Tailoring the Electronic Energy Level Alignment of Metalloporphyrins Adsorbed on Oxide Semiconductor Surfaces

Robert A. Bartynski and Elena Galoppini, Rutgers University

II. Results from Prior NSF Support

Bartynski: [1-20]

NSF-ECS-0224166: *"Development of ZnO Based Room Temperature Spintronics"* [$255,000 (09/02 – 08/06) w/ Y. Lu] We have investigated both epitaxial ZnO thin films (c-axis in plane on r-sapphire) and nanopillars (c-axis □ substrate) grown by MOCVD Fig. 1). We examined a wide range of transition metal dopants, finding Mn and Fe most promising. We have incorporated dopants by diffusion, ion implantation, and in-situ during film growth with appropriate precursors. Both the implantation doped and the in-situ doped samples exhibit ferromagnetic behavior at room temperature. More recent studies are focusing on the effects of co-doping with various metals to controlling carrier type (i.e. *n*- or *p*-) and concentration.

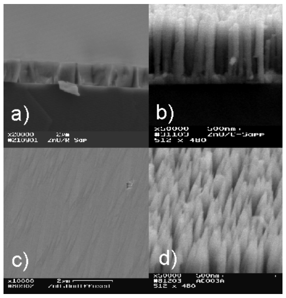


Fig. 1: As-grown (a, b) and Fe-implanted (c, d) MOCVD-grown ZnO epi-films (a, c) and nanopillars (b, d).

NSF-DMR-0304432: "*NER: Development of an Ultrafast Scanning Probe Microscope*," [$100,000 (07/03-6/06), w/ F. Zimmermann] seeking to combine apertureless near-field optical microscopy with femtosecond pump-probe methods to obtain femtosecond time-resolved "movies" of photoexcited dynamical processes at surfaces. We have successfully built a femtosecond pump-probe apparatus to probe ultrafast dynamics. We have used this apparatus to probe coherent phonon dynamics in manganite crystals (Fig. 2). In addition, we have built a combined apertureless near-field optical microscope/atomic force microscope that has yielded excellent topographic images of a test sample. We are currently combining the femtosecond pump-probe apparatus with the microscope to obtain time-resolved microscopic images.

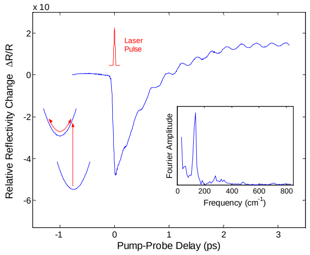
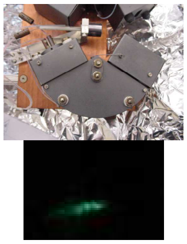


Fig. 2: Coherent phonon excitation of LuMnO3 with 20fs laser pulses observed in pump-probe reflectivity studies.

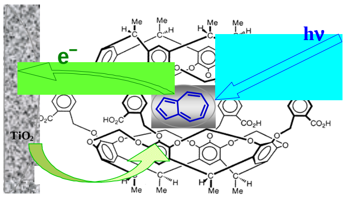
DMR-0421177, *"Development of a high resolution and low current density inverse photoemission spectrograph for research and education"* [$331,560 (9/04-8/07), with R. Opila]: We have constructed a novel inverse photoemission spectrograph in a near-normal incidence geometry that takes advantage of parallel photon energy detection, both in and out of the dispersion plane, so as to obtain good count rates while maintaining either high electron energy resolution or low electron flux. We have developed a new electron source (Fig. 3), modified an existing system to accept the new source, grating and detector, we have tested the high-resolution electron source and will commission the system in the early Spring.



DMR-0421028 *"Development of an integrated thin film growth system with comprehensive in-situ characterization for research and education"* [$525,000 (9/04-8/07), with Y. Chabal] The objective of this project is the development of a modular system for Atomic Layer Deposition (ALD) with *in-situ* IR characterization and UHV sample transfer to a wide array of analytical techniques, in particular our novel Medium Energy Ion Scattering (MEIS). The system, which is now fully designed and currently under construction, will be used primarily to grow epitaxial high-K dielectric films on a variety of substrates.

DMR-9801681: *"Auger-Photoelectron coincidence spectroscopy (APECS) of surface alloys, ultrathin films and layered compounds"* [$264,000 (7/98 – 6/04)] We have used the novel technique of APECS, in conjunction with a range of other approaches, to investigate surface alloys, oxide surfaces, and metallic quantum wells: systems where engineering the electronic structure gives rise to interesting physical properties. We have also used APECS to probe magnetic oxides in a spin-specific manner and performed the first angle resolved APECS measurements.

Galoppini



PI. NSF-NIRT-CHE0303829; \$1,030,760; 09/1/03-07/31/08 *Electronic Interactions in Hybrid Organic-Nanoparticle Materials* The objective of this project was to tune the interfacial electronic interactions through systematic molecular-level variation between dyes and dyes@host and nanoparticles. Two classes of molecular scaffolds were studied: rigid linkers with multiple anchoring groups for surface binding; and “hemicarcerands” cage hosts for encapsulation of organic guests (azulene). TiO_2 and ZnO nanocrystals, assembled in colloidal solutions and in mesoporous thin films were functionalized with the organic dyes. Electronic interactions of the hybrid organic-nanoparticle interface were probed electrochemically, spectroscopically on ultrafast time scales. The study showed that the electronic processes are influenced by varying the conjugation and length of the linkers, the size of the nanoparticle or hemicarcerand, and by the multipodal footprint. The work resulted in twenty eight publications, five to six papers in preparation, numerous presentations at meetings, and in the collaborative work of students, postdoctoral associates and high school students, with frequent exchanges between labs. Six Ph.D. theses and 2 M.S. were based on this work. 2 project SEED students participated to the research and 6 undergraduate. Travel supplements by REU allowed summer research in Sweden for one undergraduate student and the team to take turns in work visits of laboratory of collaborators abroad (Berlin, Stockholm).

