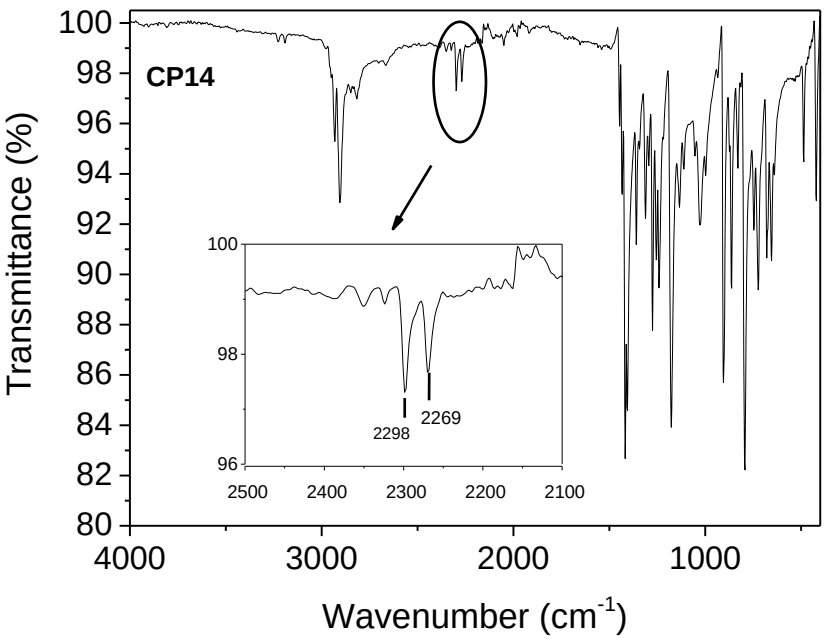

Figure S32. ATR-IR spectrum of **CP14**.

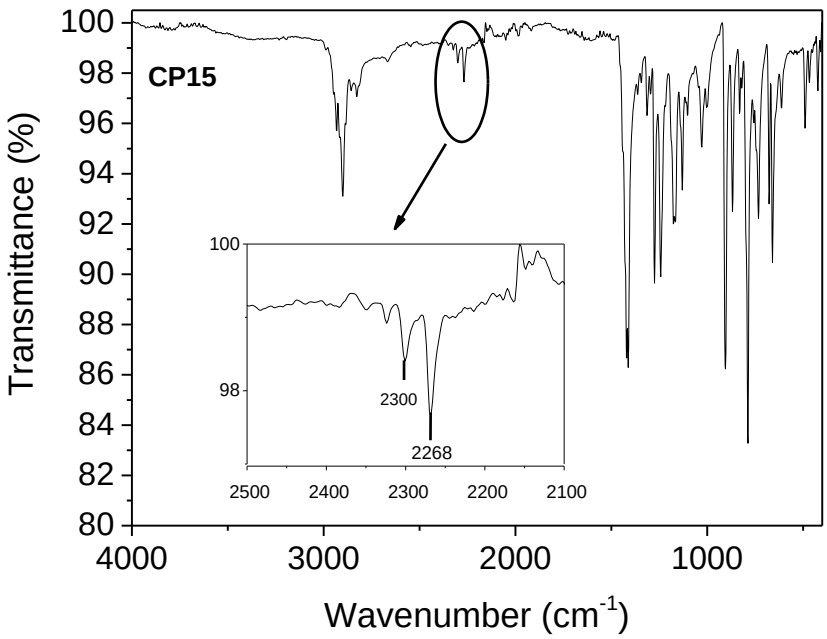

Figure S33. ATR-IR spectrum of **CP15**.

