Self-assembled monolayer engineered interfaces: Energy level alignment tuning through chain length and end-group polarity

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ARTICLE INFO

ABSTRACT

We explore the different mechanisms through which self-assembled monolayers can tailor energy level alignment at metal–organic semiconductor interfaces. We show that the large work function variation that can be induced by the self-assembled monolayer on gold has limited ability to tailor the interface energy level alignment of a subsequent organic semiconductor overlayer.

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1. Introduction

In organic-based electronics, device performance and life-time strongly depend on the properties of the interfaces between the active organic material(s) and the electrodes. In order to achieve efficient and balanced charge injection at low voltages in for example OLEDs [1,2] and efficient charge extraction in organic photovoltaic devices [3–6], proper matching of the energy levels between electrodes and active organic material is needed. One attractive method to tune the work function of a metal electrode is the use of surface modification through a self-assembled monolayer (SAM). SAMs are used in a wide variety of applications [7,8] and SAM-based engineering of electrode work functions in organic electronics is extensively studied and the mechanisms through which the SAM introduce an interface dipole is well understood [9–20]. A SAM interlayer does more than just modify the work function of a surface, it also separates the original surface from the organic semiconductor (OSC) overlayer. This property has been used to great effect in organic field effect transistors, where a SAM deposited on top of the silicon oxide gate reduces electron trapping by the oxide and hence improves electron mobility in the device [21].

The use of SAM interlayers thus have a two-fold effect: it modifies the work function of the electrode and creates a non-interacting spacer layer between the OSC and the electrode ensuring physisorbed rather than chemisorbed OSC films. The integer charge transfer (ICT) model [22–24] was developed to describe

the energy level alignment at such weakly interacting interfaces featuring OSC molecules. Contacts formed by depositing OSC molecules onto weakly reactive electrodes typically exhibit vacuum level (VL) alignment when the work function of the electrode is within energy gap defined by the so-called pinning energies: E_{ICT-} and E_{ICT+}. In the other regions, the Fermi level becomes pinned at the ICT density of states formed by spontaneous charge transfer across the interface via tunneling. The most easily oxidized/reduced molecules (or segments on polymers) adjacent to the interface are thus "used up" until enough charge has been transferred across the interface to create a potential step that equilibrates the Fermi level. The ICT model states that the oxidation (and reduction) energies of the OSC molecules/polymers present at an interface strongly depends on the local inter- and intramolecular order [23,25], a consequence of the well-known effects on ionization energies going from gas phase to solid films [26] and the effect of counter ions on polaron formation energies. Moreover, other effects can also play a role in determining the so-called pinning energies such as: intrinsic molecular dipole, chemical modification or doping [27–29]. The ICT state distribution is thus different than the bulk polaron distribution, see Fig. 1. The effects contributing to the ICT state formation, such as intermolecular screening of the ionized OSC molecules and electrostatic interaction with the image charge on the metal electrode, are non-trivial to treat computationally in realistic systems, but several methods recently have been developed to obtain the ICT pinning energies [30–34].

In this paper we use ultraviolet photoelectron spectroscopy (UPS) and ellipsometry to investigate in detail how an insulating SAM can change energy level alignment at metal–organic interfaces. In particular, we explore how the distance between the metal and organic semiconductor across the interface affects the

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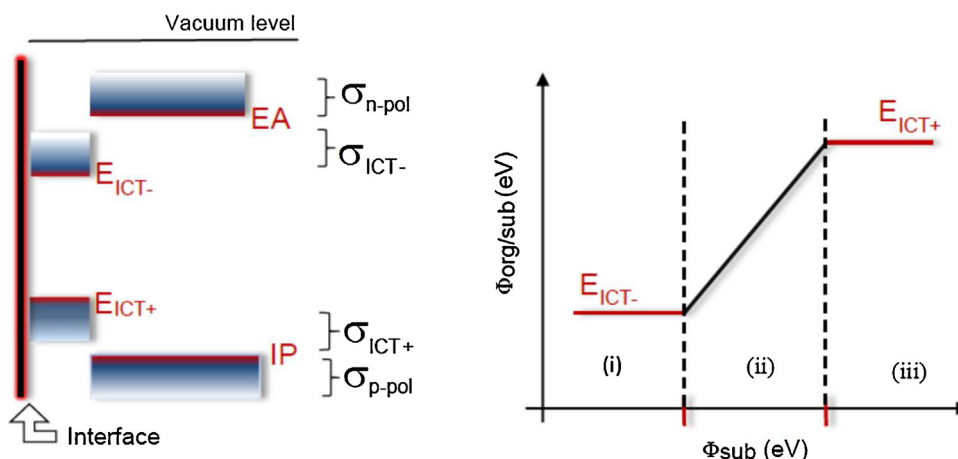*E-mail address:* mafah@ifm.liu.se (M. Fahlman).