NSF-MRI-0443538 *Acquisition of x-Ray Instrumentation for Materials Chemistry at Rutgers-Newark* \$100,700(02/2/05-01/31/08) [EG co-PI.] A new single-crystal X-ray CCD diffractometer with fast and reliable data collection at low T replaced a 32-year old instrument, allowing the new faculty to routinely have access to this technique, resulting in numerous publications. The instrument has been used for experiments for an advanced undergraduate laboratory course and in minority outreach programs (ACS SEED and local high schools).

NSF-Chem.Instr.-0342432 *Acquisition of a Dual Non-Collinear Optical Parametric Amplifier (NOPA) System for Ultrafast Electron Transfer Studies* 07/2004/-06/2007; \$220,000 [EG co-PI.] Two sub-15 fs NOPAs were integrated with an existing kHz Ti:sapphire amplifier to expand tenability and are now being used to study a wide variety of ultrafast photo-chemical processes. This grant has greatly enhanced fs spectroscopy resources at Rutgers University and has had a crucial impact on the progress of NSF-sponsored projects.

III. Preliminary Remarks

III. A: Introduction

In this proposal we describe a collaborative research program aimed at establishing the atomistic and molecular level properties of novel porphyrin-bridge-anchor dyes bound to oxide semiconductor surfaces. This class of systems has shown great promise as mediators of light harvesting and photochemical processes. However, a detailed study determining, for example, the surface bonding geometry, electronic structure, energy level alignment, and intermolecular interactions, and how these properties influence optical absorption, charge transfer and electrochemistry is lacking In the proposed work we will employ a series of systematic synthetic modifications to model porphyrin-bridge-anchor group compounds to engineer the molecular energy level spacing and alignment with the substrate, modify orbital densities to influence charge transfer efficiency, control the surface bonding geometry, and regulate molecular-molecule interactions. The dye molecule/oxide semiconductor interface will be explored using a series of advanced surface characterization techniques including direct and inverse photoemission, low temperature scanning tunneling microscopy and spectroscopy, near edge x-ray absorption spectroscopy, and other synchrotron radiation-based techniques. These results will be correlated with solution-phase analysis including UV-vis absorption spectroscopy and cyclic voltammetry. The dye-semiconductor system will be modeled using density functional theory to facilitate the interpretation of experimental results. The objective is to perform a comprehensive study of this important class of dye/semiconductor systems and obtain a fundamental understanding of the key properties that underlie the practical use of these systems.

The goal of the program described in this proposal is to develop synthetic and adsorption strategies that tailor the properties of novel porphyrin-based complexes bound to oxide-semiconductor substrates in order to enhance their desirable properties for practical applications..

To achieve this goal, we propose a **collaborative program** that brings together two PI's with highly complementary skills: one (EG) an organic chemist who will synthesize a series of porphyrin complexes with novel functionalizations, designed to have differing orbital energies, different intermolecular interactions and different surface bonding, and will study their optical absorption and electrochemical properties in solution; the other (RAB) a surface scientist who will determine the bonding geometries and measure the electronic and geometric properties of the same porphyrin complex/oxide surface systems under well-characterized and controlled ultrahigh-vacuum conditions. This research team has been collaborating informally during the past year and obtained initial results (shown below) that are very promising. The PIs also have on-going collaborations with theoreticians who can provide additional insight into the properties of these systems. The objective is to develop principles that will have a broad impact on other areas, ranging from photovoltaics and photocatalysis to organic electronics and interface engineering, where the properties of the organic molecule/semiconductor interface are critical.

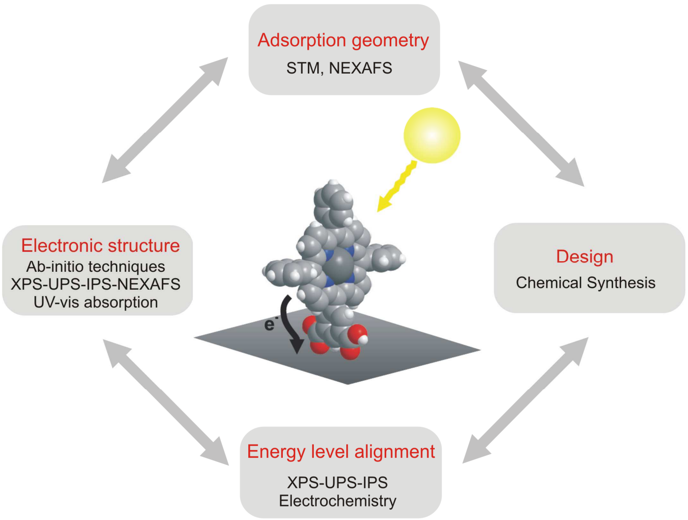


Figure 1:test.

MOTIVATION:

WHY PORPHYRIN-BASED SYSTEMS: The study of the interface between organic molecule (*e.g.,* dye, redox active compound) and wide bandgap semiconductor (*e.g*., TiO_2, ZnO) is both fundamentally important and of great technical and practical interest for the development of sensors, solar cells, electrochromic windows, and other devices. Metalloporphyrins and porphyrin arrays of various complexity bound to semiconductors have attracted considerable attention in this area owing to: **(a)** their role as active sites for oxygen transfer (hemoglobin), electron transfer (cytochrome) or energy conversion (chlorophyll) [21, 22] in biological systems; **(b)** their ability to bind and release gases and to act as active center in photo-catalytic reactions in chemical and gas sensors, or nanoporous catalytic materials [23-25]; and, **(c)** their stability and the close match of their photoabsorption properties to the solar spectrum which makes them appealing candidates for efficient photovoltaic applications [26-30].

