Electronic Supplementary Material (ESI) for CrystEngComm.


# Supporting Information

## Strong Luminescent Copper(I)-halide Coordination Polymers and Dinuclear Complexes with Thioacetamide and N,N-donor ligands

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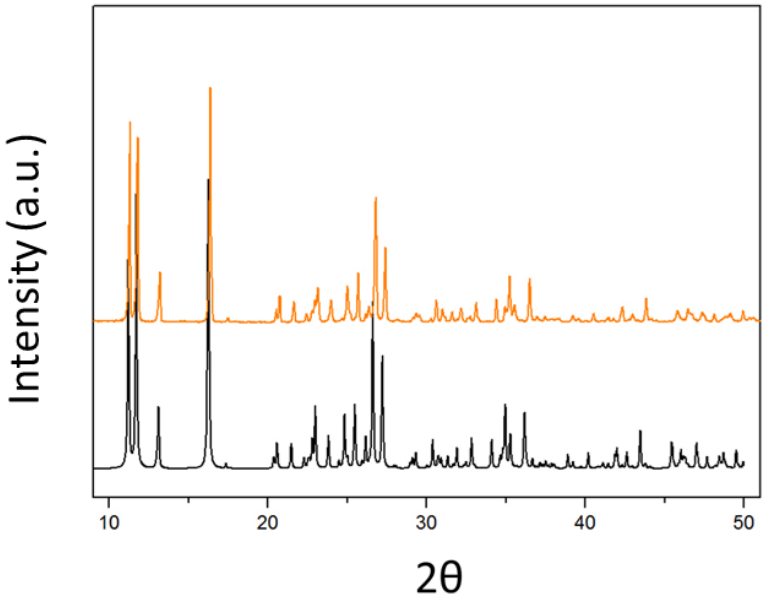


