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| 14. ABSTRACT Despite the technological and scientific importance of semiconducting organic materials, there have been few studies of their valence band electronic structure using modern synchrotron radiation-based spectroscopic methods. The combination of high resolution soft x-ray emission, soft x-ray absorption, and high resolution photoemission spectroscopy was used in this program to measure the detailed electronic structure of a selection of organic semiconductor thin films. The films were grown in a custom built organic molecular beam epitaxy chamber attached to a multi-technique spectrometer chamber stationed on a soft x-ray undulator beamline at the National Synchrotron Light Source. Information was obtained on the element and site specific valence band partial density of states, chemical state, and orbital bonding in the films. Materials studied include aluminum tris-8-hydroxyquinoline (Alq ₃), titanyl phthalocyanine (TiO-Pc), and vanadyl phthalocyanine (VO-Pc) | | | | | |
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1. Introduction

Organic semiconductors have been the subject of intense study due to technological interest in developing carbon-based electronic devices, and due to the challenge they pose to our understanding of the physical properties of complex solids. While much progress has been made in the synthesis and doping of thin film organic semiconductors, there is a remarkable lack of comprehensive, detailed measurements of electronic structure in these materials. The objective of this program was to rectify this situation. Specifically, the electronic structure of *in-situ* grown thin film organic semiconductors was studied using synchrotron radiation-excited soft x-ray emission spectroscopy (XES), x-ray photoemission spectroscopy (XPS), soft x-ray absorption spectroscopy (XAS) and resonant inelastic x-ray scattering (RIXS). The goals of the program included using XES and XAS to measure the element specific partial density of states for both the valence and conduction bands, using RIXS to measure on-site and charge transfer excitations, using XPS to measure core level binding energies and bonding interactions, studying the effect of doping on the electronic structure, and finally investigating the nature and severity of x-ray photon beam damage to these materials. Each of these goals was attained.

2. Accomplishments/New Findings.

We have performed a number of successful experiments supported by this award. Our experiments are performed at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory on Long Island, New York, with all films grown *in-situ* using organic molecular beam deposition. The highlights of our work are as follows:

a) Alq₃: We have studied the electronic structure of aluminum tris-(8-hydroxyquinolate) (Alq₃) which is one of the key electroluminescent materials used today in OLED devices.¹ We used our combination of synchrotron radiation-excited spectroscopies, together with density functional theory (DFT) calculations to present a thorough joint experimental and theoretical investigation of the electronic structure of Alq₃.² XPS and XAS have previously been used to investigate the occupied and unoccupied states of Alq₃ with comparison to DFT calculations of the density of states.^{3,4} Our C, N and O K-edge emission spectra are in excellent agreement with the corresponding DFT calculated partial densities of states (PDOS), but differ from previous x-ray emission studies.⁵ Due to the long acquisition time required for the weak signal from this second order process, any organic material can suffer significant synchrotron beam damage, and Alq₃ is no exception.⁴ We circumvent this by continuously translating our samples during the measurement, at a rate of approximately 40 microns per second, and explain the difference between our results and previous x-ray emission studies in terms of the latter exhibiting beam damage.⁵ Valence band XPS (VB-XPS) of thin Alq₃ films was found to be in agreement with earlier studies by Curioni *et al.*³

b) F₁₆CuPc and CuPc: The fundamental properties⁶ and technological applications⁷ of metal phthalocyanines (M-Pc) have been the subject of much research, and indeed M-Pcs are one of the foremost planar organic molecular semiconductors used in many organic optoelectronic devices.⁸ Of this family, there has been increased attention in recent years paid to CuPc and its derivatives F₁₆CuPc and K-doped CuPc.^{9,10} While CuPc semiconductor films are *p*-type in air,¹¹ F₁₆CuPc is one of the few organic molecules exhibiting high performance and stability in air in *n*-type operation.¹² Aside from providing insight into the role of hydrogen in the observed proclivity towards *p*-type character of organic semiconductors,¹³ F₁₆CuPc is naturally advantageous from the perspective of future device applications, for example in organic field effective transistors.¹⁴⁻¹⁶ As a result, there is a need for information regarding the bulk electronic properties of F₁₆CuPc, as well as regrading interface electronic structure. Synchrotron radiation-excited photoemission spectroscopy and x-ray absorption spectroscopy (XAS) studies have previously been undertaken to investigate the energy alignment of acceptor-like CuPc and donor-like F₁₆CuPc heterojunctions.¹⁷ The importance of the energetic location of the charge-neutrality level (CNL) of organic semiconductors in determining the formation of the interface organic interfaces has been highlighted recently both experimentally and theoretically,¹⁸⁻²⁰ including for CuPc and for partial fluorinated F₄CuPc metal interfaces.²¹ By analogy with inorganic semiconductors (where the CNL plays an important role in the formation of the interface),²² further manipulation of their near-surface/interface properties can only be achieved following improved understanding of their bulk electronic structure.