But the key reason we have selected porphyrin-based systems for this molecular-level study is their synthetic versatility: easily accepting different transition metal ions to form metalloporphyrins, and the relative ease with which they can be synthetically modified and functionalized to form model compounds of varying complexity, from simple monomers to sophisticated arrays. Moreover, the porphyrin macrocycle is particularly suitable for the preparation of model porphyrine-bridge dyes giving control over the orientation of the prophyrine unit with respect to the surface (for instance planar or perpendicular to the surface) as recently shown by the co-PI (refs). Recent exciting results have found that A wide variety of large porphyrin arrays has prepared by research groups, using a building-block approach or by self assembly.[i] The binding of such arrays (antennae) to the surface of planar semiconductor surfaces could greatly increase the light harvesting and , most interestingly, *it could lead to configurations (branched, linear, with an energy gradient etc..) with great control of energy and electron transfer processes.*[ii] Aas a results, porphyrins are promising building-block molecules for the sensitization of **<u>planar semiconductor surfaces</u>** that could ultimately lead to "thin" solar devices.

MOTIVATION:

THE NEED FOR COMPREHENSIVE CHARACTERIZATION AND ANALYSIS: The interaction of dye molecules at oxide surfaces is highly complex, depending, among other things, on adsorption site, molecular geometry and charge redistribution at the surface. Tetraphenyl porphyrin-derived systems are particularly attractive because, for symmetric cases, the properties of the phenyl rings (typically central in bonding to the surface) are essentially decoupled from those of the porphyrin macrocycle (the portion of the molecule typically responsible for its desirable optical properties). Therefore, to first approximation on can separately explore these two critical aspects of the molecule/surface interaction. Moreover, by appropriate functionalization, one can tune the degree and nature of the macrocycle and the phenyl through which surface bonding is expected to occur, thereby facilitating photoexcited charge transfer. The multitude of parameters that may be modified upon adsorption to an oxide surface indicates that a comprehensive experimental and theoretical study is required to obtain a complete understanding of the problem (need better phrasing here). Below we give a brief description of the properties that will be characterized in the proposed research.

ELECTRONIC STRUCTURE: The description above enables on to anticipate how the electronic structure if a porphyrin derivative may change upon functionalization, whether it be adding bridging and/or anchoring groups to the phenyl rings to manipulate bonding to the surface or intermolecular interactions, or if it is functionalization of the porphyrin macrocycle in an effort to tailor energies of the HOMO and LUMO levels. While this approach may be useful as a guideline, many factors must be considered in order to obtain a more realistic picture of the true situation. For example, functionalizing the phenyl rings in an effort to influence the molecule-molecule interactions at a surface can also shift the phenyl levels so that they are nearly degenerate with the

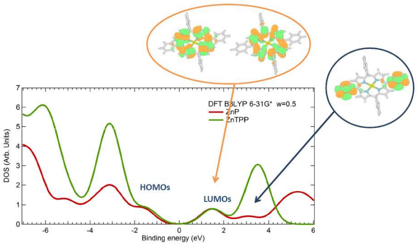


Fig. 4: The energy level alignment of molecular levels with respect to the substrate band edges can influence performance in photovoltaic

frontier orbitals of the macrocycle. This may have the deleterious effect of disrupting a favorable band alignment, or it may have a beneficial effect of actually enhancing molecule-to-substrate charge transfer, once again illustrating the need for a broad-based study of these systems.

ENERGY LEVEL ALIGNMENT: When bound to semiconductor substrates, the alignment of the frontier orbitals of the porphyrin molecule with the conduction band and valance band edges of the semiconductor is key to the function and efficiency of the structure. This is schematically illustrated in Fig. 5 for two important cases: photocatalysis and dye-sensitized solar cells (DSSC). In the former case, if the levels of a porphyrin with a given HOMO-LUMO gap could be adjusted so that the LUMO level were just above the conduction band edge of the substrate, then a larger portion of the solar spectrum might contribute to the photochemical process. [23] In the case of DSSCs, improved energy alignment of the LUMO with the oxide CBE, and HOMO with the redox potential of the electrolyte, could improve efficiency and provide new options in the design of photovoltaic cells. While the HOMO – LUMO gap may depend largely on the nature of the porphyrin macrocycle, factors that depend on bonding geometry, such as intermolecular interactions, can significantly alter the alignment. In addition, the introduction of dipoles between the macrocycle and the anchoring group can shift the levels of the molecule with respect to those of the substrate.
[SHOULD PROBABLY SAY SOMETHING ABOUT ELECTROCHEMISTRY HERE]

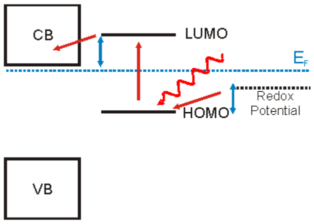


Fig. 5: The energy level alignment of molecular levels with respect to the substrate band edges can influence performance in photovoltaic applications

OPTICAL ABSORPTION: Complexes based on the Zn-porphyrin molecule will be central to the studies described in this proposal. The structure of the molecule, along with electron distribution diagrams of two of the frontier HOMO and LUMO orbitals primarily involved in optical absorption, are shown in Fig. 4. The typical UV-Vis absorption spectrum of porphyrins is composed of two main bands: The Soret (or B band) roughly at 400 nm and a weaker Q band around 550 nm. Both Q and B bands arise from π to π^* transitions that can be understood within the Goutermann model[31] as transitions between the frontier orbitals shown in Fig. 4. The ground state electronic structure of the metalloporphyrin is related to, but differs from, that of the free base porphyrin. The extent of modification depends to first order on the relative energy position of the *d*-orbitals of the metal and the free base porphyrin orbitals. The calculated HOMO-LUMO gap of a series of metals (Fe, Co, Ni, Cu and Zn) can vary from 1.7 eV for Ni to 2.5 eV for Co and Zn. [32] The fact that the optical transitions involving these orbitals are in the visible, and can be modified with relative ease by metal insertion, is part of what makes these molecules so attractive as mediators of photocatalytic and photovoltaic processes. [MAY WANT TO SAY SOMETHING ABOUT ARRAYS, PLANAR SURFACES, HOW WE CAN CONNECT UHV STUDIES TO SOLUTION STUDIES.]

