

Experimental and Theoretical Studies of the Near Edge X-ray Absorption Fine Structure Spectra and Dominant Nanoelectronic Transport Process in Organic Molecules

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The investigation of the electronic structures of hole transporting layers are very important to understand their proprieties in the process of charge transfer. The compounds most used as hole transporting layers are *N,N'*-di(naphthalene-1-yl)-*N,N'*-diphenyl-benzidine (NPB) and *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), but few works about inner shell spectroscopy have been performed to study of the electronic structure of these materials. The *Near Edge X-ray Absorption Fine Structure* (NEXAFS) spectra are interpreted with help of partial and total density of states calculation for each molecule. The molecules present a transition at $N_{1s} \rightarrow \pi^*$ for *lowest unoccupied molecular orbitals* (LUMOs) of the naphthyl and biphenyl groups from NPB and TPD molecules, respectively. The molecular systems present a typical behavior of bi-directional diode with the electrons do not tunnel through vacuum but through the LUMO.

Keywords: Photoabsorption, Organic Light-Emitting Devices, NEXAFS Spectroscopy, Synchrotron Radiation, Density of States.

1. INTRODUCTION

The *organic light-emitting diodes* (OLEDs) are devices that nowadays have been largely studied due to its luminescent proprieties in relation at the inorganic LEDs. The organic electroluminescent materials have attracted much attention because their potential applications to produce full color and flexible flat panel organic light-emitting displays.¹ Intensive investigations on OLEDs have been motivated to develop new generation display and lightening devices with low energy consumption.² OLEDs represent a promising technology for large, flexible, lightweight and flat-panel displays.

Near Edge X-ray Absorption Fine Structure (NEXAFS)³ is an element-specific electron spectroscopic technique, which is sensitive to bond angles, bond lengths and the presence of adsorbates. The NEXAFS spectroscopy is one of the powerful tools for studying organic materials by means the electronic structure of atoms or

molecules through the excitation of core electrons to *Lowest Unoccupied Molecular Orbital* (LUMO). It requires a monochromatic light source with enough energy to promote the electron from the core to an unoccupied orbital. The *density of states* (DOS) of a system describes the number of states at each energy level that are available to be occupied.⁴ The comparing DOS simulation results for molecular systems provide a detailed description of the structure to the measured NEXAFS.⁵

The *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)(1,1'-biphenyl)-4,4'-diamine (or TPD) molecule is often used in OLEDs like hole transporting layer, but in the last year new materials have been used due to highest stability (for example, with respect to the degradation process^{6–8}) like is the case of the *N,N'*-di(naphthalene-1-yl)-*N,N'*-diphenyl-benzidine (or NPB) molecule. When an electric field is applied, electrons are injected by the cathode into the LUMO of the adjacent molecules and holes are injected by the anode into the HOMO (Highest Occupied Molecular Orbital).⁹ The study of these molecules may

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provide important information on the carrier transporting mechanism and lead to some useful clues on designing better hole transporter. It is essential to know the detailed bonding configurations of the constituent elements in order to understand their hole-transporting properties; the electronic structure of these materials have not been studied in detail.⁹

In resume, NEXAFS is the excitation of atomic core electrons (for light elements such as Carbon, Nitrogen and Oxygen) to unoccupied valence orbital; which this may be interpreted by use of molecular orbital theory. The energies of the core levels, HOMOs and LUMOs, may be easily identified by theoretical calculations of the ground state, which predicts values that are few eV lower than experimental data, due to neglecting the core hole effect. The *projected or partial DOS* (PDOS) of the constituent atoms provide information about contribution of the individual atoms for *total DOS* (TDOS) in the electronic structures by the qualitative analyses. The PDOS to individual atom-orbital would not only reveal the properties of electronic states in the bands and in the gap as well as their relationship with the atoms involved, but would also provide information of bonding between the atoms.