Fig. 1. Left panel: schematic picture of energy levels in an OSC film versus the vacuum level (VL): bulk n-polarons and their distribution σ_{n-pol}, bulk electron affinity (EA) defined as the n-polaron distribution edge, bulk p-polarons and their distribution σ_{p-pol}, bulk ionization potential (IP) defined as the p-polaron distribution edge, ICT energy distributions $\sigma_{ICT+,-}$ and pinning energies ($E_{ICT+,-}$) defined as the ICT$_{+,-}$ distribution edges. Note that the respective ICT and bulk polaron distributions partially may overlap depending on the e.g. the strength of the electrostatic interaction with the substrate upon forming an ICT state. Right panel: energy level alignment regimes according to the ICT model (see text): work function of the (hybrid) organic interface ($\Phi_{ORG/SUB}$) as a function of the substrate work function (Φ_{SUB}).
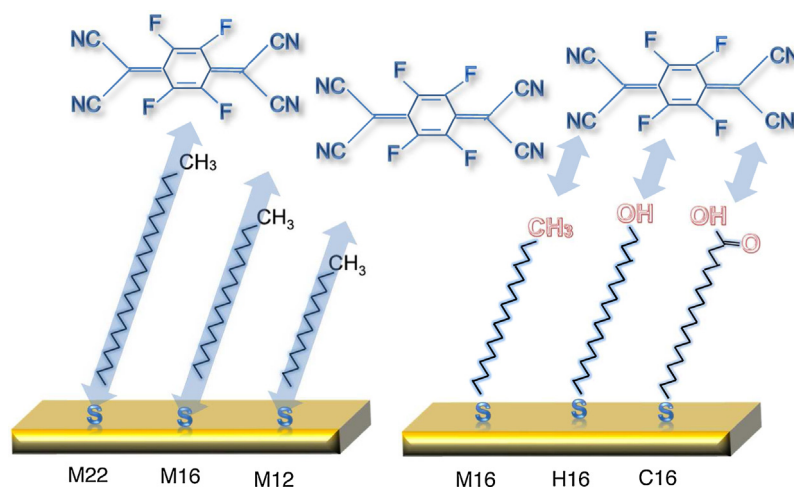

Fig. 2. A schematic picture of the F_4-TCNQ/SAM/Au systems used in the study.

energetics of the interface (and hence the efficiency of charge injection processes). We study this phenomenon by inserting a layer of non-conducting alkanethiol-based SAMs as spacer layers in-between an organic semiconductor of strong acceptor nature, 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquino-dimethane (F_4-TCNQ) [35] and an electrode material, Au. Alkanethiols on gold are an extensively studied SAM system and as they tend to form robust well-defined dense layers and have a non-conjugated backbone, they are ideal for this study. For the first part of the experiment we vary the length of the inserted SAMs to change the tunneling distance using methyl-terminated alkanethiols (HS-$(CH_2)_n$-CH_3), with an increasing number of carbons in the chain $n \equiv 11, 15, 21$ denoted as: M12, M16 and M22, using the total number of carbons in the naming. Maintaining the same anchoring- and tail-groups makes it possible to have a good control of the tunneling distance of the charges while keeping all other aspects as constant as possible. For the second part of the study we vary the tail-group of the SAM while keeping the number of carbons in the SAM constant ($C=16$) to achieve different substrate work functions while maintaining good control of the tunneling distance. Small polar groups such as the hydroxyl group —OH and the carboxyl group —COOH is used since this change tends not to affect the ordering of the SAMs on the gold surface [8]. The three different SAMs are hereafter

denoted as M16, H16 and C16. The organic semiconductor, F_4-TCNQ, is chosen since it has a sufficiently high E_{ICT-} value to keep the system in the negative pinning regime for both "pristine" Au and SAM-modified Au substrates [35,36]. A schematic picture of the resulting F_4-TCNQ/SAM/Au systems is depicted in Fig. 2. The SAM molecules are drawn with a tilt angle, α, which in the real system probably is close to 30° for all the included SAMs [8].

2. Experimental methodology

The gold substrates were prepared by deposition onto silicon surfaces using an electron beam evaporation system according to the following procedure. First, single-crystal silicon (1 0 0) surfaces are cleaned in a so-called TL-1 solution containing MilliQ water, NH_3 (25%) and H_2O_2 (28%) at a ratio of 5:1:1 at 80 °C for about 15 min to remove organic contaminations. The surfaces are then carefully rinsed 10 times with MilliQ water, dried in N_2-gas and placed in the evaporation system. The silicon surfaces are then pre-coated with a 25 Å thick titanium layer and thereafter coated with a 2000 Å thick gold layer. The base pressure was ∼10^{-9} Torr and the evaporation pressure was ∼10^{-7} Torr.

All the thiols used in this study were dissolved in ethanol. The concentration of the solutions was 1 mM and the incubation time