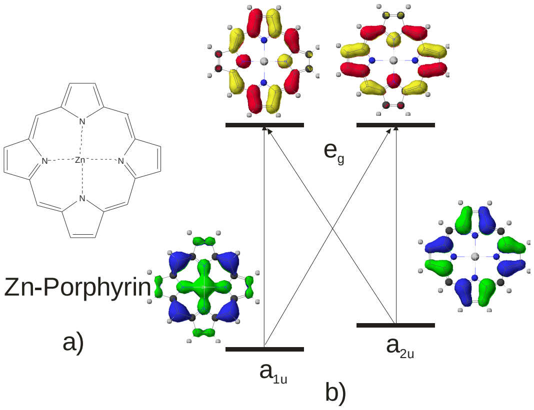


Fig. 6: (a) Molecular structure of Zn porphyrin; (b) e_g LUMOs and a_{2u} and a_{1u} HOMOs of the molecule, and important optical transitions.

BONDING GROUPS AND BONDING GEOMETRY: Because of the essential role played by porphyrins in photosynthetic mechanisms, these molecules are also natural candidates for the electron transfer mediator in DSSCs. Novel DSSC architectures may increase cell efficiencies by employing absorbers that capture different portions of the solar spectrum. Creating a series of molecules with similar binding to the substrate, but different HOMO-LUMO gaps, would be a straight forward way to implement such an approach.

[26, 23, 28, 30]

The Zn porphyrin molecule can be functionalized with phenyl rings to form zinc tetra phenyl porphyrin (Zn-TPP), shown in

Fig. 6, an important starting point for our studies. Derivatives of ZnTPP have similar electron injection and charge recombination properties as the ruthenium-based N3 dye commonly used for DSSCs.[30] To control the binding of Zn-TPP to the semiconductor substrate, the molecule can be functionalized with carboxylic (or phosphonate) end groups that form either unidentate, chelating or bridging-bidentate structures on oxides substrates. These configurations are shown in

Fig. 6.[33, 28] These molecules exhibit reasonable performance in DSSCs using either TiO_2 or ZnO as substrates, opening the possibility of different wide band gap oxides to this platform.[28, 26, 27] Recently, it has been shown that Zn-TPP could increase the photocatalytic activity of N-doped TiO_2 nanoparticles by extending the absorption range of the catalysts to visible radiations.[23]

An important feature of these molecules is their flexibility upon functionalization. Functional groups, such as the phenyl groups of ZnTTP, attached to the meso-phenyl ring of the porphyrin have little influence on the ground state frontier orbitals of the dye. This is in part because the phenyl rings are oriented essentially perpendicular to the porphyrin macrocycle.[34] The insensitivity of the frontier orbitals to functionalization of the phenyl rings provides the opportunity to independently test the effect that several other critical factors, such as macrocycle orientation upon adsorption, π/π molecular interactions that may result from aggregation, or modification of the molecule-substrate linker groups, have on the absorption properties of the molecule.[26, 35, 27] In addition, as seen in Fig. 4, the frontier orbitals reside on the macrocycle, and their orbital energies can be modified by appending electron donors/acceptors groups to the pyrrolic portion of the macrocycle, and/or by inserting a different transition metal (TM) ion into the ring. Systematically studying the effect of such modifications on the orbital energies and their alignment with the bands of the oxide substrate is the central theme of the research proposed below.

IV. Research Plan

IV. A: Overview

The overall approach of the proposed research is to spectroscopically determine the energy alignment of the HOMO and LUMO levels of dye molecules with respect to the VBM and CBM of oxide surfaces onto which the dyes are adsorbed.[36-45] This study will focus on a range of novel TMTPP-based dyes specifically synthesized for this project. By judicious functionalization, we will attach anchoring groups to one of the peripheral phenyl rings, through which the molecule will attach to the surface. By functionalizing the other peripheral phenyl groups, we will attempt to modify intermolecular interactions at the surface. We will then explore ways to tailor the relative energy of the porphyrin HOMO and LUMO levels with respect to the band edges of the substrate. This will first be done by selectively functionalizing a linker chain between the anchor group and the porphyrin ring so as to introduce a dipole. We will also investigate the effect of attaching electron withdrawing and donating groups to the pyrrolic portion of the porphyrin macrocycle and substitution of different transition metal ions in the porphyrin ring. To maintain a high degree of control in this part of the research, we will initially perform these measurements using atomically well-ordered single crystal $TiO_2(110)$ and ZnO $\left(11\bar{2}0\right)$ surfaces. After characterizing these molecules on the single crystal surfaces, we will expand our studies to include adsorption on anatase TIO_2 nanoparticles and single crystal ZnO nanorods. We have performed successful preliminary measurements of the N3 dye molecule on these single crystal surfaces, [46] compared them to similar measurements performed on anatase nanoparticles and MOCVD-grown single crystal ZnO nanorods of the sort that may be used in practical systems, and found very similar results.

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IV. B: Experimental Approach

IV. B1: Synthesis of functionalized model porphyrins The co-Pi's synthetic organic group at Rutgers University-Newark has developed over the years a variety of **dye-linker-anchor group** model compounds [47], including rigid-rod and planar ("spider") model porphyrins to study the influence of binding geometry on charge transfer and solar cells efficiency