**Figure S1.** XRPD pattern of **1**. Experimental (orange) and simulated (black).

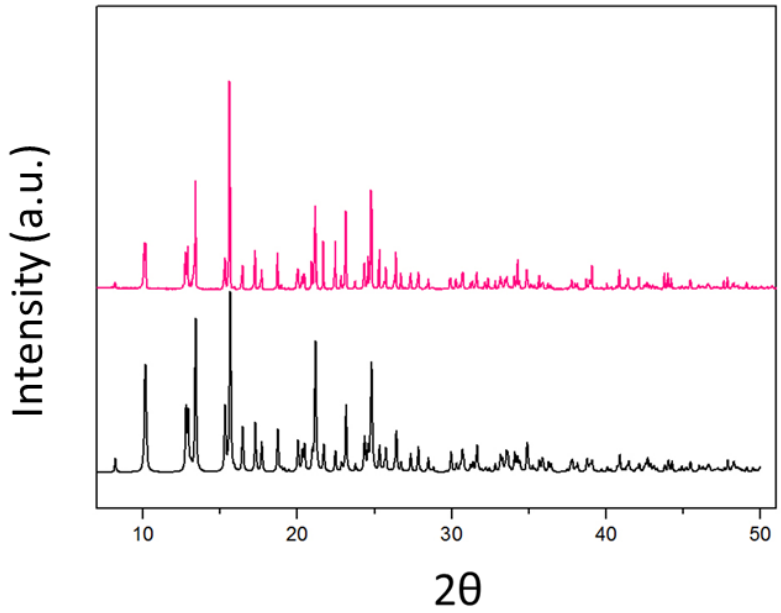


**Figure S2.** XRPD pattern of **2**. Experimental (pink) and simulated (black).

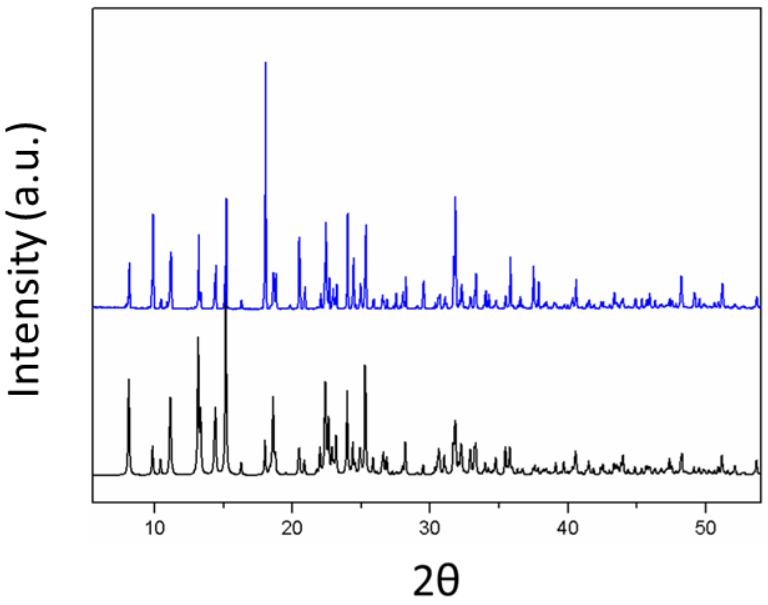


**Figure S3.** XRPD pattern of **3**. Experimental (blue) and simulated (black).

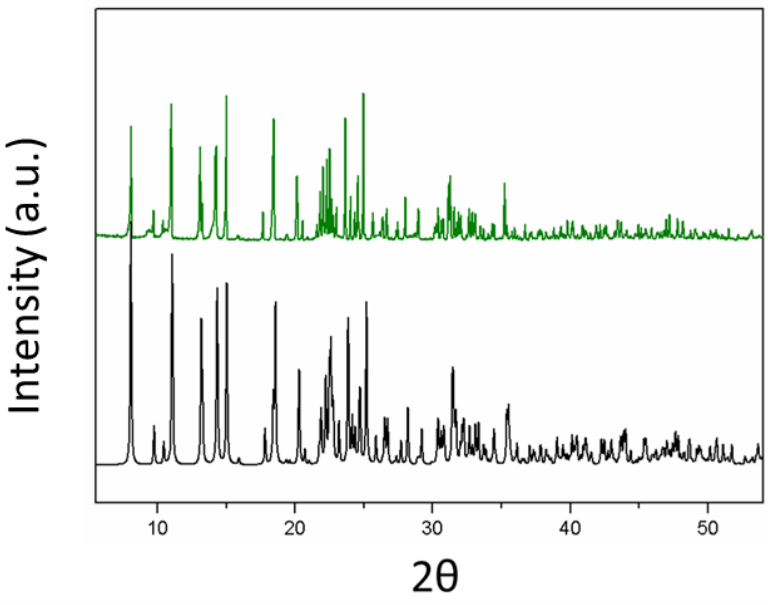


**Figure S4.** XRPD pattern of **4**. Experimental (green) and simulated (black).

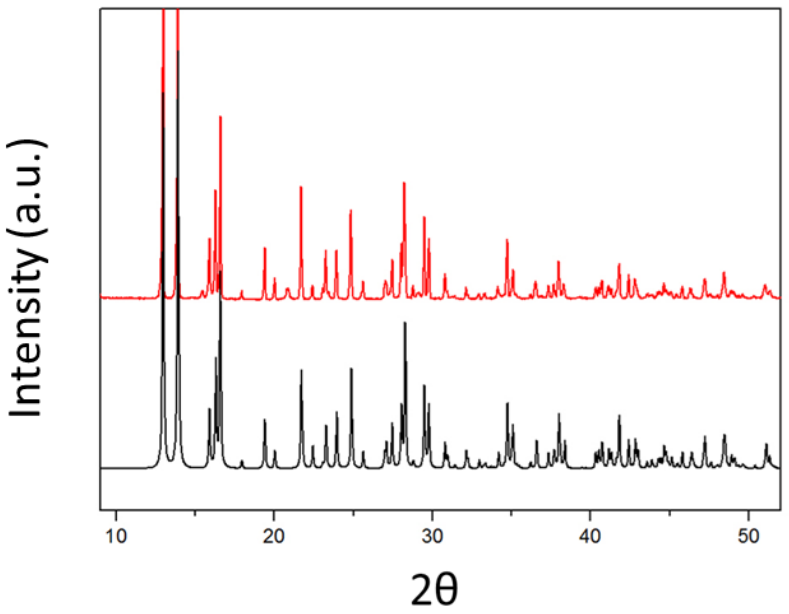


**Figure S5.** XRPD pattern of **5**. Experimental (red) and simulated (black).

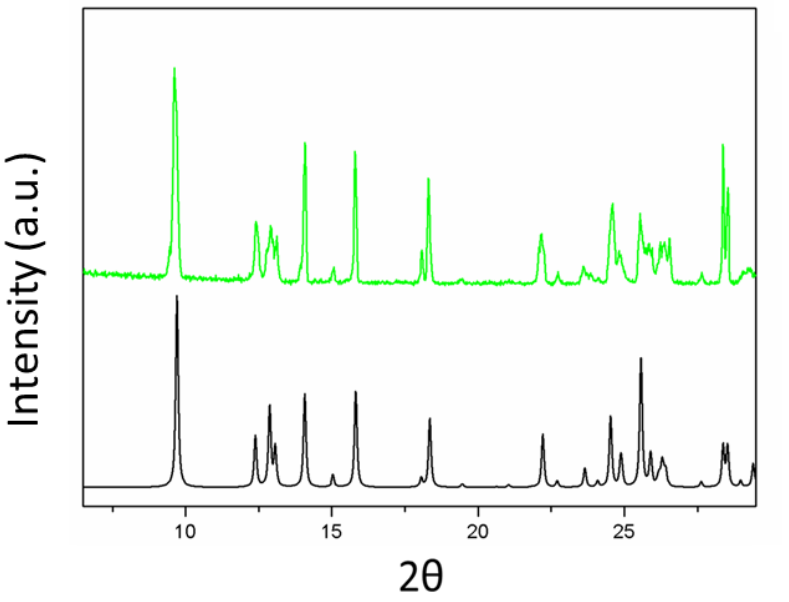


**Figure S6.** XRPD pattern of **6**. Experimental (green) and simulated (black).

## *Single crystal X-ray diffraction supplementary information for 1-6*

### *a) Single crystal X-ray diffraction supplementary information for 1*

A clear yellow prismatic-like specimen of $C_7H_9ClCuN_2S$, approximate dimensions 0.02 mm x 0.05 mm x 0.23 mm, was used for the X-ray crystallographic analysis.

*Data collection and integration*

A total of 864 frames were collected. The total exposure time was 2.40 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 7463 reflections to a maximum θ angle of 25.10° (0.84 Å resolution), of which 1698 were independent (average redundancy 4.395, completeness = 99.9%, $R_{int}$ = 2.40%, $R_{sig}$ = 2.18%) and 1375 (80.98%) were greater than $2\sigma(F^2)$. *Unit cell*

The final cell constants of *a* = 8.127(3) Å, *b* = 15.76(1) Å, *c* = 8.041(3) Å, β = 111.816(9)°, volume = 956.4(8) $Å^3$, are based upon the refinement of the XYZ-centroids of 2637 reflections above 20 σ(I) with 5.218° < 2θ < 55.53°.

*Scaling*

Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.782. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5729 and 0.9475.

*Structure solution and refinement*

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_7H_9ClCuN_2S$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 110 variables converged at $R_1$ = 2.64%, for the observed data and $wR_2$ = 6.74% for all data. The goodness-of-fit was 1.000.

The largest peak in the final difference electron density synthesis was 0.454 $e^-/Å^3$ and the largest hole was -0.482 $e^-/Å^3$ with an RMS deviation of 0.055 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.752 $g/cm^3$ and F(000), 508 $e^-$.

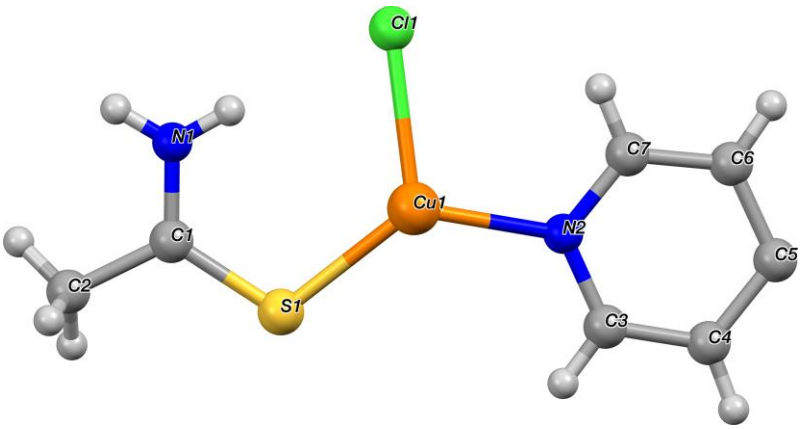


**Figure S7.** Asymmetric unit of compound **1**

**Table S1.** Sample and crystal data for **1**.

| | | |
|---|---|---|
| **Chemical formula** | $C_7H_9ClCuN_2S$ | |
| **Formula weight** | 252.21 | |
| **Temperature** | 296(2) K | |
| **Wavelength** | 0.71073 Å | |
| **Crystal size** | 0.02 x 0.05 x 0.23 mm | |
| **Crystal habit** | clear yellow prismatic | |
| **Crystal system** | monoclinic | |
| **Space group** | $P2_1/c$ | |
| **Unit cell dimensions** | $a$ = 8.127(3) Å | α = 90° |
| | $b$ = 15.76(1) Å | β = 111.816(9)° |
| | $c$ = 8.041(3) Å | γ = 90° |
| **Volume** | 956.4(8) $Å^3$ | |
| **Z** | 4 | |
| **Density (calculated)** | 1.752 $Mg/cm^3$ | |
| **Absorption coefficient** | 2.725 $mm^{-1}$ | |
| **F(000)** | 508 | |

**Table S2.** Data collection and structure refinement for **1.**

| | | |
|---|---|---|
| **Theta range for data collection** | 2.70 to 25.10° | |
| **Index ranges** | -9<=h<=9, -18<=k<=18, -9<=l<=9 | |
| **Reflections collected** | 7463 | |
| **Independent reflections** | 1698 [R(int) = 0.0240] | |
| **Coverage of independent reflections** | 99.9% | |
| **Absorption correction** | multi-scan | |
| **Max. and min. transmission** | 0.9475 and 0.5729 | |
| **Structure solution technique** | direct methods | |
| **Structure solution program** | SHELXS-97 (Sheldrick, 2008) | |
| **Refinement method** | Full-matrix least-squares on $F^2$ | |
| **Refinement program** | SHELXL-97 (Sheldrick, 2008) | |
| **Function minimized** | $\Sigma\, w(F_o^2 - F_c^2)^2$ | |
| **Data / restraints / parameters** | 1698 / 0 / 110 | |
| **Goodness-of-fit on $F^2$** | 1.000 | |
| **Final R indices** | 1375 data; I>2σ(I) | $R_1 = 0.0264$, $wR_2 = 0.0627$ |
| | all data | $R_1 = 0.0362$, $wR_2 = 0.0674$ |
| **Weighting scheme** | $w=1/[\sigma^2(F_o^2)+(0.0319P)^2+0.5895P]$ where $P=(F_o^2+2F_c^2)/3$ | |
| **Largest diff. peak and hole** | 0.454 and -0.482 eÅ$^{-3}$ | |
| **R.M.S. deviation from mean** | 0.055 eÅ$^{-3}$ | |

***b) Single crystal X-ray diffraction supplementary information for 2***

A clear orange prismatic-like specimen of $C_{14}H_{18}ClCuN_4S_2$, approximate dimensions 0.14 mm x 0.18 mm x 0.25 mm, was used for the X-ray crystallographic analysis.