The bulk electronic structure F₁₆CuPc is less well understood than that of CuPc.^{23,24} We used XES of the C, N and F *K*-edge electronic structure of pristine F₁₆CuPc films and made direct comparisons with similar measurements from CuPc. XES is an element- and orbital-selective probe of the occupied states within these planar organic compounds, and two earlier XES studies of these molecules exist.^{9,25} We observed distinct differences in the carbon environment (in contrast to the nitrogen environment) between the two molecules in XAS and x-ray photoemission spectroscopy (XPS) measurements, which are in agreement with other metal fluorinated and non-fluorinated Pc molecules.^{17,23,24,26,27} While the N *K*-edge XES spectra of the two samples are similar (as for the XAS), we found significant differences between the C *K*-edge XES of the two molecules. This finding is in contrast to earlier reports F₁₆CuPc and CuPc,⁹ and we attribute this to x-ray induced sample degradation in earlier work. Our experimental emission results are in agreement with theoretical calculations of based on DFT within the Stockholm-Berlin (StoBe) method,²⁸ for not only the C *K*-edge of the two molecules but also the N and F *K*-edge emission spectra of F₁₆CuPc. The agreement between theory and experiment enables us to assign spectral features in terms of contributions from particular atomic sites. Additional site-specific information is obtained from examining the C *K*-edge resonant x-ray emission spectroscopy (RXES), which provides detailed electronic information regarding specific carbon sites, as shown for example with benzene,²⁹ CuPc,²⁵ and Alq₃.²

c) **AlCIPc/C₆₀:** Despite significant recent advances in photovoltaic cell performance, current power conversion efficiencies remain too low to make such cells commercially viable. One key issue that remains poorly understood is the energy level alignment at the organic-electrode and organic heterojunction interfaces. The interfacial energetics play a key role in determining important cell parameters such as the open circuit voltage (V_{OC}). Recent studies in small molecule multilayer heterojunctions devices^{30,31} and in polymeric bulk heterojunctions^{32,33} have shown that the magnitude of the V_{OC} appears to correlate with the energy difference between the HOMO level of the donor and the LUMO level of the acceptor molecules. The energy level alignments at organic/metal, organic/insulator, and organic/organic interfaces have been studied by several research groups.³⁴⁻³⁷ As part of a new collaboration with Professor Tim Jones from the University of Warwick in the U.K., we measured the energy level alignment of a fullerene (C₆₀)/chloro-aluminum phthalocyanine (CIAIPc)/indium tin oxide (ITO) bilayer system. CIAIPc/C₆₀ organic PV cells have recently been shown to display a greater V_{OC} than that routinely observed for CuPc/C₆₀,³⁸ however little is known about the detailed interfacial electronic structure. The interface electronic structure of C₆₀/CIAIPc/ITO bilayers, grown *in situ* using OMBD, was measured using synchrotron radiation-excited photoelectron spectroscopy. This spectroscopy allows the energy difference between the HOMO level of CIAIPc and the LUMO level of C₆₀ to be determined. XAS was used to estimate the molecular orientation of the CIAIPc grown on ITO. We found that the CIAIPc deposition rate affects the molecular orientation relative to the ITO substrate, and that this in turn modifies the energy level alignment at the organic heterojunction interface.^{38,39}

d) **TFAC:** In collaboration with Professor Linda Doerrer, we have started to study a new copper organic material that exhibits similar UV-vis properties and similar packing in the solid state as CuPc, and may therefore exhibit similar or perhaps greater conductivity. This material, is N,N'-Ethylene-bis(1,1,1-trifluoropentane-2,4-dioneiminato)-copper(ii), and is abbreviated Cu(TFAC). We have undertaken an extensive experimental and theoretical investigation of the electronic structure of thin films of Cu(TFAC) using synchrotron radiation-excited XES, XAS, and photoelectron spectroscopy, together with density functional theory (DFT) calculations.