Fig 6 here

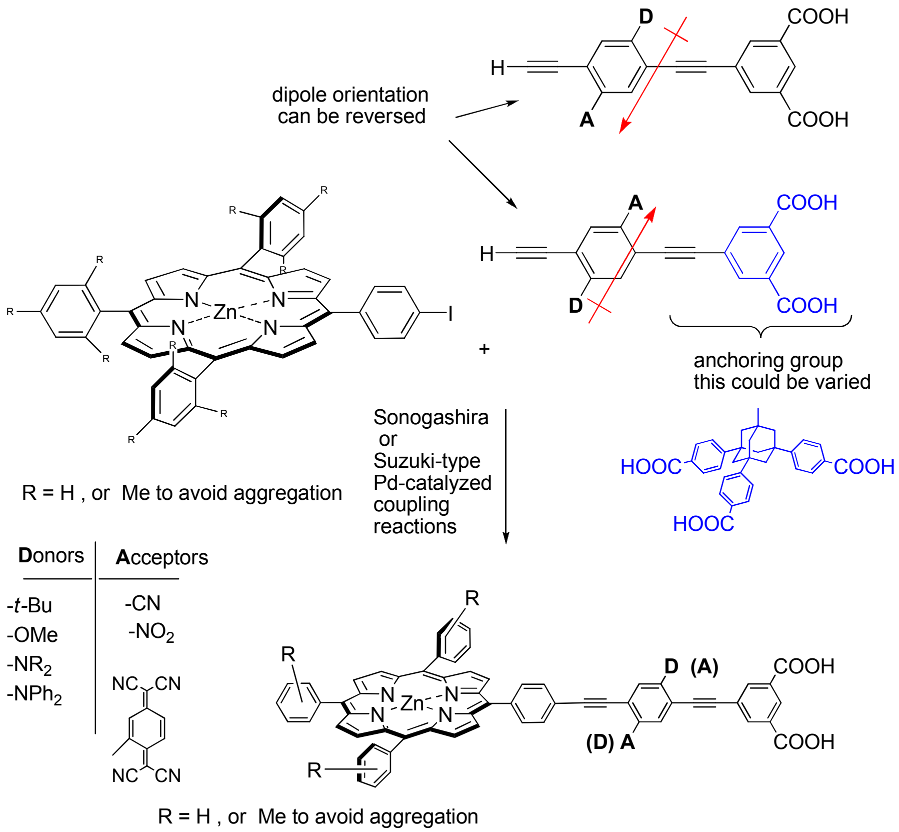


Fig. 7: Strategies for linker functionalization.

For this project we plan to develop two new classes of model porphyrins:

a) **Porphyrin –Ipa rods with built-in dipole** The synthetic strategy will be the same that we have developed for the synthesis of rigid-rod porphyrins [48, 35, 49] except that the central phenyl ring in the OPE bridge will be substituted with a donor and an acceptor. The relative position of the donor and acceptor will be switched (by varying the order of the cross-coupling procedures) so that the dipole orientation will respect to the semiconductor surface can be reversed. The presence of methyl groups on the meso phenyl rings (mesityl-derivative) will avoid aggregation of the models. Variations of the anchoring group will be considered (See Scheme) to ensure anchoring to the surface that is close to the normal. The Ipa rods are expected to bind though both the COOH groups but at an angle of about ~45 deg. [50]

b) Capped porphyrins

Charge transfer studies by Sundström and calculations by Persson suggests that rotational freedom about the anchoring "legs" in the tetrachelate porphyrins greatly complicate the ability to correlate kinetics with the expected binding geometry.

To address this question, in the past year we have developed novel capped porphyrins, Fig. 2. The purpose of the cap is to restrict the conformational freedom of the linker group, to prevent (or limit) both direct contacts with the semiconductor and porphyrin stacking.

Figure

C) "spiders" vs. rigid rods. Finally we will continue to study utilize some of the already available model compounds (# # and # in figure 6) to determine their orientation on the surface

……….

. IV. B2: Analysis of functionalized porphyrins bound to oxide surfaces

Another important aspect of this study is the possibility of determining the dye adsorption modes on oxides surfaces using STM. Most studies of porphyrins at surfaces have used *in-situ* sublimation to deposit the molecule. [53-64] The more complicated functionalized metalloporphyrins to be examined in this study need to be deposited by a solution immersion method where a sample surface is prepared in UHV, passivated with a monolayer of pivalic acid, removed from the chamber via a load-lock, sensitized by immersion in a dye-solvent solution, dried, and reinserted into the UHV chamber for further analysis.

As mentioned above, the effect that different linker groups and endgroups can have on the alignment of both the HOMO and LUMO levels of the dye molecule with respect to the band edges of the oxide are key issues to be addressed in the proposed work.
Energy alignment should be only a part of the project. Important issues are: molecular geometry, electronic structure of system dye/substrate. These will determine the electron transfer processes.

Elena: UV-vis, Test solar cells?

The adsorption properties of a range of metalloporphyrins to well-characterized single crystal surfaces of wide band gap oxide semiconductors surfaces will be studied using an array of surface science techniques. Central to our approach is the use of direct and inverse photoemission which provide a very direct way of determining from the electronic structure, the orbital energies and their alignment with the substrate bands. [51, 52, 46] As illustrated in **Error! Reference source not found.**, in UPS a photon that is incident on the system is absorbed and an electron is ejected. The kinetic energy distribution of ejected electrons contains features associated with the occupied electronic states of the system, particularly the HOMO levels of interest in these studies. In IPS, a monoenergetic (~ 20 eV) beam of electrons is directed towards the sample and these electrons couple to high lying unoccupied states of the system. A small fraction undergo optical transitions to lower-lying unoccupied states, in particular the LUMOs, emitting a photon in the process. By measuring the energy distribution of emitted photons, one can determine the energy of the unoccupied states in a way that is very analogous to how the occupied levels are determined in UPS. An important novel aspect of our instrumentation is that UPS and x-ray photoemission [XPS] and IPS capabilities are housed in a single UHV experimental chamber.[52, 51] In that way, not only can we explore the HOMO and LUMO energy alignment on an equal footing, but measurements of the occupied and unoccupied electronic states of the surface resulting from a particular preparation can be performed sequentially on the sample, and thus remove any artifacts that may arise from variations in sample preparation conditions.[52, 51]

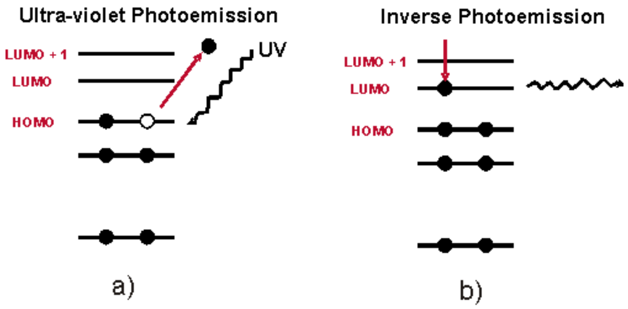


Fig. 8: Schematic diagrams illustrating the principle of (a) UPS and (b) IPS spectroscopies.

