Organic Electronic Devices: Investigation of the Electronic Transport Properties at the Molecular Level

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DOTTORANDO
Giorgia Olivieri

COORDINATORE
Prof. Paolo Camerini

SUPERVISORE
Prof. Alberto Morgante

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It is expected that in the next few years devices based on organic (carbon-based) molecular thin films will play a crucial role in many different fields, ranging from nanomedicine to electronics, from photovoltaics to coating technology. This large diffusion is driven by the high variability of electronic, mechanical and chemical properties of organic molecules which allow them to fit in a number of different applications. Furthermore organic molecules are light, highly supple, easy to process, low-cost and are composed by non-toxic, abundantly available materials [1]. Beside the properties listed above, in 1977 the class of conjugated molecules has been found to present also non negligible electrical conductivity [2]. This fascinating discovery opened the door to the application of organic materials in the field of electronics.

Electrical conductivity can be observed both in organic polymers and organic molecules in which the conjugation is extended over the whole molecule or at least over a big portion of it. These two classes of materials form together the class of organic semiconductors which is nowadays a hot scientific topic. The interest in organic semiconductors is intimately connected to their multiple technological applications. Indeed due to their semiconductive properties they can be used as active materials in potentially any electronic device, leading to the realization of organic field effect transistors (OFETs) [3, 4], organic light-emitting diodes (OLEDs) [5, 6] or organic solar cells (OPVs) [7, 8]. The devices made with organic semiconductors have all the properties of plastic materials and allow applications that were not possible with the standard semiconductors. One attractive application is, for example, the integration of electronic devices in flexible materials to obtain, among other things, the electronic newspaper. Moreover, due to the ease of fabrication processes, organic solar cells represent a less expensive alternative to inorganic ones and could help the production of solar energy to go beyond its market niche.

Despite the numerous advantages, organic semiconductors suffer from several issues.
They are poor electrical conductors with respect to their inorganic counterparts and they have a very low stability (they degrade very fast with time and in ambient conditions); ways to overcome these drawbacks are subject of intensive research in the last few years. Even if in the last years also the second topic has been investigating [9, 10], major recent research efforts focus on the charge transport problem, both to understand the charge transport mechanism inside organic semiconductors and to study charge injection at the interfaces between different materials. The topic of charge transport in organic semiconductors is not a simple task to deal with. Electrical properties of organic semiconductors are related to the conjugation of their atomic $\pi$-orbitals that leads to the delocalization of the valence electrons over the whole system. Since in organic semiconductors the molecules are bound by weak intermolecular forces (often Van der Waals), organic solids do not form a proper valence and a conduction band and therefore the transport mechanism cannot be described by making use of the usual band theory. Beside the theoretical complications, the strong sensitivity of the experimental data from the device fabrication conditions, which affect primarily the molecular order and the material purity, makes even more difficult the generation of an unified model for organic charge transport.

The second big issue arises when an organic semiconducting material is interfaced with another material, either organic or non-organic. Hybrid interfaces are present in all electronic devices when, for example, the active organic material is connected to the external world through metal electrodes or more than one different organic materials are used inside the same device. One of the most important processes characterizing the electrical behaviour of a hybrid interface is the charge injection, which has been demonstrated to be strongly affected by the structural and electronic properties of the system [11, 12]. Morphology and electronic structure at hybrid interface are therefore critical parameters which affect the overall device performances.

Our approach for the investigation of the fundamental processes mentioned above, is to make use of synchrotron based spectroscopic techniques to study the electronic, morphological and the structural properties of organic semiconductors. With respect to the transport measurements usually performed to probe macroscopic electrical properties of organic devices, spectroscopic techniques give a description at the molecular level of the electronic structure of the materials. With these techniques it is possible indeed to probe both the occupied and unoccupied molecular orbitals to gather information about the local molecular structure and how it affects both structural and electronic properties. This results in the understanding of the transport mechanisms at the molecular level with the possibility to discriminate the molecular orbitals involved. Moreover, this approach has the advantage to be predictive, in a sense that it is possible to design new complex hetero-architectures relying on the experimental results obtained on archetypal systems.
Among the numerous spectroscopic techniques available, in this work we will deal with X-ray Photoemission Spectroscopy (XPS), Near Edge X-ray Absorption Fine Structure (NEXAFS) and Resonant Photoemission Spectroscopy (RPES). The latter is particularly interesting since beside the typical advantages of spectroscopy (e.g. chemical selectivity), it allows to study the charge-transfer dynamics through the determination of the charge-transfer time.

After the description of the spectroscopic techniques used in the thesis (Chapter 1), I tackle the issues of organic semiconductors studying two different model systems, namely an organic semiconducting single crystal (OSSC) and an hetero-organic interface.

OSSCs are very good candidates to study the intrinsic behaviour of charge carriers in organic semiconductors, since their long range molecular order and reduced contribution of defects allow to exclude phenomena due to structural defects and grain boundaries. The OSSC I deal with in Chapter 2, is made of the organic molecule 4-hydroxycyanobenzene (4HCB). In order to understand the charge transport properties and the origin of the observed electrical anisotropy in 4HCB based OFET [13, 14], I have performed a full investigation of the 4HCB molecule using XPS, NEXAFS and RPES. I first show the results for the molecule in its gas phase that I use then as a reference to analyze the solid phase. In particular I will show how exploiting the RPES measurements and comparing the results between gas and solid phase, I can calculate the charge-transfer time in 4HBC crystal to understand the origin of its directionality. Moreover, through the deposition of a 4HCB thin film onto a gold substrate I will model also the organic/metal interface and study its morphological properties.

The problem of hetero-organic interfaces is tackled in Chapter 3 where I present a study of a model donor/acceptor interface. The processes occurring at this interface are critical for the behaviour of organic solar cell based on heterojunctions since the donor/acceptor interface is the place where the exciton dissociation takes place. In the systems that we investigated, the shape complementarity between donor and acceptor molecules is exploited in order to drive the formation of efficient charge transfer hetero-organic interface. We studied, as donor materials, a special class of molecules that derivate from hexabenzocoronene (HBC) and we coupled different HBC derivatives to the fullerene (C60) acceptor. The different shape matching observed for three different HBC derivative molecules with C60, drives the formation of different interfaces. We study the detailed morphology of these interfaces to understand the consequence of shape-complementarity on solar cell efficiency.

In the last chapter (Chapter 4) an application of organic semiconductors in the fabrication of a real device is presented. The work aims to built a novel graphene-based tandem solar cell to push the organic solar cell efficiency toward the one of inorganic devices. Some of the practical aspects related to the fabrication processes are pointed
out and in particular a process specifically developed to transfer graphene onto organic substrate is shown.

The work presented in Chapter 2 was carried out in collaboration with dr. Alessandro Fratelli Morgera and its group from Elettra laboratory in Trieste. The study of Chapter 3 was performed in collaboration with the group of prof. Ioannis Kymissis from University of Columbia in New York and prof. Dean Cvetko and dr. Gregor Kladnik from University of Ljubljana. The work of Chapter 4 is the result of a four months period I spent in the CLUE laboratory of Columbia University working under the supervision of prof. Ioannis Kymissis. All the spectroscopic measurements have been executed at the Elettra synchrotron where I did my PhD on the ALOISA beamline.
In this chapter I give first a brief description of the experimental apparatus and then I recall the principles of the experimental synchrotron-based spectroscopic techniques used in chapters 2 and 3: X-ray Photoemission Spectroscopy (XPS), Near Edge X-ray Absorption Fine Structure (NEXAFS) and Resonant Photoemission Spectroscopy (RE-SPES).

All the synchrotron-based experiments have been performed at the ALOISA and GAS-PHASE beamlines of the Elettra Synchrotron in Trieste, Italy, that are part of the TASC laboratories at the IOM-CNR institute. Elettra is a 3\textsuperscript{rd} generation light source operating at a storage ring electron energy of 2 or 2.4 GeV in top-up mode. The outcoming beams, provided by wigglers and undulators, have a wide photon energy range (10-30000 eV) and high spectral brilliance.

1.1 ALOISA Beamline

ALOISA (Advanced Line for Over-layer, Interface and Surface Analysis) is a multi-purpose beamline for surface science experiments. Since it was designed to work in a wide spectral range (from 130 to 8000 eV) and its experimental chamber hosts several kind of different detectors, it is possible to perform a number of different experiments from photoemission spectroscopies to photoelectron and X-ray diffraction. Moreover a switching mirror can deflect, when inserted, the photon beam towards a second experimental chamber, HASPES, which offers the addional ultraviolet spectroscopy and scattering of the helium atoms.

The outline of the beamline is shown in Fig.1. The ALOISA photon beam is produced by the U7.2 Wiggler/Undulator Insertion Device (ID). It consists of two parallel series of alternately oriented magnets, separated by a user-tunable gap. The orbit of the electrons that pass through the ID is deflected by the ID magnetic field in a series of wiggles. The radiation emitted at each wiggle is summed together along the direction of the ID axis to give the final X-ray source at the pinhole separating the storage ring from the beamline optics. Depending on the gap size, the ID con operate either as undulator in the high gap values region (\(\sim 40-80\) mm) or as wiggler in the low gap values one (\(\sim\))
20 mm). In particular when the gap is large compared to the distance of two adjacent magnets, the electron orbit can be approximated to a sinusoidal curve and the ID is said to operate in the undulator regime. On the other hand, when the gap is comparable to the magnets distance the sinusoidal path becomes heavily distorted and the ID is said to operate in the wiggler regime. Fig. 1.2 shows the photon beam intensity as a function of the photon energy for different values of the ID gap [15]. For small gap values the oscillations in the spectrum become very dense resulting in an intensity spectrum similar to that of a bending magnet. The outcoming light is linearly polarized (polarization degree > 95%) in the horizontal plane of the synchrotron ring.

The full optical layout of the beamline is sketched in Fig. 1.3. The light coming from the pinhole is collected by a first parabolid mirror (P1) and is collimated towards the dispersing system. The main characteristic of the ALOISA monochromator is the possibility to switch between two types of dispersing systems accordingly to the desired photon energy: a Plane Mirror/Grating Monochromator (PMGM), for the 120-1600 eV range, and a Si(111) channel-cut crystal for the 2.8-8.0 keV range [15, 16]. The two systems lay side by side and they can be inserted by means of a slide mechanism. The monochromatic beam is then focused at the exit slits (ES) by a second paraboloidal mirror (P2) and the diverging beam is refocused on the sample, placed at the center of the experimental chamber, by a toroidal mirror (RT). The final beam spot size is about 20-30 μm in the vertical direction and 150-200 μm in the horizontal one. The system is characterized by the absence of the entrance slits. All the optics are designed to work at grazing incidence with a deflection angle of 1° for P1, P2 and RT. Moreover they are used in the sagittal focusing configuration (i.e., perpendicular to the scattering plane) to minimize the aberration in the dispersive plane due to slope errors and their surfaces have gold coating to minimize chemical contaminations and losses in the photon flux. Due to the high power density generated by the insertion device, P1 PMGM and the channel-cut crystal are water cooled.

Figure 1.1: Outline of the ALOISA/HASPES beamline
A third paraboloid mirror is used to deviate the beam to the HASPES bench-line chamber. In this case no additional refocusing mirrors are used due to the long focussing distance of P3.

1.1.1 Experimental Chamber

The ALOISA experimental chamber depicted in Fig. 1.4 is composed of two parts: a hemispherical element dedicated to the sample preparation and a cylindrical one which hosts the electron analyzers and the photon detectors for sample investigation. This two parts are coupled by a large bronze ball bearing and a system of O-rings. This configuration allows the complete rotation of the experimental chamber, with all the detectors, around the photon beam axis, while the preparation chamber stands still. Two differential pumping stages maintain a constant base pressure of $10^{-11}$ mbar inside the main chamber also during its rotations. In this Ultra-High Vacuum (UHV) condition the signal to noise ratio is high enough to detect also the low-energy electrons. Moreover the UHV environment is necessary because of the surface sensitivity of the techniques \[17\]. The preparation chamber is equipped with a molecular Beam Epitaxy (MBE) cryopanel which hosts four evaporation cells and two quartz microbalances for deposition flux calibration. The ion gun for the Ar$^+$ bombardment enables sample sputtering with ion energy up to 3 keV. A RHEED (Reflection High Energy Electron Diffraction) system,
with the beam impinging the surface at a grazing angle, is also available to check the surface symmetry *in-situ* during the deposition. The preparation chamber is additionally equipped with the sample transfer system and fast entry-lock for quick sample exchange.

In the main chamber, the detectors are hosted on two frames which are mounted
inside the rotating elements. The axial frame is placed at the end of the cylindrical element and hosts five 33 mm electron analyzers that are primarily dedicated to the APECS (Auger Photoelectrons Coincidence Spectroscopy). On this frame also a phosphorous plate with a CCD camera is mounted and it is used for the beam alignment with respect to the sample. The bimodal frame is placed inside the cylindrical chamber and can rotate around an axis perpendicular to the photon beam. This axis can further rotate around the photon beam axis together with the main chamber. The bimodal frame hosts a 66 mm hemispherical electron analyzer for angle resolved photoemission (ARXPS) and photoelectron diffraction (PED). The bimodal frame additionally hosts two energy resolved photodiodes operating in single-photon counting mode for X-ray diffraction. A wide-angle-acceptance channeltron is mounted on the axis of the bimodal frame and it is used to measure the Partial Electron Yield (PEY) in Near Edge X-ray Absorption Fine Structure experiments (NEXAFS). The channeltron is equipped with an additional grid in front of it which can be polarized with respect to the collector. In order to cut off the low energy tail of the secondary electrons and reduce in this way the background signal, the applied potential is negative.

The sample is placed onto a six-degree of freedom manipulator which can be inserted in the main chamber through the fast entry-lock. The photon beam passes through the whole manipulator and impinges the sample at a grazing incidence. Three rotations of the sample holder allow the sample to be rotated around the synchrotron beam ($R_1$) in order to select the desired surface orientation with respect to the photon polarization, the required incidence angle ($R_3$) and the azimuthal orientation of the surface with re-
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1.2 GASPHASE Beamline

The Gas Phase Photoemission beamline is a high resolution, high flux versatile beamline designed to work with gases, vapours and metastable species. It consists of an undulator source, a variable-angle spherical-grating monochromator and two end stations. The design value of the energy range is 20-800 eV with a specified resolving power of over 10 000 that gives a resolution significantly better than the natural line-widths of the main atomic excitation in this range.

The light source is provided by the U6.2 undulator insertion device which delivers light in the range from 13.5 up to 900 eV. A sketch of the beamline is reported in Fig.1.6. There are two pre-focussing mirrors before the entrance slits; a plane mirror with five gratings between the entrance and the exit slits; and two re-focussing mirrors afterwards. The first mirror focuses the beam vertically so it enters the entrance slits. The monochromator can be scanned in two different modes: energy scan mode and fixed mirror mode. In the former mode both the mirror and the gratings are scanned simultaneously and it is used for low to medium energy resolving power, up to about 4000. Since the scanning of two mechanical systems doubles the contribution of the mechanical errors to the final resolution, at high resolving power the second scanning mode is preferred. The mirror...
1.3. Experimental methods

is set to the average value for the range of energy to be scanned and only the grating is scanned. The disadvantage is that the defocus contribution to the resolution changes slightly over the scan. The use of fixed exit slits and two re-focussing mirrors afterwards, provided a very stable spot in which changes in spot size, shape and position as a function of energy are minimized.

The beamline is connected to the experimental section through a differential pumping section to decouple the ultra high vacuum of the mirrors to the high vacuum in the experimental region. The end-station comprises two chambers, the Multi-coincidence Chamber and the Angle Resolved Photoemission Chamber, and it also allows the possibility that users bring their own chamber.

1.2.1 Angle Resolved Photoemission Chamber

The ARPES chamber consists of a 500 mm cylindrical vessel lined with a double μ-metal shield. Gaseous and volatile liquid can be introduced into the ionization region through a hypodermic needle mounted on a XYZ manipulator. Solids can be vaporized in a high temperature, anti-inductively wound oven, in which temperature can reach up to 1400 K. The oven and the ionization volume are enclosed in a cooled jacket designed to minimize contaminations. An efficient cryo and turbo pumping system and a quartz capillary mounted between the beamline and the chamber prevent contamination of the beamline.

Two hemispherical 50 mm analyzers can be inserted with a mutual angle of 90° on a turntable. The four-element system of each analyzer has an acceptance angle of approximately ±3°. Pass energies from 1 to 50 eV can be selected. The modular design of the chamber and the large side flanges also allow users’ spectrometers to be mounted. For further detail on the GasPhase beamline we remand the reader to references [18, 19].

1.3 Experimental methods

1.3.1 Photoemission theory

When an electromagnetic radiation interact with the matter, the transition probability between the N-electron initial and final states is given, in the framework of time-dependent perturbation theory, by the Fermi’s Golden Rule [20, 21]

\[ W_{fi} \propto \frac{2\pi}{\hbar} \left| \langle f | H_{\text{int}} | i \rangle \right|^2 \delta(E_f - E_i - \hbar \nu) \]  

(1.1)

where the perturbation operator \( H_{\text{int}} \) describes the interaction between an electron and the electromagnetic field. In the gauge of \( \phi = 0 \) (absence of electromagnetic source) it
can be derived by substituting the momentum operator $p$, in the unperturbed Hamiltonian $H_0$, with the new operator $p-eA$ (neglecting the interaction with the electronic spin), with $A$ being the vector potential of the electromagnetic field. The total Hamiltonian can be written as a sum of the unperturbed and perturbed contributions as following

$$H = H_0 + H_{int} = \frac{p^2}{2m} + eV(r) + \frac{e}{2m}(A \cdot p + p \cdot A) + \frac{e^2}{2m}A \cdot A$$  \hspace{1cm} (1.2)

The quadratic term in $A$ gives rise to the two photon (photon in, photon out) scattering processes and, when the perturbation intensity is small, its contribution can be neglected. The linear term can be rewritten using the commutation relation $[A, p] = i\hbar \nabla \cdot A$ and the interacting Hamiltonian becomes

$$H_{int} = \frac{e}{m}A \cdot p + \frac{e\hbar}{2mi} \nabla \cdot A$$  \hspace{1cm} (1.3)

Assuming the translational invariance inside the solid, $\nabla \cdot A = 0$ and only the first term remains. The usual form of the matrix element in Eq.1.1 is then given by

$$M_{fi} \propto \langle f | A \cdot p | i \rangle$$  \hspace{1cm} (1.4)

In the semi-classical approximation the vector potential is written as a plane wave with wave vector $k$, frequency $\omega$ and polarization $\epsilon$

$$A = \epsilon A_0 \cos(kr - \omega t) = \epsilon A_0 \frac{1}{2} (e^{i(kr - \omega t)} + e^{-i(kr - \omega t)})$$  \hspace{1cm} (1.5)

Since we are interested only in the absorption process we can omit the second exponential term that represents photon emission. Combining Eq. 1.4 and 1.5 the interacting matrix element becomes

$$M_{fi} \propto \langle f | e^{ikr} \epsilon \cdot p | i \rangle$$  \hspace{1cm} (1.6)

For $kr \ll 1 = |r| \ll \lambda/2\pi$, where $\lambda$ is the wavelength of the X-rays and $r$ the estimation of the K-shell diameter, the equation can be simplified by retaining only the first term in the expansion. By doing this we confine to the dipole approximation. For $h\nu \sim 100eV$ one has $\lambda \sim 10^2\AA$ and therefore the wavelength is large compared to the atomic distances and the dipole approximation can be applied in most cases. Expanding the vector potential to the first order and introducing the dipole operator $\mu = e r$, the transition probability is then proportional to

$$W_{fi} \propto |\langle f | e \cdot \mu | i \rangle|^2$$  \hspace{1cm} (1.7)
1.3.2 X-ray Photoemission Spectroscopy (XPS)

The physical principle behind the photoemission spectroscopy is the photoelectric effect, the phenomenon in which an electron is emitted from matter after the absorption of electromagnetic radiation. Since its discovery in 1887 by Hertz [22] and the subsequent rationalization by Einstein in 1905 [23], this spectroscopic technique has been widely used to investigate the composition and electronic structure of matter. When the electromagnetic radiation is in the X-ray range, the technique is called X-ray Photoemission Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA). With ultraviolet radiation, on the other hand, the technique is called Ultraviolet Photoemission Spectroscopy (UPS). The use of synchrotron radiation as source for the photons has several advantages since it allows to tune the photon energy as required, to have high photon flux and high resolution. For XPS the typical photon energies are up to 1000 eV. In this range the penetration power in a solid is on the order of 1-10 \( \mu \text{m} \) [23]. However not all the generated photoelectrons are emitted from the solid because of the high probability they have to interact with matter with the consequent loss of kinetic energy. So while the path length of photons is of the order of micrometers that of electrons is of the order of tens of Ångstroms as predicted by theory and confirmed in many different materials (see Fig.1.7). For this reason only the electrons generated within tens of Å below the surface can leave the solid without energy loss and can contribute to the relative peak in the spectrum. On the other hand the electrons that are scattered before coming out from the solid contribute to the background signal while that generated deeper in the solid are not detected. From these considerations it is evident the surface sensitivity of the XPS. The intensity of the electrons emitted from all depths larger than \( d \) is given by the Beer-Lambert law [17]

\[
I(d) = I_0 \exp \left( -\frac{d}{\lambda \cos \theta} \right)
\]

where \( I_0 \) is the intensity of an infinitely thick, \( \lambda \) the attenuation length of electrons and the \( \cos \theta \) term account for electrons emitted at an angle \( \theta \) with respect to the surface normal. There are several relationships to relate the attenuation length to the inelastic mean free path (IMFP) of electrons. The one proposed by Seah and Dench [24] is the following:

\[
\lambda = 0.316a^{3/2} \left\{ \frac{E}{Z^{0.45} \ln(E/27) + 3} \right\} + 4 \}
\]

where \( a \) is the lattice parameter, \( E \) the kinetic energy of the electrons and \( Z \) the mean atomic number. The electrons that leave the sample are detected by a spectrometer according to their kinetic energy that depends on the exciting photon energy \( h\nu \), the
binding energy of the atomic orbital from which the photoelectrons originates $E_b$ and the work function of the sample $\phi_S$ through the following relationship

$$E_k = h\nu - E_b - \phi_S$$  \hspace{1cm} (1.10)

The electrons that arrive to the detector experience the contact potential $\phi_S - \phi_A$ that exists between the sample surface and the analyzer when they are electrically connected and their kinetic energy changes accordingly. Usually the analyzer work function is smaller than the sample work function and so the contact potential results in an acceleration of the electrons as they fly through the analyzer. Adding the contact potential to the previous equation we get the similar equation

$$E_k = h\nu - E_b - \phi_A$$  \hspace{1cm} (1.11)

However in practice neither the sample work function nor the analyzer one can be used because it is not possible to know them a priori. To overcome this problem the Fermi edge of a metal surface is used as reference for the measured kinetic energies. The only definition is that the kinetic energy of the fastest electrons (the electrons coming from the Fermi edge) is not $h\nu - \phi_S$ but it is simply $h\nu$ and so the kinetic energy of all the electrons is equal to the one they have before leaving the sample. This puts the $E_b$ of the Fermi edge to zero and shifts the photoemission spectrum accordingly. The photoemission spectrum reproduces the electronic structure of the system under
1.3. Experimental methods

investigation through the map of all the occupied levels, both core and valence levels. Since each element has a unique set of binding energies, XPS can be used to identify and determine the concentration of the elements in the sample. Moreover measuring the relative $E_b$ shifts information about the chemical state of the system can be extracted.