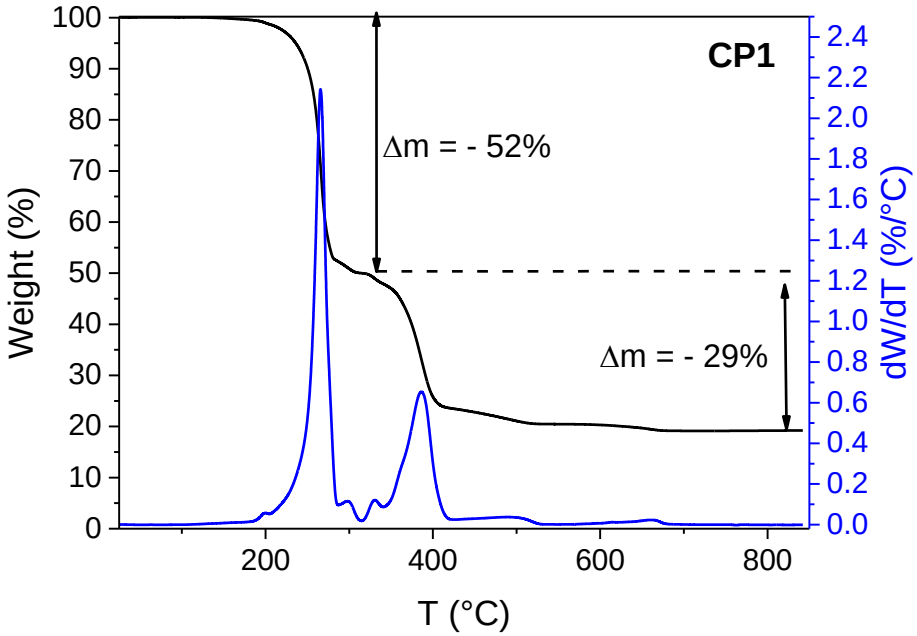

Figure S34. TGA traces and its first derivatives of **CP1** under air flow.

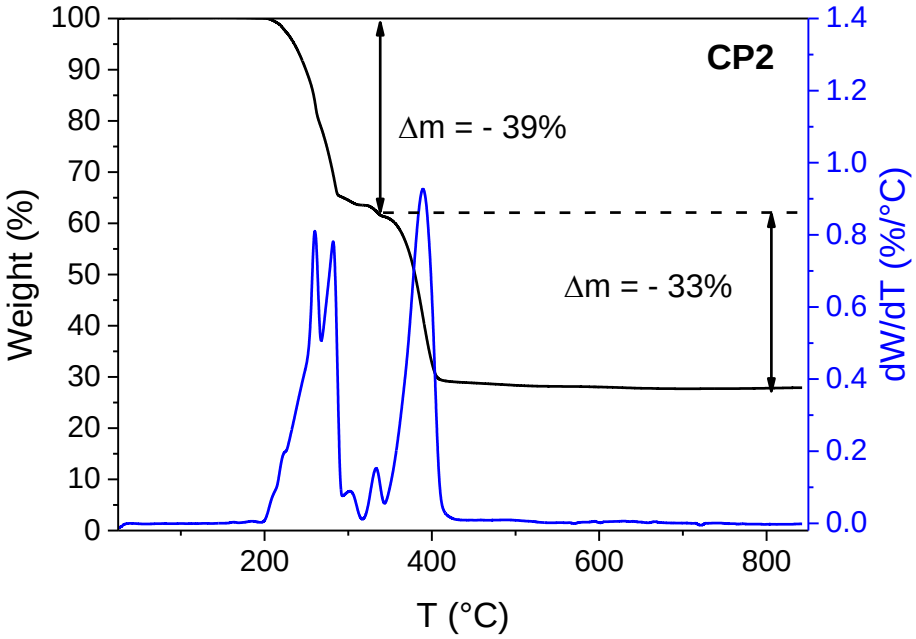

Figure S35. TGA traces and its first derivatives of **CP2** under air flow.

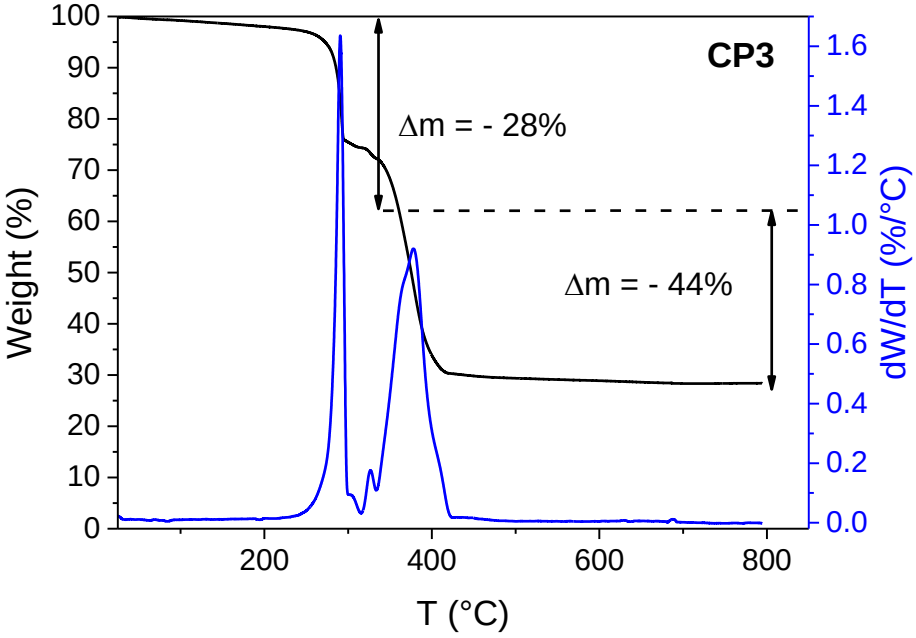

Figure S36. TGA traces and its first derivatives of **CP3** under air flow.