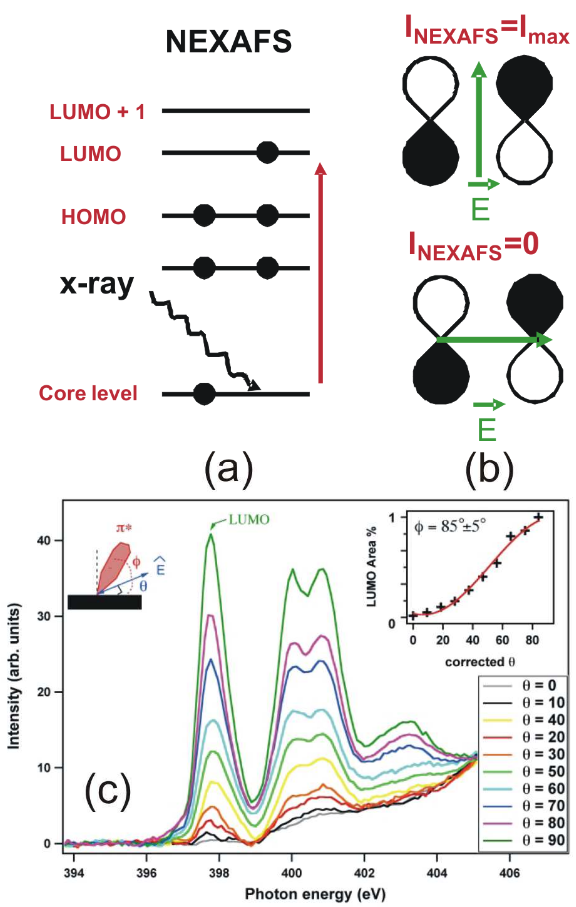


Figure 2: (a) NEXAFS transition

The interpretation of the electronic structure is facilitated by the use of ab-initio techniques to calculate the density of states of the gas phase and adsorbed dyes.

. UHV numbers theory comparison etc…

NEXAFS spectroscopy is not only sensitive to adsorbates orientation but also a powerful elemental probe, with which, through a choice of the elemental edge and keeping in mind transition selection rules, chemical bond can be characterized.

Add NEXAFS after that.
Techniques (ideally Auger Yield with possibility of probing several crystallographic directions)? Where? ALOISA, TEMPO…

Resonant photoemission?

Time resolved?

IV. B4: Concluding comments on Experimental Approach

The collaborative experimental approach to be implemented in this program offers several key features as compared to many other more traditional methods used in the field:

1) The versatility of the metalloporphyrins, and the relative insensitivity to functionalization of the phenyl groups allows to probe separately different factors (molecular interaction, adsorption geometry, linker influence and dipole creation) that can modify the energy level alignment of the dye molecule with respect to the substrate band edges and that could be then used for band alignment engineering in other systems.

2) The use of well characterized single crystals substrates in a UHV environment, allows the most efficient control of the dye/adsorbate system. For comparison, we will also measure porphyrins on technologically more relevant nanostructured oxides, in sensitization conditions similar to traditional DSSCs preparations, so as to investigate the effects of atmospheric contaminants on those systems.

3) The results of UPS and IPS, techniques where no core/valence hole is involved, allow a more direct comparison with theoretical models, and can help improve theoretical treatment of these dye/oxide substrate systems. In particular, typical DFT studies cannot describe energy gaps properly, thus making energy alignment evaluation difficult. In this perspective, we have started in parallel to our experimental studies of N3 as well as other sensitizers on oxide surfaces, a theoretical collaboration involving P. Persson (Lund University, Sweden). [71, 67, 72, 73]

IV. C: Novel Porphyrin-based dyes on oxide surfaces

In the following sections, we describe a series of experiments designed to determine the key properties and interactions that determine the behavior of several specifically designed TM-TPP-based molecules adsorbed on semiconducting oxide substrates. All of the apparatus and capabilities necessary to synthesize the proposed molecules and perform the proposed measurements is in place. In some cases, preliminary results illustrating proof-of-concept and the ability to perform the proposed measurements are presented. To fully explore all of the options and variations described in the following sections would require time and resources beyond the scope of this program; however we include them in the discussion to set the appropriate context. Our priority is to synthesize and measure the properties of two or three molecules, for each of the sections below, to establish the range with which we can control the key bonding properties in these systems. Then, for the most promising approaches, we will explore a wider range of molecular complexes.

IV C1: Electronic Structure and Band Alignment

Our initial studies will focus on the electronic structure of a set of porphyrin-linker-anchor complexes described in Section IV.B.1. As illustrate in **Error! Reference source not found.**13(a), functionalizing a member of the linker chain with appropriate electron withdrawing or electron donating ligands, will introduce a dipole moment between the anchor group and the porphyrin ring. For an overlayer of molecules at the surface, an effective dipole layer is formed, generating a change in electrostatic potential that would shift the molecular orbitals on the porphyrin ring with respect to the substrate levels. In the schematic diagram of **Error! Reference source not found.**13(a), the electric dipole is oriented towards the surface, thus increasing the electrostatic potential energy of the levels in the porphyrin ring, resulting in an upward shift of the levels, as illustrated in **Error! Reference source not found.**13 (b).

The first molecule that we will synthesize to explore this approach is shown in **Error! Reference source not found.**13(c). In this case a rigid linker chain, consisting of two phenyl rings, will be appended to a phenyl group of the TPP molecule. The terminal phenyl ring will be functionalized with a carboxylic group that will serve as the anchor to the oxide surface. The phenyl ring along the linker will be functionalized with an electron withdrawing NO_2 group and an electron donating $N(CH_3)_2$ group as shown. An ab-initio calculation of the dipole moment generated by this configuration is of order 6.5 D, orientated along the axis connecting the ligands. Even though the orientation of this dipole is not parallel to the linker chain, a simple capacitor model using realistic molecular dimensions suggests that an ordered array of such molecules would result in a significant shift of the porphyrin levels of order 1 eV.