1.3.3 Near Edge X-ray Absorption Fine Structure (NEXAFS)

NEXAFS is a synchrotron-based technique that can be viewed as complementary to XPS since in this case the unoccupied states are probed. It measures the X-ray absorption of a material when the photon energy is tuned in an energy range of about 30 eV near the excitation edge of a certain atomic shell. It is a quite new technique since the first NEXAFS spectrum on a chemisorbed system has been recorded only in 1980 [25]. Before that time the near edge structure was automatically recorded during each EXAFS (Extended X-ray Absorption Fine Structure) experiments but it was discarded as too complicated. Since then, significant progresses in the understanding of the near edge structure has been made and now NEXAFS is used as a powerful technique to

- detect the presence of specific bonds in molecules
- determine the bond lengths
- derive the molecular orientation of molecules on surfaces or in solids
- reveal the orbitals that are involved in the bond with the surface

The X-ray absorption can be measured either directly by monitoring the attenuation of the X-ray intensity passing through the sample, or indirectly by observing the intensity of the secondary processes. After the X-ray absorption an electron from a localized atomic level is excited to one of the unfilled molecular states. The secondary deexcitation process can occur either radiatively by the emission of a fluorescent photon or non-radiatively by Auger electron emission, the probability emission depending on the atomic number $Z$ and excitation shell (Fig. 1.8). Both channels are a direct measure of the probability of the existence of a core-hole created by X-ray absorption. For low-Z atoms the most probable process is the Auger emission, the process in which an electron from a higher level is ejected taking over the energy of the electron which relaxes to the core level. By detecting the Auger electrons when the photon energy is scanned across the edge we obtain a map of the unoccupied states. Since kinetic energy of the Auger electrons is independent from the photon energy it is possible, by using an electron energy analyzer, to select a kinetic energy window that is centered at the fixed energy of the Auger peak characteristic of the absorbing species. In this case the detection technique is called Auger Electron Yield (AEY). The Partial Electron Yield (PEY) detection
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Figure 1.8: Fluorescence and Auger yield of different atomic shells as a function of the atomic number. For low-Z atoms the Auger yield dominates.

The technique measures both the inelastic and elastic Auger electrons by detecting all the electrons of kinetic energy larger than a threshold energy. The threshold energy has to be chosen in order to avoid new photoemission peaks entering the kinetic energy window of the detector over the NEXAFS energy range and also to decrease the background due to the secondary electron tail. Finally it is possible to measure also all the photoemitted electrons and in this case we talk about Total Electron Yield (TEY). The three techniques produce all almost identical NEXAFS spectra except for giving different signal-to-background and signal-to-noise ratio and to probe different depth of the sample because of the IMFP.

The mechanism of exciting an electron from an atomic core shell to a molecular orbital (MO) is depicted in Fig.1.9. Here we have assumed that the transition of 1s core states to all unoccupied levels are allowed and neglect the multielectron excitations. Usually molecular orbitals are referred to by their $\pi$ or $\sigma$ symmetry and unoccupied MOs are denoted with an asterisk. As illustrated the lowest unoccupied molecular orbital (LUMO) for two bound atoms is usually a $\pi^*$ one with a $\sigma^*$ orbital at higher energy. For the ground state molecule these states typically lie above the vacuum level, while for the excited molecule with a hole in a core level, they are pulled below the vacuum level due to the screening of the positive core-hole. So in the K-shell spectra of low-Z molecules, the lowest energy structure is a $\pi^*$ resonance and its position falls below the vacuum level. Also above the vacuum level there are resonance structures correspond-
1.3. Experimental methods

Figure 1.9: The NEXAFS process (right) and corresponding X-ray absorption spectrum (left).

ing to quasi-bound $\sigma^*$ states. They are confined with the potential barrier arising from the centrifugal part in the effective potential ($\propto l(l+1)/r^2$) which becomes positive for large $l$. Because of the increasing decay probability of the electron to continuum states, the energy width of the $\sigma^*$ resonances is broader with respect to the $\pi^*$ one. As the excitation energy approaches the ionization potential (IP), the bound state cross section merges into continuum cross section through closer-spaced atomic Rydberg states.

Besides $\pi^*$ and $\sigma^*$ resonances, several step-like features can be present in a NEXAFS spectrum. They are the result of an excitation of a core-level to a continuum or quasi-continuum of final states. A step-like increase in the X-ray absorption is observed at the IP, corresponding to the transition to unbound free states. In the presence of adsorbate, the IP of the substrate may be considerably shifted with respect to the clean substrate because of the work function difference.

Additionally, the step to the Fermi level can occur due to the transition to densely spaced unfilled electronic states of the metallic substrate above the Fermi level which mix with molecular states. The height of the Fermi level step depends on the strength of hybridization of the metallic states around Fermi with molecular valence band states.

**Polarization dependence and molecular orientation**

Following the outline given by Stöhr [26] I discuss the polarization dependence of the matrix element that leads to the angular dependence NEXAFS resonances in molecular adsorption system when polarization dependent studies are carried out. I will limit the discussion to K-shell excitations and X-ray linearly polarized light, described by the
1. Experimental techniques and apparatus

Figure 1.10: Schematic illustration of spatial orientation of $\pi^*$ and $\sigma^*$ orbitals in a benzene ring.

polarization vector $\epsilon$.

The polarization dependence can be derived from the transition intensity in Eq. 1.7 and it is based to the concept that bonds and associated molecular orbitals (MOs) are highly directional.

The initial state $|i\rangle$ is represented, with a good approximation, by the atomic 1s wavefunction of the excited atom in the molecule. It is spherically symmetric and can thus be represented by the function $|i\rangle = R_{1s}(r)$. In a one-electron model the final state can be represented by a linear combination of atomic orbitals (LCAO). Despite the rough simplification, the LCAO is one of the simplest and successful way to construct electron wavefunctions in molecules. It assumes that the molecular orbitals $\phi_i$ can be expanded in the basis set of $N$ atomic orbitals according to

$$\phi_i = \sum_{l=1}^{N} a_{il} \chi_l$$  \hspace{1cm} (1.12)

where $a_{il}$ are the weight of the individual atomic orbitals. The further derivation is for simplicity confined to the atoms of the second raw in the periodic table. The final state wavefunction for low-Z atoms can thus be written as a linear combination of atomic 1s, 2s and 2p states

$$|f\rangle = a|1s\rangle + b|2s\rangle + c|2p_x\rangle + d|2p_y\rangle + e|2p_z\rangle$$  \hspace{1cm} (1.13)

Expressing the atomic wavefunctions in spherical coordinates one gets

$$|f\rangle = aR_{1s}(r) + bR_{2s}(r) + R_{2p}(r)(c \sin \theta \cos \phi + d \sin \theta \sin \phi + e \cos \theta)$$  \hspace{1cm} (1.14)

where $R_{1s}$, $R_{2s}$ and $R_{2p}$ represent the radial part of the wavefunctions. The position vector $r$ in the dipole operator is expressed in the same coordinate system as

$$r = r(\hat{e}_x \sin \theta \cos \phi + \hat{e}_y \sin \theta \sin \phi + \hat{e}_z \cos \theta)$$  \hspace{1cm} (1.15)
1.3. Experimental methods

Figure 1.11: Coordinate system of the plane orbital relative to the substrate.

where are $\hat{e}_x$, $\hat{e}_y$ and $\hat{e}_z$ are the unit vectors along the axis of the coordinate system. The matrix element is now obtained by integration

$$\langle f | \mu | i \rangle = R \frac{4\pi}{3} (c\hat{e}_x + d\hat{e}_y + e\hat{e}_z)$$

(1.16)

where $R = \int R_{1s}(r)R_{2p}(r)r^3 dr$ is the radial part of the matrix element. Thus, according to Eq.1.16 the vector matrix element points in the same direction as the p-component in the final state orbital of the excited atom.

We want to consider now two specific cases, i.e. the $\sigma^*$ and $\pi^*$ orbitals of two double-bonded atoms. We orient the coordinate system so that the interatomic axis and therefore $\sigma^*$ orbital lies along the z axis and the $\pi^*$ orbital along the the x axis. The orientation of the X-ray polarization unit vector $\epsilon$ is specified by spherical angle $\theta$ and $\phi$. The polarization dependence of resonance intensity associated with the $\sigma^*$ molecular orbital final state is given by

$$I_{if}(\sigma^*) \propto |\epsilon \cdot \hat{e}_z|^2 \propto \cos^2 \theta$$

(1.17)

The $\sigma^*$ resonance intensity is greatest for $\epsilon$ along the interatomic axis and vanishes when $\epsilon$ is perpendicular to it. The polarization dependence of the resonance associated with the $\pi^*$ orbital is correspondingly give by

$$I_{if}(\pi^*) \propto |\epsilon \cdot \hat{e}_x|^2 \propto \sin^2 \theta \cos \phi^2 \propto \sin \theta^2$$

(1.18)

having an opposite angular dependence from $\sigma^*$.

Eqs. 1.17 and 1.18 describe the origin of the linear dichroism in the NEXAFS angular spectra and are very helpful in defining the bond and molecular orientation in space.

We now examine the spatial orientation of $\pi^*$ and $\sigma^*$ systems in the molecules. Since only the spatial orientation of the orbital, i.e. the direction of maximum orbital amplitude, determines the angular dependence of $K$-shell spectra, we can divide the final states in two class depending on the number and mutual orientation of s and p orbital.
If the molecular orbital points in a specific direction it is called a vector orbital, while if it spans a plane we have a plane orbital. An example of this notation is given in Fig.1.10 where the $\sigma^*$ system of a benzene ring is characterized by the plane of the carbon atoms and the $\pi^*$ orbitals can be represented by vectors perpendicular to this plane.

As derived before and according to the notation in Fig.1.11 the angular dependence of a $\pi^*$ or $\sigma^*$ vector orbital changes as $I_v \propto \cos^2 \zeta$, where $\zeta$ is the angle between the polarization vector and the vector orbital. On the other hand for a plane orbital we need to integrate Eq.1.17 over all the azimuthal angles to get for the intensity the dependence $I_p \propto \sin^2 \delta$ where $\delta$ is the angle between the normal to the plane and the polarization vector.

Passing to the coordinate system of the surface one gets respectively for the vector and plane orbitals

$$I_v \propto (\cos \theta \cos \alpha + \sin \theta \sin \alpha \cos \phi)^2$$

$$I_p \propto 1 - (\cos \theta \cos \gamma + \sin \theta \sin \gamma \cos \phi)^2$$

In the above equations the resonance intensity explicitly depends on the azimuthal orientation $\phi$ of the molecule relative to the substrate. When we have a large number of molecules on the substrate, the NEXAFS signal averages on all the possible configurations and the corresponding equations are consequently simplified. In particular in the presence of a well ordered surface, the adsorption geometry is strongly affected with the formation of domains of equivalent molecular orientation. In the following I will consider two particular cases of useful interest: substrate with twofold symmetry and substrate with threefold or higher symmetry.

In the case of twofold symmetry we do not distinguish between molecules adsorbed with orbital tilt angle $\alpha$ and $-\alpha$ ($\gamma$ and $-\gamma$ for plane orbitals). The cross-term in Eqs.1.19 and 1.20 vanishes and the equations simplify as

$$I_v \propto \cos^2 \theta \cos^2 \alpha + \sin^2 \theta \sin^2 \alpha \cos^2 \phi$$

$$I_p \propto 1 - \cos^2 \theta \cos^2 \gamma - \sin^2 \theta \sin^2 \gamma \cos^2 \phi$$

When the substrate posses threelfold or higher symmetry the $\cos^2 \phi$ term averages to 1/2 and the above expressions becomes

$$I_v \propto \cos^2 \theta \cos^2 \alpha + \frac{1}{2} \sin^2 \theta \sin^2 \alpha$$

$$I_p \propto 1 - \cos^2 \theta \cos^2 \gamma - \frac{1}{2} \sin^2 \theta \sin^2 \gamma$$

Thus in this case the azimuthal angular dependence vanishes and the expressions are equivalent to those for cylindrical symmetry about the surface normal. This has the
1.3. Experimental methods

important consequence that for one specific molecular orientation the resonance intensities in both the vector and plane cases can become independent of the X-ray incidence angle $\theta$. In the case of perfect linear polarization, it can be easily see that for $\alpha$ or $\gamma$ equal to the magic angle of $54.7^\circ$ the angle-dependent terms vanish. Thus for this particular orientation, i.e., a $54.7^\circ$ tilt of the vector orbital from the surface normal or a $35.3^\circ$ tilt of the orbital plane from the surface normal, the intensity distribution measured in NEXAFS is indistinguishable from that for a random molecular orientation. Moreover for an X-ray incidence angle of $54.7^\circ$ the measured intensity distribution is independent of the molecular orientation. It is also possible to combine NEXAFS spectra of the same system taken in p-polarization ($\varepsilon$ perpendicular to the surface) and s-polarization ($\varepsilon$ in the surface plane) to build an artificially magic angle NEXAFS. For a plane type orbital and a high surface symmetry substrate, we can use Eq.1.24 to derive the synthetic magic angle expression.

\[ I_{p-pol} \propto 1 - \cos^2 \gamma \]  
\[ I_{s-pol} \propto 1 - \frac{1}{2} \sin^2 \gamma \]

If we take the weighted sum

\[ I_{\text{magic}} = I_{p-pol}^p + 2I_{s-pol}^p \propto \text{const} \]

the angular dependency of the NEXAFS intensity is lost and we are left with an artificially calculated magic angle NEXAFS independent of the true molecular orientation $\gamma$. The same kind of derivation also holds for the vector type orbitals.

NEXAFS spectra processing at ALOISA

NEXAFS spectra have to be calibrated and normalize before they can be used in further analysis. At ALOISA the calibration procedure can be done in two different ways. The first one can be used to calibrate NEXAFS spectra on C-, N- and O-edge and it is based on the measurement of the drain current $I_0$ on the last toroidal mirror of the optical system. During time a small amount of carbon, nitrogen and oxygen residues have deposited on the mirror yielding a distinct absorption spectrum. This spectrum has been calibrated in photon energy by reference benchmark measurements to gas absorption resonances. In cases where absorption of other edges are measured, the toroidal current cannot be used to calibrate the photon energy. It is necessary to measure, soon before the NEXAFS spectrum, a XPS scan with the Fermi step or other well known spectral
feature, to proper calibrate the photon energy. In doing so, it is assumed that during a NEXAFS scan only a rigid shift of the photon energy can occur. The toroidal current is used also to normalize the NEXAFS intensity by the photon flux. It has to be used together with the NEXAFS signal taken separately on the clean surface across the same photon energy range. The normalized spectrum is obtained as

\[ I_{\text{norm}} = \frac{I}{I_0} \frac{I_{\text{clean}}}{I_{\text{clean,0}}} \] (1.29)

The NEXAFS spectra can be further normalized putting the pre-edge intensity at 0 since there is no absorption in this region and the post-edge intensity at 1. In this way one has normalized to the same amount of scatterers per volume since in the post-edge region, where no resonances are present, the system is directly ionized and the NEXAFS intensity is proportional to the number of core-holes created per unit volume.

1.3.4 Resonant Photoemission Spectroscopy (RPES)

The Resonant Photoemission Spectroscopy (RPES) is a spectroscopic technique that combines the two techniques presented in the previous sections, XPS and NEXAFS. Indeed in the RPES the photoemission from the valence band is measured while the photon energy is tuned across a molecular absorption edge. Under these conditions two emission channels can be simultaneously present. The first is the direct photoemission from the valence band, while in the other a core-electron is first resonantly excited into an empty available level, forming an intermediate state. This intermediate state may decay via autoionization, yielding a final state identical to that of direct photoemission and giving rise to the observed resonances.

In the RPES technique the study of the core-hole decay channels is exploited to study the charge transfer dynamics in the timescale of the core-hole lifetime \( f_s = 10^{-15} \text{s} \). The shortness of this timescale gives the approach a unique place in the study of electron-transfer dynamics. Moreover it differs from the more traditional pump and probe technique by two main aspects:

- the measurements is carried out not in the time-domain but in the energy domain;
- core-electrons are involved, which enables the atomic specificity unique of the spectroscopic technique.

In Fig.1.12 different excitation and de-excitation channels of interest here are depicted. The X-ray absorption can give rise to both ionized states by the photoemission of a core or valence electron, and neutral resonantly excited states by the occupation of an empty
1.3. Experimental methods

Figure 1.12: Representation of the electronic excitations and subsequent decay processes. The different spectroscopic techniques related to each process are indicated. Among the other

molecular level with a core electron. In both cases the X-ray absorption leads to the creation of a core-hole that decays, after a time equal to its mean lifetime, by Auger decay or autoionization processes. In the case of core-electron photoemission, the core-hole can be refilled with an electron from a higher occupied state and the extra energy may
be taken over by another electron that is then photoemitted. The final state is double ionized and the decay process is a simple Auger decay.

The second scenario involves the core-hole decay with the initially excited core-electron that remains bounded in a molecular empty level. In this situation several decay channels are opened. If the excited electron participate to the core-hole decay we have the participator decay whose final state is equal to that of a direct photoemission from the valence band. The excited electron can also remains in the atomically localized resonance while the core-hole decay takes place with the other electrons of the system and in this case we have the so-called spectator or Raman decay. In both situations the final state is singly charged and the two channels are usually referred to as autoionization channels. Moreover in the Raman process a linear relation between the energy of the incoming photon and of the outgoing electron is observed and the Raman channel results at a constant binding energy.

Beyond these channels that can be observed for an isolated system, it can happen that the initial excitation involves an electronic state delocalized over many atomic centers, when the excited resonance is coupled to a continuum of states. The consequences of the electron delocalization are the lack of the autoionization channels both participator and Raman. The only decay channel is the normal Auger, that in this situation is often called charge-transfer channel. Its dispersive behaviour is that of the normal Auger which is at constant kinetic energy independently of the incident photon energy.

Owing to this different dispersive behaviour the Raman and charge-transfer can be spectroscopically separated and the ratio of Raman to charge-transfer intensity is related to the degree of atomic localization in the excited state in the timescale of the core-hole decay. Another approach to measure the charge transfer time does not take into account the Raman and Auger components of a resonant spectrum but is based on the decrease of the participator intensity in the system after charge transfer. The two approaches are schematically depicted in Fig.1.13

Core-hole Clock method

Following the paper of Bruhwiler et al. [27] I derive the equations of the core-hole clock method in which the decay channel branching are used as a measure of the charge transfer (CT) times.