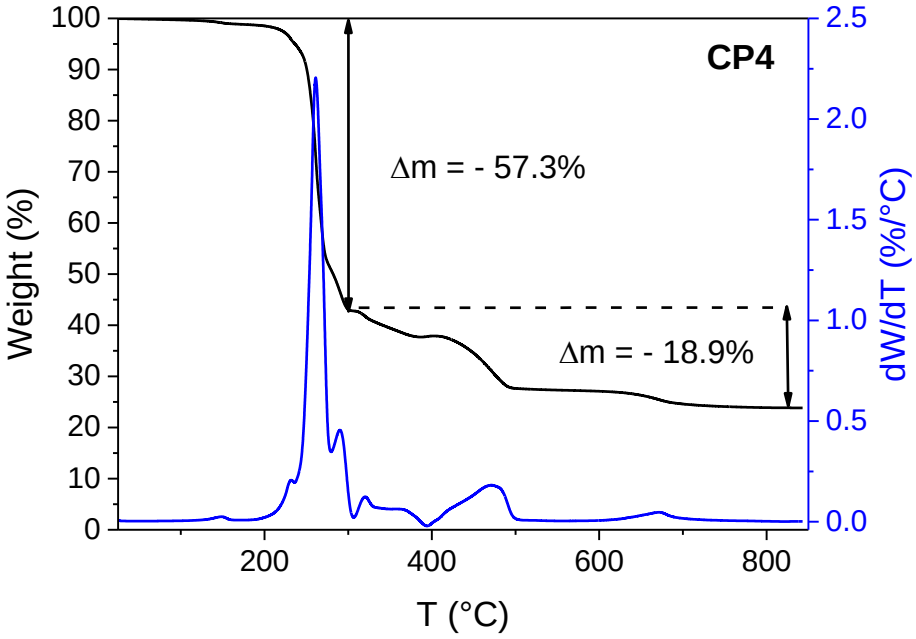

Figure S37. TGA traces and its first derivatives of **CP4** under air flow.

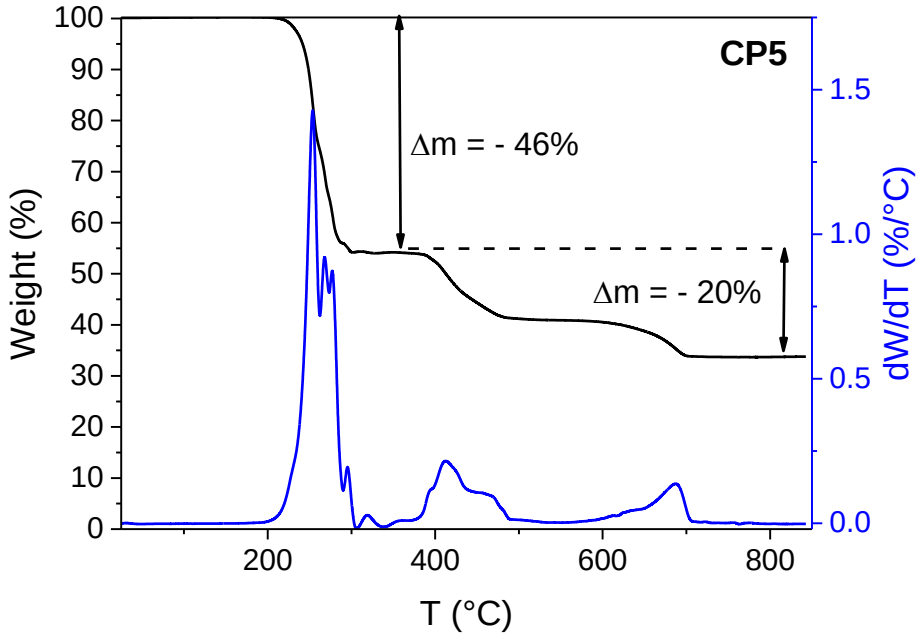

Figure S38. TGA traces and its first derivatives of **CP5** under air flow.