Our first studies of this molecule will involve sensitizing single crystal $TiO_2(110)$ surfaces by the solution immersion method. We anticipate that the presence of the dipole on the linker chain will shift the energy levels, as observed in UPS and IPS, with respect to the band edges of the TiO_2, but not with respect to each other. To verify the anticipated effect, additional studies will be made on molecules where the binding sites of the NO_2 and $N(CH_3)_2$ groups are reversed. This would reverse the sign of the dipole on the linker, and should reverse the shift of the porphyrin levels. As time allows we will explore other changes including varying the electronegativity of the ligands on the linker which is expect to impact

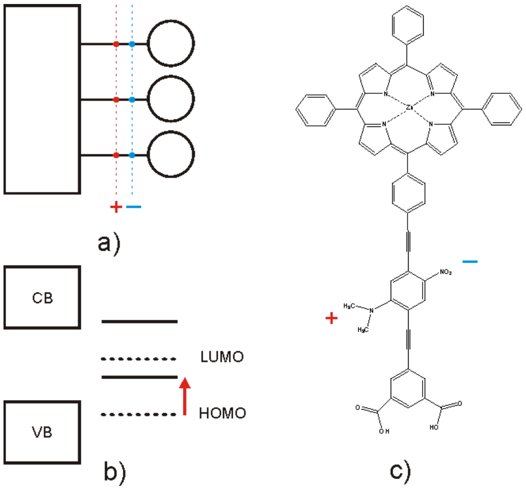


Fig. 9: (a) Schematic diagram showing dipole layer formed by functionalizing the linker chain; (b) expected effect of such a dipole layer on the energy of molecular levels; (c) one possible scheme for establishing a permanent dipole in the linker chain.

the magnitude of the shift of the porphyrin levels. Another important point is that the dipole of the linker phenyl group is not oriented along the linker axis. Therefore, modifying the anchor groups could change the bonding geometry and affect the dipole layer of an ordered array of such molecules, even if the internal structure of the linker and the porphyrin are not changed. Clearly there is a large space to explore with this class of molecules.

Preliminary results we have obtained in an exploratory study of a series of three ZnTPP derivatives, schematically shown in Fig. 1, illustrates the utility of UPS and IPS in exploring the electronic structure of this class of molecules. The occupied and unoccupied states obtained using respectively using UPS and IPS, measured for the a clean ZnO(11-20) surface before and after sensitization with each of the three ZnTPP derivatives, is shown Figure xx(d). A comparison with the calculated density of states presented in the figure xx(e) (Gamess, B3LYP, 6-31*) for each molecule allows a clear interpretation of the experimental data. In particular, the nearly degenerate HOMO/HOMO-1 and degenerate LUMOs levels which are found delocalized over the ZnP central macrocycle (indicated by ZnP), are insensitive to the meso-phenyls functionalization, due to the high level of decoupling of the ZnP center with the surrounding perpendicular meso-phenyls. Among other remarkable features, the position of the phenyl-related states (indicated by Ph), depending on the electron transfer between the phenyl ring and the CH$_3$ electron donating or COOH electron withdrawing groups, is well reproduced by the DFT approach.

Form these results, the energy level alignment of the ZnTPP derivative is directly extracted from the UPS and IPS spectra (as shown figure xx(f)). For the three dyes considered in this study, the HOMOs centroid is found 1.6 eV above the substrate VB while the LUMOs centroid is found 1.9 eV deeply above the CB.

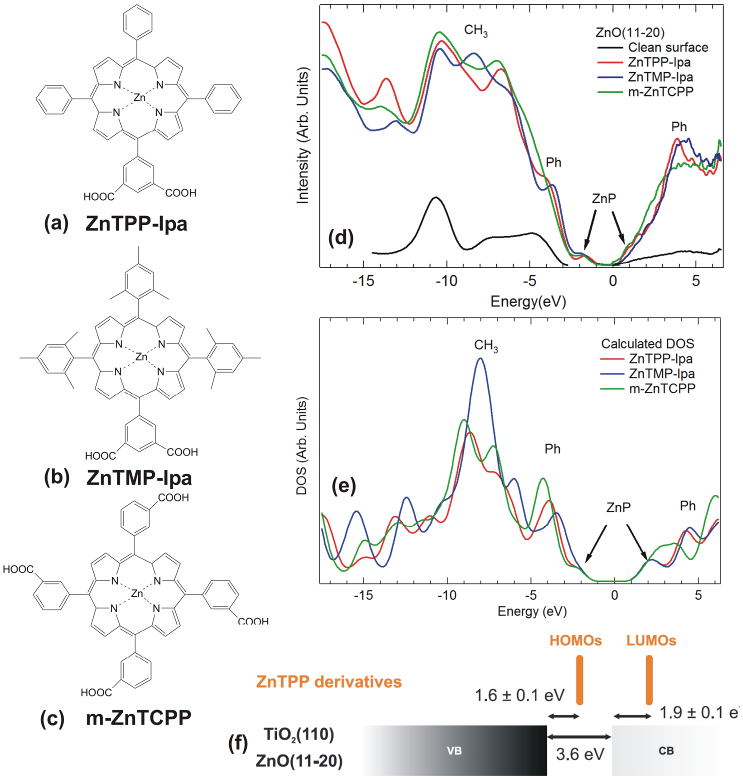


Figure 3: Text here.