If one consider the removal of the excited electron as a tunneling process with exponential probability as a function of time, then a direct comparison with the core-hole decay rate is a relatively simple matter to understand. The assumption behind the description of the two processes as exponential is that they are independent which is often the case. In general, an exponential decay law derives from the assumption that the decay rate is proportional to the number of identical systems available in the initial, unstable state,
1.3. Experimental methods

Auger vs Autoionization

Participator decreasing

Figure 1.13: Schematic of the two measurement approaches for deexcitation of the small system which is loosely coupled to a continuum. a) A spectrum is analyzed for its primary components, Auger and autoionization, here shown as overlapping components, instead of as the total spectrum. b) A spectrum at resonance is measured for the isolated system and compared to the case of the coupled system. Changes in the participant intensity are used to monitor the overall change in the autoionization intensity associated with dynamic charge transfer for the system of interest to the continuum.

i.e. the decay rate $dN/dt$ is given by

$$\frac{dN(t)}{dt} = -\frac{\Gamma}{\hbar} N(t) \quad (1.30)$$

where $\hbar/\Gamma = \tau$ is the characteristic time for the decay. The quantity $\Gamma$ in Eq.1.30 is generally given the interpretation of the imaginary part of a complex energy often denoted the self-energy. It is apparent that $\Gamma$ itself is proportional to the decay rate. For a particular core-excited state this quantity is also proportional to the total intensity in the measured spectrum. A solution of Eq. 1.30 is given by

$$N(t) = N_0 \exp \left( -\frac{t}{\tau} \right) = N_0 \exp \left( -\frac{\Gamma}{\hbar} t \right) \quad (1.31)$$

where $N_0$ is the number of “systems” prepared in the decaying state at some (arbitrarily) chosen time zero and $N(t)$ is the number of systems left in the excited state at time $t$. We can use Eq.1.30 to derive time dependent probabilities by dividing by $N_0$ and integrating to some time $T$ to determine the likelihood of no decay event for times smaller...
than or equal to that time. This yields

\[ P(T) = 1 - \int_0^T \frac{\Gamma}{\hbar} \exp \left( - \frac{\Gamma}{\hbar} t \right) dt \]  (1.32)

where \( P(T) \) is the probability that no decay has taken place up to time \( T \). By identifying \( \hbar/\Gamma \) with the characteristic times for charge transfer (\( \tau_{CT} = \hbar/\Gamma_{CT} \)) and core-hole lifetime (\( \tau_{CH} = \hbar/\Gamma_{CH} \)), respectively, we may write the relations corresponding to Eq. 1.32 for the processes in which we are interested here. This is done below, where we derive a useful relationship between the characteristic times and the intensities found in the decay spectrum. As stated above in connection to Eq 1.32 we may write the probability for no charge-transfer event to occur before time \( T \) as

\[ P(T)_{noCT} = 1 - \int_0^T \frac{\Gamma_{CT}}{\hbar} \exp \left( - \frac{\Gamma_{CT}}{\hbar} t \right) dt \]  (1.33)

The same form holds for the probability relation \( P_{CT}(T) \) that the excited state of an isolated small system has decayed before a given time \( T \) after excitation of the core electron,

\[ P(T)_{CH} = \int_0^T \frac{\Gamma_{CH}}{\hbar} \exp \left( - \frac{\Gamma_{CH}}{\hbar} t \right) dt \]  (1.34)

Note the difference in sign between Eqs. 1.33 and 1.34. This reflects the fact that we are considering the situation “nothing happened” (i.e. no charge transfer) in Eq 1.33 while we are considering the probability for “something happened” (a core-hole decay in this case) in Eq 1.34.

If we would like to consider both channels simultaneously, with independent rates, we have to consider the conditional probability for the combined events. The branching of the events is indicated in Fig. 1.9. Let us first consider the sequence: a core-excited system decays before or at some time \( T \), with no charge transfer during this time. This is given by

\[ P_{CH}^{noCT}(T) = \int_0^T \frac{\Gamma_{CH}}{\hbar} \exp \left( - \frac{\Gamma_{CH}}{\hbar} t_1 \right) \cdot \left[ 1 - \int_0^{t_1} \frac{\Gamma_{CT}}{\hbar} \exp \left( - \frac{\Gamma_{CT}}{\hbar} t_2 \right) dt_2 \right] dt_1 = \frac{\Gamma_{CH}}{\Gamma_{CH} + \Gamma_{CT}} \left[ 1 - \exp \left( - \frac{\Gamma_{CH} + \Gamma_{CT}}{\hbar} T \right) \right] \]  (1.35)

Measuring a spectrum corresponds to \( T \rightarrow \infty \) in Eq. 1.35 when the excited systems have definitely decayed, and we obtain

\[ P_{CH}^{noCT} = \frac{\Gamma_{CH}}{\Gamma_{CH} + \Gamma_{CT}} \]  (1.36)
1.3. Experimental methods

Figure 1.14: Comparison of the decay channels for an isolated system (bottom) and a coupled system (top). In the isolated system the participator decay is degenerate with the direct photoemission from the valence band and the relative occupied orbitals are resonantly enhanced. In the case of a coupled system the fast delocalization of the excited electron can open a new normal Auger channel. The excited electron cannot participate to the core-hole decay and therefore the participator intensity is reduced.

Eq. 1.36 tells us that a fraction $\Gamma_{CH}/\Gamma_{CH} + \Gamma_{CT}$ of the spectral intensity stems from decays where no charge transfer has occurred before core-hole decay. The remaining fractional intensity in the spectrum is given analogously by

$$P_{CT}^{CH} = \frac{\Gamma_{CT}}{\Gamma_{CH} + \Gamma_{CT}} \quad (1.37)$$

These equations show that, while $\Gamma_{CH}$ is proportional to the Auger transition rate which defines the absolute intensity of the entire spectrum (resonant and non-resonant), its magnitude relative to $\Gamma_{CT}$ emerges in the intensity ratios. This can also be confirmed by taking certain limits, such as $\Gamma_{CH} \rightarrow \infty$ and $\Gamma_{CH} \rightarrow 0$. Since we did not need to specify which core-excited state was originally produced, the expressions above apply, within the stated approximations, to all cases of dynamic charge transfer to be considered.

We can now apply the relationships above to obtain expressions relating the measured spectral intensities $I$ to the corresponding quantities $\Gamma$. The intensities are defined in
Here it is important to stress out, that the participator decay channels, being degenerate with direct photoemission final states, are found at constant binding energy, whereas the spectator decay channels are found at constant kinetic energy enabling to differentiate the two decay channels by observing the binding (kinetic) energy dispersion with photon energy. For the case of resonant excitation corresponding Fig.1.13(a), in which the core-excited small system transfers charge to the large system, the total intensity in the spectrum corresponds to the core lifetime broadening (transition rate) $\Gamma_{CH}$, whereas the Auger fraction corresponds to the tunneling bandwidth $\Gamma_{CT}$. Hence the relationship we seek is

$$\frac{\Gamma_{CT}}{\Gamma_{CH} + \Gamma_{CT}} = \frac{I_{Aug}}{I_{res} + I_{Aug}}$$

(1.38)

where $I_{Aug}$ represents the intensity of the Auger component in the spectrum, and $I_{res}$ that of the resonant Auger, or spectator component. Fig.1.13(a) is also relevant for non-resonant excitation followed by charge transfer from the large to the small system, yielding

$$\frac{\Gamma_{CT}}{\Gamma_{CH} + \Gamma_{CT}} = \frac{I_{res}}{I_{Aug} + I_{res}}$$

(1.39)

In this case, the “resonant” portion of the spectrum is not necessarily equivalent to what one would obtain for truly resonant excitation, but may be identified by the so-called spectator shift in kinetic energy due to the screening effect of the transferred electron and a general similarity to a truly resonant spectrum. Since the total Auger-like spectrum is not considered in Fig.1.13(b), approximations are required in order to make use of these variations on the method. The principle behind Fig.1.13(b) is that the occupied-unoccupied spatial overlap which enters the Auger matrix element for the participator intensity is only weakly dependent on the coupling with the neighbouring systems. In that case, one takes the intensity of the participator channel $I_{iso}$ for the isolated small system as proportional to the entire resonant spectral intensity in the spirit of Eqs.1.36 and 1.37 and thus $\Gamma_{CH} + \Gamma_{CT}$. One then assumes that a decrease in intensity of that feature $I_{iso} - I_{coup}$ corresponds to the charge-transfer rate, or tunneling bandwidth $\Gamma_{CT}$, for which $I_{coup}$ is the participator intensity for the coupled small-large systems, Fig.1.14.

For this approximation to be quantitatively valid, the participator matrix element must be the same for the isolated and coupled small systems. A second issue is the intensity calibration, which must correspond in the ideal case to an intensity per unit small system. With these considerations in mind, one can write

$$\frac{\Gamma_{CT}}{\Gamma_{CH} + \Gamma_{CT}} = \frac{I_{iso}}{I_{coup} + I_{iso}}$$

(1.40)
The charge transfer time is from Eq. 1.40 equal to

\[ \tau_{CT} = \tau_{CH} \frac{I_{coup}}{I_{iso} - I_{coup}} = \tau_{CH} \frac{q}{1 - q} \]  

(1.41)

using the participator signal intensity quenching \( q = I_{coup} / I_{iso} \). Or, if it is possible to separate the signal into the resonant part and normal Auger part, which is in extended (multi-atom) molecules very difficult to achieve, the CT time equals

\[ \tau_{CT} = \tau_{CH} \frac{I_{res}}{I_{Aug}} \]  

(1.42)

The Eqs. 1.41 and 1.42 are the main equations of the Core-Hole Clock method and rely on the knowledge of the core-hole lifetime \( \tau_{CH} \) which can be found from literature. Furthermore, if the charge transfer time in a non-isolated reference system is not “infinitely” long and is known from, e.g., other techniques, or if the RPES signal is possible to separate into the resonant and normal Auger part, the CT times in the coupled (e.g. monolayer) system can be nevertheless calculated. The trick is to use Eq. 1.41 to express the expected intensity of the isolated system \( I_{iso} \) with the measured intensity of the coupled reference system \( I_{coup}^{ref} \) and the measured CT time in the reference system \( \tau_{CT}^{ref} \)

\[ I_{iso} = I_{coup}^{ref} \left( 1 + \frac{\tau_{CH}}{\tau_{CT}^{ref}} \right) \]  

(1.43)

Applying Eqs. 1.41 and 1.43 one is then able to give CT times even in cases where significantly fast charge transfer times are measured in the reference system.

**RPES data processing**

The pre-processing of the RPES spectra is a crucial step for a correct application of the core-hole clock technique. Moreover, in order to compare RPES intensity from different systems (like monolayer and multilayer), a careful acquisition of the RPES data is needed. In particular, to avoid molecular orientation dependency, the spectra are usually taken at magic angle conditions with the electron detector placed along the polarization vector \( \epsilon \).

The usually procedure followed at the ALOISA beamline for data processing can be summarized in four steps:

- Normalization
- Alignment and calibration
- Non-resonant part subtraction
• Auger subtraction

In the first step the data are normalized for the photon flux and the signal coming from the substrate, using a similar procedure to the NEXAFS spectra normalization. The signal of the clean substrate is measured at the same conditions of the RPES measurement and, after the correction of the photon energy, the RPES signal is normalized using

\[ I_{\text{norm}}^{\text{RPES}} = \frac{I_{\text{raw}}^{\text{RPES}}}{I_0^{\text{NEXAFS}}/I_0} \]  

(1.44)

where \( I_0 \) is the drain current measured during the RPES scan and \( I_0^{\text{NEXAFS}} \) is the drain current during the clean NEXAFS scan (\( I_{\text{NEXAFS}}^{\text{NEXAFS}} \)). Since a RPES measurement is a collection of many valence band spectra taken at different photon energies, we need to calibrate each valence band spectrum separately. This can be done by referring to a peak of the substrate or to the Fermi edge that have to remain at a constant binding energy when the photon energy is changed. Any correction at the binding energy reflects a change in the photon energy from its nominal value and so the photon energy has to be further correct by applying

\[ h\nu = h\nu' - \Delta E(h\nu') \]  

(1.45)

where \( \Delta E(h\nu') \) is the photon energy dependent binding energy offset.

In some cases (especially multilayer depositions) after the alignment of the substrate feature, it is possible to still observe some discrepancies in the binding energy position of the adsorbate states. This is due to the charging of the adsorbate layer that can be handle by using the second order diffraction X-ray light excited core-level peak. The kinetic energy of the second order peak is equal to

\[ E_k^{\text{2nd order}} = 2h\nu - E_b \]  

(1.46)

while in the binding energy scale it is

\[ E_b^{\text{2nd order}} = h\nu - E_k^{\text{2nd order}} = h\nu - E_b \]  

(1.47)

The second order peak position is dispersing in binding energy with the photon energy and any deviation from the position given by the equation above indicate a charging effect. These should then be corrected where is important to stress out that the substrate features, after this correction, are no longer properly aligned.

The third step of data processing involves the subtraction of the non-resonant part of the spectrum, to remain only with the resonant features that can be compared. This means basically the subtraction of the signal observed in the pre-edge region where no resonances are still present and the detected intensity comes from the direct photoemission from the valence band. In the non-resonant part of the spectra there is also the
contribution of the substrate that can be subtracted by measuring a separate RPES on the clean substrate across the same energy ranges. Moreover due to the absorption of the photon inside the adsorbate, the relative intensity of the substrate varies across the photon energy scan. This can be also taken into account by attenuating the measured clean RPES by the amount of the X-ray absorption in the adsorbate film. However this last step is important only for a low coverage where the substrate signal is significant.

After remaining with only the resonant intensity we can decompose the spectra in the different decay channels. To do this we need first to measure the Auger peak shape and then subtract it from all the scans. The Auger peak shape as to be taken at high photon energy where we are certain that only a normal Auger decay can be present. We then change the scale from binding to kinetic energy and subtract the Auger shape by properly scaling the reference Auger shape. In principle two Auger components could be subtracted from each scan: one at constant kinetic energy and the other, Raman Auger, with a distinct spectator shift. In general the subtraction of two distinct Auger components is, however, very difficult, and thus we commonly apply the subtraction procedure of a single component with adjusted spectator shift. The residuum, after the Auger subtraction is the participator decay channels that are then used to calculate the CT times.

However when the participator quenching is used to apply the core-hole clock method, a correct normalization is crucial. The overall signal has to be normalized to the number of created core-holes which is proportional to the intensity measured in NEXAFS. To be consistent we use the total intensity of the subtracted Auger peak and the participator decay, both measured with the same electron analyser in a RPES scan. In most cases we integrate a wider range (up to 10–15 eV) of the participator decay channel to overcome the issue of the transition matrix element affecting the single HOMO resonances. Using the total signal of a wider range this effect is expected to be averaged out and the resulting quenching can be thus attributed just to the charge delocalization, and the CT times can be calculated after applying Eq.[1.41]
Chapter 2
Organic semiconducting single crystals: the case of 4HCB

2.1 Introduction

The problem of charge transport in organic semiconductors is of fundamental importance in the organic electronic field. However, since the discovery of the electrical conductivity in polyacetylene (1977) [2], that opened the research field of organic semiconductors (both polymers and molecules), a unified description of the charge transport mechanism in this class of materials has not been yet found. The electrical properties of the organic semiconductors are due to the high delocalization of the molecular orbital along the polymer or macromolecule, with the formation of an extended $\pi$-conjugated system that allows the charge transport in the organic systems. The electronic structure is therefore different from that of an inorganic semiconductor and, as a consequence, the mechanism of charge transport cannot be described by simply borrow the concepts of classical semiconductors theory.

The fundamental and intrinsic electronic transport parameter, that specifies a given semiconductor, is its carrier mobility $\mu$, that is the linear coefficient between the electric field-induced velocity component of the charge carriers $\langle v \rangle$ and the applied electric field $E$: $\langle v \rangle = \mu \cdot E$ [28]. Due to the low symmetry, in organic crystals the previous relation is anisotropic and the mobility becomes a tensor in which each component depends on the temperature $T$ and, in the case of a non-linear transport, also on the electric field. At present a theoretical prediction of the mobility components for an organic crystal is not possible, and therefore reliable data are needed to find out the magnitude of the transport parameters and the conditions under which the proposed models can be applied.

This task, however, is not simple because of the strong sensitivity of the experimental results from the device fabrication conditions, which affects primarily the molecular order and the material purity. The charge-transport properties in conjugated materials critically depend indeed on the molecular packing and degree of order in the solid state [29], as well as on the density of impurities and structural defects [30].

In this view, organic semiconducting single crystals (OSSCs) represent the perfect model
system to study the intrinsic electric behaviour of organic semiconductors, since their long range molecular order and reduced contribution of defects allow to exclude hopping phenomena due to grain boundaries and structural defects. Moreover due to their intrinsic spatial anisotropy it is possible to relate the electric properties to the 3D order and ultimately to the intermolecular coupling.

In highly purified molecular single crystals, transport at low temperature can be described within a band picture, as shown by Karl [31]. When temperature increases, the mobility progressively decreases as a result of scattering processes due mainly to lattice phonons, as is the case in metallic conductors. At elevated temperatures, transport operates via a thermally assisted polaron hopping regime where charge carriers jump between adjacent molecules or chains, as described, for instance, by Conwell and coworkers [32].

The realization of macroscopic self-standing crystals have been reported for different molecules and their anisotropic transport properties have been investigated connecting the crystal in a field effect transistor (FET) configuration and measuring the mobility along the different crystallographic axes. Due to the small crystal thickness, usually only a 2D electrical anisotropy has been measured, as for example for rubrene [33, 34] or dicyclohexyl-a-quaterthiophene [35], while a complete study along the three crystallographic axes has been carried out by Fraboni et al. on the 4-hydroxycyanobenzene (4HCB) based single crystal [13, 14].

We chose this last system and, exploiting synchrotron based spectroscopic techniques, we studied its detailed electronic structure to understand the origin of the electrical anisotropy from a molecular point of view. Since no spectroscopic study had been previously reported for this particular molecule, we examined first the electronic properties of the isolated 4HCB, studying the molecular gas phase. We moved than to the solid phase to investigate both the properties of a thick film and the ones of a monolayer deposited on a metal surface. The former system is used for the study of the charge transport inside the organic material, while the latter models the interface between an organic material and a possible metal electrode.

2.1.1 4HCB: molecule and crystal structure

4-hydroxycyanobenzene (4HCB) is an organic compound consisting of an aromatic ring with one cyano and one hydroxyl functional group respectively at the 1,4 carbon positions (Fig. 2.1). It has an intrinsic dipole moment caused by the simultaneously effect of the cyano and hydroxyl groups on the overall molecular charge distribution. In fact even if both nitrogen and oxygen are highly electronegative atoms, with O more electronegative than N, the hydroxyl and cyano groups have an opposite effect on the
benzene rings resulting the first in a light electron donor and the second in a strong electron acceptor. This is due to the sum of two effects, namely the isomeric and mesomeric effect. The first one consists in the deformation of the entire electronic cloud toward the functional group due to the higher electronegativity of the N (O) with respect to the C. This is an isotropic effect that influences stronger the atoms close to the electronegative one and weaker the ones far away. On the other side we have to take into account the possible resonances that the benzene ring can undergo under the presence of a particular functional group. In Fig. 2.2 the resonances of the benzonitrile and phenol are shown separately. In the first case, the benzonitrile can resonate between the totally aromatic form and the one in which the reorganization of the molecular bonds results in the presence of an additional lone pair on the N. The resulting electronic re-distribution is known as mesomeric effect. The interplay between this two effects in the 4HCB molecule results in an overall electronegativity of the \(-\text{CN}\) group, whereas the \(-\text{OH}\) termination has a light electron donor character. The donor and acceptor groups are connected by the \(\pi\)-bridge of the aromatic ring. The results is a push-pull system with a permanent dipole moment of 5.15 Debye on the molecule. The 4HCB primitive cell, determined by X-ray diffraction measurements, is orthorhombic \((a=9.19, b=10.75, c=25.46 \, \text{Å})\) with 16 inequivalent molecules. The molecules are bondend alternately head-to-tail via hydrogen bonds between their respective hydroxyl and cyano groups to form infinite helical chains around two axis parallel to \(c\). To obtain the crystals, a solution-growth procedure based on a progressive and controlled evaporation of the solvent (ethylic ether) was adopted. The resulting crystals are
2. Organic semiconducting single crystals: the case of 4HCB

![Figure 2.2: Effect of the cyano and hydroxyl groups on the charge of benzene ring. a) The benzonitrile resonances are shown where the cyano group acts as donor acceptor for the benzene ring. b) Phenol tautomerism results in a light electron donation inside the benzene ring.]

colourless, plate-like shape with \(a\) and \(b\) directions parallel to the larger face and \(c\) direction along the crystal thickness.

The molecular arrangement along \(a\) and \(b\) is shown in Fig. 2.3. The packing along \(b\) develops in a sequence of two entangled benzenic rings arranged to form a sort of square-based columns parallel to the crystallographic axis. In the first sequence the benzenic rings (A-B) lying on perpendicular planes and they do not overlap. The second sequence is composed by rings that partially overlap (C-D) to form two infinite stacks, where the rings are separated by a distance of 10.738(2) Å. Along the \(a\) axis there is a group of four molecules each of which originates an infinite column with the benzenic rings partly overlapping and separated by a distance 9.202(2) Å. We note how in this second case the distance between the benzene rings is smaller with respect to the \(b\) axis. Moreover the nitrogen atoms of the cyano group, belonging to the stack next to the one examined, are sandwiched between two overlapping rings of the column and may contribute to increase the local net electron density of the system.

The solution-growth procedure, allows to tune the crystal dimension from one to a few
2.2 Experimental Details

2.2.1 Gas-phase measurements

The gas-phase measurements have been performed at the GASPHASE beamline at ELETTRA. The 4HCB powder was inserted into the experimental chamber inside a crucible and it was introduced in the interaction region via an effusive nozzle. At room temperature the sample vapor pressure is $6 \times 10^{-7}$ mbar which allows to take the spectra with reasonable statistics. The C1s, N1s and O1s core photoemission spectra were taken at 382, 495 and 628 eV photon energy, with a overall energy resolution (photon plus analyzer) of 280 meV for C1s and N1s and 370 meV for O1s. The NEXAFS spectra were recorded by collecting the total ion yield signal using a channel electron multiplier placed close to the ionization region. The signal was normalized by the photon flux measured by a photodiode. The photon energy resolution for the C, N and O K-edges
is respectively 60, 70 and 100 meV.

Both XPS binding energies and NEXAFS photon energies have been calibrated using a mixture of the molecule with a calibration gas, namely CO$_2$ for C1s and O1s levels and N$_2$ for N1s level. For further details on the gas phase calibration I refer the reader to Ref [40] [41].

