Supporting Information belonging to the publication

Rigidity Effect of the Dithioether Spacer on the Size of the Luminescent Cluster $(Cu_2I_2)_n$ (n = 2, 3) in their Coordination Polymers

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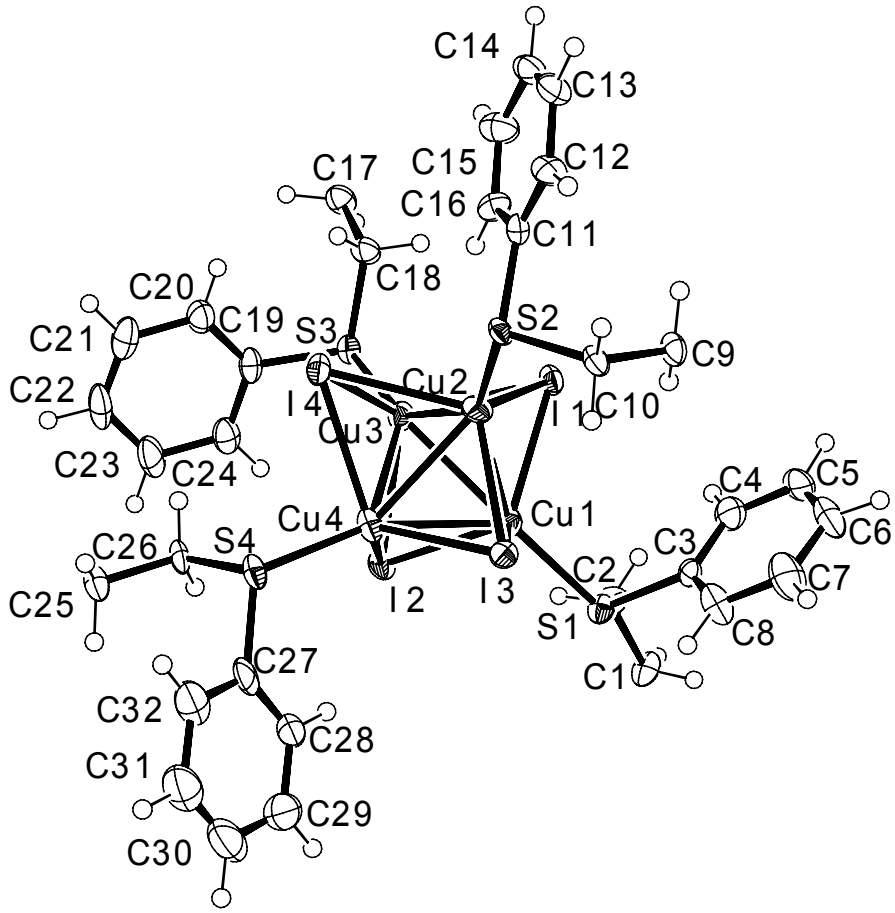

Figure S1. ORTEP plot of **1** (asymmetric unit) at 50 % probability level.

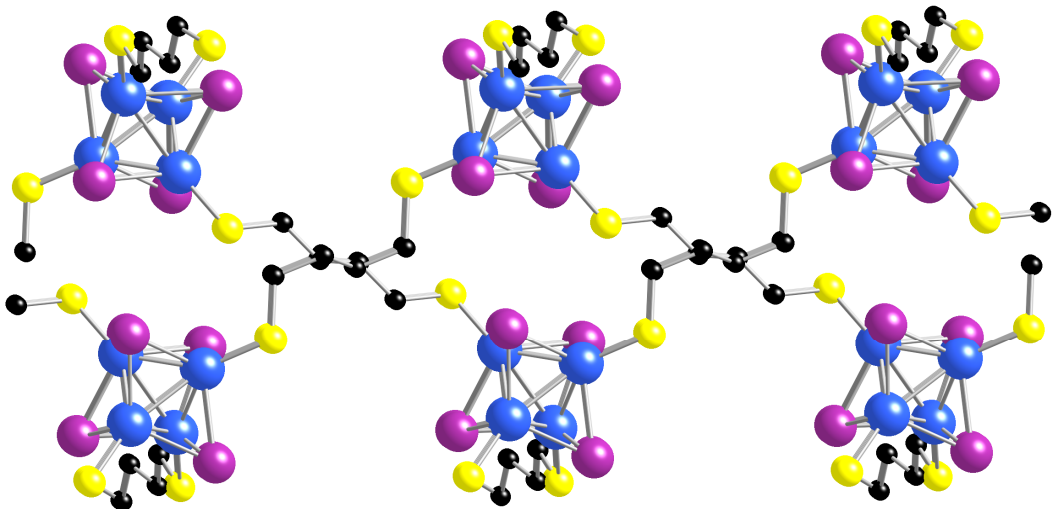

Figure S2. View on the *bc* plane of 2D polymer **1**. The phenyl groups are omitted for clarity (C = black, S = yellow, Cu = blue, I = magenta).