3. Personnel Supported.

Directly supported: Yufeng Zhang (Ph.D Student), Alex DeMasi (Ph.D. Student).

Affiliated BU personnel: Dr. Louis Piper, Dr. Sang Wan Cho.

Collaborators: Dr. Anne Matsuura (formerly AFOSR); Professor Cormac McGuinness (Trinity College Dublin); Professor James Downes (McQuarie University, Melbourne); Professor Tim Jones (University of Warwick, UK); Professor Linda Doerrer, BU.

4. Publications.

The following papers were produced:

a) "Electronic Structure of C₆₀/AlClPc/ITO Interfaces studied using Soft X-Ray Spectroscopies"

S. W. Cho, L. F. J. Piper, A. DeMasi, K.E. Smith, K.V. Chauhan, I. Hancox, P. Sullivan, R. A. Hatton, and T. S. Jones, *Appl. Phys. Lett.* (*submitted*)

b) "Electronic Structure of the Organic Semiconductor Alq₃ (aluminum tris-8-hydroxyquinoline) from Soft X-ray Spectroscopies and Density Functional Theory Calculations"

Alex DeMasi, L.F.J. Piper, Y. Zhang, I. Reid, S. Wang, K.E. Smith, J.E. Downes, N. Peltekis, C. McGuinness, and A. Matsuura, *J. Chem. Phys.* **129**, 224705, (2008)

c) "The Local Electronic Structure of Tin Phthalocyanine studied by Resonant Soft X-ray Emission Spectroscopies"

N. Peltekis, B. Holland, L.F.J. Piper, A. DeMasi, K.E. Smith, J.E. Downes, I.T. McGovern and C. McGuinness, *App. Surf. Sci.* **255**, 764 (2008)

d) "Electronic Structure of the Organic Semiconductor Titanyl Phthalocyanine (TiO-Pc)"

Yufeng Zhang, Shancai Wang, Alex Demasi, A.Y. Matsuura, and Kevin E. Smith, *J. Mater. Chem.* **18**, 1792 (2008)

e) "Electronic Structure of the Organic Semiconductor Vanadyl Phthalocyanine (VO-Pc)"

Y. Zhang, T. Learmonth, S. Wang, A.Y. Matsuura, J. Downes, L. Plucinski, S. Bernardis, C. O'Donnell, and K.E. Smith, *J. Mat. Chem.* **17**, 1276 (2007)

f) "Electronic Structure in Thin Film Organic Semiconductors studied using Soft X-Ray Emission and Resonant Inelastic X-Ray Scattering"

Y. Zhang, J.E. Downes, S. Wang, T. Learmonth, L. Plucinski, A.Y. Matsuura, C. McGuinness, P.-A. Glans, S. Bernardis, and K.E. Smith, *Thin Solid Films* **515**, 394 (2006)

5. Meetings and Seminars

- a) “Soft X-Ray Emission and Resonant Inelastic X-Ray Scattering: Novel Probes of Electronic Structure in Complex Materials”
Advanced Materials and Nanotechnology Conference (AMN4), University of Otago, Dunedin, New Zealand; (February 9, 2009)

- b) “An Introduction to Resonant Inelastic Soft X-Ray Scattering and Soft X-Ray Emission Spectroscopy as Probes of Electronic Structure in Solids, at Interfaces, and at Surfaces”
RIXS-08 Conference, Uppsala University, Uppsala, Sweden; (June 13/14, 2008)

- c) “Soft X-Ray Emission and Resonant Inelastic X-Ray Scattering: Novel Probes of Electronic Structure in Complex Materials”,
Departments of Physics and Chemistry, University of Warwick, U.K. (January 9th, 2008).

- d) “Soft X-Ray Emission and Resonant Inelastic X-Ray Scattering: Novel Probes of Electronic Structure in Complex Materials”;
Department of Physics, Case Western Reserve University, Cleveland, OH; (October 16, 2006).

- e) “Resonant Soft X-Ray Emission and Resonant Inelastic X-Ray Scattering: New Probes of Electronic Structure in Organic Semiconductors”;
2006 AVS National Symposium, San Francisco, CA. (November 15, 2006)

- f) “Electronic Structure of Copper Hexadecafluorophthalocyanine ($F_{16}CuPc$) measured using Soft X-ray Spectroscopies”;
MRS Spring Meeting, San Francisco, CA. (April, 2007) - *Presented by Yufeng Zhang*,

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