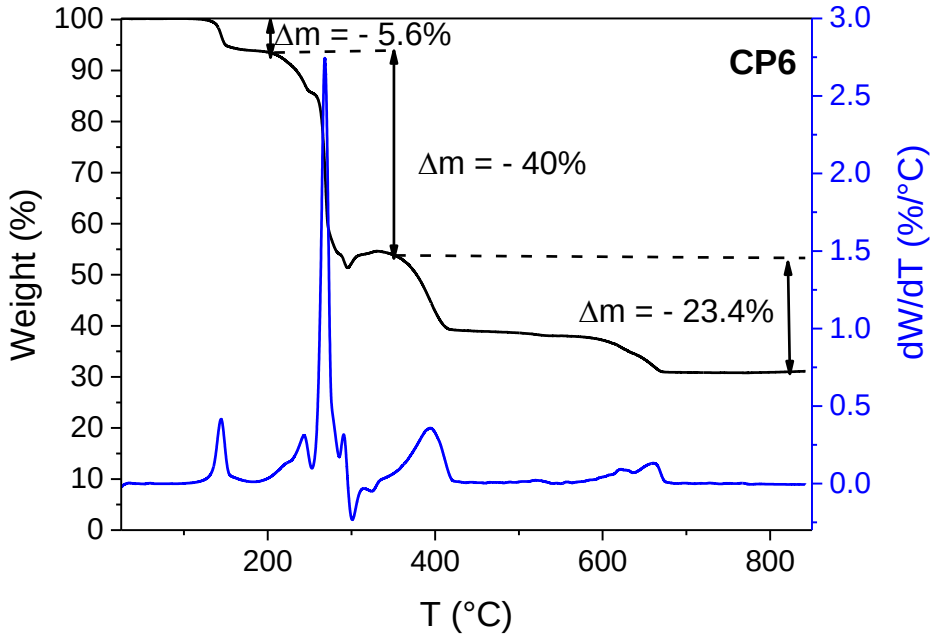

Figure S39. TGA traces and its first derivatives of **CP6** under air flow.

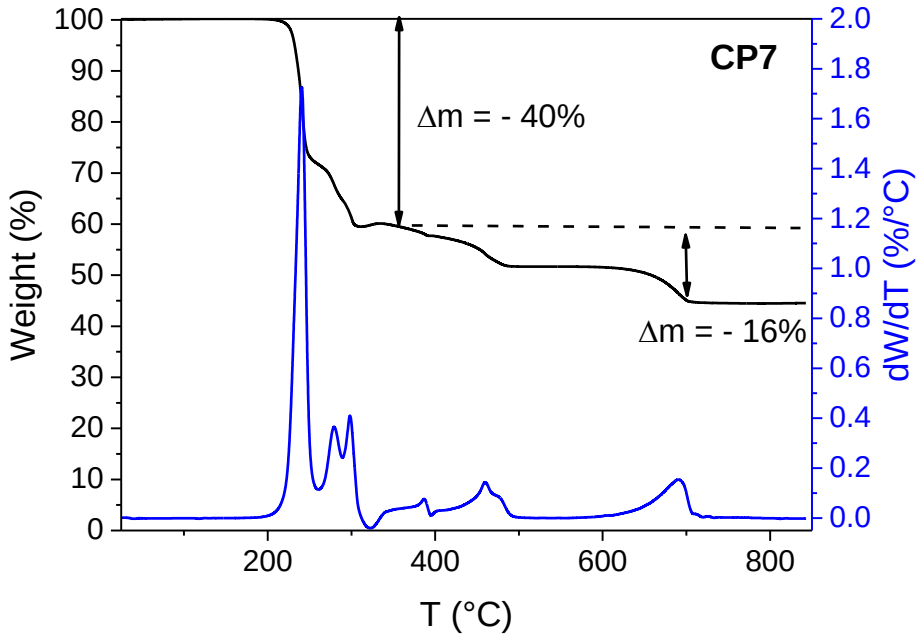

Figure S40.TGA traces and its first derivatives of **CP7** under air flow.