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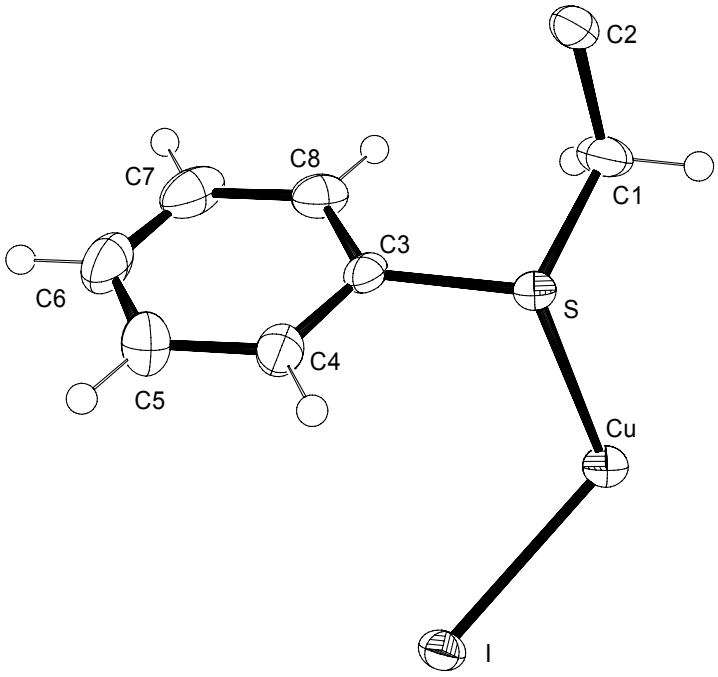

Figure S3. ORTEP plot of **2** (asymmetric unit) at 50 % probability level.

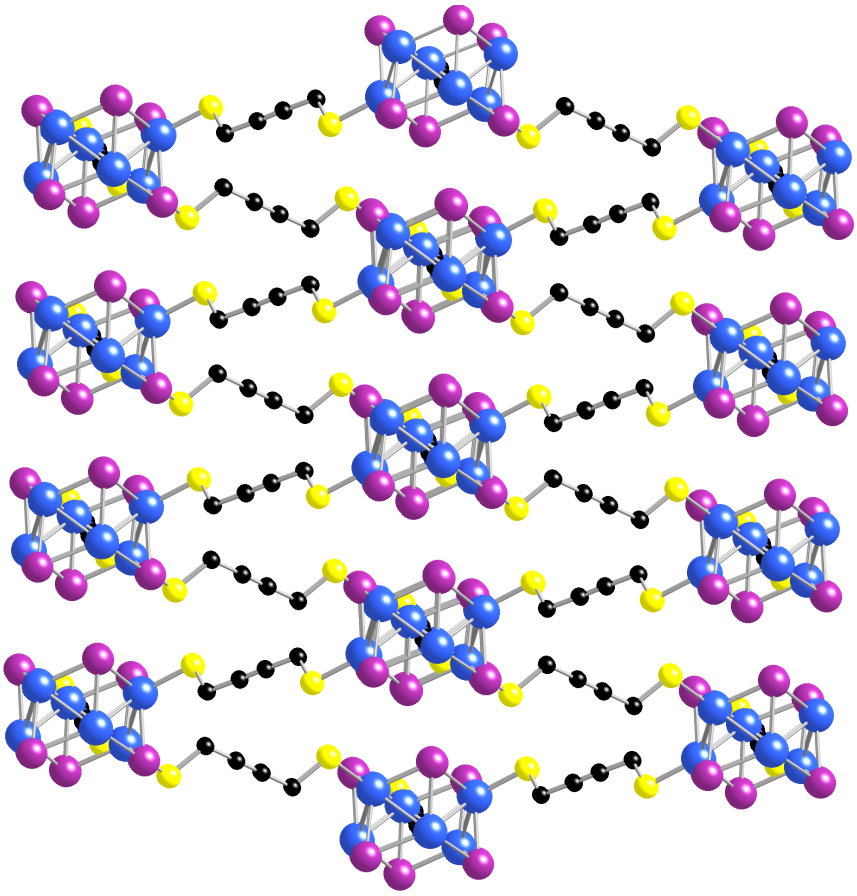

Figure S4. View on the *bc* plane of **2** showing the hexanuclear $Cu_6(\mu^2\text{-}I)_6$ SBUs (C = black, S = yellow, Cu = blue, I = magenta).

