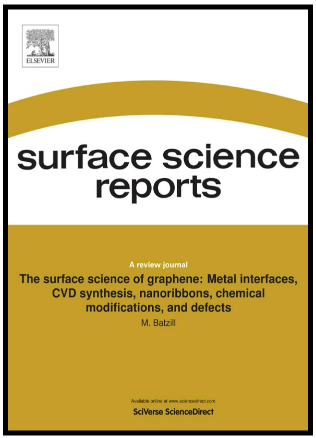

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Electronic, Structural and Chemical Effects of Charge-Transfer at Organic/Inorganic Interfaces

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Abstract

During the last decade, interest on the growth and self-assembly of organic molecular species on solid surfaces spread over the scientific community, largely motivated by the promise of cheap, flexible and tunable organic electronic and optoelectronic devices. These efforts lead to important advances in our understanding of the nature and strength of the non-bonding intermolecular interactions that control the assembly of the organic building blocks on solid surfaces, which have been recently reviewed in a number of excellent papers. To a large extent, such studies were possible because of a smart choice of model substrate-adsorbate systems where the molecule-substrate interactions were purposefully kept low, so that most of the observed supramolecular structures could be understood simply by considering intermolecular interactions, keeping the role of the surface always relatively small (although not completely negligible). On the other hand, the systems which are more relevant for the development of organic electronic devices include molecular species which are electron donors, acceptors or blends of donors and acceptors. Adsorption of such organic species on solid surfaces is bound to be accompanied by charge-transfer processes between the substrate and the adsorbates, and the physical and chemical properties of the molecules cannot be expected any longer to be the same as in solution phase. In recent years, a number of groups around the world have started tackling the problem of the adsorption, self- assembly and electronic and chemical properties of organic species which interact rather strongly with the surface, and for which charge-transfer must be considered. The picture that is emerging shows that charge transfer can lead to a plethora of new phenomena, from the development of delocalized band-like electron states at molecular overlayers, to the existence of new substrate-mediated intermolecular interactions or the strong modification of the chemical reactivity of the adsorbates. The aim of this review is to start drawing general conclusions and developing new concepts which will help the scientific community to proceed more efficiently towards the understanding of organic/inorganic interfaces in the strong interaction limit, where charge-transfer effects must be taken into consideration.

Keywords:
Organic adsorbates, Self-assembly, Charge transfer

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1. Introduction

Organic electronic and optoelectronic devices have been investigated in recent years as a potentially competitive alternative to the current inorganic semiconductor technology for applications such as Organic Light Emission Diodes (OLEDs) [1], Organic Field Effect Transistors (OFETs) [2], bulk-heterojunction [3] or dye-sensitized solar cells [4] or chemical sensors [5]. While some of these applications are already in the market (OLEDs, OFETs), some other are still far from real applications in spite of the enormous strides in efficiency registered in the last decades (bulk heterojunction solar cells) [6]. Improving the efficiency of such devices requires control over many parameters, such as the chemical nature and electronic structure of the molecular building blocks, the degree of order of the organic molecules in the active layer, the presence of dopants and impurities or the nanoscale morphology of the organic films [7].

In particular, the interface between the organic active layer and the metallic contacts is of paramount importance in determining the efficiency of the device: for example, the alignment of the molecular orbital levels of the organic layer with the vacuum and Fermi levels of the metallic leads determines the electron- and hole-injection barriers [8--10]. Alongside the purely electronic effects, the molecular organization at the interface will also determine the morphology and structure of the organic molecules in thicker films and, thus, will play an important role in steering the physical behavior of the device [11].

Thus, during the 90's and the first decade of the 21st century, research on the structure of organic monolayers deposited on metallic or passivated semiconductor surfaces progressed at a very fast pace [12--16], driven by the observation that, if the nature of the organic molecules and the substrate were properly chosen, many of the concepts that had been developed by Supramolecular