

SWITCHING OF THE FE OXIDATION STATE IN FERROCENE-CAPPED ALKANETHIOLS

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Molecular electronics has been a rapidly-growing area, due to the simplicity of building molecular devices by self-assembly and the promise of extremely low power consumption as a result of pushing the size down to a few molecules per device. As model system we have chosen a self-assembled monolayer (SAM) of ferrocene-capped alkanethiols which can be produced in two stable oxidation states of Fe (Fe^{2+} and Fe^{3+}). The oxidation states of Fe are probed with submonolayer sensitivity by Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy at the iron $L_{2,3}$ edges^[1](Figure1). NEXAFS provides a direct method to distinguish between the oxidation states of submonolayer by comparing with the bulk sample spectrum. The native Fe^{2+} layer is converted chemically to Fe^{3+} , and the Fe^{3+} layer can be switched back to Fe^{2+} or possibly Fe^0 by irradiation with soft x-rays (Figure2). The results have implications on switching mechanisms in molecular electronics.

[1] Fan Zheng, V. Pérez-Dieste, J. L. McChesney, Yan-Yeung Luk, Nicholas L. Abbott, and F. J. Himpsel, Surf. Sci. **587**, L191 (2005).

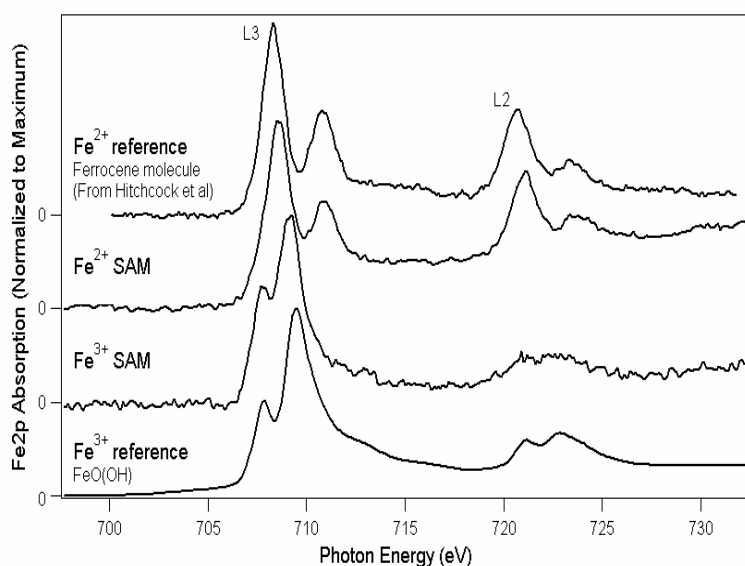


Fig. 1 NEXAFS spectra of the Fe2p ($L_{2,3}$) edge for ferrocene-capped alkanethiol layers in two oxidation states (two center curves). A reference spectrum for Fe^{2+} is given at the top (from Hitchcock et al.) and one for Fe^{3+} at bottom. Fe^{2+} and Fe^{3+} both exhibit two peaks at the L_3 edge, but Fe^{2+} has the more intense peak at lower energy, while Fe^{3+} has it at higher energy.

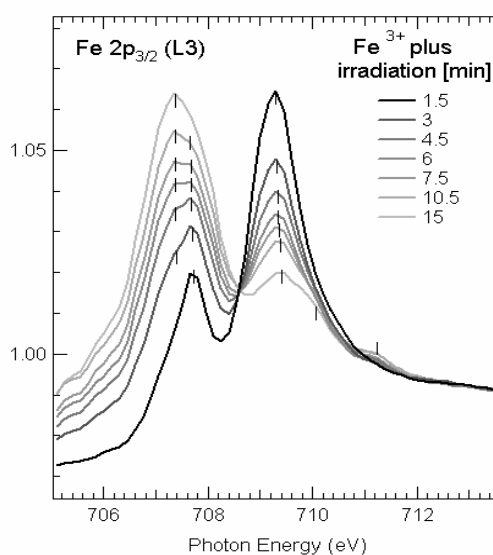


Fig. 2 Evolution of the Fe L_3 NEXAFS spectrum with irradiation ($h\nu \geq 700\text{eV}$). Fe^{3+} is reduced to Fe^{2+} (and possibly Fe^0), thereby demonstrating photo-chemical switching.