2.2.2 Films on Au substrates

4HCB molecules (Fluka, purity of 99 + %) were placed in a pirex cell and pumped down to high vacuum. All the films were grown in-situ on Au(111) and Au(110) monocrystalline surfaces. Both surfaces have been prepared by cycles of Ar$^+$ sputtering at 1 keV and subsequent annealing up to $\sim$ 750 K. The missing row pattern of the Au(110) surface has been checked by reflection high-energy electron diffraction (RHEED), while XPS has been used to ensure the absence of any contaminants on both surfaces. The 4HCB films were then obtained exposing the gold surfaces to a 4HCB vapor pressure of $5 \times 10^{-7}$ mbar through a leak valve keeping the substrate at room temperature and varying the deposition time. The operational pressure for the measurement chamber was maintained at $10^{-11}$ mbar and the sample preparation chamber at $10^{-10}$ mbar. During the measurements we kept the sample at around 200 K by means of a liquid nitrogen cooling circuit in order to avoid molecular desorption that we have been observed to start at around 240 K for a multilayer film. The monolayer was obtained by depositing the molecules on the substrate at room temperature and then it was cool down to avoid beam damaging. The sample was also continuously displaced during the measurements to minimize the beam induced damage.

XPS spectra have been taken with the X-ray beam impinging the sample at a grazing incidence angle ($4^\circ$) using a photon energy of 650 eV for O1s and C1s and 500 eV for N1s. The photoelectrons were detected in normal emission geometry using an hemispherical electron analyzer with an overall energy resolution (photon+analyzer) of about 300 meV. The binding energies were calibrated using the bulk component of the Au 4$f_{7/2}$ peak at 84.0 eV [42].

NEXAFS spectra have been collected in Partial Electron Yield mode by means of a wide acceptance angle channeltron detector. The photon energy resolution, in this case, is better than 100 meV and the beam impinges the surface with a grazing angle of $6^\circ$. Since the rotation of the manipulator allows to change the orientation of the surface with respect to the linear polarization of the X-ray, we have measured the X-ray absorption in different geometries. In particular, rotating the manipulator around the beam axis, we have probed the polar dependence of the NEXAFS measuring the spectra with E-field polarization parallel (s-pol) and perpendicular (p-pol) to the sample. A further degree of freedom of the manipulator allows to probe also the azimuthal dependence when we
2.3 Theoretical methods

In the density functional theory the many-body electron problem is attacked using the ground-state one-body electron density $n(r)$ in place of the ground-state many-electron wavefunction $\Psi_G(r_1, ..., r_N)$. The Hohenberg-Kohn theorem shows that the ground-energy of a many-particle system can be expressed as a functional of the one-body density \[43\]. The minimization of this functional allows, in principle, the determination of the actual ground-state density \[44\]. The calculations have been performed using the density functional theory (DFT) worked up in a pseudopotential scheme as implemented in the Quantum ESPRESSO open-source suite \[45\]. This method does not take into account explicitly all the electrons, it rather replaces the strong electron-ion potential with a pseudopotential that describes all the salient features of a valence electron moving through the solid. Thus the original solid is replaced by pseudo valence electrons and pseudo ion cores. The pseudo-electrons experienced exactly the same potential outside the core region as the original electrons but have a much weaker potential inside the core region. In our system we treated H(1s), C(2s), C(2p), N(2s), N(2p), O(2s) and O(2p) as valence electrons, while all the inner shells were embedded in a pseudopotential. Between all the pseudopotentials developed in the last years, we chose the norm-conserving Martins-Troullier one following the scheme already used by Bolognesi et al. \[46\]. To evaluate the inter-electronic interactions we used the BLYP (Becke Lee-Yang-Parr) exchange-correlation functional which relies on the generalized gradient approximation. To investigate the properties of the isolated 4HCB we accommodate the molecule in a large cubic supercell (15 Å) and then we make a self-consistent field (SCF) calculation to solve the Kohn-Sham equations. Satisfactory convergence on the total energy, the energy gap and the single wavefunctions, has been achieved using an energy cutoff of 80 Ry on the plane waves and 320 Ry on the electronic density. It has been demonstrated that core level binding energies can be obtained by total energy difference between ground state and core hole calculation. In the latter case a core hole is created on the desired atom when the pseudopotential is generated. In our case the core hole has been created separately on each inequivalent C atom running a SCF calculation at every step to obtain the whole photoemission C spectrum. Since we do not have a reference value for the calculated binding energy calibration, we can not directly compare the experimental and theoretical values. However the relative differ-
Figure 2.4: Gas phase C1s XPS spectrum (square blue markers). The continuus line is the data best fit obtained from the convolution of the five filled lorentzian peaks. The black sticks show the binding energy shifts calculated with the DFT. The experimental binding energy scale is referred to the vacuum level while at the calculated one an offset is applied in order to compare it with the experimental data.

<table>
<thead>
<tr>
<th></th>
<th>Binding Energy (eV)</th>
<th>Chemical shift (experimental)</th>
<th>Chemical shift (DFT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>292.44 ± 0.04</td>
<td>1.75 ± 0.06</td>
<td>1.93</td>
</tr>
<tr>
<td>C2</td>
<td>291.83 ± 0.04</td>
<td>1.14 ± 0.06</td>
<td>1.26</td>
</tr>
<tr>
<td>C3</td>
<td>291.32 ± 0.04</td>
<td>0.64 ± 0.06</td>
<td>0.75</td>
</tr>
<tr>
<td>C4'</td>
<td>—</td>
<td>—</td>
<td>0.32</td>
</tr>
<tr>
<td>C4</td>
<td>290.69 ± 0.04</td>
<td>0.21 ± 0.06</td>
<td>0.27</td>
</tr>
<tr>
<td>C5'</td>
<td>—</td>
<td>—</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Table 2.1: Absolute binding energies extracted from the fitting procedure and their chemical shifts (both experimental and calculated) relative to atom C5.
ences of the calculated binding energies are not affected by the calibration issue and so this is the quantity we will compare.

2.4 Gas Phase

2.4.1 XPS

The C1s XPS spectrum of the 4HCB in the gas phase is reported in Fig. 2.4, where it is compared with the results of DFT calculation. The experimental XPS spectrum presents four main structures. Moving from high to low binding energies, we can observe two different peaks, with approximately the same intensity, and a third one, with double intensity, which has a shoulder at higher binding energies. The different features correspond to the ionization of the C atom in the seven inequivalent sites of the molecule as indicated in Fig. 2.4 (inset). Indeed, due to the fact that the OH group is tilled with respect to the O-N molecular axis (being the OH bond angle equal to 109°), the 4HCB molecule belongs to the symmetry class Cs which has only two elements of symmetry (identity and molecular plane) and, as a consequence, all the seven C atoms should be considered inequivalent. In a first approximation, however, we can consider only five inequivalent atoms expecting the atoms C4 and C5 to be very similar to C4’ and C5’ respectively.

Looking at the XPS shape and relying on the above considerations, we have fitted the experimental spectrum with five Lorentzian functions convoluted with the overall instrumental resolution, with relative intensities following the ratio 1:1:1:2:2 for the peaks 1:2:3:44’:55’ respectively. All the binding energies have been used as free parameters, while the peak width has been constrained to be equal for all the five peaks. Moreover, since the two peaks with double intensity are each a sum of two close photoemission peaks (C4-C4’ and C5-C5’), a gaussian broadening has been added as fitting parameter. In table 2.1 the absolute binding energies, extracted from the fitting procedure, have been reported together with both the experimental and calculated energy shifts relative to the atom C5. The agreement between theory and experiment is excellent and it allows to unambiguously assign the different features of the photoemission spectrum. Moving from the highest to the lowest binding energy, we find the photoemission peak of the C directly bound to the hydroxyl group (C1), the ionization of the one belonging to the cyano group (C2), followed by its first neighbour (C3) and two other peaks for the remaining four atoms of the benzene ring (C4, C4’, C5 and C5’). The approximation made above to consider only five inequivalent atoms is justified with the calculated shifts. Indeed the position of atoms C4’ and C5’ deviates from the one of C4 and C5 respectively by 0.05 and 0.15 eV. These values are much lower than our experimental resolution of
Figure 2.5: 4HCB valence band. The experimental photoemission from the valence states (lines and markers) is compared with the calculated DOS (black) which, in turn, has been projected on the 2p atomic orbitals of C, O and N (yellow, red and light blue). On the top of the graph the first five HOMOs are plotted.

0.3 eV and they cannot be resolved as separate peaks. The binding energy difference between C1 and C2, determined theoretically, is in agreement with the donor-acceptor character of the -OH and -CN groups discussed above.

The photoemission from the other two elements of the molecule (N and O) presents a single peak structure as expected considering the presence in the molecule of only one atom for each element. It does not carry by itself any further information but it will be fundamental for the understanding of the interactions in the solid state.

On the other side, the photoemission from the valence states is much more interesting since it is the fingerprint of the molecular valence band. In Fig. 2.5, the photoemission from the valence states is shown and it is compared with the calculated density of states (DOS). As it is evident the calculated total DOS matches almost perfectly with the experimental valence band over all the energy range. Beside the total DOS I have calculated also the projected DOS (PDOS) onto the 2p atomic orbitals. The PDOS reveals that while the HOMO gets contribution from all the elements, the HOMO-1 receives the contribu-
2.4. Gas Phase

Ition only from the C atoms. Moreover the N2p atomic orbital contributes mainly to the shallow orbitals while the O2p gives its contribution also to the deepest ones. In Fig. 2.5 the first five occupied molecular orbitals (HOMOs) are also plotted. The HOMO and HOMO-1 correspond to the first two peaks and their binding energy difference is 1 eV, while the HOMO-2 and HOMO-3 are almost degenerate and give rise together to the peak at 11.7 eV. It is important to note that among these orbitals the HOMO-2 extends in the molecular plane while all the other HOMOs are out of the molecular plane. Adopting a reference system in which the molecular plane is in the xy plane with x along the oxygen-nitrogen axis, we can also say that the in-plane orbital spans the y direction and the out-of-plane ones the z direction.

2.4.2 NEXAFS

The absorption spectrum of the 4HCB in the gas phase is shown in Fig. 2.6 for N- and C-edge with a zoom on the spectral features present in the $\pi^*$ regions. In the same figure the first three lowest unoccupied molecular orbitals (LUMOs), as obtained by DFT calculations, are also plotted. The first three LUMOs have all a $\pi^*$ character, being localized perpendicular to the interatomic axis. Moreover, following the same notation adopted for the HOMOs, we observe that the LUMO and LUMO+1 have an out-of-plane symmetry whereas the LUMO+2 has an in-plane symmetry. From now on we refer to these three LUMOs as $\pi^*_1(z)$, $\pi^*_2(z)$ and $\pi^*_3(y)$, where y and z indicate the direction of the orbital spatial extension.

It is worth noting that the calculated unoccupied orbitals do not represent exactly the final state of the X-ray absorption. In fact I have calculated them directly from the density of unoccupied states and I did not take into account the core-hole effect. Indeed, when we probe the unoccupied levels, the molecule is in an internal excited states, with a hole in the core level relative to the absorption edge and an extra electron in a normally unoccupied state. In this situation the electronic density undergoes a redistribution in order to screen the core-hole and the NEXAFS final states will be different from the ground state LUMOs. To investigate the core-hole effect I have calculated the same LUMOs in the excited state with a hole in the N1s level. In this case the stabilization of the orbital due to the attractive force of the positive charge, causes a rearrangement of the electronic density as shown in Fig. 2.7. Even if there is an increase of the density around the excited atom, we notice that both the overall orbitals shape and their symmetry do not change dramatically and so we can use the ground state LUMOs as first approximation of the NEXAFS final states.

Besides this change in the orbital shape, the presence of a core-hole affects also the en-
Figure 2.6: Gas phase NEXAFS on the N-edge a) and C-edge b). On the graphs are reported the final state assigned to each peak as discussed in the text. The relative ground state LUMO orbitals are plotted on the right.

Energy and intensity of the core-LUMO transitions making impossible, in many cases, a direct comparison between NEXAFS and density of unoccupied states (DOUS). It has been demonstrated that the core-hole effect is less effective for large $\pi$-conjugated systems like $C_{60}$ or $C_{70}$ [47] due to the better screening of the core-hole by the mobile $\pi$ electrons. Moreover a reasonable agreement between DOUS and NEXAFS can be obtained when only equivalent excitation sites are present, like the N atoms in Zn-tetraphenylporphyrin [48]. This would correspond, in our case, to the excitation from N or O. In this situation the additional dependence of the excitation energies, that would arise from the difference of core ionization energies at different sites, has not to be taken into account [49].

With these considerations in mind I will discuss now the NEXAFS spectra of 4HCB. The spectrum relative to the N-edge is shown on the upper part of Fig. 2.6. It is composed of two strong and well-separate resonances that we can confidently say to correspond
2.4. Gas Phase

Ground state LUMOs

Core-excited state LUMOs

Figure 2.7: Calculated LUMO and LUMO+2 orbitals in the molecular ground state (a-b) and in the excited state with a core-hole in the N1s level (c-d).

to the transition from N1s to $\pi^*_1(z)$ and $\pi^*_3(y)$ respectively. No resonance is associated with the $\pi^*_2(z)$ orbital since it is localized mainly on the central C atoms and, in this case, the initial and final states do not overlap. This assignment is also supported by the N-edge NEXAFS on the benzonitrile that has a very similar shape and for which the experimental peaks have been unambiguously assigned after a comparison of experimental data and theoretical calculations [50, 51]. In the same work, the rich vibronic structure that surrounds the two strong resonances, has been completely explained in terms of dynamic excitation path.

In the lower part of Fig. 2.6 the absorption spectrum on the C-edge is displayed. In the region between 285.1 and 285.5 eV the NEXAFS spectrum presents twice the same peak+shoulder structure with a distance between the peak and the shoulder of $\sim 0.2$ eV and a shift between the first peak and its repetition of $\sim 0.4$ eV. After these features, the spectrum has a broad peak centered at $\sim 286.2$ eV and a second complex structure with two visible horns at $\sim 286.7$ and $\sim 286.9$ eV respectively. The rich peak structure reflects the presence of many inequivalent C atoms and a proper spectral decomposition should be supported by a full theoretical NEXAFS calculation. However, relying on the XPS chemical shifts and on the shape of the calculated LUMOs, it is possible to give a reasonable assignment of the main NEXAFS structures.

Starting from the first resonance, we notice that it appears at the same energy ($\sim 285.1$ eV) of the first transition observed in the benzene molecule and in all its derivatives,
in particular benzonitrile and phenol [52, 53]. Moreover, since the distance of \( \sim 0.2 \) eV between the peak and the shoulder is the same that the binding energy difference between C4 and C5, it is likely that the first feature (peak plus shoulder) represents the transitions from the atoms C5 (C5') and C4 (C4') to the \( \pi^*_1(z) \) orbital and the second one the transitions from the same initial states to the \( \pi^*_2(z) \) orbital.

Then, following the XPS hierarchy, we expect to find the transitions from C3, C2 and C1 to the \( \pi^*_1(z) \), being the one to the \( \pi^*_2(z) \) not allowed for these initial states. In particular the distance of 1.1 eV between the first resonance and the one at \( \sim 286.2 \) eV, correspond to the binding energy difference between atoms C5 and C2 and so we can assign the NEXAFS resonance at \( \sim 286.2 \) eV to the transition \( C2 \rightarrow \pi^*_1(z) \). Following the XPS hierarchy, the second horn of the second complex structure at \( \sim 286.9 \) eV should be caused by the transition \( C1 \rightarrow \pi^*_1(z) \), being at 1.8 eV away from the first resonance. Considering a rigid system in which the position of the LUMOs stays at the same energy irrespective of the position of the core-hole, we can predict the position of the resonance relative to the \( \pi^*_3(y) \) orbital knowing it for the N-edge. Indeed, since the energy difference between the two resonances at the N-edge is 0.7 eV, we expect to find the same energy difference in the C-edge NEXAFS. In particular, the transition to the \( \pi^*_3(y) \) is allowed only when the initial state is the cyano C (C2), and for this reason this resonance should be at 0.7 eV away from the peak assigned to the transition \( C2 \rightarrow \pi^*_1(z) \). At 0.7 eV from this position there is indeed a peak but we have already pointed out that it can be due to the transition \( C1 \rightarrow \pi^*_1(z) \). This misinterpretation arises from the fact that when I assign the peaks following only the binding energy differences I do not take into account the core-hole effects previously discussed.

However the ambiguity between these two resonances can be removed by looking at the resonant photoemission from the valence band (RPES).

### 2.4.3 RESPES

Fig.2.8 displays the resonances of the valence band while the photon energy is tuned across the N absorption edge. It is worth to keep in mind during the following discussion that the occurrence of a resonance in the gas phase RPES is determined by the simultaneously spatial overlap between the atomic core level, the intermediate LUMO state and the resonating HOMO.

The valence band spectra have been taken at six different photon energies ranging from 398.7 to 400.5 eV. They have been normalized to the photon flux and the pre-edge intensity has been subtracted in order to put in evidence the resonant part of the spectra. Due to the overall different resolution of the N-edge at these photon energies, the valence band peaks can no longer be well resolved. In particular the first two peaks, corresponding to the photoemission from the HOMO and HOMO-1 levels, merge to-
Figure 2.8: Gas phase N-edge RESPES (filled colored spectra). The 4HCB valence band taken at 100 eV photon energy is reported in the bottom part of the figure to help the comparison with the resonant spectra. The NEXAFS spectrum is reported as well and the photon energy at which the resonance spectra have been taken are highlighted by the square markers. The square markers data have been obtained by integrating each valence band scan in the all binding energy range. The HOMOs and LUMOs I refer to in the RESPES discussion are also shown.

together into a single broad one, and the same happens with the second two (HOMO-2 and HOMO-3).

Beside the broad Auger structure that starts to rise at around 17 eV we can distinguish several participator resonances in correspondence of both NEXAFS peaks. We will focus our discussion on the first two features that comprise respectively the HOMO and HOMO-1 resonances and the HOMO-2 and HOMO-3 ones. Both structures resonate in correspondence of both NEXAFS resonances at a photon energy of \(\sim 339\) eV and \(\sim 399.8\)
The first feature is highly asymmetric toward lower binding energies and, even if we cannot distinguish directly the HOMO and HOMO-1 resonances, we can conclude that the HOMO resonates much more than the HOMO-1. Moreover, when the photon energy is set at 399 eV, the intensities of the first two valence structures are comparable. On the other side, when the photon is at 399.8 eV, the intensity of the second structure becomes more than double with respect to the first one and it becomes highly asymmetric toward lower binding energies indicating a strong resonance of the HOMO-2 level in correspondence of the LUMO+2 ($\pi_3^*$ ($y$)) empty orbital.

The observed RPES resonances are in agreement with both the NEXAFS assignment, made in the previous section, and the DFT calculations for occupied and unoccupied levels. In particular, the occurrence of the HOMO-2 resonance in correspondence of the LUMO+2 empty state could be predicted considering the same in-plane symmetry.
shared by these two orbitals, as shown in Fig. 2.8.

Fig. 2.9 shows again the resonant photoemission spectra but this time the photon energy is tuned across the C-edge. Referring to the same structures discussed for the RPES on the N-edge, we see that when the photon energy is tuned between 285.1 and 285.5 eV the shape of the first RPES feature is asymmetric toward high binding energies. This kind of asymmetry is suddenly reversed in correspondence of the fifth RPES scan, when the photon energy is around 286 eV and the new shape is preserved until the last measured scan. Moreover, looking for the occurrence of the HOMO-2 resonance we clearly find that it is maximum for $\hbar \nu = 286.7$ eV. In the last measured scan, at 286.9 eV, the HOMO resonance rises again and its intensity becomes comparable to the HOMO-2 resonance. From this experimental evidence we can say that the HOMO-1, situated on the central C atoms, resonates only when the photon energy is in the range 285.1-285.5 eV, while, for the remaining photon energies, only the HOMO resonance survives. Also in this case the RPES measurements confirm the prediction about the relative NEXAFS resonances. From DFT calculation we see that the HOMO-1 and LUMO+1 have a similar spatial distribution and the presence of the HOMO-1 resonances in the photon energy range 285.1-285.5 eV, allow to conclude that in the same energy range there are the NEXAFS peaks relative to the LUMO+1, as already supposed in the previous section about NEXAFS. For the same reason the occurrence of the HOMO-2 resonance allows to unambiguously associate the first horn of the second large NEXAFS peak at $\sim 286.7$ eV to the transition to the in-plane orbital.

The 4HCB molecule has been fully characterized, in its gas phase, combining spectroscopic techniques and DFT calculations. In particular, the detail structure of occupied and unoccupied levels has been revealed by core and valence-level XPS, and NEXAFS measurements respectively. The results obtained with these techniques have been confirmed and validated by the resonant PES. This gas phase study will be the basis for the solid state investigation presented in the next sections.

2.5 Solid phase

In this section I will use the results from the gas phase measurements to describe how the electronic properties of the 4HCB molecule change when the crystal is formed. We attempted to measure directly the single crystal but we faced with several experimental issues that hampered the collection of the complete data set required for a comprehensive study. The main issues are related to the crystal damage induced by the X-ray beam, together with the non regularity of the sample. Because of the first issue we need to continuously displace the sample during the very long RPES scan (more than 10 hours). As a consequence, since the crystal thickness is not uniform and its shape not
To overcome these problems we decided therefore to deposit a thick film of 4HCB on a single crystal gold substrate. The thickness of the film has been estimated, from the attenuation of the Au4f peaks, to be more than 10 nm. This value is high enough to neglect any interaction between the molecule and the Au substrate and hence all the measurements on this system will give information about the molecule-molecule interaction. It is worth to note that the thick film has been obtained by physical vapour deposition, while the single crystal has been grown from solution and, these different preparation methods, could reflect into different intermolecular environment in the final sample.