On the other hand, by analyzing the contribution of the electronic states from individual atoms to a particular molecular orbital, it would be also convenient to obtain the localization of the states and chemical properties of the atoms. For instance, the atoms in which the HOMO resides would provide information on the sites of chemical reaction and possible excitation in the molecule.¹⁰

The theoretical prediction of unipolar molecular diodes has led to application in molecular electronics, which could to solve fundamental scaling limits in *Metal Oxide Semiconductor* (MOS) integrated circuits.¹¹ The electronic transport in single molecules has been investigated with break junctions and a variety of Scanning Probe Techniques (SPT). The conductance in the molecules differs by orders of magnitude due to the presence of an additional tunneling gap in SPT, to uncertainties in the number of molecules measured, or to poorly defined device surface areas.^{12, 13} Molecular rectifiers were first suggested by Aviram and Ratner.¹¹ Their design called for the placement of an organic molecule containing a covalently linked electron donor-acceptor pair between two metal electrodes. The hypothesis underlying this design is based on the relative energies of the HOMO of the donor and the LUMO of the acceptor: the current observed with one bias voltage (resulting from resonant electron transfer from the LUMO of the acceptor to the HOMO of the donor) would be greater than the current for the opposite bias (resulting from nonresonant transfer).^{11, 14} Once that the molecules have HOMOs and LUMOs energies very similar, we can use a simple and rapid proceeding to identify some properties and it will facilitate the interpretation of the spectra.

In this work, the NEXAFS spectra are interpreted with the help of theoretical calculation in the investigation of

the frontiers molecular orbitals (FMOs), DOS and charge transfer (current indicative) for NPB and TPD molecules. An important question that arise is about the electronic transport process, which the simulation will provide information if this process is dominated by electron tunneling through vacuum or by LUMO.

2. MATERIAL AND METHODS

2.1. Experimental Details

The NPB and TPD films was deposited on substrate of Indium-Tin-Oxide (ITO) coated glass, where they were successively thermally evaporated onto ITO at room temperature from tungsten crucibles. The NPB and TPD films present a thickness of ~ 50 nm. The system of deposition is formed by a micro quartz balance put under deposition support under a pressure $\sim 1 \times 10^{-6}$ Torr and the deposition rate ~ 0.3 nm/s. NEXAFS measurements were carried out at: 1—*Spherical Grating Monochromator* (SGM) 270–1000 eV beamline¹⁵ of the Brazilian Synchrotron Light Source (LNLS), with pressure $\sim 1 \times 10^{-9}$ Torr; 2—*Total Electron Yield* (TEY) mode and the angle of the incident photon was maintained at 30° between the incident X-ray and the sample's surface normal. Both molecules present an HOMO and LUMO with energy very similar.¹⁶

2.2. Theoretical Methodology

For the computational description of the (NPB and TPD) molecules investigated, all quantum chemical calculations like geometry optimization, PDOS, TDOS, FMOs and charge transfer (current indicative) were carrying out using the Gaussian 09 packages¹⁷ based *Density Functional Theory* (DFT) with B3LYP (Hybrid or Exchange-Correlation Potential) functional and 6-311G(d) polarized basis set, i.e., DFT/B3LYP/6-311G(d) for single molecules in a gas phase. These molecules are basically composed of biphenyl (Biph), two benzene rings (Benz-1 and Benz-2) and two nitrogen atoms (N) locating at two junctions. So, Figure 1 exhibits that these molecules were divided into five groups and the N atom, to compose the PDOS. The Figure 1(a) is NPB molecule consists of the groups: N atoms (two), benzene (Benz-1 and Benz-2), naphthalene (Naph-1 and Naph-2) and biphenyl (Biph) and the Figure 1(b) is TPD molecule, with groups: N atoms (two), benzene (Benz-1 and Benz-2), 3-methyl-benzene (Methyl-1 and Methyl-2) and biphenyl (Biph).