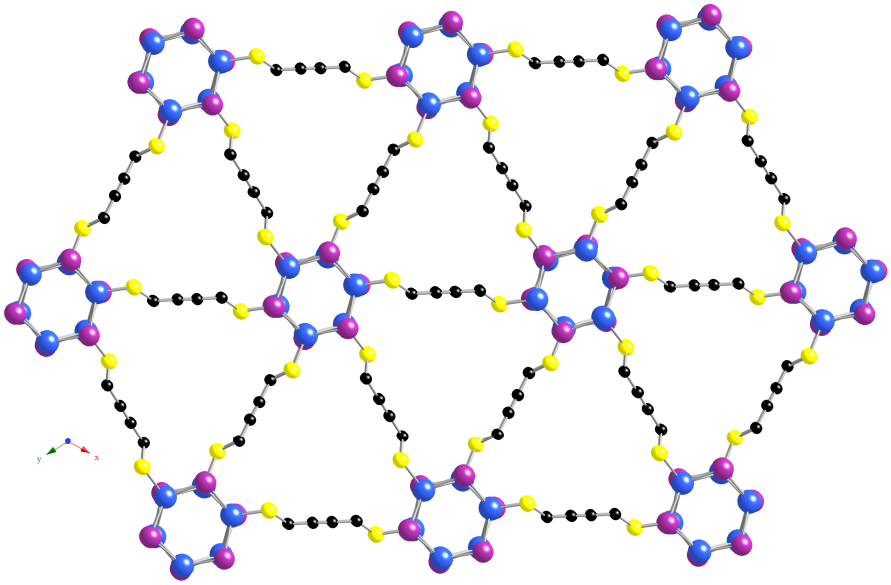

Figure S5 View on the *ab* plane of the 3D network of **2**. The phenyl groups are omitted for clarity (C = black, S = yellow, Cu = blue, I = magenta).

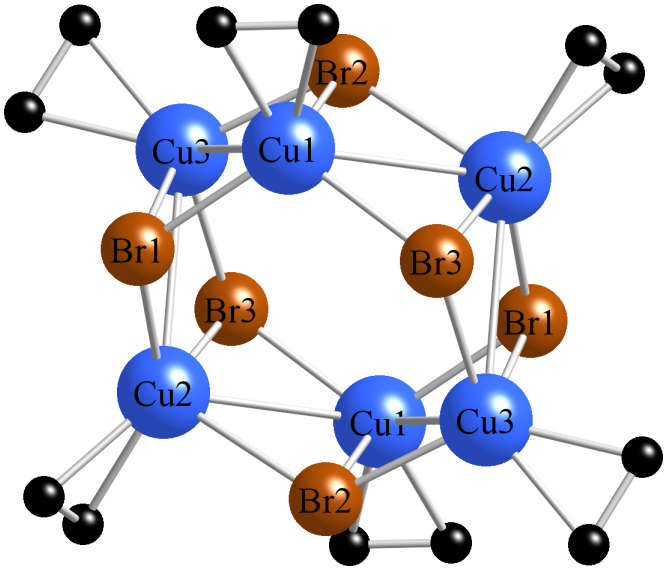

Figure S6. Picture of the core of $[Cu_6(\mu_3\text{-}Br)_6(TTT)_2]_n$ (TTT = triaallyl-1,3,5-triazine-trione) according to reference 14a. Selected bond distances(Å): Cu(1)-Br(1) 2.454, Cu(1)-Br(2) 2.669, Cu(1)-Br(3) 2.491, Cu(2)-Br(1) 2.447, Cu(3)-Br(1) 2.741.
All Cu•••Cu distances are in the range between 3.203 - 3.316 Å.

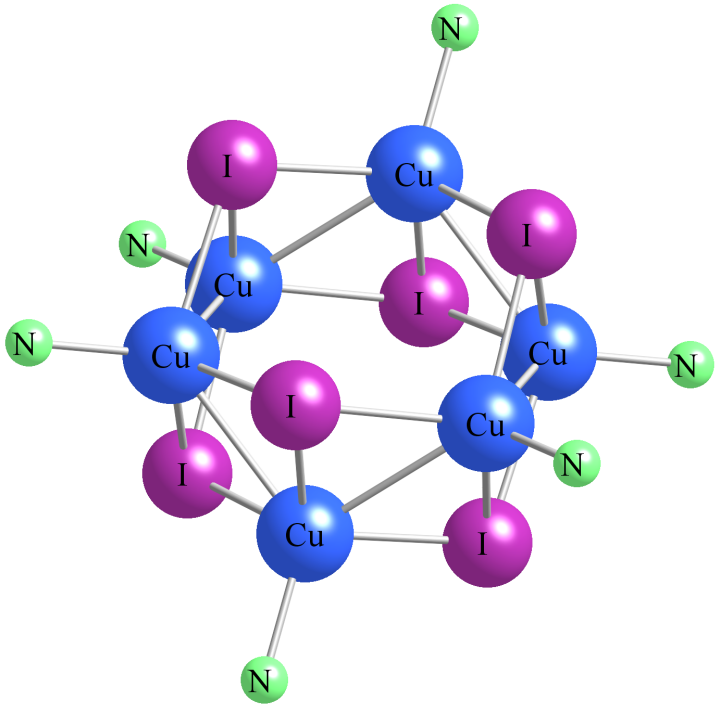

Figure S7. Picture of the core of $[Cu_6(\mu_3\text{-}I)_6py_6]_n$ according to reference 14b. Selected bond distances (Å) : Cu-I 2.7248(4), Cu-I* 2.6628(5), Cu-I# 2.5991(5), Cu-Cu# 2.9645(5)