In order to establish if our thick film can be compared to the single crystal in term of local intermolecular environment, we put in comparison the measurements we have been able to perform on both systems. In particular in Fig. 2.10 the NEXAFS on the N-edge and the valence band of the thick film are compared with that on the single crystal. The NEXAFS presents a similar shape and the same polar dichroism for both systems, suggesting that in the thick film the local molecular arrangement and the interactions between the molecules are the same than in the crystal. Also the XPS from the valence band presents the same structures and a very similar shape in the two cases, indicating a comparable hybridization of the outer molecular orbitals when the molecules interact...
2.5. Solid phase

Figure 2.11: XPS binding energy shifts between the gas phase (top) and the thick film (bottom) for the three atomic species. The experimental data (markers) are shown together with their best fits (black line). Since the gas phase binding energies are referred to the vacuum level while the solid phase ones to the Fermi edge of the gold, the two scales are shifted in order to have the C5 peak at the same position. The subsequent shift of the N1s and O1s in opposite directions suggested a head-to-tail molecule-molecule bonding.

In the solid phase.

In Fig. 2.11 the XPS from C1s, N1s and O1s of the gas phase with the one of the thick film are put in comparison. Since the reference level for the binding energies is different between the two systems, being the vacuum level in the gas phase and the Au Fermi level for the thick film, we applied an horizontal shift in order to easily compare them. In particular we shifted the gas phase binding energies until the position of the peak corresponding to the photoemission from the atom C5 (higher binding energy in the C1s spectrum) is the same in the two systems. This choice is based on the fact that the molecular interactions in the single crystal interest mainly the functional group (being the molecules linked by hydrogen bond between their respective hydroxyl and cyano groups) and the central atoms of the benzene ring are less involved in the intermolecu-
lar interactions. After this alignment we see that the C1, C2 and C3 peaks in the thick film, experienced a mean shift of +0.4 eV with a slightly higher shift of the C2 components with respect to the other two, while the C4 peak stays at the same position. Looking at the photo-emission from the other two elements, we observe how the N1s peak is shifted by 0.5 eV toward higher binding energies and the O1s peak is shifted by the same amount in the opposite direction (lower BEs). The opposite behaviour of nitrogen and oxygen indicates that the former experiences an increase of the electron density around it, while the latter undergoes to an electron depletion. In other words the nitrogen is accepting electrons from the oxygen and this is exactly what happens in the O-H · · · N hydrogen bonds. Moreover, as expected, the C4 peak, corresponding to the second species of carbon in the benzene ring, does not shift at all and so the electron density around it remains the same when the molecules are linked together.

We can conclude that molecules self-assembly is driven by the formation of O-H · · · N hydrogen bonds, the same interaction that is supposed to characterize the formation of the 4HCB single crystal. Our thick film can be therefore considered to present intermolecular arrangement similar to the one on the crystalline form. This fact allows us to adopt the system as a prototype of the single crystal.

2.5.1 RPES and charge transfer time

The RESPES map for the thick film, with the photon energy tuned across the N-edge, is reported in Fig 2.12. The presented RESPES map is shown after the intensity of the pre-edge signal and the one of the Auger peak have been subtracted as discussed in Section 1.3.3. What remains after the subtraction is the intensity of the participator resonances that can be compared to the same resonances in the gas phase system in order to extract the charge transfer time of the resonantly excited electron.

For a direct comparison with the gas phase resonances and a correct extraction of the charge transfer time, it is necessary to normalize the respective participator intensities. This can be done by normalizing to the number of core-hole generated, which is proportional to the Auger intensity. Accordingly, the participator intensity in the thick film has been rescaled by the factor $A_{gas}/A_{thick}$, that represents the ratio between the areas of the Auger peaks in gas phase and in the thick film. This procedure has been applied for the two photon energies corresponding to the main NEXAFS resonances on the N-edge, namely $h\nu = 399.1$ and $h\nu = 399.8$ eV. After the normalization it is possible to apply Eq. 1.41 to calculate the charge transfer time

$$\tau_{CT} = \frac{\tau_{ch} I_{coupl}}{I_{iso} - I_{coupl}}$$ (2.1)
2.5. Solid phase

Figure 2.12: Two-dimensional RPES map for the thick film with the photon energy tuned across the N-edge. The resonance intensities, shown with a color scale, are plotted versus the binding energy (x-axis) and photon energy (y-axis). The spectrum obtained by taking the mean value of the pre-edge spectra is plotted in red and the blue dotted line is the N-edge NEXAFS.

Knowing that the mean lifetime for a core-hole ($\tau_{ch}$) in the N1s level is 5 fs [54]. $I_{\text{coupl}}$ and $I_{\text{iso}}$ are respectively the integrated participator intensities of the coupled system (thick film) and the isolated one (gas phase). The integration range has been chosen in order to include the same occupied levels for both systems. The quenching of the RESPES intensity passing from the isolated (gas phase) to the interacting system (Fig.2.13) is due to the fast charge delocalization of the excited electron from both LUMO and LUMO+2 in the thick film. The calculated charge transfer times are summarized in Table 2.2.

The two values are comparable and indicate that both the LUMO and LUMO+2 are short lived states, being the delocalization from them very fast. Since the initial state of the RPES is the atomic N1s level, this result suggests that the charge transfer is me-

<table>
<thead>
<tr>
<th>LUMO</th>
<th>LUMO+2</th>
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<tr>
<td>$\tau_{CT}$</td>
<td>0.9 ± 0.2 fs</td>
</tr>
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</table>

Table 2.2: Calculated charge transfer times after the excitation from N1s to the LUMO and LUMO+2 empty levels.
Figure 2.13: Participator resonance in the gas phase (blue) and in the thick film (red) plotted on different vertical axis (left and right respectively). The upper panel shows the resonances relative to the transition N1s-LUMO, while in the lower panel the resonances relative to N1s-LUMO+2 are compared. The binding energy of the thick film has been shifted in order to match the valence band structures with that of the gas phase.

diated by the N atoms. The crystal structure validates the N-mediated charge transfer hypothesis, since along the direction of higher mobility (axis $a$), there is a cyano groups sandwiched between two faced benzene rings. Moreover, even if the order of magnitude is the same, the measured charge transport is faster from the LUMO than from the LUMO+2. Looking at the orbital shape this means that the preferential direction of the charge transport is perpendicular to the molecular plane as it would be in a picture of charge hopping between the $\pi^*$ of the benzene ring.
Figure 2.14: Fcc primitive cell with the two crystallographic planes discussed in the text.

2.6 4HCB on Au surfaces

In this section I will discuss the interaction of 4HCB with two different Au surfaces, namely Au(111) and Au(110). This two surfaces are obtained by cutting the FCC crystal along the two crystallographic directions shown in Fig.2.14. The resulting surfaces however are not the simple termination of the bulk because of the reconstruction process in which the minimization of the surface free energy can cause the reorganization of the outer atomic layers. In particular the Au(110) presents, at room temperature, a (1x2) reconstructed surface [55]. The peculiarity of the reconstructed phase is the missing row (MR) structure where every second row of Au atoms along (1-10) is absent. Also the Au(111) undergoes to a reconstruction of its close-packed structure and it is the only fcc metal to have a (111) reconstructed ground state [56]. However in this case the reconstruction has a much larger unit cell and the final structure is much more complicated having an unit cell of (22x√3).

2.6.1 XPS

To study the 4HCB/gold interaction we started by comparing the XPS BEs of a monolayer of 4HCB deposited on the Au(111) surface, to the BEs of the thick film. The relative shifts are pictured in Fig.2.15. All the spectra are shown together with their best fit given by one or more Voigt functions depending on the photoemitting atom. Also for the monolayer, the C1s spectrum can be deconvoluted into five different components that represent the photoemission from the inequivalent C atoms. Even in this case, the relative peak intensity is 1:1:1:2:2 moving from higher to lower binding energies. Moreover, in fitting the C1s regions we fixed the Lorentzian width to be equal to the one found in gas phase, leaving the Gaussian broadening free. This is reasonable
since the former is directly related to the core hole lifetime, which is not expected to change, while the multiple configurations the molecule can assume when it is in contact with a surface can cause a different Gaussian broadening of the components. The XPS from N1s and O1s is again single-peaked and has been fitted with one component for each element. Even if the number of components is the same, the width is different, being the peaks of the monolayer much narrower than the ones of the thick film. The peak broadening is possibly related to the different inequivalent molecules in the unit cell differently bonded one to the other.

The observed shifts, passing from the thick film to the monolayer, are equal to 0.8 ± 0.1 eV for the peaks relative to the photoemission from C1s and N1s, and equal to 1.1 ± 0.1 eV for the O1s peak. A deeper analysis of the C1s spectra reveals that the C1s components do not experience all the same shift, being the C2 peak closer to the C1 one in the monolayer than in the thick film. This non-rigid shift, already observed in the comparison thick-film/gas-phase, results in the presence of a deeper minimum between the two main carbon peaks with respect to the spectrum of the thick film. Moreover, with respect to the XPS in the gas phase, the first region of the spectrum is made up of only one peak instead of the two separate ones observed in gas phase.

The binding energy shifts can be due either to a different screening of the core-hole or
to a different chemical environment of the selected atom. The core-hole screening depends on the surface distance and it is therefore different for a monolayer and a thick film. Moreover, in our particular case, if the molecule is tilted with respect to the substrate, the different species can have a different distance from the surface, resulting in a different screening. Beside this effect, there are other effects that add together to give the final measured shifts. First of all there is a change in the molecular environment passing from the thick film, where a molecule is completely surrounded by other molecules, to the monolayer phase, where the molecules do not have anything on the top. Moreover, in a monolayer also the interaction with the substrate has to be taken into account. It can cause a change in the electronic cloud interested in the molecule-substrate bonding, leading to a different shift for the species that directly participate to the interaction.

The different shift observed for the O1s, as well as for the C2, can be a superposition of the different molecule-molecule interaction in the monolayer and of the molecule-substrate one at the gold surface. Calling this two effects as “monolayer interaction”, we can conclude that the oxygen participate more than the other elements to it.

I will discuss now the features of two 4HCB monolayers on the two Au surfaces presented above. In Fig.2.16 the XPS core level spectra from O1s, N1s and C1s recorded on the Au(111) and Au(110) surfaces are compared.

The XPS from the C1s on the Au(110) has basically the same features of that on the Au(111) (Fig.2.16a), the main difference being in the shallowness of the minimum between the two main peaks, due to the broadening of the components underneath. Also the photoemission from the O1s (Fig.2.16c) is similar on both surfaces, being characterized by a well-defined single peak structure. On the contrary the photoemission from the N1s region (Fig.2.16b) is the one that shows the major differences. In fact, while on the Au(111) the N1s is a single peak, on the Au(110) a shoulder that rises beside the main peak is visible at higher binding energy. The fit of the N1s with two Voigt functions reveals an intensity ratio of 3:1 between the major and minor component. Moreover also the N1s binding energy difference between the main N1s peaks on the two surfaces is different than the one measured for the C1s and O1s region, being $\sim 0.1$ and $\sim 0.3$ respectively. In table 2.3 the extracted binding energies are reported.

The value of the binding energy shift is consistent with the different screening experienced by the core hole on the different surfaces. In fact when the electron is photoemitted, the positive charge it leaves behind it induces an image charge inside the metal at a distance equal to the one between the core-hole and the surface. The potential arising from this charge distribution is proportional to $(z - z_0)^{-1}$ where $z_0$ is the position of the plane that separates the two charges called image plane. Strictly speaking the surface and the image planes does not correspond since the actual surface is not an ideal smooth plane. For this reason the position of the image plane is different on various surfaces.
2. Organic semiconducting single crystals: the case of 4HCB

Figure 2.16: a) C, b) N, and c) O core level XPS of the 4HCB adsorbed on the two different gold surfaces examined. Red circles are the photoemission from Au(111), green triangles the one from Au(110). All the spectra are shown together with their best fits.

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<tr>
<th></th>
<th>Binding Energies</th>
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<tr>
<td></td>
<td>C</td>
<td>N</td>
<td>O</td>
</tr>
<tr>
<td>Au(111)</td>
<td>286.2 ± 0.1</td>
<td>398.7 ± 0.1</td>
<td>532.5 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>285.9 ± 0.1</td>
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<tr>
<td></td>
<td>285.0 ± 0.1</td>
<td>398.5 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>284.5 ± 0.1</td>
<td>399.8 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>284.2 ± 0.1</td>
<td>399.8 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>Au(110)</td>
<td>286.5 ± 0.1</td>
<td>398.8 ± 0.1</td>
<td>532.8 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>286.1 ± 0.1</td>
<td>399.5 ± 0.2</td>
<td></td>
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<tr>
<td></td>
<td>285.4 ± 0.1</td>
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<td></td>
<td>284.8 ± 0.1</td>
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<tr>
<td></td>
<td>284.4 ± 0.1</td>
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Table 2.3: Comparison of the binding energies measured on Au(111) and Au(110) as extracted from the fitting procedure.
leading to a different value of the potential and ultimately to a different screening of the core hole. The calculated values for the image plane position are 2.18 a.u. for Au(111) and 1.74 a.u. for Au(110) \[57\] that, substituted in the potential, predict a higher screening (and so a lower binding energy) for the Au(111) with respect the Au(110).

The broadening of all the components, as well as the shoulder on the N1s suggest that on the Au(110) surface the 4HCB has more than one adsorption configuration. Au(110) presents indeed a higher reactivity due to the presence of lower coordination Au atom with respect to Au(111) surface. We suggest moreover that the minor N1s component is due to molecules that interact more strongly with the substrate via the CN termination. On the other side the main N1s peak comes from the adsorption on the local (111) microfacets typical of the Au(110) missing row reconstruction.

### 2.6.2 NEXAFS Dichroism

The NEXAFS on the N K-edge is shown in Fig.2.17 for both Au surfaces in p- and s-polarization, together with their best fit. Referring on the gas-phase NEXAFS I have fitted the spectra with three Lorentzian functions keeping the peaks position and width constant passing from one polarization to the other. As it is evident from the graphs, the first peak intensity is maximum in p-pol while it almost vanishes in s-pol. The opposite is true for the second peak, even if the effect, especially on the Au(110), is less strong. As in gas phase, we can assign the first peak to the transition from N1s to the out-of-plane LUMO and the second one to the transition to the in-plane LUMO+2. The third peak can be due either to a vibrational feature or to a transition to a final state higher in energy than the LUMO+2.

Looking at the NEXAFS dichroism it is evident that the LUMO orbital is almost perpendicular to the surface and, in turn, the molecular plane is parallel to the substrate on both surfaces. We can calculate the mean molecular tilt angle $\theta$ from the surface by applying

$$\theta = \arctan \sqrt{\frac{I_s}{I_p}}$$

(2.2)

for the 2-fold symmetric Au(110) surface \[58\] and

$$\theta = \arcsin \sqrt{\frac{2\cos^2 \alpha}{\frac{I_p}{I_s} + 3\cos^2 \alpha - 1}}$$

(2.3)

for the 3-fold symmetric Au(111) \[59\].
2. Organic semiconducting single crystals: the case of 4HCB

Figure 2.17: NEXAFS on N-edge: comparison of the polarization dependence of the 4HCB monolayer deposited on Au(111) (left panels) and Au(110) (right panels). Panels a-b) are in p-pol, i.e. the X-ray polarization is perpendicular to the surface, panels c-d) are in s-pol, i.e. polarization parallel to the surface. All the data (markers) are presented together with their best-fit (black line) obtained as superposition of the Voigt functions underneath (filled curves).

Figure 2.18: N-edge NEXAFS: azimuthal dependence of the s-pol NEXAFS for the Au(110) surface. The polarization vector is parallel to the [001] (orange) and [1-10] (green) directions respectively. The azimuthal dichroism suggested a molecular orientation similar to the one depicted in the bottom.
2.6. 4HCB on Au surfaces

Figure 2.19: NEXAFS on C-edge: comparison of the polarization dependence of the 4HCB monolayer deposited on Au(111) (left panels) and Au(110) (right panels). Like as the N-edge NEXAFS, panels a-b) are in p-pol and panels c-d) are in s-pol.

We obtain $\theta = 21^\circ \pm 5^\circ$ for both surfaces. The mean tilt angle of the LUMO+2 otherwise is different on the two surfaces being $58^\circ \pm 5^\circ$ for Au(111) and $47^\circ \pm 5^\circ$ for Au(110). As in the photoemission spectra, where the N1s has two peaks on the Au(110), this difference can be due to the multiple adsorption sites present on that surface, that drive the different dichroism for the NEXAFS orbital closer related to the cyano group. Because of its 2-fold symmetry, the azimuthal dependence for Au(110) does not vanish, as it is evident in Fig. 2.18 where the azimuthal NEXAFS is reported. Leaving the surface parallel to the polarization vector, we probed the two azimuthal surface directions that are parallel and perpendicular to the MR reconstruction, namely [1-10] and [001]. The change in intensity passing from one to the other is indicative of a molecular distribution partly ordered with the MR motif. In particular since the intensity is higher along [001] the LUMO+2 orbital is preferentially oriented along that direction and in turn the molecular axis is parallel to the surface rows as sketched in Fig. 2.18. However the non zero intensity along the other direction [1-10] suggested that the molecular distribution is not simply that depicted in Fig. 2.18 where all the molecules are well-ordered along the rows. The remaining intensity along the [1-10] azimuthal polarization can be due to
other adsorption geometries, even if we cannot discriminate them using only spectroscopic techniques.

The same dichroism is observed for the C-edge NEXAFS reported in Fig. 2.19. In this case, due to the peak broadening, the multiple features observed in the gas phase are grouped into two main peaks that can be deconvoluted into five different components. Passing from p- to s-pol the only component that survive is the fifth one at 286.7 eV while all the others drop. This is a further confirmation that the peak at 286.7 eV is due to the transition from C1s to LUMO+2 as already derived from the gas phase RESPES.

The tilt angles extracted from the C-edge spectra are 19° ± 5° and 17° ± 5° for the LUMO orbital on (111) and (110) respectively and 43° ± 5° and 34° ± 5° for the LUMO+2.

2.7 Conclusions

The electronic structure of 4HCB molecule has been fully characterized by means of XPS, NEXAFS and RPES. For the gas phase the combination of experimental techniques and ab initio theoretical methods allowed to assign all the spectroscopic features relative to both occupied and unoccupied molecular levels and therefore the gas phase system can be used as a reference for the interpretation of the measurements on the solid phase. In particular by comparing the RPES intensities of the gas phase system with the same in the thick film we were able to apply the core-hole clock method to calculate the charge transfer time of a resonantly excited core electron inside a 4HCB solid. From the RPES on the N-edge results that both LUMO and LUMO+2 are short lived states and the charge transfer time is equal to 0.9 and 1.4 fs respectively. This evidence suggests that the charge transport is mediated by the cyano groups of the molecules which are sandwiched between two benzene rings. Moreover, the two different calculated values suggest that the charge transport is preferentially directed perpendicular to the molecular plane.

The conclusions obtained for a thick film can be extended to the single crystal system since we have observed from the relative shifts of XPS that the local inter-molecular arrangement in the thick film is driven by the same head-to-tail interaction that characterized the single crystal.

The 4HCB monolayer deposited onto a gold substrate is a model for the hybrid metal/organic interface. We used two different Au substrates with a different reactivity, namely Au(111) and Au(110). On both substrates the molecule/surface interaction is weak and the molecules lie with their molecular plane almost parallel to the surface plane. On Au(111) the oxygen has been observed to be involved more than the other elements to the ”monolayer interaction”, being the O1s XPS shift with respect to the thick film different than the shift for the other elements. On the Au(110) the appearance of a new
component in the N1s region suggests that part of the molecules interact more strongly with the substrate via their -CN termination.
Chapter 3
Shape complementary donor-acceptor systems

3.1 Introduction

One of the main applications of organic semiconductors can be found in the field of organic photovoltaics (OPV), which promise to enable a new generation of low-cost and light-weight solar cells. The major drawback, to make OPV a component of the solar energy economy, is the low efficiency with respect to their inorganic counterpart. The power conversion efficiency (PCE) of small-molecule and polymer OPV cells has increased steadily over the past decades and nowadays PCEs over 10% have been reported [60, 61]. A major turning point in the progress can be attributed to the introduction of the donor-acceptor heterojunction [62], that functions as a dissociation site for the strongly bound photogenerated excitons (for the details of the operation of an organic solar cell see chapter 4). Further progress was realized in polymer devices through the use of blends of the donor and acceptor materials [63, 64]. In this case the formation of a bulk heterojunction removes the exciton diffusion bottleneck by creating an interpenetrating network of donor and acceptor materials.

Small molecule semiconductors offer a number of advantages for OPVs relative to their polymeric counterparts, including a well-defined molecular structure, fewer traps, higher purity and superior batch-to-batch consistency. The realization of bulk heterojunctions using small molecular-weight materials has also been demonstrated [65], even if the design rules to optimize the morphology at the donor/acceptor interface are not as efficient as the ones developed for their polymeric counterparts [66]. In the case of small molecules, supramolecular assembly between donor and acceptor materials can be exploited to create ordered nanostructures with extended interfaces available for exciton dissociation. This would correspond to a bulk heterojunction obtained with small molecules in which the increase in the effective volume leads to an increase in the device efficiency.

The supramolecular assembly between hexabenzocoronene (HBC) derivatives and fullerene (C60) has been exploited in OPV devices in order to improve overall photovoltaic efficiency and address both active layer morphology and electronic interaction at the D/A interface [67, 68]. Here we probe the heterojunction morphology in bilayers composed
with different HBC as donor materials as a function of their shape matching with C60 (acceptor) using X-ray spectroscopic techniques. Shape complementarity drives self-assembly that in turn increases both the interfacial volume available for exciton dissociation, as well as the rate of exciton dissociation itself, to improve the efficiency of the OPV device.

