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Reactions of dihalogenated 3,4-ethylenedioxythiophenes on metal surfaces

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Conducting polymers are a key component of modern technologies: they are used in batteries and in displays, and they have a promising future in solar conversion and emerging technologies like flexible electronics. The polymer formed from 3,4-ethylenedioxythiophene, known as poly-3,4-ethylenedioxythiophene or PEDOT, is used in a variety of applications, primarily because of its low bandgap, transparency and stability. PEDOT is typically solution processed, and although this technique is simple, it offers limited control over the structure of the polymer. Surface-confined polymerization is emerging as an important technique for the structurally-controlled synthesis of materials like PEDOT.[1,2]

In order to explore possibilities for the surface-confined synthesis of structurally well-defined PEDOT, we have studied the reactions of dibromoEDOT and dichloroEDOT on Cu(111), Ag(111) and Au(111). The function of these surfaces is twofold: they provide an ordered template for epitaxial growth, and they act as catalyst for the Ullmann dehalogenation of the precursor molecules. X-ray photoelectron spectroscopy (XPS) measurements were performed at the SXR beamline of the Australian Synchrotron to benchmark the reaction temperatures for the successive steps in the on-surface reaction for both molecules on all three surfaces. Angle-resolved near-edge x-ray absorption fine structure (NEXAFS) spectra complement the information provided by XPS, and provide insight into the molecular adsorption geometry throughout the reaction pathway. Together, these data elucidate the benefits and drawbacks of different metal surfaces and different halogens in the context of the surface-confined synthesis of ordered PEDOT.

[1] M. El Garah, J.M. MacLeod and F Rosei, Surf. Sci. 613, 6-14 (2013)
[2] J.A. Lipton-Duffin et al., Proc. Nat. Acad. Sci. 107 (25), 11200-11204 (2010)

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