The parameters obtained of the geometry for the analyzed structures were fully optimized with DFT/B3LYP contained in Gaussian package¹⁷ in the presence of an external electrical field, using a closed shell model for the Roothaan-Hall matrix equation that is similar the Kohn-Sham equation, because are solved by expanding the atomic orbitals by means of the Linear Combination of Atomic Orbitals (LCAO) approximation over a 6-311G(d) basis set that is an approximate representation

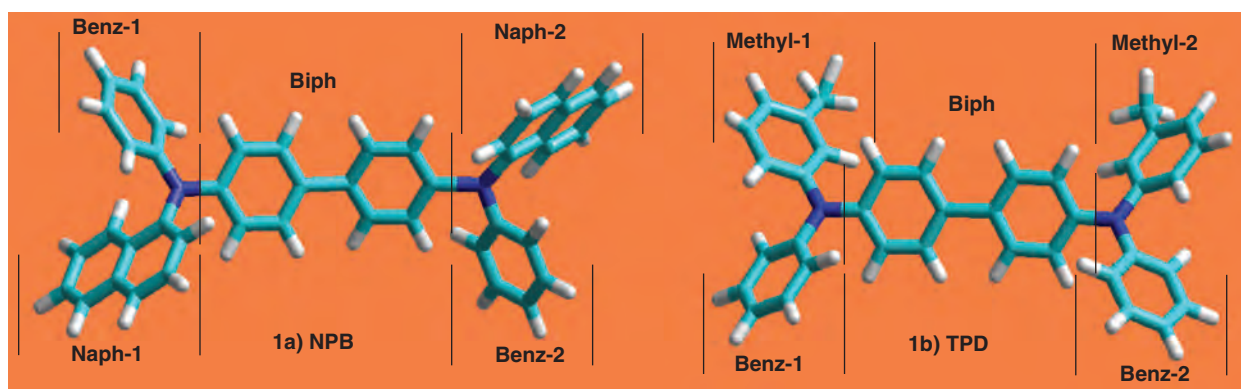


Figure 1. Molecular structure and how the molecules were divided to represent the different contributions of the partial or projected density of state (PDOS) for (a) NPB and (b) TPD.

of the Atomic Orbitals (AOs) for the Molecular Orbitals (MOs),

$$FC = SCE \quad (1)$$

with S (overlap integral matrix), C (coefficient matrix in the linear combination of atomic orbitals), E (orbital energy diagonal matrix), F (Fock matrix) as

$$F_{\mu\nu} = \int dv v_{\mu} \left[-\frac{1}{2} \nabla^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} \right] \varphi_{\nu} + \sum_{\lambda=1}^K \sum_{\sigma=1}^K P_{\lambda\sigma} \left[(\mu\mu | \lambda\nu) - \frac{1}{2} (\mu\mu | \nu\sigma) \right] + V_{\mu\nu} \quad (2)$$

where the three terms in $F_{\mu\nu}$ describe the core energy, the Coulomb and exchange interaction, and the external fields (V), respectively. The $(\mu\nu | \lambda\sigma)$ and $(\mu\lambda | \nu\sigma)$ are two electronic integrals that may involve up to four different gaussian basis function as Φ_{μ} , Φ_{ν} , Φ_{λ} , Φ_{σ} . If these two terms remains unknown, they must be approximated by local-density approximation (LDA). From the Roothaan-Hall matrix we obtain the charge distribution through of the molecular system.^{18,19} The DFT/NEGF methodology has proven to be quite efficient to investigate the electronic transport in molecules^{20–23} and molecular junctions.²⁴

3. RESULTS AND DISCUSSION

Figure 2 exhibits experimental NEXAFS spectrum:

(a) at the N_{1s} -edge of the NPB films. The peaks located at energies of 401, 407, 410 and 420 eV, which correspond to at $N_{1s} \rightarrow \pi^*$, σ_1^* , σ_2^* and σ_3^* transitions, respectively. (b) at N_{1s} -edge of the of the TPD films. The peaks located at energies 401, 407 and 410 eV correspond to $N_{1s} \rightarrow \pi^*$, σ_1^* and σ_2^* transitions.