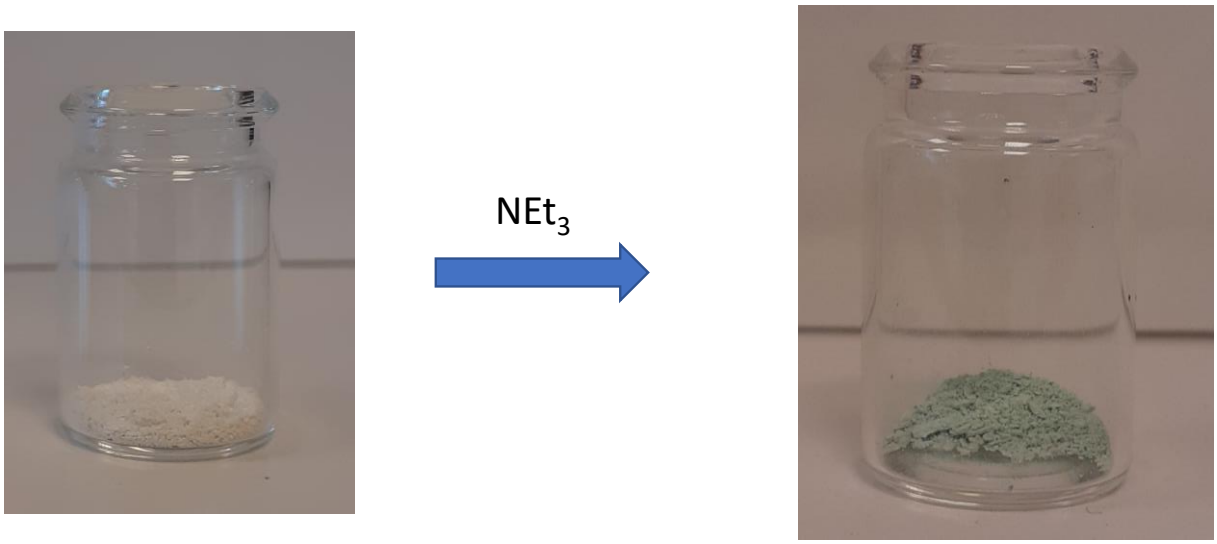

Figure S41. Images of **CP6** before and after exposure to NEt_3 vapor.

Table S1. Crystal Data, Data Collection and Structure Refinement for **L1** and **CP1**.

Compound	**L1**	**CP1**
Formula	$C_{10}H_{18}S_4$	$C_{40}H_{72}Cu_4I_4S_{16}$
Formula weight	266.48	1827.69
Temperature/K	100.0	100.0
Wavelength/Å	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	4.8578(3)	18.4505(6)
b/Å	10.6581(6)	18.2209(5)
c/Å	12.0302(11)	19.1191(7)
α /°	90	90
β /°	92.676(4)	110.0440(10)
γ /°	90	90
Volume/ $Å^3$	622.18(8)	6038.2(3)
Z	2	4
Density (calc.) g/cm^3	1.422	2.010
Absorption coefficient/mm^{-1}	0.725	4.018
F(000)	284.0	3584.0
Crystal size/mm^3	1.177 × 0.158 × 0.14	0.453 × 0.384 × 0.062
2θ range for data collection/°	5.108 to 72.732	4.394 to 59.998
Index ranges	$-8 \le h \le 8$, $-17 \le k \le 17$, $-18 \le l \le 20$	$-25 \le h \le 25$, $-25 \le k \le 25$, $-26 \le l \le 26$
Reflections collected	12460	121045
Independent reflections	3000 [R_{int} = 0.0306]	17609 [Rint = 0.0322]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3000/0/64	17609/0/588
Goodness-of-fit on F^2	1.057	1.082
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0215, wR_2 = 0.0545	R_1 = 0.0205, wR_2 = 0.0449
R indices (all data)	R_1 = 0.0255, wR_2 = 0.0566	R_1 = 0.0253, wR_2 = 0.0478
Largest diff. peak and hole/e. $Å^{-3}$	0.44/-0.28	2.09/-1.05

Table S2. Crystal Data, Data Collection and Structure Refinement for **CP2** and **CP3**.

Compound	**CP2**	**CP3**
Formula	$C_{10}H_{18}Cu_2I_2S_4$	$C_5H_9Cu_2I_2S_2$
Formula weight	647.36	514.12
Temperature/K	100.0	100.0
Wavelength/Å	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	6.0654(2)	6.6244(19)
b/Å	8.2884(3)	7.837(3)
c/Å	8.4381(3)	11.230(4)
α /°	88.411(2)	83.032(11)
β /°	87.976(2)	73.216(10)
γ /°	86.729(2)	75.644(12)
Volume/ $Å^3$	423.11(3)	540.0(3)
Z	1	2
Density (calc.) g/cm^3	2.541	3.162
Absorption coefficient/mm^{-1}	6.635	9.981
F(000)	306.0	470.0
Crystal size/mm^3	0.114 × 0.062 × 0.059	0.416 × 0.075 × 0.065
2θ range for data collection/°	4.832 to 56.984	3.794 to 52.01
Index ranges	$-8 \le h \le 8$, $-11 \le k \le 11$, $-11 \le l \le 11$	$7 \le h \le 8$, $-9 \le k \le 9$, $-13 \le l \le 13$
Reflections collected	14022	2113
Independent reflections	2144 [R_{int} = 0.0465]	2113 [R_{int} = ?,]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2144/0/82	2113/0/101
Goodness-of-fit on F^2	1.108	1.085
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0257, wR_2 = 0.0559	R_1 = 0.0269, wR_2 = 0.0753
R indices (all data)	R_1 = 0.0328, wR_2 = 0.0592	R_1 = 0.0285, wR_2 = 0.0767
Largest diff. peak and hole/e. $Å^{-3}$	0.96/-0.81	1.88/-0.82

Table S3. Crystal Data, Data Collection and Structure Refinement for **CP4** and **CP5**.