*Data collection and integration*

A total of 5959 frames were collected. The total exposure time was 8.28 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 40400 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 3302 were independent (average redundancy 12.235, completeness = 99.8%, $R_{int}$ = 3.77%, $R_{sig}$ = 1.63%) and 2913 (88.22%) were greater than $2\sigma(F^2)$.

*Unit cell*

The final cell constants of *a* = 8.8605(2) Å, *b* = 9.6615(2) Å, *c* = 11.7506(2) Å, α = 66.423(1)°, β = 82.850(1)°, γ = 78.316(1)°, volume = 901.79(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 9981 reflections above 20 σ(I) with 4.666° < 2θ < 52.28°.

*Scaling*

Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.886. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6918 and 0.8080.

*Structure solution and refinement*

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{14}H_{18}ClCuN_4S_2$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 201 variables converged at $R_1$ = 2.72%, for the observed data and $wR_2$ = 10.89% for all data. The goodness-of-fit was 1.006.

The largest peak in the final difference electron density synthesis was 0.479 $e^-/Å^3$ and the largest hole was -0.443 $e^-/Å^3$ with an RMS deviation of 0.150 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.493 $g/cm^3$ and F(000), 416 $e^-$.

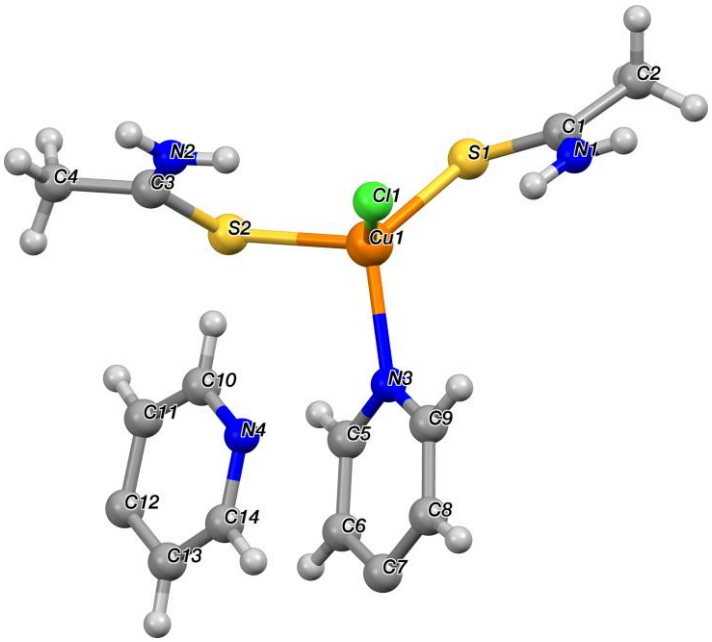


**Figure S8.** Asymmetric unit of compound **2**

**Table S3.** Sample and crystal data for **2**.

| | | |
|---|---|---|
| **Chemical formula** | $C_{14}H_{18}ClCuN_4S_2$ | |
| **Formula weight** | 405.43 | |
| **Temperature** | 296(2) K | |
| **Wavelength** | 0.71073 Å | |
| **Crystal size** | 0.14 x 0.18 x 0.25 mm | |
| **Crystal habit** | clear orange prismatic | |
| **Crystal system** | triclinic | |
| **Space group** | *P*-1 | |
| **Unit cell dimensions** | *a* = 8.8605(2) Å | α = 66.4230(10)° |
| | *b* = 9.6615(2) Å | β = 82.8500(10)° |
| | *c* = 11.7506(2) Å | γ = 78.3160(10)° |
| **Volume** | 901.79(3) $Å^3$ | |
| **Z** | 2 | |
| **Density (calculated)** | 1.493 $Mg/cm^3$ | |
| **Absorption coefficient** | 1.591 $mm^{-1}$ | |
| **F(000)** | 416 | |

**Table S4.** Data collection and structure refinement for **2.**

| | | |
|---|---|---|
| **Theta range for data collection** | 1.89 to 25.35° | |
| **Index ranges** | -10<=h<=10, -11<=k<=11, -14<=l<=14 | |
| **Reflections collected** | 40400 | |
| **Independent reflections** | 3302 [R(int) = 0.0377] | |
| **Coverage of independent reflections** | 99.8% | |
| **Absorption correction** | multi-scan | |
| **Max. and min. transmission** | 0.8080 and 0.6918 | |
| **Structure solution technique** | direct methods | |
| **Structure solution program** | SHELXS-97 (Sheldrick, 2008) | |
| **Refinement method** | Full-matrix least-squares on $F^2$ | |
| **Refinement program** | SHELXL-97 (Sheldrick, 2008) | |
| **Function minimized** | $\Sigma\, w(F_o^2 - F_c^2)^2$ | |
| **Data / restraints / parameters** | 3302 / 0 / 201 | |
| **Goodness-of-fit on $F^2$** | 1.006 | |
| **Final R indices** | 2913 data; I>2σ(I) | $R_1$ = 0.0272, $wR_2$ = 0.0886 |
| | all data | $R_1$ = 0.0351, $wR_2$ = 0.1089 |
| **Weighting scheme** | $w=1/[\sigma^2(F_o^2)+(0.0783P)^2+0.2906P]$ where $P=(F_o^2+2F_c^2)/3$ | |
| **Largest diff. peak and hole** | 0.479 and -0.443 $eÅ^{-3}$ | |
| **R.M.S. deviation from mean** | 0.150 $eÅ^{-3}$ | |

***c) Single crystal X-ray diffraction supplementary information for 3***

A clear yellow prismatic-like specimen of $C_{14}H_{18}BrCuN_4S_2$, approximate dimensions 0.06 mm x 0.12 mm x 0.16 mm, was used for the X-ray crystallographic analysis.

*Data collection and integration*

A total of 1986 frames were collected. The total exposure time was 16.55 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 31747 reflections to a maximum θ angle of 25.34° (0.83 Å resolution), of which 3319 were independent (average redundancy 9.565, completeness = 100.0%, $R_{int}$ = 4.75%, $R_{sig}$ = 2.69%) and 2638 (79.48%) were greater than $2\sigma(F^2)$.

*Unit cell*

The final cell constants of *a* = 21.7441(8) Å, *b* = 9.8378(5) Å, *c* = 16.9298(8) Å, β = 90.766(2)°, volume = 3621.2(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 7271 reflections above 20 σ(I) with 4.544° < 2θ < 50.84°.

*Scaling*

Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.910. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5932 and 0.8110.

*Structure solution and refinement*

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *C*2/*c*, with Z = 8 for the formula unit, $C_{14}H_{18}BrCuN_4S_2$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 201 variables converged at $R_1$ = 2.51%, for the observed data and $wR_2$ = 8.86% for all data. The goodness-of-fit was 1.000.

The largest peak in the final difference electron density synthesis was 0.401 $e^-/Å^3$ and the largest hole was -0.316 $e^-/Å^3$ with an RMS deviation of 0.097 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.650 $g/cm^3$ and F(000), 1808 $e^-$.