3.1.1 Donor and acceptor molecules

The three different molecules taken in consideration to form the donor layer in the three investigated systems are shown in Fig. 3.1. They share a common coronene core in the central part with six outer rings surrounding it. The position of the outer rings as well as the atoms of the rings, lead to the three coronene derivatives called flat- and contorted-hexabenzocoronene (f-HBC, c-HBC), and dibenzotetrathienocoronenes (DBTTC).

f-HBC consists of six 3-carbons annulations at the periphery of the coronene core. This configuration results in a flat molecular geometry in which all the atoms lie on the same plane. The molecule possesses a $\pi$-electronic system extending above and below the molecular plane that is available for electronic coupling. On the other side the six 4-carbons rings in the c-HBC lead to steric congestion between adjacent benzo groups, yielding a non-planar motif. c-HBC consists of three fused interpenetrating pentacenes and possesses a doubly concave shape, since the outer rings are tilted both up and down with respect to the coronene plane (Fig.3.2).

DBTTC is a tetra thiophene-fused version of the c-HBC. With respect to its c-HBC cousin, DBTTC is flatter due to reduced steric interactions among the smaller thiophene rings at the periphery, as shown by DFT calculations. Moreover, the thiophene rings give a more flexible structure which allows the molecule to shift its shape and sample multiple conformations. Indeed, it has been shown that the isolated DBTTC can adopt distinct but energetically similar conformations in which the outer rings are arranged in different ways. In Fig.3.3 two isoenergetic configurations are shown. They are referred to as up-down and butterfly respectively.

Another class of bowl-shaped molecules is obtained by joining the proximal carbons of c-HBC to form five-membered rings around the coronene core. The higher the number of these five-membered rings, the more concave is the resulting molecule. The extreme case is the 4-closed-HBC that results in a complete bowl-shaped molecule.

The acceptor layer in the systems under investigation is made up by fullerene (C60) molecules. Its ball like shape results to be complementary to the bowl-shaped donors presented above (c-HBC and DBTTC) while no shape complementarity is observed with f-HBC.
3.1. Introduction

Figure 3.1: Coronene derivatives examined.

Figure 3.2: Side view of f-HBC and c-HBC. The doubly concave shape of c-HBC is visible.

Figure 3.3: Side and top view of two DBTTC conformations.
3. Shape complementary donor-acceptor systems

3.1.2 Shape complementarity drives performance in photovoltaics

The shape complementarity of c-HBC and DBTTC donors with C60 acceptor leads to the formation of co-crystals between these two classes of molecules. It has been shown that it is possible to co-crystallize c-HBC and C60 using horizontal physical vapour transport [67]. The c-HBC and C60 organize in an ABAB nested complex in a “ball-and-socket” assembly motif, as shown in Fig. 3.4a). In this structure every c-HBC has two C60 nearest neighbours with the C60 having two non-identical neighbours. The c-HBC/C60 interface structure obtained depositing a thin film of C60 on top of c-HBC, has been investigated as well using grazing incidence X-ray diffraction (GIXD). This study suggests that C60 introduces an additional degree of order at the bilayer interface with the formation of some small co-crystalline region when a thin film of C60 is deposited on top of a film of c-HBC [67]. DBTTC was also shown to form co-crystals with C60 [69]. In DBTTC single crystals the molecules are arranged into a columnar stack with a triclinic unit cell, whereas a spin-cast film of DBTTC is amorphous at room temperature and forms 1-D crystalline π-stacked fibers after annealing to around 100°C. These fibers then coalesce into millimeter-size cables to form a 3-D network of cables, as shown in Fig. 3.4b). This net-
work works as a scaffold to template a reticulated heterojunction with interpenetrating donor and acceptor phases when the C60 acceptor is deposited on top of it (Fig. 3.4 b)).

To understand the consequences of this molecular organization in the device performance, OPV devices have been made out of both donor/acceptor systems. Their electrical properties have been put in comparison with that of the OPV where the donor/acceptor interface is f-HBC/C60, which does not present any supramolecular co-crystalline structure. The efficiency of the three systems has been observed to increase with the increasing of shape-complementarity. In particular the efficiencies for f-HBC, c-HBC and DBTTC are measured to be 0.07%, 0.55% [67] and 1.9% [68] respectively. The reason for this increased efficiency can be related to the increase of the interface region between active materials that lead, in turn, to an increase of the volume available for exciton dissociation.

However, a full understanding of the reasons that lead to improved device performance is difficult to ascertain through macroscopic device analysis. With this motivation we modeled the three D/A interfaces depositing a bilayer D/A film for each system on a gold substrate and exploiting XPS and NEXAFS to investigate in detail the morphology of the interfaces.

3.2 Experimental details

All the experimental data were acquired at the ALOISA beamline. The Au(111) substrate was cleaned prior to deposition with the same procedure discussed in section 2.2.2. The operational pressure for the measurement chamber was maintained at $10^{-11}$ mbar and the sample preparation chamber at $10^{-10}$ mbar.

The molecules were placed in a valved quartz Knudsen-type cell in line-of-sight with the sample preparation chamber. Deposition techniques for all the molecules were similar. The Au(111) substrate was maintained at room temperature and the proper Knudsen cell was heated to $\sim 650 – 700$ K to maintain a constant molecular flux which was monitored using quartz microbalances. c-HBC was deposited at a pre-chamber pressure of $6 \cdot 10^{-9}$ mbar for 110 minutes which yielded a multilayer film of about 15 Å thickness. f-HBC was deposited at a pressure of $4 \cdot 10^{-9}$ mbar for 70 minutes which resulted in a multilayer of about 15 Å thickness. DBTTC was deposited at a pressure of $3 \cdot 10^{-9}$ for 50 min which results in a film thickness of about 26 Å. Similarly a pristine multilayer of C60 was grown at a pressure of $2 \cdot 10^{-8}$ mbar for 30 minutes producing a film of approximately 23 Å thickness. For the overlayer depositions of C60 atop of HBCs we deposited C60 at a pressure of $10^{-8}$ mbar for 15 minutes yielding an overlayer thickness of about 9 Å. For the C60 overlayer on top of DBTTC the thickness was
about 11 Å. These thicknesses were approximated from the measured molecular flux and deposition time. After each deposition, XPS spectra of oxygen 1s and nitrogen 1s were checked to ensure no contamination was present. The films were then characterized using core level XPS and C K-edge NEXAFS.

### 3.3 Analytical model for an intermixed heterojunction

In this section we derive an analytical model to describe hybrid interfaces as sum of the signals of the two components. The model takes into account the photon absorption inside the film, the inelastic mean free path of the outgoing electrons and the possibility for the pristine materials to intermix at the interface. We discuss first the case of a single layer and then the results will be generalized to a bilayer conserving the overall “as deposited” bilayer thickness.

When a photon flux of intensity $I_0$ impinges on a pristine layer of thickness $D$, at a distance $x$ from the surface it will be attenuated by a factor

$$I_{ph}(x) = I_0 e^{-\mu x}$$  \hfill (3.1)

where $\mu$ is the absorption coefficient of the material which depend on the photon energy. The number of electrons generated by a thickness $dx$ is then proportional to the number of absorbed photons and the intensity of the outgoing electrons is further attenuated by the inelastic scattering

$$dI_{el} = I_{ph}(x) \mu e^{-\frac{x}{\lambda}} = I_0 \mu e^{-x(\mu + \frac{1}{\lambda})} dx$$  \hfill (3.2)

where $\lambda$ is the attenuation length that in the general case is written as $\lambda \cos \phi$ to take into account the position of the detector with respect to the surface normal. Integrating over the entire thickness $D$ we get the total electron intensity of a pristine film as a function of the incoming photon flux.

$$I_{el} = I_0 \frac{\mu}{\mu + 1/\lambda} \left(1 - \exp \left[-D \left(\mu + \frac{1}{\lambda}\right)\right]\right)$$  \hfill (3.3)

The absorption coefficient $\mu$, the attenuation length $\lambda$ and the thickness $D$ are intrinsic properties of the pristine film.

Introducing $\bar{\mu} = \mu + \frac{1}{\lambda}$ the above expression simplifies to

$$I_{el} = I_0 \frac{\mu}{\bar{\mu}} (1 - e^{-\bar{\mu}D})$$  \hfill (3.4)

The previous calculation can be easily extended to the case of two intermixed layers of thicknesses $d_1$ and $d_2$, absorption coefficients $\mu_1$ and $\mu_2$ and attenuation lengths $\lambda_1$ and $\lambda_2$.
3.3. Analytical model for an intermixed heterojunction

The electron intensity from an infinitesimal slab $dx$ is given, similarly as for the pristine film, by

$$dI_{el} = I_0 \exp \left[ - \left( \frac{\tilde{\mu}_1 d_1}{d_1 + d_2} + \frac{\tilde{\mu}_2 d_2}{d_1 + d_2} \right) x \right] \left( \frac{\mu_1 d_1 + \mu_2 d_2}{d_1 + d_2} \right) dx$$

(3.5)

The pure phases can either remain separate as in a perfect bilayer or they can intermix at the interface (Fig. 3.5). To quantify the amount of intermixing of the two phases we introduce a parameter $\beta$ that can take all the values between 0 and 1, where $\beta = 0$ corresponds to the case of a sharp interface, while for $\beta = 1$ the two phases are fully mixed. The signal from the intermixed region is obtained by integrating the previous equation on the thickness of the intermixed region given by $\beta(d_1 + d_2)$

$$I_{el}^{mix} = I_0 \frac{\mu_1 d_1 + \mu_2 d_2}{\tilde{\mu}_1 d_1 + \tilde{\mu}_2 d_2} \left( 1 - e^{-\beta(\tilde{\mu}_1 d_1 + \tilde{\mu}_2 d_2)} \right)$$

(3.6)

where the attenuation effects of the pristine overlayer, as sketched in Fig. 3.5, are not taken into account yet.

We want to derive now the overall intensity from the whole heterojunction in the general case of bottom pristine+intermixed region+top pristine like in Fig. 3.5 under the assumption that the total volume remains constant whether the pure phases intermix or not. The calculation for the general case is straightforward since we simply need to sum up the different contribution from the different layers. The signal from the outmost
material is then given by

\[ I_1 = I_0 \frac{\mu_1}{\tilde{\mu}_1} (1 - \exp[-(1 - \beta)\tilde{\mu}_1 d_1]) + 
\quad + I_0 \frac{\mu_1 d_1}{\tilde{\mu}_1 d_1 + \tilde{\mu}_2 d_2} (1 - \exp[-\beta(\tilde{\mu}_1 d_1 + \tilde{\mu}_2 d_2)]) \exp[-(1 - \beta)\tilde{\mu}_1 d_1] \]  

(3.7)

where the first term describes the signal from the topmost layer of thickness \((1 - \beta)d_1\) and the second one the signal of material 1 from the blended layer that is attenuated by the pure phase on the top.

Similarly the signal of the material 2 can be decomposed as

\[ I_2 = I_0 \frac{\mu_2}{\tilde{\mu}_2} \exp(-\tilde{\mu}_1 d_1)[\exp(-\beta\tilde{\mu}_2 d_2) - \exp(-\tilde{\mu}_2 d_2)] + 
\quad + I_0 \frac{\mu_2 d_2}{\tilde{\mu}_1 d_1 + \tilde{\mu}_2 d_2} (1 - \exp[-\beta(\tilde{\mu}_1 d_1 + \tilde{\mu}_2 d_2)]) \exp[-(1 - \beta)\tilde{\mu}_1 d_1] \]  

(3.8)

where the first term describes the signal from the attenuated bottom layer and the second the signal from the blended layer. The equations above can be simplified by expressing the intensities of the pure phases in the bilayer with the ones from pristine films of thickness \(D_{1(2)}\)

\[ I_1 = \frac{I_{1\text{Prist}}}{1 - \exp(-\tilde{\mu}_1 D_1)} \left\{ (1 - \exp[-(1 - \beta)\tilde{\mu}_1 d_1]) + 
\quad + I_0 \frac{\mu_1 d_1}{\tilde{\mu}_1 d_1 + \tilde{\mu}_2 d_2} (1 - \exp[-\beta(\tilde{\mu}_1 d_1 + \tilde{\mu}_2 d_2)]) \exp[-(1 - \beta)\tilde{\mu}_1 d_1] \right\} \]  

(3.9)

and similarly for material 2

\[ I_2 = \frac{I_{2\text{Prist}}}{1 - \exp(-\tilde{\mu}_2 D_2)} \left\{ \exp(-\tilde{\mu}_1 d_1)[\exp(-\beta\tilde{\mu}_2 d_2) - \exp(-\tilde{\mu}_2 d_2)] + 
\quad + I_0 \frac{\mu_2 d_2}{\tilde{\mu}_1 d_1 + \tilde{\mu}_2 d_2} (1 - \exp[-\beta(\tilde{\mu}_1 d_1 + \tilde{\mu}_2 d_2)]) \exp[-(1 - \beta)\tilde{\mu}_1 d_1] \right\} \]  

(3.10)

In the following sections material 1 will be the acceptor C60 deposited on top of the three different coronene derivatives (material 2) considered in this study to form three heterojunctions, namely f-HBC/C60, c-HBC/C60 and DBTTC/C60. The signal of the heterojunctions is then decomposed into the ones of the pristine films using the single parameter (\(\beta\)) model just presented.
3.3. Analytical model for an intermixed heterojunction

Figure 3.6: Attenuation of the substrate due to an adsorbate film of thickness D on top of the substrate.

<table>
<thead>
<tr>
<th>Deposition</th>
<th>Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>f-HBC</td>
<td>15</td>
</tr>
<tr>
<td>c-HBC</td>
<td>15</td>
</tr>
<tr>
<td>DBTTC</td>
<td>26</td>
</tr>
<tr>
<td>C60</td>
<td>23</td>
</tr>
<tr>
<td>f-HBC/C60</td>
<td>15/9</td>
</tr>
<tr>
<td>c-HBC/C60</td>
<td>15/9</td>
</tr>
<tr>
<td>DBTTC/C60</td>
<td>27/11</td>
</tr>
</tbody>
</table>

Table 3.1: Film thicknesses as calculated from Au4f attenuation.

3.3.1 Parameter extraction

To successfully apply the $\beta$-model we need to carefully extract the non-fitting parameters that appear inside Eq.3.9 and 3.10, namely thicknesses, absorption coefficients and inelastic mean free paths.

The thicknesses of the films can be measured by inspecting the attenuation of the intensity of the peaks typical of the substrate on which the films are deposited. Since we deposited everything on a gold substrate, we refer to the 4f peaks of gold and we measure their attenuation passing from the clean substrate to the substrate with the
adsorbate. We can then calculate the adsorbate thickness by

\[ D = -\lambda \ln \frac{I}{I_0} \quad (3.11) \]

where \( \lambda \) is calculated using Eq.1.9, \( I_0 \) is the clean Au signal and \( I \) the attenuated one. An example of the Au4f attenuation is reported in Fig.3.6 while in table 3.1 all the thicknesses of the deposited films are given, both for pristine and sandwich. It is worth to note that this is an indirect measure of the film thickness and it gives a correct assessment of the amount of deposited material only if the substrate is uniformly covered by the adsorbate. This means that if the growth is not layer-by-layer but it proceeds in a 3D way, some substrate area will be less attenuated and the overall evaluated thickness will be smaller than the effective one. In this case it would not be possible to apply the \( \beta \)-model that is limited to the case of uniform adsorbate layers.

The second parameter to calculate is the absorption coefficient which is an intrinsic property of the material and depends on the photon energy. When the photon energy is far from an absorption edge however, the absorption coefficient is very low while it becomes critical when the photon energy is scanned across an absorption edge of the material being stronger in correspondence with an absorption peak. The absorption coefficient is then directly related to the absorption spectrum and so a direct measure of it is in our case the NEXAFS measurement. In this case the NEXAFS spectrum has to be normalized in order to normalize the absorption coefficient to the per atom X-ray absorption. It is necessary to normalize the pre-edge NEXAFS intensity to 0 and the post-edge to 1, since in the pre-edge no absorption is expected and in the post-edge, without the presence of any resonances the signal is proportional to the number of the scatterers.

After the NEXAFS normalization we need to scale the measured peak intensities to the absorption coefficient scale. This can be done using the Au 4f intensity attenuation measured across the resonance, i.e., during a RPES scan. Indeed the Au signal is differently attenuated depending on the amount of photons absorbed by the top layer and this attenuation sets the scale for the absorption coefficient. Using Eq.3.1 the absorption coefficient can be calculated from the Au 4f attenuation with the following formula

\[ \mu(\hbar \nu) = -\frac{1}{d} \ln \frac{I}{I_0} - \frac{1}{\lambda} \quad (3.12) \]

An exemple of calibration is given in Fig.3.7 for pristine C60 where it can be noted how the absorption coefficient \( \mu \) calculated from the attenuation of the Au 4f follows the NEXAFS shape.
Figure 3.7: Comparison of the calculated X-ray absorption coefficient for C60 (red) and the measured C60 NEXAFS (black). The similar shape of the two spectra allows to use the measured NEXAFS (after a proper rescaling) as the X-ray absorption coefficient.

3.3.2 XPS and NEXAFS analysis

We applied the $\beta$-model to fit the C1s XPS of the three bilayer systems as shown in Fig. 3.8. The $\beta$-model fit reproduces very well the experimental spectra in all three systems. Each spectrum can be seen as a superposition of the XPS spectra of the pristine films as shown by the deconvolution underneath them. From the fit the $\beta$ parameter has been extracted. C1s XPS has been measured soon after the deposition of C60, i.e. at a time $t=0$. The corresponding $\beta$ values at this time are equal to $0 \pm 0.2$, $0.7 \pm 0.2$ and $0.9 \pm 0.1$ for the flat, contorted and DBTTC system respectively. The two phases do not intermix at all in the f-HBC/C60 bilayer, while they display a significant intermixing in both c-HBC/C60 and DBTTC/C60 bilayers.

At the interface the molecules are not expected to preserve their orientation, however the magic angle NEXAFS do not depend on the molecular orientation and therefore we can apply the $\beta$-model also to the magic angle NEXAFS spectra. The NEXAFS for the f-HCB/C60 and c-HBC/C60 systems have been measured about 1 hour after the formation of the bilayer, while the same measurement is missing for the DBTTC/C60 system. As we explained in section 1.3.2, it is possible to build a synthetic NEXAFS at the magic angle taking a superposition of the p-pol and s-pol NEXAFS spectra. The validity of
Figure 3.8: C1s XPS for the three bilayer systems. The experimental data (grey dotted curves) are shown together with the best-fit with the $\beta$-model (black lines). Under each bilayer spectrum also the deconvolution into its pristine components is reported (filled curves).

This method is tested in Fig. 3.9 where the measured magic angle NEXAFS for the f-HBC pristine system is compared to the synthetic one. The synthetic spectrum obtained as simple sum of the p- and s- spectra is also displayed and it evidently does not match
with experimental data. The $\beta$-model fit for the magic angle NEXAFS on the C K-edge is shown in Fig. 3.10. The value of the $\beta$ parameter has been extracted separately also from this set of measurements. In this case $\beta$ passes from $0 \pm 0.1$ to $0.3 \pm 0.1$ for the f-HBC/C60 bilayer whereas it remains the same for the other two systems. The f-HBC/C60 system undergoes a change in the interface morphology with time. The C60 molecules start to interdiffuse slowly inside the f-HBC layer underneath and the initial sharp interface starts to present a certain degree of intermixing. The contorted systems, on the other hand, seem to reach an equilibrium condition soon after the C60 is deposited. Moreover, the appearance of no new features in the spectra of the sandwiches indicates that no chemical interaction between the donor and acceptor molecules is present at the interface. It is worth to note that this direct comparison between different interfaces is possible because the thicknesses of the relative layers are of the same order of magnitude. We attempted to measure also the 2closed-HBC/C60 interface (not reported here) in which the 2closed-HBC thickness was of the order of several nm. In that case we noticed that the interdiffusion process continues for more than 10 hours due to the higher interaction energy of the donor/acceptor molecules and the higher donor thickness.

### 3.4 Molecular orientation study with NEXAFS

In this section we investigate how the mean molecular orientation changes from the pristine stacks to the bilayer heterojunctions.
Figure 3.10: C K-edge NEXAFS for the three bilayer systems at the magic angle. The experimental data (gray) are showed together with their β-model best-fit (black). The NEXAFS for the pristine films are reported in each graph with different colours.
The dichroic NEXAFS for the DBTTC pristine film is shown in Fig.\ref{fig:nexafs}. The change in intensity passing from p- to s-polarization indicates that in the pristine stack DBTTC molecules tend to grow in ordered co-facial stacks along the surface normal even in a multilayer film where the substrate induced ordering is usually lost. The same behaviour is observed for f-HBC and c-HBC. The mean molecular orientation with respect to the surface can be in principle easily calculated from the ratio between the NEXAFS signals measured in s- and p-polarizations. Indeed, knowing that the NEXAFS intensity in s-pol is proportional to $\frac{1}{2} \sin^2 \theta$ and the one in p-pol to $\cos^2 \theta$, the mean tilt angle $\theta$ is given by $\frac{I_s}{I_p} = \frac{1}{2} \tan^2 \theta$.