The $N_{1s} \rightarrow \pi^*$ transition of the NPB films at 401 eV, which has less intensity due to the orientation of the molecule with respect to the polarization of the photon beam, corresponds to a transition to the LUMO, with the electronic density localized at the naphthalene. The σ^*

transitions are due to the contribution from different rings as benzene and biphenyl, which compose the NPB molecule.²⁵ The $N_{1s} \rightarrow \pi^*$ transition of the TPD films at 401 eV is due to orbital of the carbon of p character of the biphenyl group. The N_{1s} photoabsorption spectrum does not exhibit a π^* related LUMO. The σ^* transition presents a contribution of different benzene rings, which make difficult to point out its contribution to that transition. The N atoms in TPD are nominally sp^3 hybridized but with some planarization of the molecule to take advantage of the resonance delocalization with benzene rings.

From theoretical calculations, we analyze the different contributions associated to the TPD and NPB molecules. The first absorption feature (at 401 eV) is due to transitions from N_{1s} levels to mixed states of LUMOs that contains only C.

Treusch et al.²⁶ reported that the HOMO of the TPD is strongly delocalized over benzene rings with significant contribution from the lone pair of electrons of the N. According to computational method employed, the LUMO of the TPD molecule is localized over biphenyl, i.e., mainly over the C atoms of the two-phenyl rings that interconnect the two N atoms, which has sp^3 hybridization. However, the NPB molecular orbitals show that HOMO electronic density is localized over biphenyl group with a contribution from the lone pairs of the N atoms (the reaction sites more probable).²⁷ The N atom present a highest contribution in the process of charge transport due to its pair of electrons weakly bound and it due to the localization, and its sp^3 hybridization. The LUMO electronic density is localized over the naphthalene group.

Figure 3 exhibit the HOMO and LUMOs of the (a) NPB and (b) TPD molecules calculated by DFT at the B3LYP/6-311G(d) level for the ground state. The previous DFT study for HOMO and LUMOs levels is agreed with resulted shown for Moewes et al.²⁸ to the NPB molecule that have shown the molecular orbitals (HOMO, LUMO up LUMO + 3) much more localized in the naphthyl groups. These molecular orbitals also present a p features

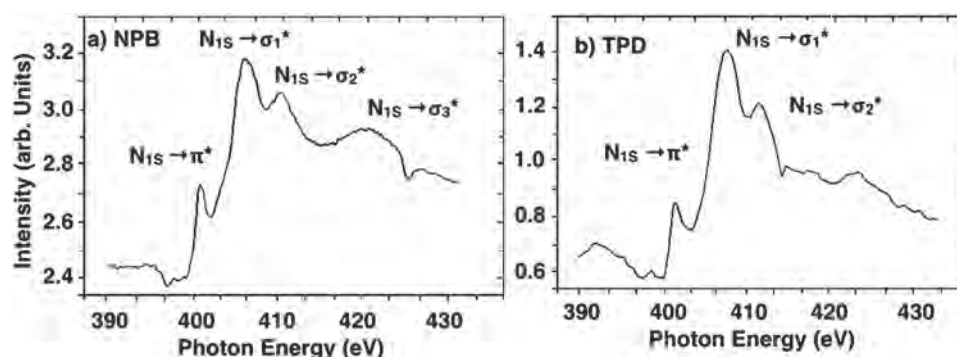


Figure 2. NEXAFS spectrum of the: (a) NPB and (b) TPD molecules at N_{1s} -edge obtained from SGM beamline.

dominant. The HOMO, LUMO and LUMO + 3 of the TPD molecule calculated at the B3LYP/6-311G(d) level obtained by ground state calculation have shown an electronic density much more localized in the biphenyl group, while LUMO + 1 to LUMO + 2 are more localized in the

benzene and methyl groups (end of the TPD molecule). The difference of energy between them is small, resulting in an asymmetry in the π^* transition of the experimental measure. These molecular orbitals also present a p features dominant.