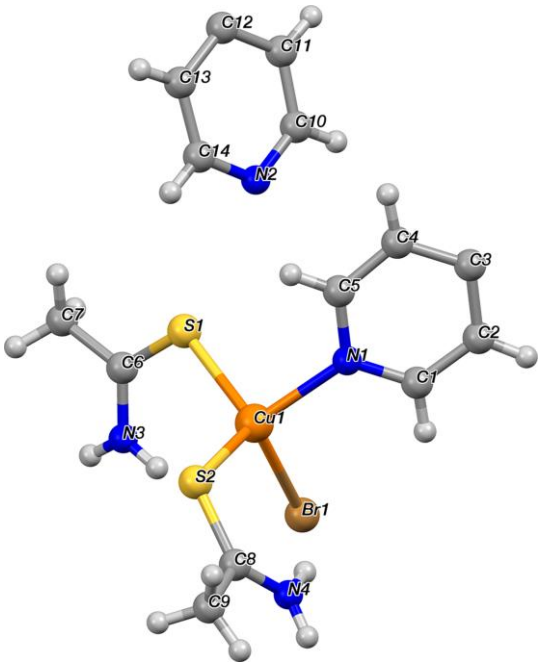


**Figure S9.** Asymmetric unit of compound **3**

**Table S5.** Sample and crystal data for **3.**

| | | |
|---|---|---|
| **Chemical formula** | $C_{14}H_{18}BrCuN_4S_2$ | |
| **Formula weight** | 449.89 | |
| **Temperature** | 296(2) K | |
| **Wavelength** | 0.71073 Å | |
| **Crystal size** | 0.06 x 0.12 x 0.16 mm | |
| **Crystal habit** | clear yellow prismatic | |
| **Crystal system** | monoclinic | |
| **Space group** | *C*2/*c* | |
| **Unit cell dimensions** | *a* = 21.7441(8) Å | α = 90° |
| | *b* = 9.8378(5) Å | β = 90.766(2)° |
| | *c* = 16.9298(8) Å | γ = 90° |
| **Volume** | 3621.2(3) $Å^3$ | |
| **Z** | 8 | |
| **Density (calculated)** | 1.650 $Mg/cm^3$ | |
| **Absorption coefficient** | 3.644 $mm^{-1}$ | |
| **F(000)** | 1808 | |

**Table S.6** Data collection and structure refinement for **3.**

| | | |
|---|---|---|
| **Theta range for data collection** | 1.87 to 25.34° | |
| **Index ranges** | -26<=h<=26, -11<=k<=11, -20<=l<=20 | |
| **Reflections collected** | 31747 | |
| **Independent reflections** | 3319 [R(int) = 0.0475] | |
| **Coverage of independent reflections** | 100.0% | |
| **Absorption correction** | multi-scan | |
| **Max. and min. transmission** | 0.8110 and 0.5932 | |
| **Structure solution technique** | direct methods | |
| **Structure solution program** | SHELXS-97 (Sheldrick, 2008) | |
| **Refinement method** | Full-matrix least-squares on $F^2$ | |
| **Refinement program** | SHELXL-97 (Sheldrick, 2008) | |
| **Function minimized** | $\Sigma\, w(F_o^2 - F_c^2)^2$ | |
| **Data / restraints / parameters** | 3319 / 0 / 201 | |
| **Goodness-of-fit on $F^2$** | 1.000 | |
| **Final R indices** | 2638 data; I>2σ(I) | $R_1$ = 0.0251, $wR_2$ = 0.0691 |
| | all data | $R_1$ = 0.0415, $wR_2$ = 0.0886 |
| **Weighting scheme** | $w=1/[\sigma^2(F_o^2)+(0.0595P)^2+0.0000P]$ where $P=(F_o^2+2F_c^2)/3$ | |
| **Largest diff. peak and hole** | 0.401 and -0.316 $eÅ^{-3}$ | |
| **R.M.S. deviation from mean** | 0.097 $eÅ^{-3}$ | |

***d) Single crystal X-ray diffraction supplementary information for 4***

A clear orange prismatic-like specimen of $C_{28}H_{36}Cu_2I_2N_8S_4$, approximate dimensions 0.08 mm x 0.17 mm x 0.19 mm, was used for the X-ray crystallographic analysis.

*Data collection and integration*

A total of 1949 frames were collected. The total exposure time was 8.12 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 32680 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 3364 were independent (average redundancy 9.715, completeness = 99.6%, $R_{int}$ = 3.60%, $R_{sig}$ = 2.01%) and 3092 (91.91%) were greater than $2\sigma(F^2)$.

*Unit cell*

The final cell constants of *a* = 21.910(3) Å, *b* = 9.944(2) Å, *c* = 16.891(3) Å, β = 90.414(7)°, volume = 3680.1(9) $Å^3$, are based upon the refinement of the XYZ-centroids of 9985 reflections above 20 σ(I) with 4.498° < 2θ < 56.52°.

*Scaling*

Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.767. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5911 and 0.7900.

*Structure solution and refinement*

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *C*2/*c*, with Z = 4 for the formula unit, $C_{28}H_{36}Cu_2I_2N_8S_4$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 201 variables converged at $R_1$ = 1.84%, for the observed data and $wR_2$ = 7.03% for all data. The goodness-of-fit was 1.001.

The largest peak in the final difference electron density synthesis was 0.645 $e^-/Å^3$ and the largest hole was -0.783 $e^-/Å^3$ with an RMS deviation of 0.143 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.794 $g/cm^3$ and F(000), 1952 $e^-$.

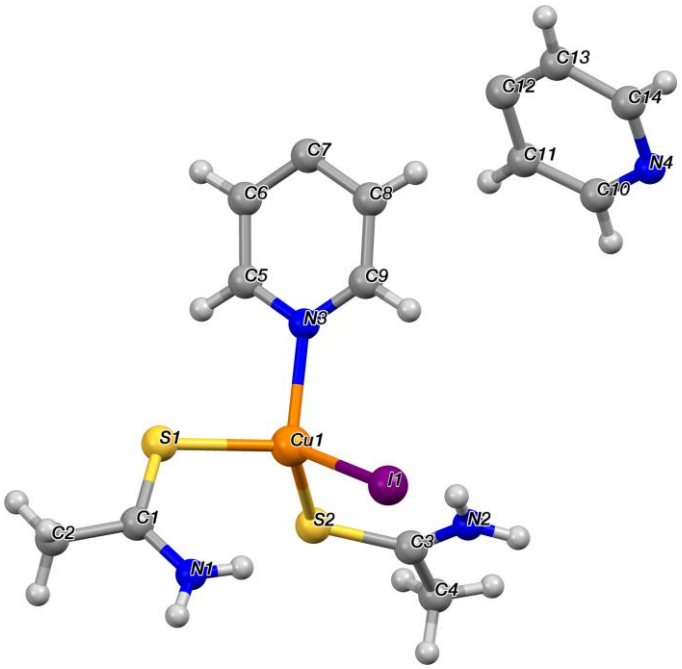


**Figure S10.** Asymmetric unit of compound **4**

**Table S7.** Sample and crystal data for **4.**

| | | |
|---|---|---|
| **Chemical formula** | $C_{28}H_{36}Cu_2I_2N_8S_4$ | |
| **Formula weight** | 993.77 | |
| **Temperature** | 100(2) K | |
| **Wavelength** | 0.71073 Å | |
| **Crystal size** | 0.08 x 0.17 x 0.19 mm | |
| **Crystal habit** | clear orange prismatic | |
| **Crystal system** | monoclinic | |
| **Space group** | *C*2/*c* | |
| **Unit cell dimensions** | *a* = 21.910(3) Å | α = 90° |
| | *b* = 9.944(2) Å | β = 90.414(7)° |
| | *c* = 16.891(3) Å | γ = 90° |
| **Volume** | 3680.1(9) $Å^3$ | |
| **Z** | 4 | |
| **Density (calculated)** | 1.794 $Mg/cm^3$ | |
| **Absorption coefficient** | 3.092 $mm^{-1}$ | |
| **F(000)** | 1952 | |