However when the molecule has a non-flat geometry, like for c-HBC and DBTTC, the dichroic NEXAFS signal will depend also on the specific molecular shape that we need to explicitly consider in extracting the mean tilt angle. We can take into account the distinct molecular geometry of the contorted molecules considering that the coronene core is flat and the outer rings are tilted either up or down with respect to the coronene plane by an angle $\theta_0$. We can then calculate, knowing the tilt angle of every single ring, the expected NEXAFS intensities in s- and p-pol separately. Therefore when the coronene core lies flat on the surface $\theta_c = 0^\circ$ we would measure a mean tilt angle $\theta_{exp}$, due to the molecular wings, given by

$$\frac{1}{2} \tan^2 \theta_{exp} = \frac{\sum_{i=0}^{N} c_i I_{si}}{\sum_{i=0}^{N} c_i I_{pi}}$$  \hspace{1cm} (3.13)
where \( c_i \) are the weights due to the spatial distribution of the LUMO, \( I_{s,p} \) are the calculated intensities for each wing and the number 7 gives the intensity of the seven benzene rings in coronene. The above expression can be applied for an arbitrary rotation of the coronene around an axis. In this case the only thing to do is to recalculate the wing angles after the rotation. To know the molecular tilt angle we can then simply compare the angle extracted from the measured \( I_s/I_p \) with the set of \( \theta_{exp} \) calculated for different values of \( \theta_c \).

<table>
<thead>
<tr>
<th>( \theta_c )</th>
<th>( \theta_{exp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>10°</td>
</tr>
<tr>
<td>10°</td>
<td>14°</td>
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<tr>
<td>20°</td>
<td>22°</td>
</tr>
<tr>
<td>30°</td>
<td>31°</td>
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<tr>
<td>40°</td>
<td>40°</td>
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<tr>
<td>50°</td>
<td>50°</td>
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<tr>
<td>60°</td>
<td>59°</td>
</tr>
<tr>
<td>70°</td>
<td>68°</td>
</tr>
<tr>
<td>80°</td>
<td>72°</td>
</tr>
<tr>
<td>90°</td>
<td>81°</td>
</tr>
</tbody>
</table>

Table 3.2: Calculated tilt angle for a set of rotation of the coronene plane.

For DBTTTC the six outer rings are tilted with respect to the coronene plane by 21°, 17° and 26°, being the first the tilt angle of the two benzene rings (one up and one down), and the other two the angles of the four thiophene rings that are symmetric two by two. However we can confidently say that the LUMO relative to first NEXAFS peak is not localized on the thiophene rings being the one derived from the LUMO of the benzene. For this reason the contribution of the four thiophene rings can be neglected in the above equation and only the benzene flaps will be considered. In this situation we calculate that when the coronene plane lies flat on the surface, we would measure a mean tilt angle of 10°.

We chose to rotate the whole molecule around an axis perpendicular to the one that connects the benzene flaps. For this choice the new angles of the benzene flaps with respect to the surface plane will be equal to \( \theta_0 + \theta_c \), where \( \theta_0 \) is the flap angle with respect to the coronene plane. It is worth to note that for this particular molecular configuration and for this choice of the rotation axis, we need to mediate between the up-down and down-up configurations, being up and down the directions of the wings tilt with respect to the coronene plane.

A list of the expected tilt angle for a set of coronene rotations is given in table 3.2. The
angle measured for the pristine DBTTC, as obtained directly by the NEXAFS measurement, is $\theta = 25^\circ$. Looking at table 3.2 we see that between $20^\circ$ and $60^\circ$ $\theta_{\text{exp}}$ is almost the same as $\theta_{\text{c}}$, so our measured tilt angle can be considered the actual molecular tilt with an error of $\pm 2^\circ$.

Similar considerations have been done also for the c-HBC obtaining in that case a tilt angle of $25^\circ \pm 2^\circ$, whereas for the f-HBC film the measured tilt angle is identical to coronene orientation and it is equal to $14^\circ \pm 3^\circ$.

To find how the molecules are rearranged when the C60 film is deposited on top of them, we need to apply a modified version of the $\beta$-model.

### 3.4.1 Application of the $\beta$-model to the study of NEXAFS dichroism

The $\beta$-model can be directly applied to decompose both XPS and magic angle NEXAFS signals of a bilayer system. However to study the polarization dependent NEXAFS some modifications of the model need to be taken into account.

The first thing to note is that since $\mu$ is proportional to the NEXAFS, it will also depend on the X-ray polarization $\epsilon$ and it will be different for p-pol, s-pol and magic angle. RPES measurements are usually taken at magic angle conditions so while we have a direct measure of the Au 4f attenuation (and so of the absorption coefficient) at the magic angle, the same is not true for the polarization dependent one. However, as we already pointed out in the previous section, it is possible to build a synthetic spectrum corresponding to the one measured at magic angle and get the correct scaling factor for the absorption coefficient in both polarizations.

Moreover the absorption coefficient depends also on the film morphology and it will be different for the three regions of the heterojunction where the morphology is different. We assume that the molecular orientation is preserved in the pure phases of the bilayer while it changes only in the intermixed region. Moreover, in the particular case examined here, HBC-derivatives/C60 interfaces, any changes in the molecular orientation have to be attributed to the HBC-derivative molecules since the C60 film has a non-dichroic signal due to its molecular symmetry. Therefore we can express the signal from the mixed layer as a superposition of the measured p- and s-pol NEXAFS of the pristine HBC-derivatives ($I_{p(s)}$) as

$$I_{p(s)}^{\text{mix}} = \alpha_{p(s)} I_{p(s)} + (1 - \alpha_{p(s)}) I_{s(p)}$$

(3.14)

where $\alpha_{p(s)}$ is a parameter that describes the change in molecular orientation.

Accordingly the absorption coefficient $\mu$ for the intermixed region can be written with the same expression

$$\mu_{p(s)}^{\text{mix}} = \alpha_{p(s)} \mu_{p(s)} + (1 - \alpha_{p(s)}) \mu_{s(p)}$$

(3.15)
Figure 3.12: C K-edge NEXAFS for the DBTTC/C60 bilayer in p- and s-pol. The spectra have been fitted separately using the $\beta$ value already found as a constant parameter.

To obtain the signal of the whole bilayer we need to sum at Eq. 3.14 the contributions of the non-intermixed phases which gives

$$I_{p(s)}^{mix} = k(\mu_{C60}^{p(s)}, \mu_{mix}^{p(s)})I_{C60}^{prist} + l(\mu_{C60}^{p(s)}, \mu_{HBC}^{mix})I_{p(s)} + m(\mu_{C60}^{p(s)}, \mu_{mix}^{p(s)})(\alpha_{p(s)}I_{p(s)} + (1 - \alpha_{p(s)})I_{s(p)})$$  

(3.16)

where $k, l, m$ are coefficients related to the pre-factors already found for the non-modified $\beta$-model in Eq. 3.9 and 3.10. In particular the first coefficient is equal to

$$k = (1 - \exp[-(1 - \beta)\tilde{\mu}_{C60}^{p(s)}d_1]) +$$

$$+ I_0 \frac{\mu_{C60}^{p(s)}d_1}{\mu_{C60}^{p(s)}d_1 + \mu_{mix}^{p(s)}d_2}(1 - \exp[-\beta(\tilde{\mu}_{C60}^{p(s)}d_1 + \tilde{\mu}_{mix}^{p(s)}d_2)])\exp[-(1 - \beta)\tilde{\mu}_{C60}^{p(s)}d_1]$$  

(3.17)

and it gives the signal of the C60 molecules both in the pristine and in the intermixed layer. The second coefficient takes into account the attenuation experienced by the pristine bottom layer of HBC-derivatives and can be written as

$$l = \exp[-(\tilde{\mu}_{C60}^{p(s)}d_1 + \beta\tilde{\mu}_{mix}^{p(s)}d_2)](1 - \exp[-(1 - \beta)\tilde{\mu}_{HBC}^{p(s)}d_2])$$  

(3.18)

and the third one, $m$, defined as

$$m = \left\{ \frac{\tilde{\mu}_{mix}^{p(s)}d_2}{\tilde{\mu}_{mix}^{p(s)}d_2 + \tilde{\mu}_{C60}^{p(s)}d_1}\exp[-(1 - \beta)\tilde{\mu}_{C60}^{p(s)}d_1](1 - \exp[-\beta(\tilde{\mu}_{C60}^{p(s)}d_1 + \tilde{\mu}_{mix}^{p(s)}d_2)]) \right\}$$  

(3.19)
3.4 Molecular orientation study with NEXAFS

Figure 3.13: NEXAFS intensities of the intermixed region in the DBTTC/C60 heterojunction in p-pol (black) and s-pol (red).

Gives the signal of the HBC-derivatives from the intermixed layer of unknown molecular orientation $\theta_{mix}$. The new orientation of the donor molecules in the intermixed region can be then easily calculated from

$$\frac{I_s}{I_p} = \frac{m(\mu_{C60}, \mu_{mix}^s)(\alpha_s I_s + (1 - \alpha_s)I_p)}{m(\mu_{C60}, \mu_{mix}^p)(\alpha_p I_p + (1 - \alpha_p)I_s)} = \frac{1}{2} \tan^2 \theta_{mix}$$

(3.20)

In Fig. 3.12, the dichroic NEXAFS for the DBTTC/C60 system is shown together with the best fit using the modified $\beta$-model. In the fits the $\beta$ value has been fixed to be equal to the one already found with the XPS and magic angle NEXAFS analysis. As one can see, the fits are reasonably good and the whole peak structure is well reproduced. The same has been done also for the f-HBC/C60 and c-HBC/C60 heterojunctions (not reported here) obtaining a similar fit quality [71].

After applying this model, we can also plot the NEXAFS of the interface component present in the bilayer NEXAFS. This is shown in Fig. 3.13. Comparing these spectra with the ones for the pristine DBTTC (Fig. 3.11), it is evident that there is a reorientation of the intermixed phase in which the DBTTC molecules are tilted toward a higher angle. Applying Eq. 3.20 and looking at table 3.2, we find that the DBTTC angle passes from $25^\circ \pm 2^\circ$ to $36^\circ \pm 2^\circ$.

The reorientation for the three systems are summarized in Table 3.3. These results indicate that the inclusion of C60 on top of f-HBC has less significant effect on the orientation of both f-HBC and DBTTC molecules, when on the other hand in the case of
Table 3.3: Comparison of the mean tilt angles for the pristine stack and the intermixed region.

<table>
<thead>
<tr>
<th></th>
<th>Pristine</th>
<th>Intermix</th>
</tr>
</thead>
<tbody>
<tr>
<td>f-HBC</td>
<td>$14^\circ \pm 2^\circ$</td>
<td>$30^\circ \pm 2^\circ$</td>
</tr>
<tr>
<td>c-HBC</td>
<td>$25^\circ \pm 2^\circ$</td>
<td>$50^\circ \pm 2^\circ$</td>
</tr>
<tr>
<td>DBTTC</td>
<td>$25^\circ \pm 2^\circ$</td>
<td>$36^\circ \pm 2^\circ$</td>
</tr>
</tbody>
</table>

c-HBC there is a more significant rearrangement of the c-HBC molecules. This observation is consistent with theoretical DFT calculations of the interaction energies of different dyads. Due to stronger intermolecular interaction between f-HBC molecules than C60/f-HBC they tend to remain together in a columnar fashion, whereas on the contrary the c-HBC/c-HBC interaction energy is similar to the C60/c-HBC dyad’s and it is therefore energetically more convenient for the C60 molecules to rearrange themselves between the c-HBC molecules than between f-HBC. In the case of DBTTC we suggest that the reticulated heterojunction promotes an interdiffusion of the C60 molecules between the cables and therefore we observe a lower rearrangement of the DBTTC phase.

**Self-absorption**

Let’s discuss now the self-absorption phenomenon and how it affects the molecular tilt angle in a thick film determined by NEXAFS dichroism. Self-absorption effects occur when the penetration depth of the X-rays varies strongly near an X-ray absorption edge. This effect can suppress the peak intensity in the measured spectra due to the smaller amount of material illuminated by the photon flux when the X-ray absorption is stronger. The measured signal could be non-linear with respect to the absorption coefficient and when the NEXAFS intensity ratio measured in p- and s-polarization is used to get the molecular tilt angle we could overestimate it. To model the self-absorption we assume that the thick film is well ordered and it is made up by a superposition of single layers of thickness d which have all the same morphology and orientation. In this case we can write the electron yield for the Nth layer as

$$I^{p,s}(hv) = I_0 d \mu_{p,s}(hv) \exp \left[ - \left( \mu_{p,s}(hv) + \frac{1}{\lambda} \right) \right] Nd \quad (3.21)$$

where the total thickness is N times the thickness of one layer and the incoming photon flux has been absorbed by the top N-1 layers before arriving to the Nth one. The same equation holds for s and p polarization with the absorption coefficients taken accordingly. To get the signal from the whole thickness we have to sum over all the layers.
3.4. Molecular orientation study with NEXAFS

Figure 3.14: Correction of the tilt angle due to self-absorption effects. The colour scale shows the difference between the measured $\theta$ and the actual tilt angle $\theta_0$. The difference is plotted versus the original molecular tilt angle and the number N of layers.

\[
I_{p,s}(h\nu) = \sum_{i=0}^{N} I_0 d \mu_{p,s}(h\nu) \exp \left[ - \left( \mu_{p,s}(h\nu) + \frac{1}{\lambda} \right) id \right]
\]  

(3.22)

Without the self-absorption the intensity ratio in p- and s- polarization would give the molecular tilt angle according to the formula

\[
\frac{I_s}{I_p} = \frac{1}{2} \tan^2 \theta_0
\]

(3.23)

Taking into account the self-absorption effects the intensity in both polarization is given by (3.22) and the measured angle $\theta$ is related to the actual angle $\theta_0$ by the following equation

\[
\frac{I_s}{I_p} = \frac{1}{2} \tan^2 \theta_0 \sum_{i=0}^{N} \frac{e^{-(\mu_s + \frac{1}{\lambda})id}}{\sum_{i=0}^{N} e^{-(\mu_p + \frac{1}{\lambda})id}} = \frac{1}{2} \tan^2 \theta
\]

(3.24)

where we exploited the relation between the absorption coefficient and the NEXAFS spectrum $\mu_{p,s} = c I_{p,s}^0$, where $c$ is the scaling factor between the two. From equation (3.24) we can evaluate the role of the self-absorption in the tilt angle analysis. In Fig. 3.14 the difference between $\theta$ and $\theta_0$ is plotted for a system composed up to 20 layers. The actual angle $\theta_0$ is reported on the x axis and the number of layers on the y axis. The
color scale is the quantity $\theta - \theta_0$. As expected the first layer is not affected by the self-absorption and so the measured angle is equal to the actual one. The same is true for the extreme cases in which the molecule is totally flat or standing-up and the corresponding tilt angle $\theta_0$ is $0^\circ$ or $90^\circ$. In both of these conditions one of the two measured intensities is zero and the ratio is the same regardless of the other intensity. For the magic angle condition ($\theta = 54.7^\circ$) the angle dependance in the measured NEXAFS vanishes and again $\theta - \theta_0 = 0$. The variation calculated for a thick film in which the molecules are oriented at an angle that is different from $0^\circ$, $\sim 55^\circ$ or $90^\circ$ is on the scale of several degrees and does not go beyond the range $\pm 6^\circ$. This maximum value is of the same order of magnitude of the error bar that is usually associated with the calculated tilt angle.

### 3.5 Conclusions

We have studied the morphology of three hybrid systems, namely $f$-HBC/C60, c-HBC/C60 and DBTTC/C60 to model the donor/acceptor interface of OPV devices. Combining spectroscopic techniques with a specific theoretical model we have been able to analyze the detailed structure of the intermixed interface. In particular we have found that the two materials produce an intermixed phase at the interface and that the degree of intermixing depends on the shape complementarity between coronene derivatives and C60. Indeed whereas for the $f$-HBC the intermixing is less pronounced ($\beta = 0.3$), both c-HBC and DBTTC form a thick intermixed layer ($\beta = 0.7$ and $\beta = 0.9$ respectively). The larger intermixed volume would correspond to a higher active volume available for exciton dissociation that leads in turn to the higher power conversion efficiency measured in the devices.

Moreover, we have shown that the HBC molecules rearrange in the intermixed layer changing their molecular orientation due to the interactions with fullerenes. The orientation of $f$-HBC changes from $14^\circ$ in pristine films to $30^\circ$ in the intermixed layer, whereas the mean molecular orientation of c-HBC changes from $25^\circ$ to $50^\circ$ and the one of DBTTC from $25^\circ$ to $36^\circ$. We have attributed the high reorientation of c-HBC to the higher interaction energy between c-HBC and C60. The lower molecular rearrangement for DBTTC is probably due to the fact that in this system the reticulated network of the DBTTC pristine phase drives a stronger intermixing and not the interaction energy between the single DBTTC/C60 dyads.

The results show that shape-complementarity represents a promising route to increasing the efficiency of OPV devices through interfaces and morphologies tailored at the molecular level.
4.1 Introduction

The term photovoltaic effect (PV) means in general the generation of a tension under illumination and its discovery is ascribed to Becquerel, who observed a photocurrent when platinum electrodes, covered with silver bromide, were illuminated in aqueous solution \[72\]. A solar cell is an electronic device which exploits the PV effect to produce electric energy. The first solar cell was realized in 1954 at Bell Laboratories \[73\]. It was based on silicon and had an efficiency of 6%. Today Si-based solar cells are the main type of PVs since over the years the efficiency has reached 24% for crystalline Si solar cells in the laboratory \[74\].

Organic semiconductors PVs (OPV) are a less expensive alternative to inorganic ones. Also, organic molecules can be processed by techniques not available to crystalline inorganic semiconductors. For example various printing and coating technologies have been proven to be compatible with semiconducting polymer processing, illustrating that polymer solar cells can be manufactured using standard printing processes \[75\]. Moreover the plastic properties of organic semiconductors and the low temperatures required in the fabrication processes make OPVs compatible to a number of different substrates including flexible materials. Despite their advantages, OPVs suffer from a range of issues, including low efficiency and limited stability.

The field of OPV can be divided in two main categories: dye sensitized solar cells and heterojunction solar cells. The latter, in turn, can be broken down into conjugated polymer and small molecules solar cells. In this chapter I will deal with heterojunctions based on small molecules, focusing in particular to the tandem structure in which two or more solar cells are connected in series. I will show also a method to realize non-series tandem cells exploiting graphene as an electrode.

4.2 Organic Photovoltaic

The active region of an organic solar cell is a junction of two different organic materials which act one as electron donor and the other as electron acceptor. The organic light-
absorbing layer is sandwiched between two electrodes, one of which must be transparent or semi-transparent. The process of conversion of the light into electricity by organic solar cells can be summarized into four different steps:

- exciton (electron-hole pair) creation after photon absorption;
- exciton diffusion toward the donor/acceptor interface;
- exciton separation at the donor/acceptor interface;
- charge transport of the separated electron and hole toward the respective electrodes.

With respect to the inorganic p-n junction, there are few but notable differences in the basic principles. The first thing is that in organic materials the LUMOs and HOMOs levels do not interact strongly enough to form a conduction band and a valence band like in inorganic semiconductors. Thus the charge transport mechanisms are different in the two cases leading to a generally lower mobility for organic semiconductors. Also, whereas in organic semiconductors the excited electron is bound to the hole, in many inorganic ones the light absorption produces a free electron and a hole. This is due to the lower dielectric constant organic semiconductors have with respect to the inorganic ones. The electrostatic attractive force between the holes and the electrons is proportional to $1/\varepsilon$. While this interaction can be neglected in the inorganic semiconductors, the organic ones have a dielectric constant of about 3 [76] and require a force more than 0.4 eV to separate the exciton [77].

### 4.2.1 Characteristics of PV cells

In this section I will recall the characteristic parameters of a p-n junction which are common to both organic and inorganic devices.

If a nonirradiated junction is biased with a voltage $V$, the current of the minority carriers is the saturation current denoted by $I_S$, while the majority current is exponentially reinforced to become [78]

$$I_{Maj} = I_S \exp \left( \frac{qV}{kT} \right)$$  \hspace{1cm} (4.1)

where $q$ is the elementary charge, $k$ the Boltzman constant and $T$ the temperature. The resulting current density is thus:

$$i = I_S \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right]$$  \hspace{1cm} (4.2)
4.2. Organic Photovoltaic

Figure 4.1: I-V curves of a photovoltaic cell under dark (left) and illuminated (right) conditions.

When the junction is irradiated, a reverse current $I_{ph}$ appears and the current density becomes

$$I = I_S \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right] - I_{ph}$$  \hspace{1cm} (4.3)

Under irradiation the I-V curve does not pass through the origin anymore (see Fig. 4.1) and the irradiated biased junction can work as:

- a rectifier with a forward bias in the first quadrant;
- a photodiode with a reverse bias in the third quadrant;
- a photovoltaic cell without external bias, but with a current flowing through a load resistance $R_L$ in the fourth quadrant.

In the latter case power and electrical energy can be produced by the device since, in the fourth quadrant, the product $V \cdot I$ is negative. The maximum voltage difference attainable between the two electrodes is equal to the open-circuit voltage $V_{OC}$. Whenea cell is placed in an open circuit and illuminated, electrons and holes separate and start to flow towards the electrons. At some point the build-up charge will reach a maximum equal to $V_{OC}$. The maximum current that can run through the cell is determined by the short circuit current $I_{SC}$. This quantity yields information about the charge separation and transport efficiency in the cell and its magnitude depends on the illumination strenght. The square $I_{max}V_{max}$ is the maximum power ($P_{max}$) the cell is able to yield, while the fill factor (FF) is defined as

$$FF = \frac{P_{max}}{V_{OC}I_{SC}}$$  \hspace{1cm} (4.4)
4. Organic Photovoltaic Tandem Cells

The external power conversion efficiency (PCE), defined as the power output divided by the incident light power, can be written using the above expression as

$$PCE = \frac{FF \cdot I_{SC} \cdot V_{OC}}{\Phi}$$

(4.5)

where $\Phi$ is the photon flux.