Compound	**CP4**	**CP5**
Formula	$C_{15}H_{27}Br_2Cu_2S_6$	$C_{10}H_{18}Br_2Cu_2S_4$
Formula weight	686.62	553.38
Temperature/K	100.0	100.0
Wavelength/Å	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	12.9413(15)	8.1301(12)
b/Å	13.0872(11)	13.8417(14)
c/Å	14.5879(17)	14.591(2)
α /°	90	90
β /°	115.754(5)	95.315(7)
γ /°	90	90
Volume/ $Å^3$	2225.3(4)	1634.9(4)
Z	4	4
Density (calc.) g/cm^3	2.049	2.248
Absorption coefficient/mm^{-1}	6.065	7.979
F(000)	1364.0	1080.0
Crystal size/mm^3	0.294 × 0.125 × 0.043	0.133 × 0.084 × 0.034
2θ range for data collection/°	4.392 to 61.136	5.608 to 64.994
Index ranges	$18 \leq h \leq 18$, $-18 \leq k \leq 15$, $-20 \leq l \leq 20$	$-12 \leq h \leq 12$, $-20 \leq k \leq 20$, $-22 \leq l \leq 22$
Reflections collected	47344	62361
Independent reflections	6754 [R_{int} = 0.0547]	5923 [Rint = 0.0370]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F2
Data / restraints / parameters	6754/0/226	5923/0/163
Goodness-of-fit on F^2	1.047	1.088
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0346, wR_2 = 0.0596	R_1 = 0.0303, wR_2 = 0.0721
R indices (all data)	R_1 = 0.0543, wR_2 = 0.0665	R_1 = 0.0351, wR_2 = 0.0740
Largest diff. peak and hole/e. $Å^{-3}$	0.81/-0.81	1.57/-1.09

Table S4. Crystal Data, Data Collection and Structure Refinement for **CP6** at 100K and 200K.

Compound	**CP6**	**CP6**
Formula	$C_{24}H_{42}Br_6Cu_6N_2S_8$	$C_{24}H_{42}Br_6Cu_6N_2S_8$
Formula weight	1475.77	1475.77
Temperature/K	100.0	200K
Wavelength/Å	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	7.8786(4)	7.8928(11)
b/Å	9.8046(5)	9.8456(14)
c/Å	26.8573(15)	26.928(4)
α /°	87.562(2)	87.555(2)
β /°	83.924(2)	84.017(2)
γ /°	87.249(2)	87.229(2)
Volume/ $Å^3$	2059.14(19)	2077.2(5)
Z	2	2
Density (calc.) g/cm^3	2.380	2.359
Absorption coefficient/mm^{-1}	9.293	9.212
F(000)	1424.0	1424.0
Crystal size/mm^3	0.163 × 0.107 × 0.043	0.163 × 0.107 × 0.043
2θ range for data collection/°	4.162 to 72.658	4.144 to 67.504
Index ranges	$-13 \leq h \leq 13$, $-16 \leq k \leq 16$, $0 \leq l \leq 44$	$-12 \leq h \leq 12$, $-15 \leq k \leq 15$, $0 \leq l \leq 42$
Reflections collected	19959	16608
Independent reflections	19959 [R_{int} = 0.0504]	16608 [R_{int} = 0.0501]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	19959/0/417	16608/0/417
Goodness-of-fit on F^2	1.021	1.000
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0279, wR_2 = 0.0686	R_1 = 0.0276, wR_2 = 0.0683
R indices (all data)	R_1 = 0.0356, wR_2 = 0.0714	R_1 = 0.0369, wR_2 = 0.0715
Largest diff. peak and hole/e. $Å^{-3}$	0.83/-1.91	1.36/-1.57

Table S5. Crystal Data, Data Collection and Structure Refinement for **CP7** and **CP8**.

Compound	**CP7**	**CP8**
Formula	$C_5H_9ClCuS_2$	$C_{10}H_{18}HgI_2S_4$
Formula weight	232.23	720.87
Temperature/K	100.0	100.0
Wavelength/Å	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	C2/m	P-1
a/Å	18.3202(9)	9.3903(3)
b/Å	6.7228(3)	9.8817(3)
c/Å	6.1576(3)	10.0545(3)
α /°	90	68.8700(10)
β /°	100.814(2)	79.6750(10)
γ /°	90	86.6570(10)
Volume/ $Å^3$	744.92(6)	856.14(5)
Z	4	2
Density (calc.) g/cm^3	2.071	2.796
Absorption coefficient/mm^{-1}	3.751	13.062
F(000)	468.0	656.0
Crystal size/mm3	0.232 × 0.172 × 0.035	0.459 × 0.254 × 0.174
2θ range for data collection/°	4.528 to 61.046	4.408 to 61.156
Index ranges	$-26 \le h \le 26$, $-9 \le k \le 9$, $-8 \le l \le 8$	$-13 \le h \le 13$, $-14 \le k \le 13$, $-14 \le l \le 13$
Reflections collected	12880	14810
Independent reflections	1227 [R_{int} = 0.0375]	5243 [R_{int} = 0.0289]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	1227/0/49	5243/0/155
Goodness-of-fit on F^2	1.426	1.189
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0348, wR_2 = 0.0858	R_1 = 0.0242, wR_2 = 0.0590
R indices (all data)	R_1 = 0.0387, wR_2 = 0.0871	R_1 = 0.0244, wR_2 = 0.0591
Largest diff. peak and hole/e. $Å^{-3}$	1.64/-0.70	3.11/-2.46