**Table S8.** Data collection and structure refinement for **4.**

| | | |
|---|---|---|
| **Theta range for data collection** | 1.86 to 25.35° | |
| **Index ranges** | -26<=h<=26, -11<=k<=11, -19<=l<=20 | |
| **Reflections collected** | 32680 | |
| **Independent reflections** | 3364 [R(int) = 0.0360] | |
| **Coverage of independent reflections** | 99.6% | |
| **Absorption correction** | multi-scan | |
| **Max. and min. transmission** | 0.7900 and 0.5911 | |
| **Structure solution technique** | direct methods | |
| **Structure solution program** | SHELXS-97 (Sheldrick, 2008) | |
| **Refinement method** | Full-matrix least-squares on $F^2$ | |
| **Refinement program** | SHELXL-97 (Sheldrick, 2008) | |
| **Function minimized** | $\Sigma\, w(F_o^2 - F_c^2)^2$ | |
| **Data / restraints / parameters** | 3364 / 0 / 201 | |
| **Goodness-of-fit on $F^2$** | 1.001 | |
| **Final R indices** | 3092 data; I>2σ(I) | $R_1$ = 0.0184, $wR_2$ = 0.0582 |
| | all data | $R_1$ = 0.0224, $wR_2$ = 0.0703 |
| **Weighting scheme** | $w=1/[\sigma^2(F_o^2)+(0.0553P)^2+1.3229P]$ where $P=(F_o^2+2F_c^2)/3$ | |
| **Largest diff. peak and hole** | 0.645 and -0.783 $eÅ^{-3}$ | |
| **R.M.S. deviation from mean** | 0.143 $eÅ^{-3}$ | |

***e) Single crystal X-ray diffraction supplementary information for 5***

A clear yellow prismatic-like specimen of $C_4H_7ClCuN_2S$, approximate dimensions 0.08 mm x 0.10 mm x 0.19 mm, was used for the X-ray crystallographic analysis.

*Data collection and integration*

A total of 1985 frames were collected. The total exposure time was 16.54 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 11822 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 1378 were independent (average redundancy 8.579, completeness = 100.0%, $R_{int}$ = 2.41%, $R_{sig}$ = 1.16%) and 1317 (95.57%) were greater than $2\sigma(F^2)$.

*Unit cell*

The final cell constants of a = 7.9771(1) Å, b = 10.6730(1) Å, c = 8.9210(1) Å, β = 97.182(1)°, volume = 753.57(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 8366 reflections above 20 σ(I) with 5.979° < 2θ < 56.75°.

*Scaling*

Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.810. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5610 and 0.7704.

*Structure solution and refinement*

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_4H_7ClCuN_2S$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 83 variables converged at $R_1$ = 1.87%, for the observed data and $wR_2$ = 5.27% for all data. The goodness-of-fit was 1.000.

The largest peak in the final difference electron density synthesis was 0.333 $e^-/Å^3$ and the largest hole was -0.567 $e^-/Å^3$ with an RMS deviation of 0.056 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.888 $g/cm^3$ and F(000), 428 $e^-$.

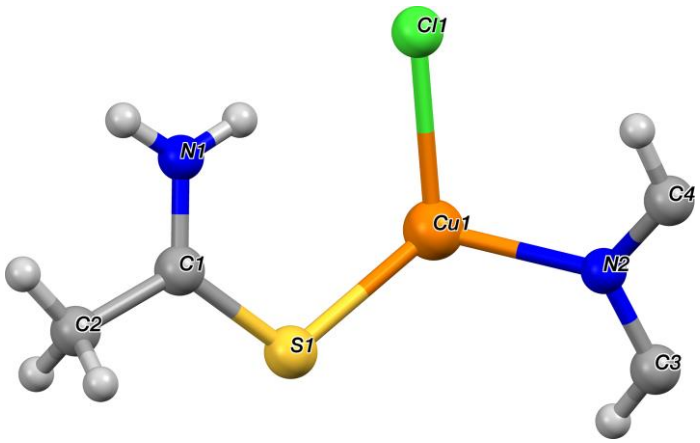


**Figure S11.** Asymmetric unit of compound **5**

**Table S9.** Sample and crystal data for **5.**

| | | |
|---|---|---|
| **Chemical formula** | $C_4H_7ClCuN_2S$ | |
| **Formula weight** | 214.17 | |
| **Temperature** | 296(2) K | |
| **Wavelength** | 0.71073 Å | |
| **Crystal size** | 0.08 x 0.10 x 0.19 mm | |
| **Crystal habit** | clear yellow prismatic | |
| **Crystal system** | monoclinic | |
| **Space group** | $P2_1/n$ | |
| **Unit cell dimensions** | $a$ = 7.9771(1) Å | α = 90° |
| | $b$ = 10.6730(1) Å | β = 97.182(1)° |
| | $c$ = 8.9210(1) Å | γ = 90° |
| **Volume** | 753.57(2) $Å^3$ | |
| **Z** | 4 | |
| **Density (calculated)** | 1.888 $Mg/cm^3$ | |
| **Absorption coefficient** | 3.439 $mm^{-1}$ | |
| **F(000)** | 428 | |

**Table S10.** Data collection and structure refinement for **5.**

| | | |
|---|---|---|
| **Theta range for data collection** | 2.99 to 25.35° | |
| **Index ranges** | -9<=h<=9, -12<=k<=12, -10<=l<=10 | |
| **Reflections collected** | 11822 | |
| **Independent reflections** | 1378 [R(int) = 0.0241] | |
| **Coverage of independent reflections** | 100.0% | |
| **Absorption correction** | multi-scan | |
| **Max. and min. transmission** | 0.7704 and 0.5610 | |
| **Structure solution technique** | direct methods | |
| **Structure solution program** | SHELXS-97 (Sheldrick, 2008) | |
| **Refinement method** | Full-matrix least-squares on $F^2$ | |
| **Refinement program** | SHELXL-97 (Sheldrick, 2008) | |
| **Function minimized** | $\Sigma\, w(F_o^2 - F_c^2)^2$ | |
| **Data / restraints / parameters** | 1378 / 0 / 83 | |
| **Goodness-of-fit on $F^2$** | 1.000 | |
| **Final R indices** | 1317 data; I>2σ(I) | $R_1$ = 0.0187, $wR_2$ = 0.0520 |
| | all data | $R_1$ = 0.0197, $wR_2$ = 0.0527 |
| **Weighting scheme** | $w=1/[\sigma^2(F_o^2)+(0.0311P)^2+0.4035P]$ where $P=(F_o^2+2F_c^2)/3$ | |
| **Largest diff. peak and hole** | 0.333 and -0.567 $eÅ^{-3}$ | |
| **R.M.S. deviation from mean** | 0.056 $eÅ^{-3}$ | |

***f) Single crystal X-ray diffraction supplementary information for 6***

A clear colourless prismatic-like specimen of $C_4H_{10}CuIN_2S_2$, approximate dimensions 0.08 mm x 0.17 mm x 0.18 mm, was used for the X-ray crystallographic analysis.

*Data collection and integration*

A total of 4017 frames were collected. The total exposure time was 11.16 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 16592 reflections to a maximum θ angle of 25.34° (0.83 Å resolution), of which 1872 were independent (average redundancy 8.863, completeness = 100.0%, $R_{int}$ = 2.17%, $R_{sig}$ = 1.13%) and 1747 (93.32%) were greater than $2\sigma(F^2)$.

*Unit cell*

The final cell constants of *a* = 7.4292(2) Å, *b* = 8.0762(2) Å, *c* = 9.6140(2) Å, α = 107.059(1)°, β = 90.971(1)°, γ = 110.972(1)°, volume = 510.10(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 9474 reflections above 20 σ(I) with 5.703° < 2θ < 56.50°.

*Scaling*

Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.814. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4368 and 0.6667.

