Study of frontier orbitals of a non-interacting PBI derivative thin film by UPS/IPS, Cyclic Voltammetry and optical absorption spectroscopy

Caroline Arantes[1*] (PG), Markus Scholz[2] (PG), Volker Dehm[4] (PG), Frank Würthner[4] (PQ), Achim Schöll[2] (PQ), Friedrich Reinert[2] (PQ), Maria Luiza M. Rocco[1] (PQ). *luiza@iq.ufrj.br

1 Universidade Federal do Rio de Janeiro, Instituto de Química,, 21941-909, Rio de Janeiro, Brazil
2 University of Würzburg, Experimental Physics II, 97074, Würzburg, Germany
4 University of Würzburg, Organic Chemistry, 97074, Würzburg, Germany

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Introduction

Charge carrier levels with respect to the electrode are needed for understanding and improving the performance of electronic devices based on organic thin films. Charge carrier injection and transport occurs in the frontier orbitals of the organic semiconductors: highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). These frontier orbitals have been estimated, directly or indirectly, by two different experimental approaches. The first one is based on photoemission and inverse photoemission spectroscopies and, the second one is based on cyclic voltammetry and optical absorption spectroscopy. Perylene tetracarboxylic acid bisimides (PBI) are electron-acceptor dye molecules that represent a class of highly thermostable n-type semiconductors with relative high electron affinity, excellent transport properties and versatile physical, chemical and electronic properties. As reported earlier, these molecules are very interesting due to the possibility of tailoring their redox and, by consequence, electronic properties (in terms of band gap and type of conductivity) by appropriated functionalization. The main goal of this work was to evaluate how the correlation between the frontier orbital energies (HOMO and LUMO) and electrochemical potentials (oxidation and reduction) of a non-interacting perylene bisimide derivative (PBI-Ph(iPr)$_2$) will fit in the experimental linear relationship proposed in the literature using different organic semiconductor films. The importance of verifying how appropriate is this relation to determine the frontier orbital from the electrochemical potentials is straighforward, since compared with other available techniques, the CV is simple, non-expensive and fast to run, so that it might be used in routine work to control the frontier orbital energies and energy diagrams during the production of the organic molecular films.

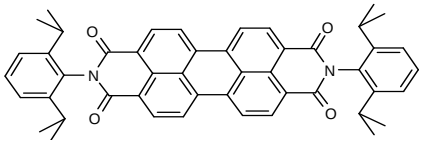

Figure 1. Molecular structure of PBI-Ph(iPr)$_2$.

Results and Discussion

We have employed UPS/IPS measurements to probe the frontier orbital energies and transport gap of the PBI-Ph(iPr)$_2$ thin solid film, and CV and optical absorption spectroscopy to probe the electrochemical potentials and optical gap energy in solution. This non-interacting PBI derivative could be an ideal system to evaluate and compare these parameters obtained at different conditions, since neither in solution nor in solid film there is strong intermolecular interaction in this system, being considered as single molecule or monomer. The ionization energy, electron affinity and energy diagram were also determined using the spectroscopic and electrochemical techniques. The obtained values are compared between them. Optical absorption spectra of PBI-Ph(iPr)$_2$ showed no aggregation in solution as well as in thin films, which turns it an ideal molecular system to evaluate the correlation between frontier orbital energies and electrochemical potentials, since there would be no strong intermolecular interactions in solution-based CV and UPS/IPS measurements in solid film.

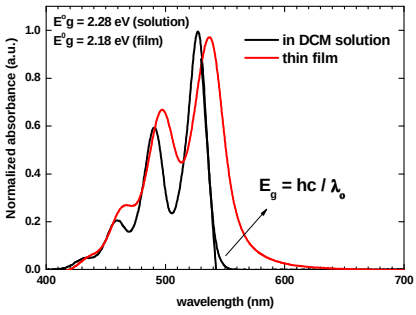

Figure 2. Optical absorption spectra of PBI-Ph(iPr)$_2$.

The correlation between HOMO and oxidation potential fits better to the empirical equation than those obtained for LUMO and reduction potential. Even so, the energy levels and electrochemical potentials obtained in this work are still in good agreement with the empirical linear equation described in the literature. The frontier orbital

energies estimated by CV and UV-visible have shown higher values than those obtained by UPS and IPS.

This result suggests that image charge effects can play a significant role due to adsorption of the molecules during the redox process in CV measurements. The influence of different surface and solution effects to estimate the energy level values obtained by these different techniques is an issue and, a fully comprehension of these effects is still a challenge for the researches.

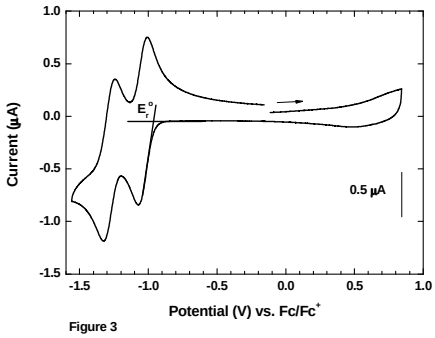

Figure 3. Cyclic voltammetry of PBI-Ph(iPr)$_2$ in CH_2Cl_2 solution.

Conclusions

In this work, we investigate N,N'-di(2,6-diisopropylphenyl)perylene-3,4,9,10-tetracarboxylic acid bisimide, (PBI-Ph(iPr)$_2$) molecule using ultraviolet photoemission spectroscopy (UPS), inverse photoemission spectroscopy (IPS), optical absorption spectroscopy and cyclic voltammetry (CV). The relationship between the transport energy levels or frontier orbitals (HOMO and LUMO) with the electrochemical potentials (E_{ox} and E_{red}, respectively) obtained for this molecule was evaluated taking into account the linear regression obtained empirically in the literature. The correlation between the HOMO/LUMO energies and the oxidation/reduction potentials has shown good agreement with the experimental linear relations using different organic semiconductor films. Different solid and solution effects play significant role in the measured values, being still an issue. Since these parameters are important for understanding electrical, electronic and optical phenomena in organic semiconductor films, such as charge carrier generation, charge carrier injection and charge transfer phenomena, it is very important to perform more research using different systems to get reliable information about these parameters.

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