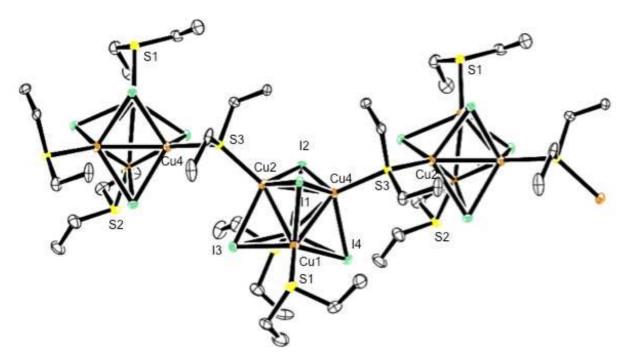
## **Supporting Information**

## Reactivity of CuI and CuBr towards $Et_2S$ ; a Reinvestigation on the Self-Assembly of Luminescent Copper(I) Coordination Polymers

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**Figure S1.** ORTEP view of the polymer chain of **1** at 115K. Thermal ellipsoids are drawn at the 50% probability

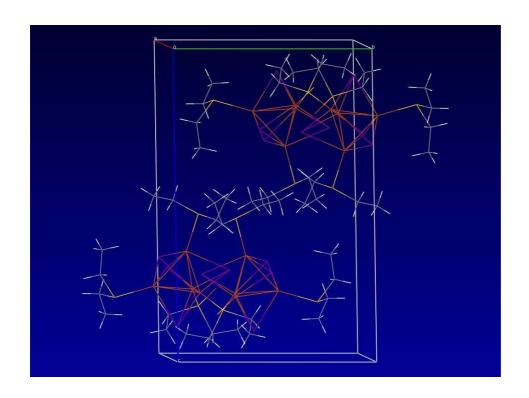


Figure S2a. Projection of the unit cell of 1 on bc plane.

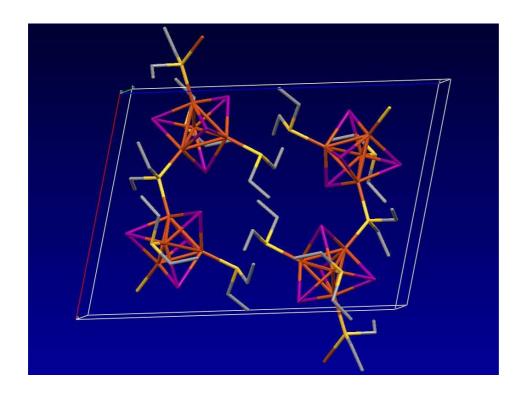
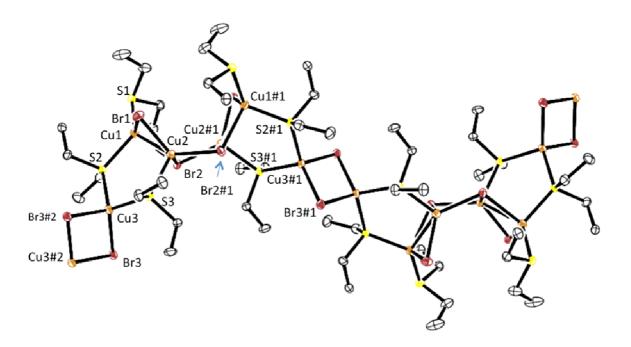


Figure S2b. Projection of the unit cell of 1 on ac plane.



**Figure S3.** ORTEP view of the polymer chain of **2.** Thermal ellipsoids are drawn at the 50% probability level. Symmetry operations: #1) -1-x, y, 0.5-z (2; -0.5, y, 0.25), #2) -1-x, 1-y, -z (i; -0.5, 0.5, 0)

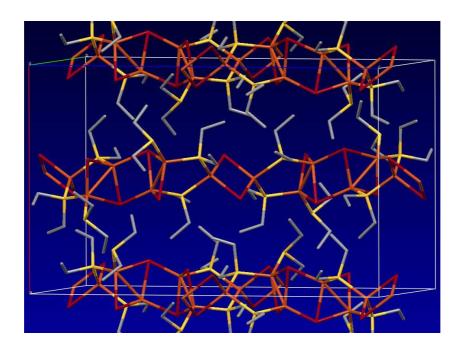
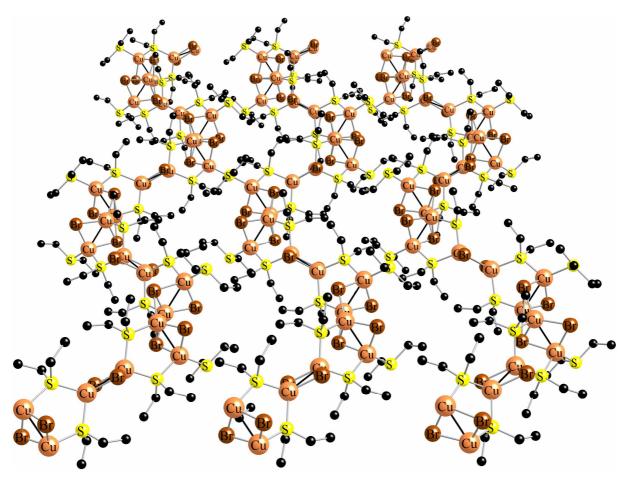
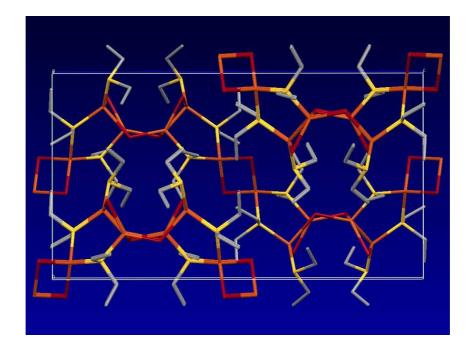


Figure S4a. Projection of the unit cell of 2 down y axis.



**Figure S4b.** Perspective view down the *x* axis of **2.** 



**Figure S4c.** Projection of the unit cell of **2** (on *bc* plane) showing the presence of twofold axes and symmetry centers.



**Figure S5.** Intense luminescence of  $[(Et_2S)_3\{Cu_4(\mu_3-I)_4\}]_n$  (right Schlenk tube) and  $[(THT)_2Cu(\mu_2-I)_2Cu(THT)_2]$  (left Schlenk tube) under UV-light at 366 nm.