The LDOS provides the major contributors to the DOS. Although calculating the isolated molecule in gas phase, the calculations suggest a correlation in the study of structures in condensed state.²⁹ The TDOS and PDOS (individuals groups that form the molecules) calculated of the NPB and TPD molecules are presented in the Figures 4(a and b). Figures 4(a) shows that the LUMO of the NPB is localized on naphthalene group, and Figures 4(b) shows that LUMO is localized on biphenyl part of the TPD molecule, i.e., on the carbon atoms of the two-phenyl rings that interconnect the two N atoms. They present a p features dominant.

The energies of the core levels and unoccupied (virtual) molecular orbital obtained by computational simulation for gas phase may construct a schematic molecular orbital diagram relevant for the NEXAFS spectra for NPB and TPD molecules.

The $N_{1s} \rightarrow \pi^*$ transition are for naphthalene and biphenyl orbitals for NPB and TPD molecules, respectively. The σ^* orbital type has contribution of more than one molecule group. The σ^* resonances is related to the lifetime of the quasi-bound electronic state and the theoretical description for electron excitation from inner shell does not consider the increasing decay probability of the electron in the continuum state.³ For the case of the $N_{1s} \rightarrow \sigma_1^*$ transition, there is contribution of Benz-1, Benz-2 and biphenyl groups, for both molecules. Computational procedures are very important to the characterization of compound chemical, but the correlation with experimental measures (mainly in NEXAFS measure) are necessary in many cases, principally when we are comparing molecules with similarities in its molecular geometry.

To understand better the process of hole injection, an electron will be excited at N atom involving the HOMO state (in your case N_{1s}) from LUMO state, and due to electron deficiency the molecule will be stabilized by the delocalized π characters of adjacent carbon atoms,³⁰ and a new excitation will happen from N atom to LUMO states.

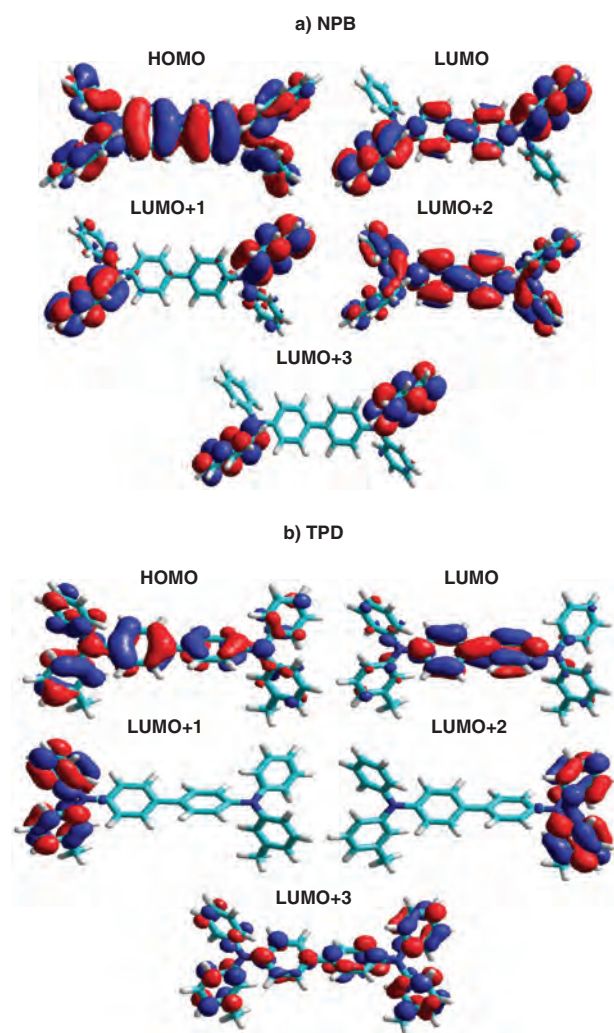


Figure 3. HOMO and LUMOs for molecules: (a) NPB and (b) TPD carried out by DFT at B3LYP/6-311G(d).