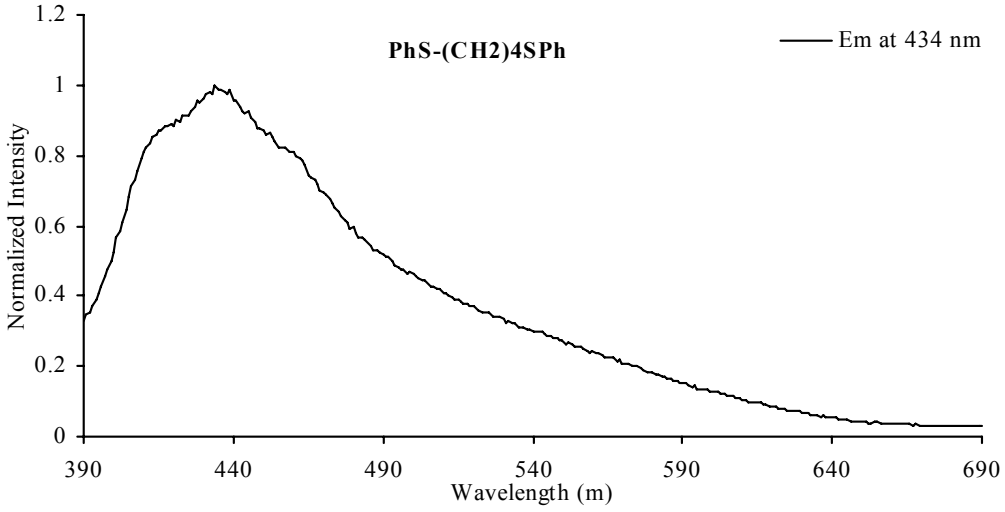

Figure S8. Normalized solid-state emission spectrum of ligand **L1** (λ_{excit} = 360 nm).

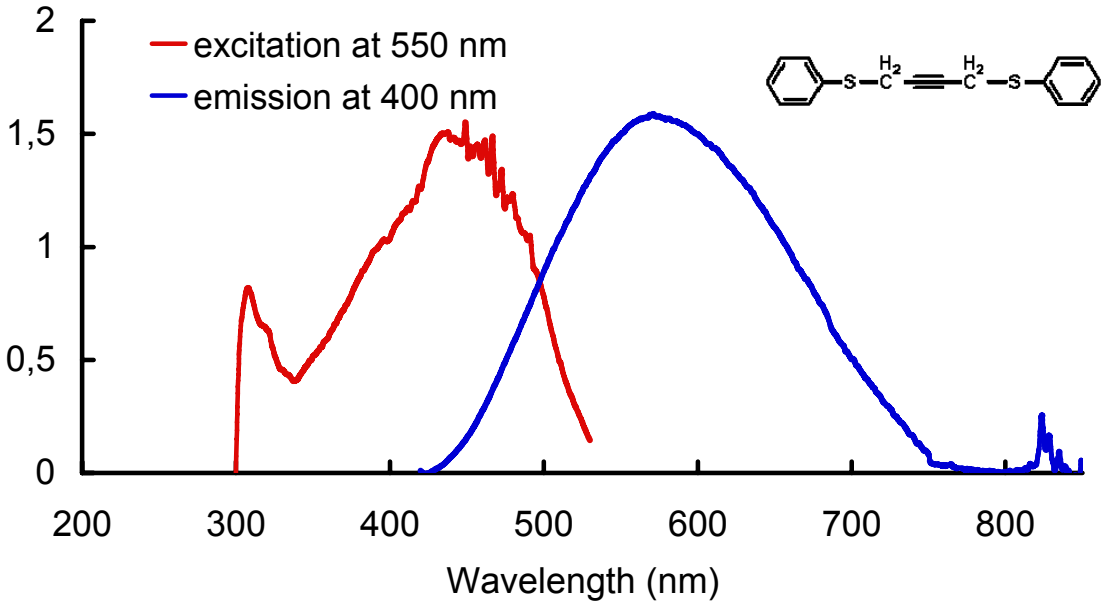

Figure S9. Solid-state emission spectrum of ligand **L2** recorded at 77 K.