*Structure solution and refinement*

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_4H_{10}CuIN_2S_2$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 93 variables converged at $R_1$ = 1.99%, for the observed data and $wR_2$ = 5.16% for all data. The goodness-of-fit was 1.004.

The largest peak in the final difference electron density synthesis was 0.513 $e^-/Å^3$ and the largest hole was -0.479 $e^-/Å^3$ with an RMS deviation of 0.073 $e^-/Å^3$. On the basis of the final model, the calculated density was 2.218 $g/cm^3$ and F(000), 324 $e^-$.

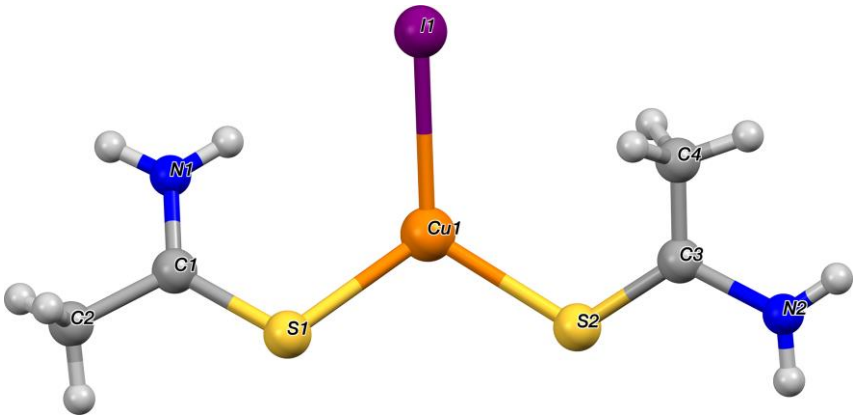


**Figure S12.** Asymmetric unit of compound **6**

**Table S11.** Sample and crystal data for **6.**

| | | |
|---|---|---|
| **Chemical formula** | $C_4H_{10}CuIN_2S_2$ | |
| **Formula weight** | 340.70 | |
| **Temperature** | 296(2) K | |
| **Wavelength** | 0.71073 Å | |
| **Crystal size** | 0.08 x 0.17 x 0.18 mm | |
| **Crystal habit** | clear colourless prismatic | |
| **Crystal system** | triclinic | |
| **Space group** | *P*-1 | |
| **Unit cell dimensions** | *a* = 7.4292(2) Å | α = 107.059(1)° |
| | *b* = 8.0762(2) Å | β = 90.971(1)° |
| | *c* = 9.6140(2) Å | γ = 110.972(1)° |
| **Volume** | 510.10(2) $Å^3$ | |
| **Z** | 2 | |
| **Density (calculated)** | 2.218 $Mg/cm^3$ | |
| **Absorption coefficient** | 5.515 $mm^{-1}$ | |
| **F(000)** | 324 | |

**Table S12.** Data collection and structure refinement for **6.**

| | | |
|---|---|---|
| **Theta range for data collection** | 2.24 to 25.34° | |
| **Index ranges** | -8<=h<=8, -9<=k<=9, -11<=l<=11 | |
| **Reflections collected** | 16592 | |
| **Independent reflections** | 1872 [R(int) = 0.0217] | |
| **Coverage of independent reflections** | 100.0% | |
| **Absorption correction** | multi-scan | |
| **Max. and min. transmission** | 0.6667 and 0.4368 | |
| **Structure solution technique** | direct methods | |
| **Structure solution program** | SHELXS-97 (Sheldrick, 2008) | |
| **Refinement method** | Full-matrix least-squares on $F^2$ | |
| **Refinement program** | SHELXL-97 (Sheldrick, 2008) | |
| **Function minimized** | $\Sigma\, w(F_o^2 - F_c^2)^2$ | |
| **Data / restraints / parameters** | 1872 / 0 / 93 | |
| **Goodness-of-fit on $F^2$** | 1.004 | |
| **Final R indices** | 1747 data; I>2σ(I) | $R_1$ = 0.0199, $wR_2$ = 0.0503 |
| | all data | $R_1$ = 0.0221, $wR_2$ = 0.0516 |
| **Weighting scheme** | $w=1/[\sigma^2(F_o^2)+(0.0238P)^2+0.8331P]$ where $P=(F_o^2+2F_c^2)/3$ | |
| **Largest diff. peak and hole** | 0.513 and -0.479 $eÅ^{-3}$ | |
| **R.M.S. deviation from mean** | 0.073 $eÅ^{-3}$ | |

