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Molecular orientation and electronic structure at organic heterojunction interfaces☆

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ABSTRACT

Due to the highly anisotropic nature of π-conjugated molecules, the molecular orientation in organic thin films can significantly affect light absorption, charge transport, energy level alignment (ELA) and hence device performance. Synchrotron-based near-edge X-ray absorption fine structure (NEXAFS) spectroscopy represents a powerful technique for probing molecular orientation. The aim of this review paper is to provide a balanced assessment on the investigation of molecular orientation at the organic–organic heterojunction (OOH) interface by NEXAFS, as well as the gap-states mediated orientation dependent energy level alignment at OOH interfaces. We highlight recent progress in elucidating molecular orientation at OOH interfaces dominated by various interfacial interactions, gap-states controlled orientation dependent energy level alignments at OOH interfaces, and the manipulations of molecular orientation and ELA in OOH.

1. Introduction

The orientation of organic molecules can have a significant effect in the performance of organic devices. Due to the anisotropic nature of organic semiconductors, molecules with different orientations can display different properties such as charge transport, energy level alignment (ELA), light absorption, electronic coupling and charge dissociation energetics [1–6]. Synchrotron-based near-edge X-ray absorption fine structure (NEXAFS) spectroscopy is a powerful method for studying the molecular orientation [7–19]. The rest of this introduction briefly reviews published work on molecular orientation, and the NEXAFS working principle for probing molecular orientation.

In organic semiconductors, charge transport is mainly facilitated by the electron hopping process rather than coherent band transport due to their narrow intermolecular band width of less than 0.4 eV [20]. The highly anisotropic packing geometry in molecular solids has a strong effect on charge transport [21,22]. Different organic electronic devices may have contrasting requirements with regard to preferred molecular orientation. For example, in organic solar cells (OSCs) and organic light emitting diodes (OLEDs), since the photocurrent flow is essentially normal to the electrodes, the vertical π–π stacking (lying configuration) of the conjugated organic semiconductors is desirable; while in horizontal organic field-effect transistors (OFETs), the parallel π-stacking direction relative to the gate dielectric (standing configuration) facilitates efficient charge transport along the channel [3,6,12,23–25].

Besides charge transport, molecular orientation has an important influence on interfacial ELA at organic–organic heterojunctions (OOHs). Duhm et al. reported orientation-dependent ionization potential (IP) in organic thin films, analogous to the dependence of metal or compound semiconductor work function (WF) on crystal face orientation [26]. Large variation in IPs up to 0.6 eV was observed for α,ω-dihexyl-sexithiophene (DH6T) and α-sexithiophene (6T) films on Au (1 1 1), depending on whether the molecules were lying flat or standing upright on the substrates as shown in Fig. 1. Combined with density functional theory (DFT) calculations, they attributed the increased IP of the lying 6T and DH6T thin films to intrinsic surface dipoles built into the ordered lying-down molecular assemblies; while no such dipole was present at the surface of standing 6T and DH6T films [26]. The same group also reported that molecules terminated by strongly electronegative atoms such as fluorine possessed more pronounced orientation dependent IP [27]. Consequently, understanding and controlling

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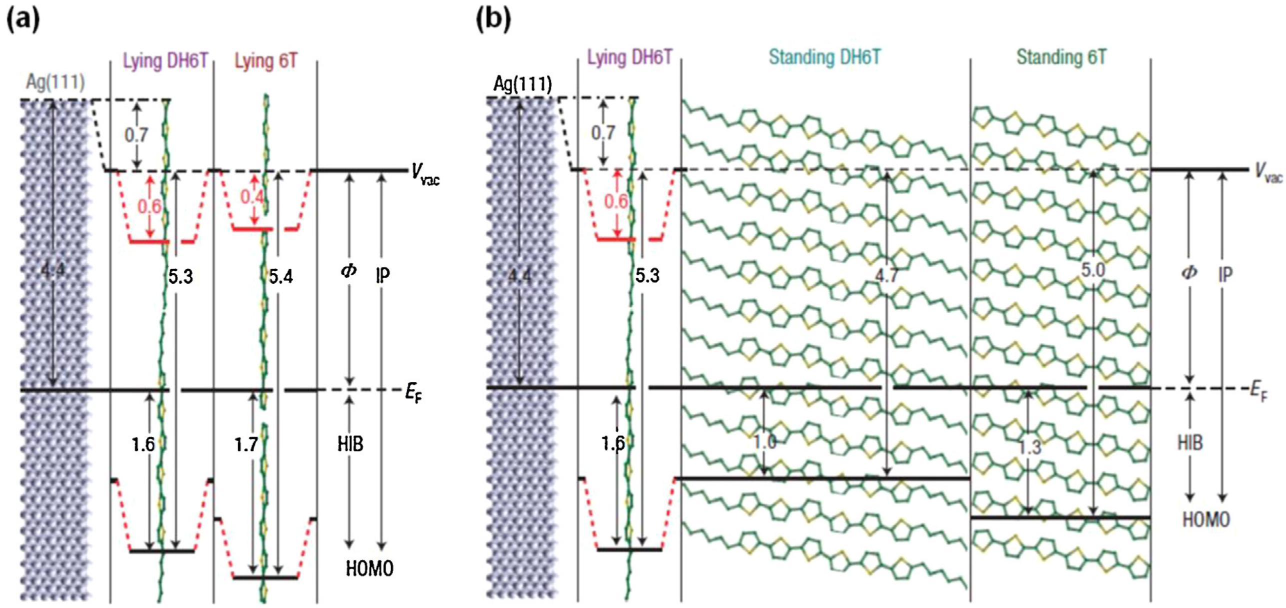