Table S6. Crystal Data, Data Collection and Structure Refinement for **CP9** and **CP10**.

Compound	**CP9**	**CP10**
Formula	$C_{10}H_{18}Br_2HgS_4$	$C_5H_9Br_2HgS_2$
Formula weight	626.89	493.65
Temperature/K	100.0	100.0
Wavelength/Å	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	$Pna2_1$	C2/c
a/Å	18.1737(10)	8.2012(3)
b/Å	4.5256(2)	13.2979(5)
c/Å	19.0929(10)	18.6993(7)
α /°	90	90
β /°	90	93.1840(10)
γ /°	90	90
Volume/ $Å^3$	1570.33(14)	2036.17(13)
Z	4	8
Density (calc.) g/cm^3	2.652	3.221
Absorption coefficient/mm^{-1}	15.399	23.309
F(000)	1168.0	1768.0
Crystal size/mm^3	0.217 × 0.105 × 0.034	0.25 × 0.079 × 0.074
2θ range for data collection/°	4.266 to 54.996	5.842 to 61.08
Index ranges	$-23 \le h \le 23$, $-5 \le k \le 5$, $-24 \le l \le 24$	$-11 \le h \le 11$, $-18 \le k \le 19$, $-26 \le l \le 26$
Reflections collected	53635	30365
Independent reflections	3609 [R_{int} = 0.0639]	3110 [R_{int} = 0.0563]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3609/1/159	3110/0/91
Goodness-of-fit on F^2	1.066	1.096
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0182, wR_2 = 0.0441	R_1 = 0.0214, wR_2 = 0.0614
R indices (all data)	R_1 = 0.0204, wR_2 = 0.0451	R_1 = 0.0231, wR_2 = 0.0621
Largest diff. peak and hole/e. $Å^{-3}$	0.63/-0.53	1.58/-1.94

Table S7. Crystal Data, Data Collection and Structure Refinement for **CP11** and **CP13**.

Compound	**CP11**	**CP13**
Formula	$C_{10}H_{20}Br_4Hg_2S_4$	$C_9H_{15}CuHgI_3N_2S_2$
Formula weight	989.32	860.18
Temperature/K	100.0	100.00
Wavelength/Å	0.71073	0.71073
Crystal system	orthorhombic	triclinic
Space group	Ama2	P-1
a/Å	14.1565(12)	8.3763(8)
b/Å	15.7413(13)	9.3131(8)
c/Å	4.5260(3)	14.2531(9)
α /°	90	94.414(4)
β /°	90	102.209(4)
γ /°	90	113.075(4)
Volume/ $Å^3$	1008.58(14)	983.86(14)
Z	2	2
Density (calc.) g/cm^3	3.258	2.904
Absorption coefficient/mm^{-1}	23.529	13.780
F(000)	888.0	766.0
Crystal size/mm^3	0.128 × 0.122 × 0.046	0.287 × 0.098 × 0.096
2θ range for data collection/°	5.756 to 66.326	5.202 to 64.998
Index ranges	$-21 \le h \le 21$, $-24 \le k \le 24$, $-6 \le l \le 6$	$-12 \le h \le 12$, $-14 \le k \le 14$, $-21 \le l \le 21$
Reflections collected	8550	185883
Independent reflections	1968 [R_{int} = 0.0341]	7116 [R_{int} = 0.0381]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	1968/1/51	7116/0/165
Goodness-of-fit on F^2	0.969	1.116
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0176, wR_2 = 0.0385	R_1 = 0.0204, wR_2 = 0.0543
R indices (all data)	R_1 = 0.0196, wR_2 = 0.0397	R_1 = 0.0212, wR_2 = 0.0556
Largest diff. peak and hole/e. $Å^{-3}$	1.00/-0.97	2.80/-2.03

Table S8. Crystal Data, Data Collection and Structure Refinement for **CP14** and **CP15**.