The cell can be thought of as a current source where $I_{ph}$ is a reverse current proportional to the incident light, in parallel with a diode in the dark which delivers a current equal to Eq.4.2. We thus obtain the equivalent circuit for an ideal solar cell which consists of a current source with an ideal diode in parallel (Fig.4.2). Since the contact resistance, due to the electrode-organic interfaces, and the ohmic losses due to the bulk resistivity of the materials, generate a non-negligible resistance in relation to the load resistance, we need to include a series resistance $R_S$ in the equivalent circuit. Furthermore, when leakage currents arise across the cell, we can take into account this component by introducing a parallel resistance $R_{SH}$ such that $R_{SH} \rightarrow \infty$ when the leakage current is zero. The effects of these additional resistances is to cause the deviation of the I-V characteristic from its ideal shape [78].

4.3 Reaching inorganic cell efficiency: tandem cells

Each of the mechanisms that from the photon absorption lead to generation of an electric current are characterized by a specific efficiency, the multiplication of which, in the total energy transfer process, gives to the external quantum efficiency (EQE). The EQE is therefore the quantity that measures the ratio of the output electrons to the incident photons and is equal to

$$EQE = \eta_{abs}\eta_{diff}\eta_{tc}\eta_{tr}\eta_{cc}$$

(4.6)

where $\eta_{abs}$ is the photon absorption efficiency and the last four parameters give the internal quantum efficiency (IQE), that, in turn, is the number of collected charge carriers.
4.3. Reaching inorganic cell efficiency: tandem cells

per absorbed photon. The IQE depends then on the efficiencies of the exciton diffusion process $\eta_{\text{diff}}$, the hole-electron separation process $\eta_{\text{tc}}$, the carrier transport process $\eta_{\text{tr}}$ and the charge collection process $\eta_{\text{cc}}$ respectively.

The energy transfer process efficiencies in an organic solar cell can be viewed as a pyramidal process. At each step there is a bottleneck to overcome and the total efficiency decreases.

The first cause of loss is the mismatch between the solar spectrum and the large bandgap of organic materials that leads to a poor photon absorption. In general the thermodynamical limitation of the energy conversion efficiency in a solar cell (Shockley-Queisser limit [79]) can be evaluated taking into account two phenomena: 1) only the photons with a energy larger than the band gap $E_g$ can be absorbed and 2) hot charge carriers created upon photon absorption relax to the conduction band of the photoactive material giving rise to the so-called thermalization. The direct consequence of these two assumptions is that the maximum charge extraction potential at open circuit ($V_{\text{OC}}$) is given by the band gap of the photoactive material. It has been calculated that the optimal value for $E_g$ is 1.1 eV that would give a theoretical efficiency of 48% [79]. When the bandgap is larger, as in the case of organic materials, the amount of harvested photons dramatically decreases and the same does $\eta_{\text{abs}}$. In the specific case of organic solar cells the efficiency is not limited only by $E_g$ but also by the offset between the LUMO

![Band diagram of a tandem cell](image)
of the donor and the LUMO of the acceptor since for organic materials $V_{OC}$ follow the empirical equation \cite{66}

$$V_{OC} = \frac{1}{e}(|E^{\text{donor}}_{\text{HOMO}}| - |E^{\text{acceptor}}_{\text{LUMO}}|) - 0.3$$

(4.7)

where 0.3 is an additional loss whose origin is still under debate \cite{80, 81}. In addition to the bandgap limit, the photon absorption depends also on the thickness of the absorbing material. Indeed, if the sample is too thin, some of the incident radiation will pass through the sample unabsorbed and will not contribute to the charge generation. However, if the sample is too thick the exciton generation zone is too far from the interface where exciton dissociation occurs and a too big series resistance appears. The thickness of the active region is therefore limited by the ability of excitons to diffuse towards the donor-acceptor interface, since the diffusion length is much shorter than the optical absorption length (typically $L_D \leq 10\text{nm}$ \cite{82}). If the exciton does not separate in time, it will recombine or decay via thermalization. \(\eta_{\text{diff}}\) represents the efficiency of the exciton diffusion to the separation point. When the exciton meets an interface between electron acceptor with high electronic affinity and electron donor with high ionization energy, it will be separated in the time scale of femto-seconds \cite{83}. This process is much faster than other competition processes like photoluminescence (ns) and charge recombination ($\mu$s). As a result, \(\eta_{\text{cc}}\) is approximately 100%. The separated free carriers are transported inside the relative electron and hole transport materials hopping between localized states. Traps can reduce the mobility, however, if carriers are not infinitely trapped we can consider \(\eta_{\text{tr}}\) = 100%. For the charge collection at the electrodes the conditions to be fulfilled are $(E_F)_{\text{cathode}} < (E_{\text{LUMO}})_{\text{acceptor}}$ and $(E_F)_{\text{anode}} > (E_{\text{HOMO}})_{\text{donor}}$. Under these conditions $\eta_{\text{cc}} \sim 100\%$.

As result from the above discussion, the two major losses occurring in solar cells are the sub-band gap transmission and the thermalization of hot carriers. One way to circumvent both effects simultaneously is the realization of a tandem solar cell, that consist of stacking two or more standard cells in series. In the case of OPVs the tandem approach allows to combine materials with different band gap in order to cover more efficiently the emission spectrum of the sun. Moreover using the tandem cell architecture it is also possible to overcome the thickness limit imposed by the exciton diffusion length and realize a thick active layer to absorb the maximum of the light.

Fig. 4.3 depicts a simplified band diagram of an organic tandem cell comprised of two distinct devices stacked on top of each other, each of them being based on a donor/acceptor composite. The light which is not absorbed in the first device can further impinge on the second one. Moreover, the thermalization losses are lowered due to the use of materials having different band gaps. The two cells involved in the device can be connected either in series (two-terminal) or in parallel (three-terminal) depending on the nature of
4.3. Reaching inorganic cell efficiency: tandem cells

Figure 4.4: Comparison of the I-V characteristics for a single solar cell and a tandem solar cell whose architecture is shown in the inset. The arrow indicate the $V_{OC}$ increase.

the intermediate layer and on the way the intermediate layer and the two electrodes are connected. The intermediate layer should allow the recombination of holes coming from one sub-cell with electrons coming from the other. Following the same principle, an infinite number of devices can be theoretically piled up this way.

In Fig. 4.4 a very basic tandem cell we made as reference cell for subsequent studies is shown and it is compared with a standard cell. It has been obtained by connecting in series two standard cell in which the active layer is made up by Subphthalocyanine (SubPc) as donor material and C60 as acceptor, whose thicknesses are 20 nm and 40 nm respectively. The front cell and the back cell are connected in series through a layer of Ag nanoparticles. The whole structure comprises also 5 nm of molybdenum oxide ($MoO_{3}$), which is used as hole injection layer, and 5 nm of 3,4,9,10perylenetetracarboxylic bisbenzimidazole (PTCBI), which serves both as hole blocking layer as well as protection cap for the organic layers beneath. Finally Indium Tin Oxide (ITO) and Al electrodes are used as anode and cathode respectively.

Even if the structure is not optimized, we observed that the $V_{OC}$ increases from $\sim 0.8$ to $\sim 1.6$ V passing from the single to the tandem cell. This leads to an efficiency increase
from 0.6% to 1.6%. Although $V_{OC}$ increases, $I_{SC}$ is limited by the weakest of the two currents being the two sub-cells connected in series.

**Non-series tandem cells**

Currently, tandem cells are almost exclusively series tandem cells, as each cell is intimately integrated with its adjacent cell. This is a consequence of the need to, first, aid hole and electron recombination at the interface of different cells and, second, to maintain the highest transparency so as not to absorb light traversing to subsequent cells. Since recombination requires only a very small amount of metallic material, most organic tandem solar cells employ a $\sim 1\text{nm}$ layer of metal as a recombination layer [84–89]. These thin metal layers, during deposition, coalesce into metal nanoparticles. The resulting structure provides the basis for charge recombination while remaining highly transparent ($\sim 98\%$ [84]), but do not have lateral conductivity, necessitating a series integration.

Graphene represents a significant opportunity as a recombination layer in tandem organic photovoltaics. Its high transparency ($\sim 97.5\%$) coupled with its high conductivity could enable a recombination layer that is laterally conductive, enabling a non-series tandem cell [90]. If one takes two identical cells and connects them in series, the first cell will absorb a greater amount of light than the second. The result of this is that more current is generated in the first cell than the second, a phenomenon well known in OPV device physics. Despite the higher current being generated by the first cell, the tandem cell will generate only as much current as the weakest cell, throwing away the additional power being generated by the first. If that tandem cell is fabricated as a non-series tandem, however, all of this power can in theory be harnessed.

### 4.4 Graphene transfer strategies

A significant barrier to the incorporation of graphene into OPV devices, apart from the synthesis of graphene itself (which is a wide area of research), is the process of transfer. Since graphene is a single atom thick it is macroscopically fragile, and great care must be taken during any transfer process. To compound this process difficulty, for OPVs, any process parameter that itself is harmful to organic semiconducting materials cannot be tolerated, such as heat, most solvents, and mechanical strain. To date, transfer process development has concentrated on the transfer of chemical vapour deposition (CVD) graphene onto high surface energy materials, such as glass and silicon. This has been sufficient for the bulk of organic electronics graphene research where graphene has been used as bottom electrodes for OPVs [91–93] and field effect transistors
Graphene transfer strategies

Where the initial transfer of graphene onto silicon or glass represented a first or early step in the fabrication process. Since CVD graphene is grown on a metal film, any integration process for single or few-layer graphene must first remove the growth substrate via chemical etching. To keep graphene intact during and following this step, a transfer substrate must be introduced, such as PDMS or polymethylmethacrylate. After the growth substrate is removed, this transfer substrate is used to apply graphene to the surface to which transfer is desired. Once in contact, the method for transfer substrate removal varies. A typical process includes a period of applied pressure at elevated temperatures, after which the polymer is removed mechanically or chemically from the graphene. This process, while effective, has been shown to leave behind polymer residue. Many transfer processes are followed by an annealing step where residual polymer materials is effectively burned off.

Recently the process of graphene transfer via PDMS was successfully used to integrate graphene onto a polymeric semiconductor thin-film for OPVs. This device process allowed the use of moderately elevated temperatures, though likely suffered from residual polymeric residue. To date there has not been a transfer process demonstrated that allows the integration of graphene onto an organic thin-film material that retains the mechanical, electronic, and semiconducting properties of the graphene and OPV materials.

Fluorinated transfer

The integration of graphene into small molecule OPVs could provide significant benefits to the OPV field. In order to develop such a process, we investigated the use of an Orthogonal resist layer as a low-energy transfer substrate whose removal could be accomplished via one of the few solvent systems that do not interact with organic small molecules (the particular solvent in this case is proprietary to Orthogonal, Inc.). Below we describe a process developed in the CLUE Columbia laboratory, that allows for the non-destructive high-quality transfer of single-layer graphene onto an organic semiconductor thin film enabling for the first time the use of graphene as a transparent electrode for all small-molecule organic transparent electronic devices.

As a target small-molecule organic substrate, 2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) films, for Raman Spectroscopy and Scanning Electron Microscopy (SEM) transfer analysis, were evaporated on ITO-coated glass at 1 Angstrom per second to a thickness of 40nm via an Angstrom Engineering thermal evaporator mated to an MBraun glovebox. To evaluate the electrical quality of fluorinated resist transferred graphene, organic LED (OLED) devices were evaporated on pre-patterned ITO substrates for graphene cathode lamination. PEDOT:PSS was spin-coated
4. Organic Photovoltaic Tandem Cells

Figure 4.5: Schematic of the fabrication of a transfer stamp, above, and graphene lamination and transfer, below.

on cleaned substrates at 3000rpm at 1000rpm/s and baked at 120°C for 1 hour. Following PEDOT deposition the substrates were taken into the nitrogen environment of the glovebox. 40nm of N,N’-Bis(3-methylphenyl)-N,N’-diphenyl-9,9-spirobiﬂuorene-2,7-diamine (E105) and followed by the evaporation of 40nm of Tris(8hydroxyquinolinato) aluminium (Alq3, LumTec).

A 60nm Aluminum cathode was evaporated on Control devices. All OLED devices were kept in nitrogen for the duration of the experiment. The transfer of graphene is accomplished via a treated PDMS (DuPont) stamp with a proprietary FL material manufactured by Orthoganol, Inc. PDMS was cured in a petri dish at 80°C for 1 hour. Small stamps of PDMS were cut from this mold, and coated with 0.4g (approximately 400nm) of Parylene-C via a Specialty Coating Systems Labcoter. These PDMS-Parylene stamps were then spin-coated with FR at 3000rpm and 1000rpm/s acceleration.

Large-area films of graphene were grown using previously reported CVD processes on copper foil. Small sections of graphene/copper was cut and placed, graphene-side down, on the PDMS-Parylene-Orthoganol stamp (referred hereafter as “transfer stamp”). A schematic of this process is depicted in Fig.4.5. Copper is then etched in ammonium persulfate (Transene APS-100 copper etchant) until no copper is evident.
4.4. Graphene transfer strategies

Figure 4.6: a-b) Raman spectra and c-d) STM images of graphene on TPBi (left) and of graphene on Silicon Oxide (right).

(periodic removal of bubbles via deionized water is typically required). It is important, after the application of Parylene and for the remainder of the experiment, to avoid ex-ring the stamp, as graphene/copper delamination will result. To effectively adhere the graphene/copper foil to the stamps without significant flexion the transfer stamp was placed on a non-adhesive side of scotch tape (3M), while uniform pressure was applied to the top of the graphene/copper foil by a glass-backed PDMS stamp with an additional scotch tape layer. The non-adhesive side of scotch tape does not adhere to PDMS. In order to transfer graphene onto organic thin-films the transfer stamp was placed, graphene-side down, onto the organic thin films in the desired location (Fig 4.5). Pressure was applied with a thumb for 5 seconds. The stamp was then removed from the substrate. What is left on the substrate is single-layer graphene along with a thin film of the Orthoganol resist. This resist was removed by two subsequent spin-coats of the Orthoganol resist stripper.

To evaluate the presence and quality of transferred graphene on organic films Raman spectroscopy was performed on graphene transferred using this method onto a TPBi thin-film. The Raman signature of the background thin-film without graphene was also measured, and the background corrected Raman signature is shown in Fig 4.6a). The presence of a strong signal from the G and 2D peaks, located at 1590.54 cm$^{-1}$ and
2683.0 cm\(^{-1}\) respectively, indicate that graphene is successfully transferred by the FR method onto organic small-molecule substrates. The small D-peak, located at 1352.5 cm\(^{-1}\), demonstrate that not only is CVD graphene grown with high quality, but that the transfer process does not induce significant defects in the transferred graphene film.

Graphene was also transferred onto Si substrates and Raman was measured for comparison (Fig. 4.6b)). Peak position and full-width-half-maximum (FWHM) for G and 2D peaks of graphene transferred on both substrates are listed in Table 3.1. The close agreement demonstrates the effectiveness of the Fl transfer process of graphene onto both high and low energy substrates and that Raman Microscopy can be used as an effective tool for characterization of graphene cathodes on organic substrates. Broadening of the peak FWHMs on organic vs Si can be attributed to increased substrate-induced corrugation in graphene films on organic versus silicon. Slight deviations in the G and 2D peak positions between the two substrates is likely due to transfer-induced local dopent concentrations and local strain.

In order to probe surface morphology and transfer cleanliness, we inspected the transferred films via SEM. Fig. 4.6c-d) shows SEM images taken at 10,000 times magnification at an energy of 2kV. Fig. 4.6d) shows Fl-transferred graphene on silicon, with expected morphology and a high level of cleanliness. Fig. 4.6c) shows graphene transferred on an organic thin-film of TPBi, illustrating the high fidelity transfer of graphene onto a low-energy surface with a transfer quality similar to that expected on silicon with existing transfer techniques.

As a final demonstration of the quality, chemical orthogonality (i.e. significant differences in chemical reactivity), and capabilities of this process, an organic LED was fabricated with Fl-transferred graphene serving as the cathode. OLED devices are typically
4.5 Conclusions

Graphene was successfully transferred via a modified PDMS fluorinated transfer-stamp in a process that is compatible with low-energy, fragile, and chemically vulnerable surfaces. Raman spectroscopy indicates high-quality graphene transfer, while SEM shows good surface morphology and little contamination. An OLED was fabricated using this process to transfer a graphene cathode. This functioning OLED is evidence of long-range high-fidelity graphene transfer to vulnerable substrates. As graphene quality improves with further research this process may allow large-scale, patternable transfer to various substrates of choice enabling flexible and transparent OLEDs, OPVs, as well as provide a new and promising material integration process for tandem organic photovoltaics.
Conclusions

In the present work I have tackled some of the main issues related to the use of organic semiconductors in electronic devices using two different model systems. The charge transport mechanism has been investigated taking a highly pure and ordered system, i.e. an organic semiconducting single crystal. The almost total lack of defects and the presence of long range order, make possible to exclude effects due to impurities or grain boundaries in the charge transport mechanism. Moreover, the intrinsic anisotropy, due to the low molecular symmetry which cause also a low crystal symmetry, allows to relate the observed anisotropic charge transport properties to the molecular structure and molecular interactions.

Making use of synchrotron based spectroscopic techniques, I have studied the detailed electronic structure of the 4-hydroxycyanobenzene (4HCB) molecule, which has been previously observed to form macroscopic single crystals with highly anisotropic mobility along the three crystallographic axes. After a full characterization of 4HCB molecule in its gas phase, where I have used three different experimental techniques (XPS, NEXAFS and RPES) together with *ab initio* theoretical calculations based on DFT, to probe both occupied and unoccupied molecular levels, I have studied the various condensed phases: single crystal and thin film. I have demonstrated that the molecules that form a thick film deposited on a gold substrate, present an inter-molecular arrangement similar to the one of the crystalline form where they are supposed to interact by $O – H \cdots N$ hydrogen bonds. Therefore I have adopted the thick film as a prototype of the single crystal system. Relying on the results of the gas phase experiments and exploiting the core-hole clock method, I have calculated the charge transfer time related to the fast de-localization of a resonantly excited core electron inside the 4HCB solid. The results of the charge transfer time calculation, suggest that the transport is mediated by the nitrogen atoms of the 4HCB. Moreover the measured charge transfer values indicate that the preferential direction for charge transport is perpendicular to the molecular plane as it
would be in a picture of charge hopping between $\pi^*$ orbitals of adjacent benzene rings. The second important issue in the field of organic semiconducting devices is related to the presence of hybrid interfaces, e.g. the ones between different organic active layers or between the organic materials and the other components of the device. The processes occurring at such interfaces have to be more deeply understood in order to control the properties of the devices. I have studied both a metal/organic interface and an organic heterojunction model system. The first one has been obtained again with 4HCB by depositing a monolayer onto a gold substrate. The comparison of the effects of two different Au surfaces has been presented. In particular 4HCB has been found to lie flat on both Au(111) and Au(110). The interaction is weak in both cases even if on the Au(110) surface some of the molecules are found to interact strongly via their -CN group.

The other hybrid interface presented in this thesis is an organic donor/acceptor heterojunction, which is the interface where exciton separation process is expected to occur and it is therefore critical for the organic photovoltaics efficiency.

I have studied the detailed morphology of three different donor/acceptor systems as a function of the shape complementarity between donor and acceptor molecules. In particular I have investigated the coupling of three different hexabenzocoronene (HCB) derivatives, namely f-HBC, c-HBC and DBTTC with the fullerene (C60) acceptor. The different degree of contortion between the three donor molecules is reflected in a different morphology at the interface with C60. The signal coming from the interface region has been analyzed making use of the specific developed theoretical model, that we called $\beta$-model, in which the $\beta$ parameter describes the degree of intermixing between the donor and acceptor film deposited one on top of the other. We have demonstrated that the degree of intermixing increases with the degree of contortion. Indeed the $\beta$ parameter is equal to 0.3 in the case of f-HBC/C60 system, where f-HBC presents a flat shape which does not show any complementarity with C60, and equal to 0.7 and 0.9 for c-HBC/C60 and DBTTC/C60 respectively. However the higher $\beta$ value has not been found for the most contorted donor molecule, i.e. c-HBC, but for DBTTC whose degree of contortion is slightly less than c-HBC.

Moreover, the study of the reorientation of the donor molecules passing from the pristine film to the heterostructure shows a rearrangement of the molecules in the intermixed phase for all the three systems. The application of the $\beta$-model to the polarization dependent NEXAFS allows to calculate the change in the mean molecular tilt angle of the donor molecules when the C60 film is deposited on top of the pristine donor film.

In particular f-HBC has a mean angle of 14° in the pristine phase that becomes 30° in the intermixed region, c-HBC changes from 25° to 50° and DBTTC from 25° to 36°. The stronger intermixing in the case of DBTTC is therefore probably not due to a higher interaction energy between DBTTC and C60 which would produce also a higher molecular rearrangement in the interface region. It is rather driven by the reticulated network
that DBTTC presents in its pristine phase, which would support the C60 interdiffusion through its cable-like pristine structure. The larger intermixed volume corresponds to a higher active volume available for exciton dissociation and indeed the OPVs made with the three systems present an efficiency that increased with the degree of intermixing. Moreover molecular shape matching drives self-assembly into an extended intermixed interface in which the physical alignment of the nested donor/acceptor partners enables optimal charge transfer efficiency, giving a faster charge transfer time for the contorted than for the flat system [71].

The study of both charge transport phenomena and hybrid interfaces organization is crucial to make progress in the organic electronics field. Therefore this more fundamental kind of research has to be coupled with the application of organic semiconductors into real devices. I have presented a study on a graphene based tandem solar cell whose perspective is that to reach the efficiency of inorganic solar cells. In particular I have shown a novel technique to transfer the graphene onto organic substrate, that make possible the integration of graphene into organic devices.
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