Fig. 1. ELA diagram for (a) the lying 6T/DH6T monolayer and (b) the standing 6T/DH6T monolayer on Ag(1 1 1) substrate. Figure adapted from ref. [26] with permission from Nature Publishing Group. Copyright 2008.

the orientation of conjugated molecules on various substrates have significant implications for optimizing ELA in organic electronic devices.

Molecular orientation also influences light absorption and exciton dissociation in OSCs. It is reported that larger absorption strength is achieved when the transition dipole moment of planar molecules is aligned with the electric field of the incident light [6]. Other reports indicate a larger exciton dissociation rate in the lying configuration due to enhanced electronic coupling and driving force [28]. The enhanced electronic coupling originates from improved orbital overlap between the lying donor and acceptor materials [29,30].

Synchrotron-based NEXAFS spectroscopy is a powerful technique to measure the molecular orientation of conjugated molecules. It can probe the resonant excitations from the core-level of specific atomic species of a molecule (e.g., C 1s or N 1s) to its unoccupied electronic states (e.g., π^* or σ^* anti-bonding orbitals). When the electric field vector **E** of the linear-polarized synchrotron light has a large projection along the π^* or σ^* orbitals, the related π^* or σ^* resonance would be strong. Conversely, when the electric field vector is perpendicular to these orbitals, their related resonance would vanish. To be more specific, the resonance intensity has a $\cos^2\delta$ dependence on the angle $|\delta|$ between **E** and the direction of the molecular orbital. For a planar π-conjugated molecule, the π^* or σ^*

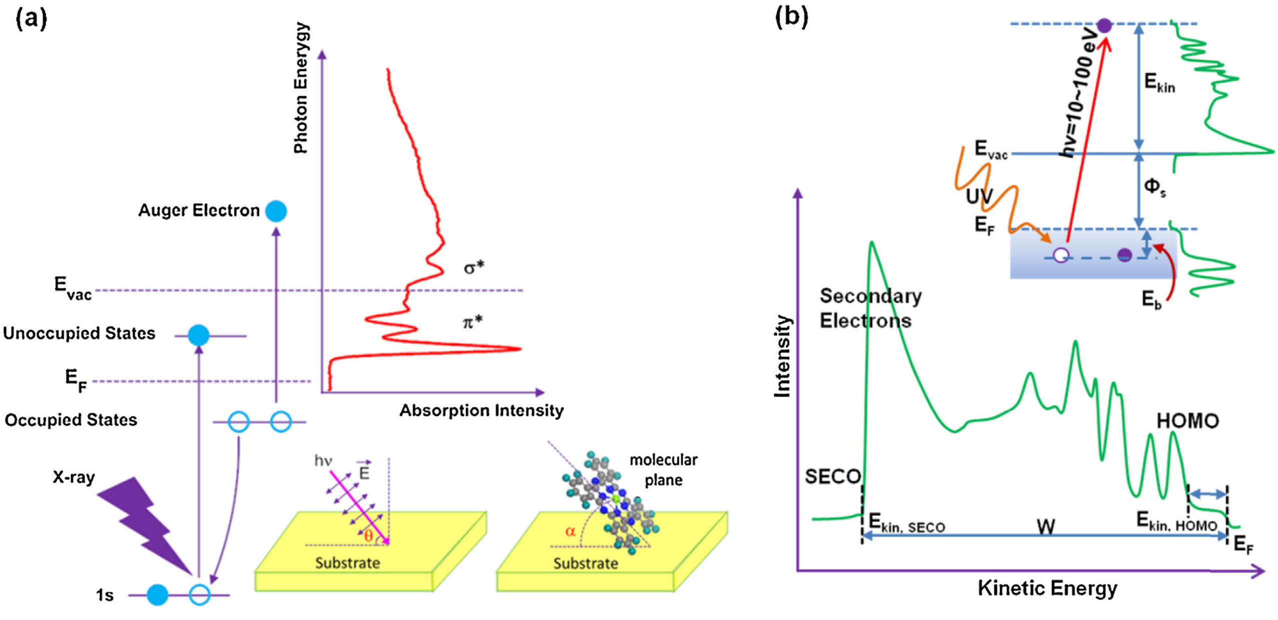

Fig. 2. (a) Schematic diagram of the X-ray absorption transition with the Auger decay channel and the related NEXAFS spectrum with distinguishable π^* and σ^* resonance. The bottom schematic shows the definition of angles in the experiment. When the electric field vector **E** of the incident linear polarized synchrotron light has a large projection along the π^* orbital, a strong π^* resonance of the molecule occurs. (b) Schematic diagrams of photoelectron emission process in a UPS experiment and a typical UPS spectrum of a molecular solid showing various energy levels.