Contribution ID : **99** Type : **Oral**

Substrate dependent ultrafast charge transfer dynamics in self-assembled monolayers with intramolecular orbital coupling – a combined spectroscopic and computational study

Friday, 23 November 2018 11:45 (15)

Abstract: Metal surfaces coated with self-assembled monolayers (SAMs) are often used in large area based molecular junctions. However, characterizing these junctions still eludes chemists and physicists alike because of the complexity associated with the orbitals involved in charge transport and their behaviour under varying temperature. The metal-molecule interaction in such a system helps to understand the mechanism of charge transport, whether it is the Landauer (coherent transport) model or the Marcus model (incoherent transport) or an "in-between" regime, and thus, is crucial to the field of molecular electronics [1]. Recently, we reported that SAMs terminated with ferrocenyl (Fc) units and attached to a conjugated diphenylacetylene (DPA) backbone via an alkyl bridge showed diode behaviour in that "in-between" regime. Tuning intramolecular orbital coupling between Fc and DPA resulted in the diode being in either the inverted Marcus regime or the direct Marcus regime [2]. While the number of alkyl units separating the conjugated units is one variable to change the metal molecule coupling, it can also be varied by changing the surface dipole at the metal-sulphur interface. Here we used synchrotron-based core-hole clock measurements to study the ultrafast charge transfer dynamics (in the order of a few fs) of the series shown in Figure 1 (FcCn(DPA)CS SAMs on M where M = Ag, Au, Pt; n = 0-3). In addition to the spectroscopic characterization, we also attempt to understand the quantum chemical picture of the metal-molecule interface by performing density functional theory calculations. The coupling of Fc is in the order Ag > Au > Pt.

Keywords: charge transfer dynamics, core-hole clock spectroscopy, self-assembled monolayers, molecular electronics, density functional theory

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Session Classification : Parallel Session 11

Track Classification : Surfaces