***g) Hydrogen bonds in compounds 1-6***

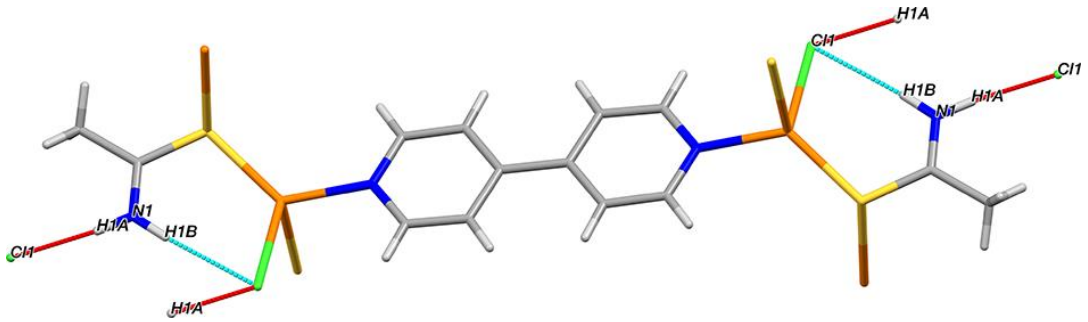


**Figure S13.** Intra- (in blue) and interlayer (in red) hydrogen bonds in **1**.

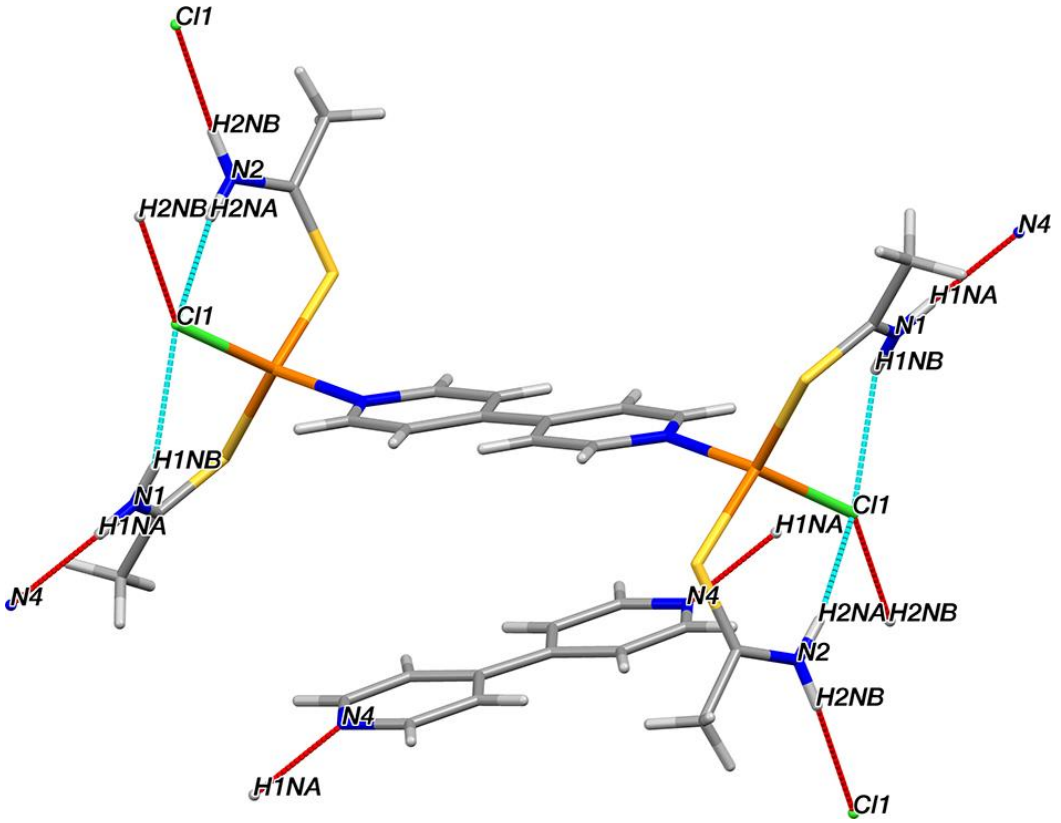


**Figure S14.** Intra- (in blue) and intermolecular (in red) hydrogen bonds in **2**.

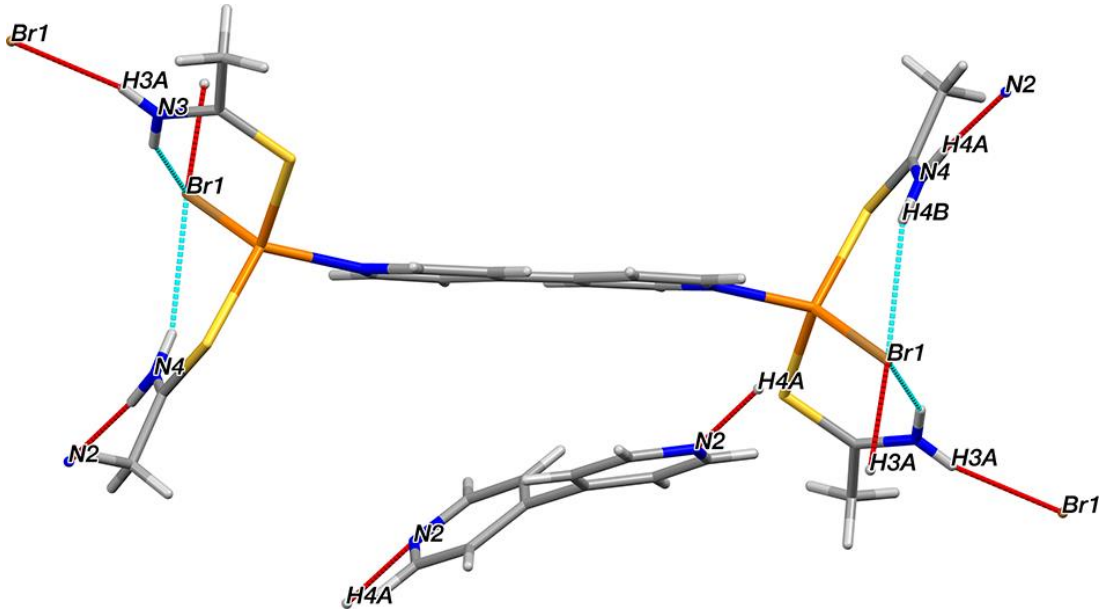


**Figure S15.** Intra- (in blue) and intermolecular (in red) hydrogen bonds in **3**.

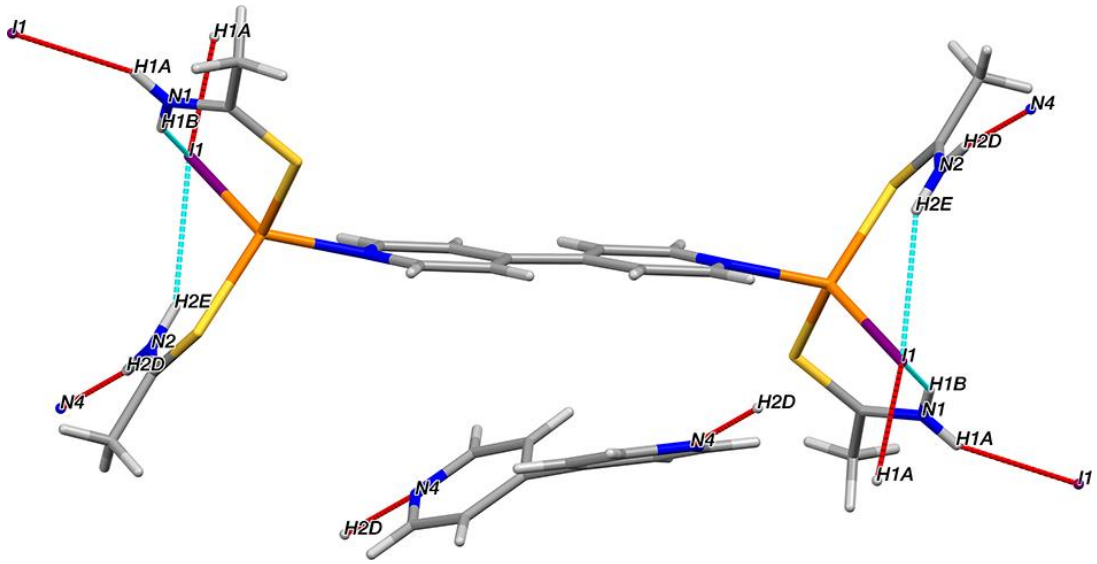


**Figure S16.** Intra- (in blue) and intermolecular (in red) hydrogen bonds in **4**.

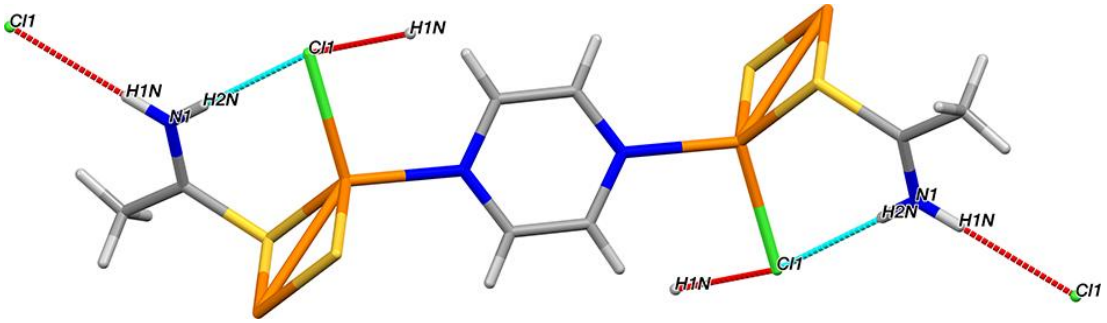


**Figure S17.** Intra- (in blue) and interchain (in red) hydrogen bonds in **5**.

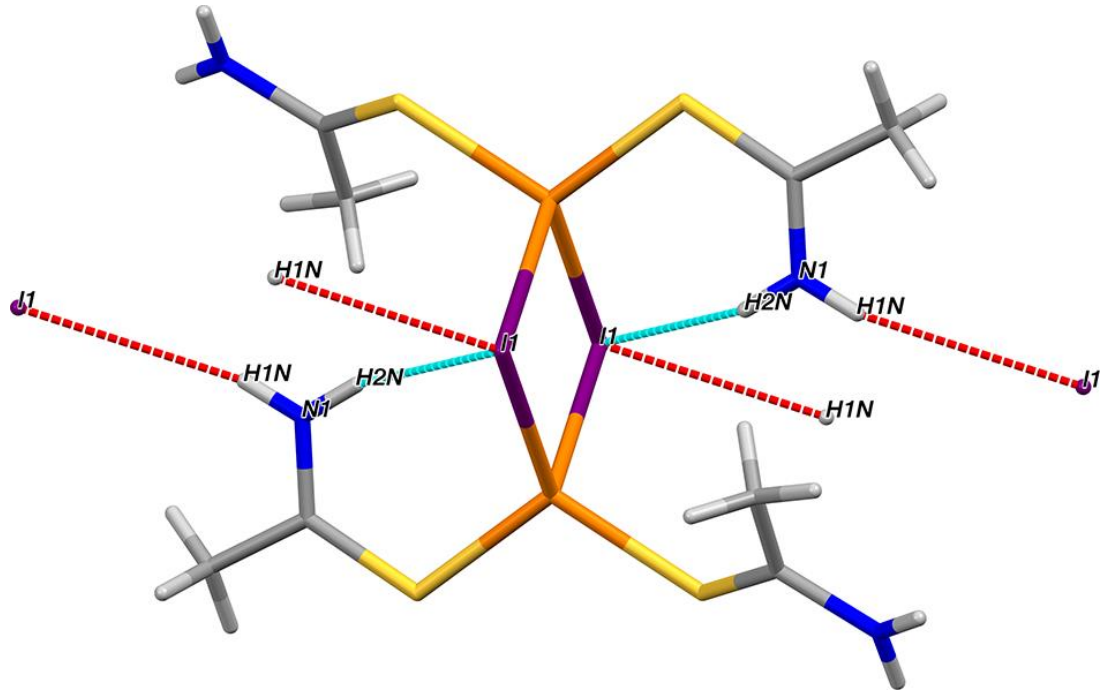


**Figure S18.** Intra- (in blue) and intermolecular (in red) hydrogen bonds in **6**.

**Table S13.** Hydrogen bonds in compounds **1-6**.

| | D-H | d(D-H)/ Å | d(H···A)/ Å | <DHA/° | d(D···A)/ Å | A |
|---|---|---|---|---|---|---|
| **1** | N1-H1A | 0.860 | 2.428 | 155.88 | 3.232 | Cl1 [ -x+1, -y+2, -z ] |
| | N1-H1B | 0.860 | 2.379 | 175.05 | 3.237 | Cl1 |
| **2** | N1-H1NA | 0.860 | 2.109 | 177.82 | 2.968 | N4 [ -x+1, -y+1, -z+1 ] |
| | N1-H1NB | 0.860 | 2.589 | 152.02 | 3.373 | Cl1 |