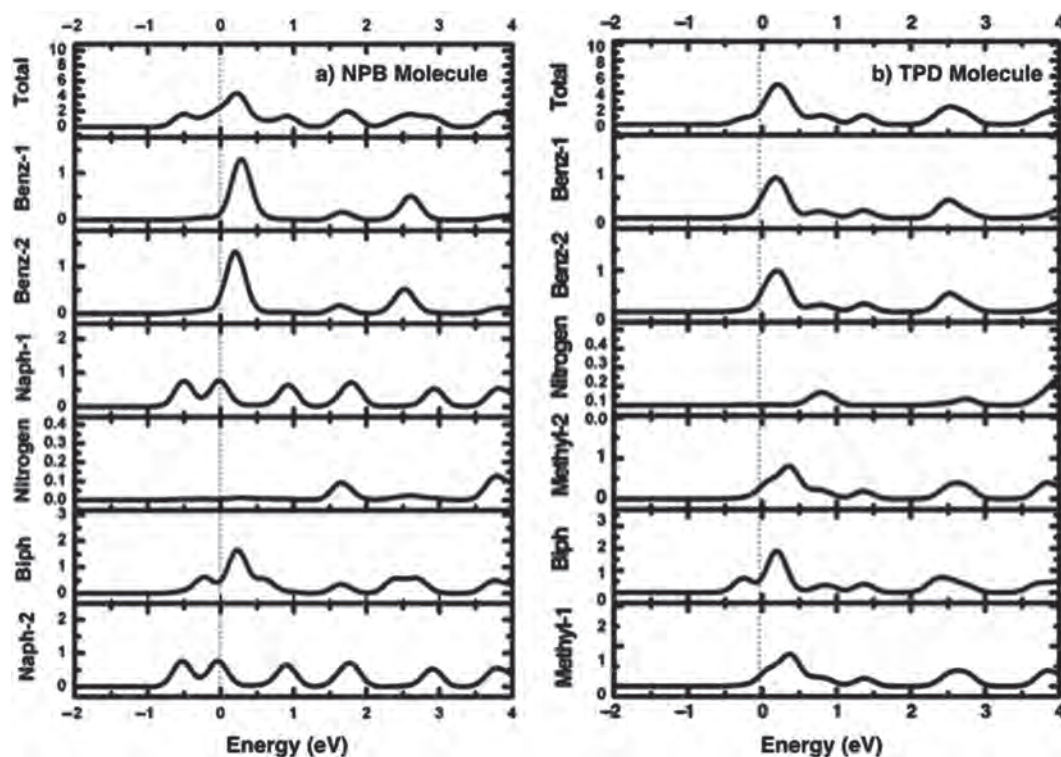


Figure 4. The figures show the different contributions in the formation of the TDOS and LDOS for the NPB (a) and TPD (b) molecules and yours respective groups from DFT calculation.

However, is charge mobility (due to at the excitation) a process dominated by electron tunneling through vacuum or by LUMOs?

From theoretical methods we can determine the electronic transport by means charge transfer (or charge transport) in the molecules subject to an external electric field^{31–34} whose lengths of the NPB and TPD molecules are $L_{\text{NPB}} \approx 21 \text{ \AA}$ and $L_{\text{TPD}} \approx 19 \text{ \AA}$, respectively. The devices can be seen at the Figures 5(a and b) below, where they were submitted the external voltage (V) for forward and reverse bias.

Figures 6(a and b) show that these molecular systems have one resonance for forward and reverse bias.

