

# SUPPORTING INFORMATION

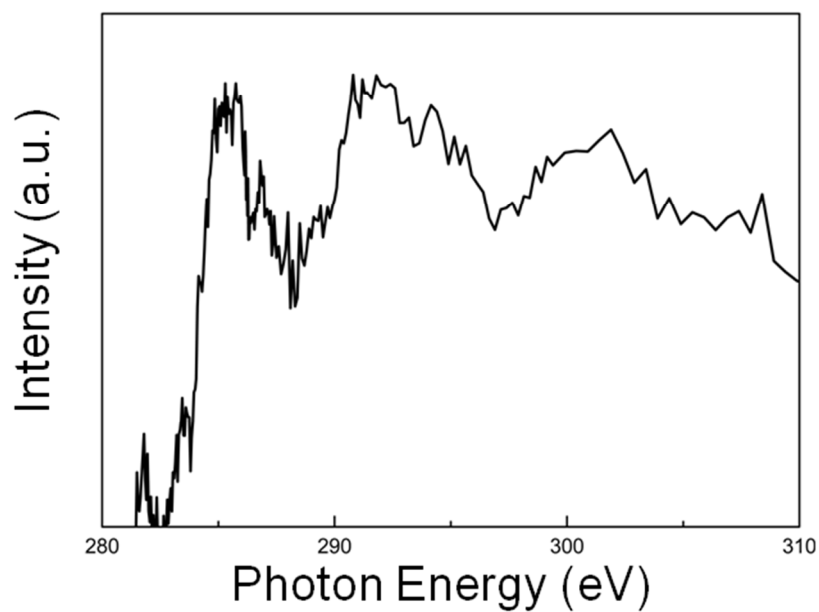
## From Benzenetrithiolate Self-Assembly to Copper-Sulfide Adlayers on Cu(111): Temperature-Induced Irreversible and Reversible Phase Transitions

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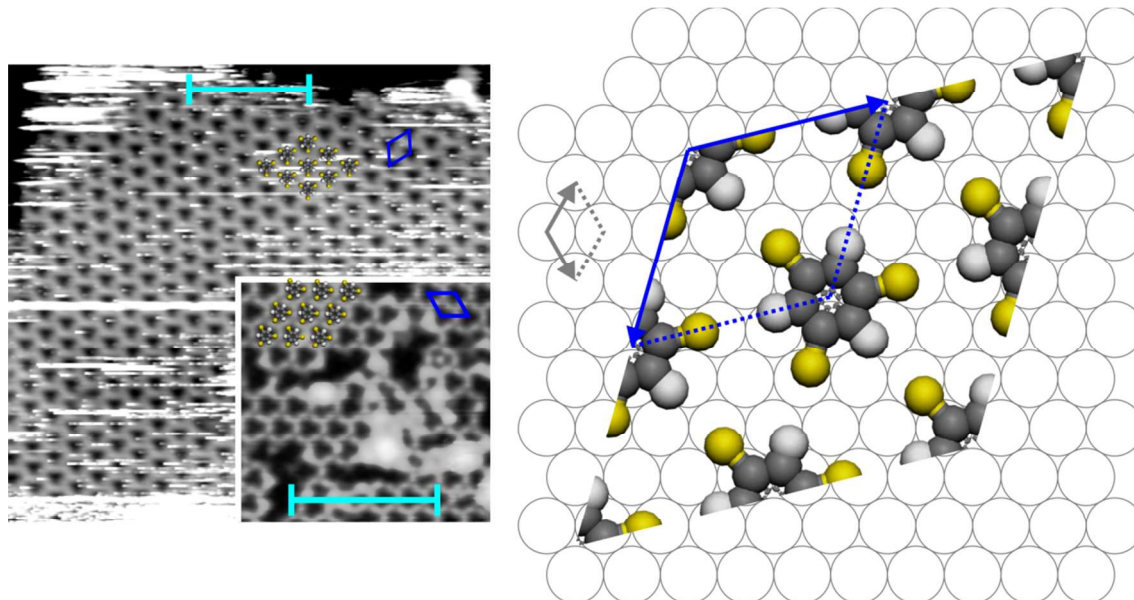
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### Additional NEXAFS data



**Figure S1.** Single NEXAFS spectrum of the  $\gamma$ -phase obtained at an incidence angle of  $45^\circ$ . This NEXAFS spectrum shows only a broad unspecific  $\pi^*$  resonance without any angular dependence, indicating a statistical orientation of the molecular units relative to the surface.

## Alternative structure model for the $\alpha$ -phase



**Figure S2.** STM topographs from Figure 1A of the manuscript (left) and alternative structure model for the  $\alpha$ -phase (right). BTT molecules are arranged in head-to-tail configuration. For the overlay BTT molecules were geometry optimized by force field calculations and are depicted to scale. For the overlay it is assumed that the phenyl rings are imaged as apparent depression. This STM contrast assignment is rather unusual, but has previously been observed. The proposed structure is not based on copper adatoms, but the thiolate groups form direct covalent bonds to copper surface atoms. This model is analogous to self-assembled monolayers of 1,3,5-tris(4-mercaptophenyl)benzene on Cu(111).<sup>1,2</sup>

## References

1. Walch, H.; Dienstmaier, J.; Eder, G.; Gutzler, R.; Schlögl, S.; Sirtl, T.; Das, K.; Schmittl, M.; Lackinger, M. Extended Two-Dimensional Metal-Organic Frameworks Based on Thiolate-Copper Coordination Bonds. *J. Am. Chem. Soc.* **2011**, *133*, 7909-7915.
2. Sirtl, T.; Jelic, J.; Meyer, J.; Das, K.; Heckl, W. M.; Moritz, W.; Rundgren, J.; Schmittl, M.; Reuter, K.; Lackinger, M. Adsorption Structure Determination of a Large Polyaromatic Trithiolate on Cu(111): Combination of Leed-I(V) and Dft-Vdw. *Phys. Chem. Chem. Phys.* **2013**, *15*, 11054-11060.