Compound	**CP14**	**CP15**
Formula	$C_{22}H_{38}Cu_2Hg_2I_6N_4S_4$	$C_{17}H_{30}Br_2CuHgINS_6$
Formula weight	1776.46	991.86
Temperature/K	100.0	100.00
Wavelength/Å	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	9.8483(8)	10.1654(12)
b/Å	14.9259(16)	12.582(2)
c/Å	15.2501(13)	13.033(2)
α /°	108.914(3)	67.070(7)
β /°	95.043(5)	69.373(5)
γ /°	94.515(3)	76.469(6)
Volume/ $Å^3$	2098.7(3)	1427.8(4)
Z	2	2
Density (calc.) g/cm^3	2.811	2.307
Absorption coefficient/mm^{-1}	12.924	10.439
F(000)	1596.0	934.0
Crystal size/mm^3	0.199 × 0.169 × 0.142	0.199 × 0.072 × 0.041
2θ range for data collection/°	4.694 to 64,998	4.716 to 61.124
Index ranges	$-14 \le h \le 14$, $-22 \le k \le 22$, $-23 \le l \le 23$	$-13 \le h \le 14$, $-17 \le k \le 17$, $-18 \le l \le 18$
Reflections collected	732333	38896
Independent reflections	15174 [R_{int} = 0.0705]	8594 [R_{int} = 0.0318]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	15174/0/452	8594/0/284
Goodness-of-fit on F^2	1.115	1.098
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0153, wR_2 = 0.0366	R_1 = 0.0229, wR_2 = 0.0354
R indices (all data)	R_1 = 0.0160, wR_2 = 0.0370	R_1 = 0.0316, wR_2 = 0.0377
Largest diff. peak and hole/e. $Å^{-3}$	1.20/-1.43	0.80/-0.93

Table S9. Crystal Data, Data Collection and Structure Refinement for **D1** and **M1**.

Compound	**D1**	**M1**
Formula	$C_{10}H_{20}Hg_2I_4S_2$	$C_{10}H_{20}Br_2HgS_4$
Formula weight	1177.28	628.91
Temperature/K	100.0	100.0
Wavelength/Å	0.71073	0.71073
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_12_12$
a/Å	9.7802(8)	8.2203(3)
b/Å	10.0351(10)	22.7657(9)
c/Å	11.6340(10)	4.4494(2)
α /°	90	90
β /°	90.652(3)	90
γ /°	90	90
Volume/ $Å^3$	1141.75(18)	832.66(6)
Z	2	2
Density (calc.) g/cm^3	3.424	2.508
Absorption coefficient/mm^{-1}	19.194	14.521
F(000)	1032.0	588.0
Crystal size/mm^3	0.308 × 0.157 × 0.134	0.332 × 0.044 × 0.037
2θ range for data collection/°	5.472 to 58	6.114 to 55.962
Index ranges	$-13 \le h \le 13$, $-13 \le k \le 13$, $-15 \le l \le 15$	$-10 \le h \le 10$, $-30 \le k \le 30$, $-5 \le l \le 5$
Reflections collected	50811	18946
Independent reflections	3029 [R_{int} = 0.0528]	2004 [R_{int} = 0.0500]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3029/0/93	2004/0/85
Goodness-of-fit on F^2	1.187	1.139
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0202, wR_2 = 0.0462	R_1 = 0.0192, wR_2 = 0.0326
R indices (all data)	R_1 = 0.0203, wR_2 = 0.0463	R_1 = 0.0213, wR_2 = 0.0334
Largest diff. peak and hole/e. $Å^{-3}$	1.73/-2.73	0.76/-0.92

Table S10. Hydrogen bond geometry (Å, °) in **CP6**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3*A*···S7[1]	0.99	3.05	3.698(4)	124.2
C7—H7···Br3[2]	1.00	2.70	3.649(4)	157.8
C8—H8*B*···Br2[2]	0.99	2.86	3.598(4)	132.4
C9—H9*A*···Br2[3]	0.99	3.05	3.695(4)	124.2
C17—H17···Br6[4]	1.00	2.72	3.678(4)	161.2
C18—H18*A*···N1[5]	0.99	2.85	3.679(6)	141.2
C20—H20*B*···Br1[6]	0.99	2.95	3.679(4)	131.3
C22—H22*B*···Br1[4]	0.98	2.85	3.692(5)	144.2
C22—H22*C*···Br5[6]	0.98	2.94	3.621(5)	127.2

Symmetry codes: [1]1+X,-1+Y,+Z; [2]1+X,+Y,+Z; [3]1-X,-Y,1-Z; [4]-1+X,+Y,+Z; [5]+X,1+Y,+Z; [6]1-X,1-Y,2-Z

Table S11. Hydrogen bond geometry (Å, °) in **CP11**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*B*···Br1[1]	0.99	3.10	3.758(4)	124.7
C1—H1*B*···Br1[2]	0.99	2.87	3.667(4)	138.3