| | N2-H2NA | 0.860 | 2.412 | 167.18 | 3.257 | Cl1 |
| | N2-H2NB | 0.860 | 2.570 | 147.00 | 3.325 | Cl1 [ -x+2, -y+1, -z+1 ] |
| **3** | N3-H3A | 0.860 | 2.725 | 158.25 | 3.538 | Br1 [ -x+3/2, y-1/2, -z+3/2 ] |
| | N3-H3B | 0.860 | 2.752 | 153.14 | 3.540 | Br1 |
| | N4-H4A | 0.860 | 2.107 | 174.58 | 2.964 | N2 [ -x+3/2, y-1/2, -z+3/2 ] |
| | N4-H4B | 0.860 | 2.645 | 157.71 | 3.457 | Br1 |
| **4** | N1-H1A | 0.880 | 2.795 | 155.98 | 3.617 | I1 [ -x+1/2, y+1/2, -z+3/2 ] |
| | N1-H1B | 0.880 | 2.826 | 150.78 | 3.620 | I1 |
| | N2-H2D | 0.880 | 2.059 | 170.48 | 2.930 | N4 [ -x+1/2, y+1/2, -z+1/2 ] |
| | N2-H2E | 0.880 | 2.826 | 149.72 | 3.613 | I1 |
| **5** | N1-H1N | 0.860 | 2.350 | 177.24 | 3.210 | Cl1 [ x+1/2, -y+1/2, z+1/2 ] |
| | N1-H2N | 0.860 | 2.320 | 168.66 | 3.167 | Cl1 |
| **6** | N1-H1N | 0.860 | 2.981 | 156.77 | 3.787 | I1 [ -x, -y+1, -z+1 ] |
| | N1-H2N | 0.860 | 2.985 | 150.11 | 3.755 | I1 |

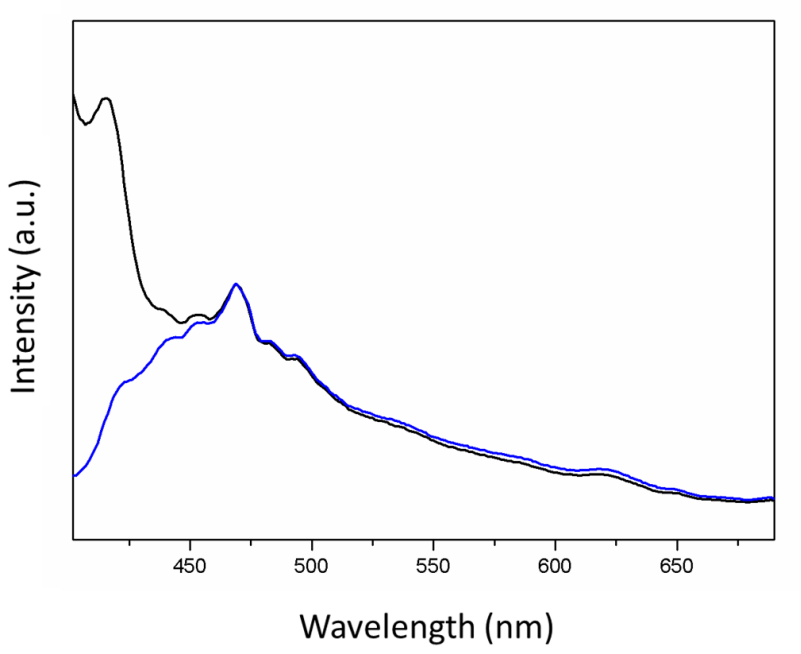


**Figure S19.** Emission spectra of **6** (blue) and thioacetamide (black) in the solid state at 359 nm.

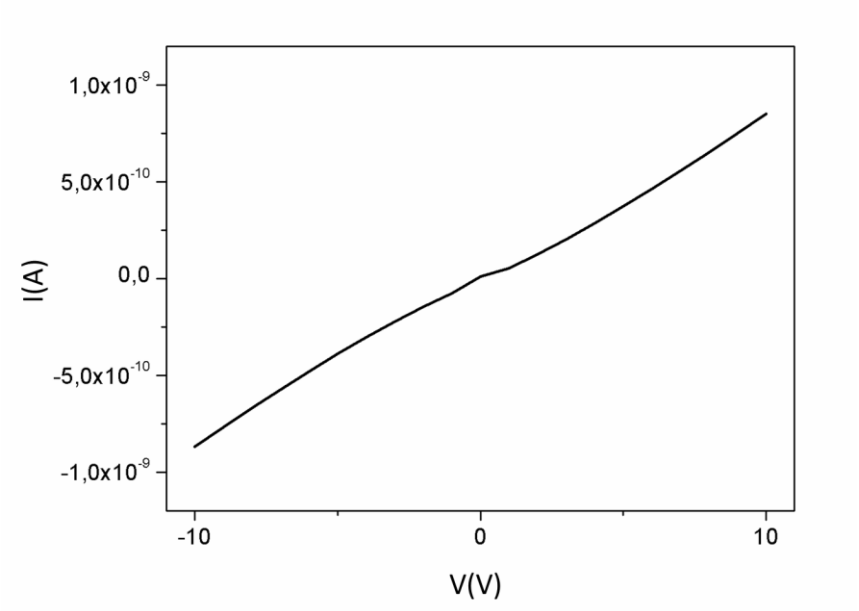


**Figure S20.** Intensity versus voltage corresponding to one crystal of compound **1**, obtained using two contact method, with graphite paint at 300 K.