Carboranethiols: Building Blocks for Self-Assembled Monolayers on Copper Surfaces, or a Novel Class of Etchants?

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Resume: This contribution aims at showing an unprecedented behavior of carboranedithiols on copper surfaces. Two different positional isomers of 1,2-dicarba-closo-dodecaborane-dithiol, 1,2-(HS)2-1,2-C2B10H10 (1) and 9,12-(HS)2-1,2-C2B10H10 (2), have been used as a convenient molecular system in which the attachment of -SH groups at different positions on the skeleton affects their acidic character and thus determines their reactivity with a copper surface. While the latter isomer represents a weak acid and forms a self-assembled monolayer (SAM) similarly to various aliphatic and aromatic thiols reported previously, the former isomer shows etching of copper leading to a complete dissolution of the films used in our experiments at a rate of approx. 70 nm per hour (in 7.5 mM EtOH solution of 1 at 20 ºC). A detailed investigation of the experimental conditions showed that the acidic character of -SH groups and the presence of oxygen at the copper surface play crucial role in how the surface reaction proceeds: whether towards the formation of a 1-SAM or towards etching and dissolution of a copper film. Reaction between 1 and a freshly prepared copper surface in vacuum or in a dry and oxygen-free solvent such as toluene, or dichloromethane yields a 1-SAM. This study shows the first thiol derivative that possesses the ability to etch copper films. A number of methods including XPS, RBS, PIXE have been used and the results will be presented and discussed. Acknowledgement: P205/10/0348, GACR