This behavior is typical of bi-directional diode and they begin the light emitter as an OLED in ± 1.06 Volts (for NPB) and ± 1.15 Volts (for TPD). When the current level reach the resonance around 1.0 Volts for positive and -1.0 Volts for negative bias, a rectification is seen in the current graphic, which it is related at the frontier molecular orbitals delocalized through all molecule. In zero bias, the current increases linearly with applied bias. This is expected for a metal–insulator–metal junction when the

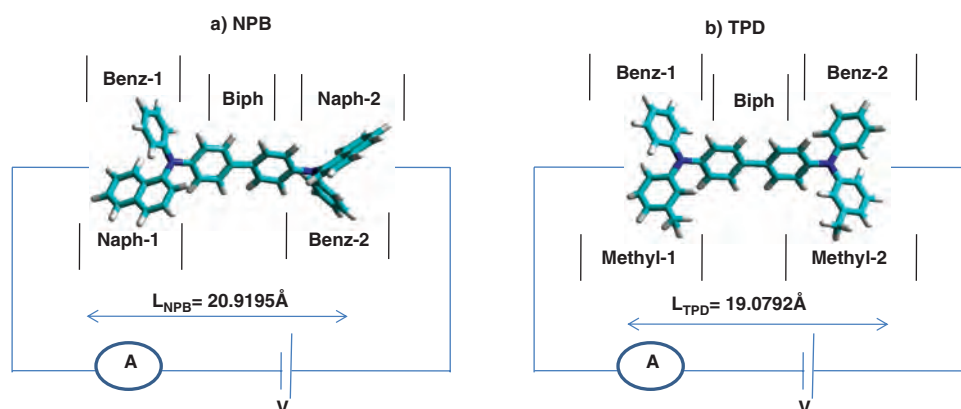


Figure 5. Exhibit a pictogram of the molecular systems under applied voltage where the current reading can be done with amperimeter (A). (a) NPB and (b) TPD devices.

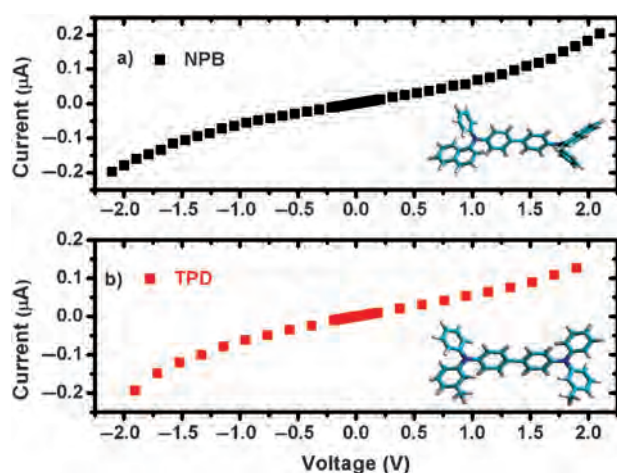


Figure 6. It presents the charge transfer versus voltage for the (a) NPB and (b) TPD device. In between -1.0 and 1.0 Volts the results present an Ohmic behavior, i.e., a linear straight curve obeying the first Ohm's Law. It comes from the alignment between the emitter Fermi level and the tail of the broaden higher level.

mean tunnel barrier height is larger than the applied voltage. Furthermore, tunneling is a nondependent process of the temperature in both molecules. Supposed that the molecular junction is with metal, it implies that the mean tunnel barrier height from the Fermi level of the metal to the LUMO is smaller than the work function of the metal. In this case, the electrons do not tunnel through vacuum but through the LUMO (which it is possible to see in the heterojunction in OLEDs).

4. CONCLUSION

We have studied two compounds hole transporter a lot used in organic light-emitting devices (OLEDs) by NEXAFS spectroscopy to investigate the element-specific electronic structure. The similarity of the spectra does not allow obtaining an interpretation in relation to the LUMO involved in the excitation from an inner shell electron, which it could lead to a wrong interpretation of the spectra. The LUMO for both present similarities but NPB molecule has the electronic density on naphthyl group, while TPD molecule has electronic density on biphenyl group. The charges transfer versus voltage for the NPB and TPD devices show that the electrons tunnel through of the LUMOs. The use of the theoretical tools is important in the interpretation of NEXAFS spectrum and have shown excellent result in X-ray absorption process.

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