In addition to the novel approach discussed above, we will also explore direct functionalization of the porphyrin macrocycle, as well as transition metal substitution, as ways of shifting key orbitals and changing the HOMO-LUMO gap. Functionalizing the macrocycle with electron withdrawing groups is expected to raise the electrostatic potential of the ring and thus lower the energy of the HOMOs and LUMOs in a relatively rigid manner. In contrast, incorporating different transition metal ions within the macrocycle is expected to have profound effects on the HOMO – LUMO gap, as well as change the nature of the levels themselves (for example, from being the delocalized pi-manifold to an orbital with substantial metal d-character) which can have a large effect on absorption efficiency and eventual charge transfer to the substrate.

Using the functionalized TPP and TM-TPP molecules of**Error! Reference source not found.**

adsorbed on the TiO$_2$(110) surface as a reference, we will investigate, with UPS and IPS, how the different TM ions in the macrocycle affects level position and alignment with the substrate bands. We will begin by comparing the Fe-based TTP and TMTTP molecules with the Zn-based complexes with which we start our studies. As time allows we will investigate other TM substitutions, such as Ni and Cu to determine the degree to which the HOMO and LUMO levels can be independently modified will be explored.

IV. C1: Adsorption geometry and control of intermolecular coupling

Complementary to our electronic structure and level alignment studies we will probe the bonding geometry of the same series of ZnTPP derivatives using, primarily, STM and NEXAFS. The location of the anchoring group on different meso-phenyl rings of the molecule is expected to lead to different molecular orientations, and thus different interactions between the porphyrin macrocycle and the surface. In addition, functionalizing other phenyl rings should modify molecule-molecule interactions. As the preliminary results in Fig. XX indicate, such modifications appear to have little effect on the HOMO and LUMOs (although the phenyl-derived states systematically shift). Upon completing these studies and correlating the results with the optical and electronic structure properties, we will explore the capped porphyrins that are designed to introduce new constraints on molecular orientation and intermolecular coupling.

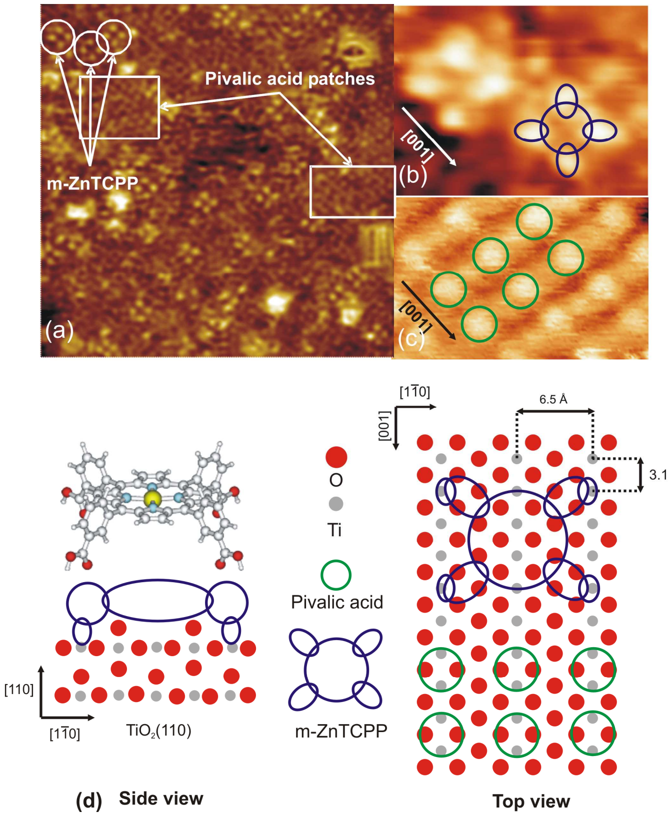


Figure 4: (a) STM image m-ZnTCPP dye adsorbed on TiO$_2$(110), previously passivated with pivalic acid. (b) (15Å× 20Å) and (c) (15Å× 20Å) close-up STM images of m-ZnTCPP and pivalic acid molecules. (d) Pivalic acid and m-ZnTCPP adsorption models on the TiO$_2$(110) rutile surface deduced from STM measurements

The ZnTPP derivatives of Fig. XX are expected to bond to the surface through an anchoring (typically carboxlyate) group appended to one or more meso-phenyl ring. Moreover, the particular functionalization of the meso-phenyls is expected to lead to different adsorption geometries when the molecules are bound to the surface of the oxide. In particular, the ZnTPP-Ipa molecule of Fig. 1(a) possesses one isophatlic acid- (Ipa-) like termination in the para position [AREN'T THE COOH's AT TWO META POSITIONS?], and thus can only bind to the surface through one functionalized phenyl. As a consequence, ZnTPP-Ipa is expected to bond nearly upright, with a large angle between the plane of the porphyrin ring and the plane of the substrate surface. A similar adsorption geometry is expected for the ZnTMP-Ipa molecule of Fig. 1(b) as it also possesses a single Ipa-like termination in the para position. However, in this case the other three phenyl groups have methyl terminations which are expected to act as spacers between the molecules thus preventing dye aggregation at high coverages. Finally the m-ZnTCPP molecule of Fig. 1(c) has four identical meso-phenyls functionalized in meta position with a COOH anchoring group which is expected to result in a flat adsorption geometry on the oxide surface.

Preliminary STM measurements obtained for solution-deposited m-ZnTCCP on (pivalic acid-passivated) TiO_2(110) are shown in Fig. XXX. In this case, a highly dilute dye solution was used in order to produce a low concentration of M-ZnTCCP molecules on the surface. The large-scale image of Fig. XXX(a), a series of bright four-fold feature can be seen along with a regular periodic array of dimmer features. From STM images of passivated surfaces that have not been sensitized, we associate the latter features with pivalate species bound to the TiO_2(110) surface. During solution sensitization of the passivated TiO_2(110) surface, a few m-ZnTCPP dye molecules replaced the pivalic acid, resulting in the brighter 4-fold features. A close-up image, as shown in Fig. XXX (c) strongly suggests that the four bright features are associated with the phenyl groups of adsorbed m-ZnTCCP, indicating that it does indeed assumes the anticiapted flat adsorption geometry. Fig. XX(d) shows a tentative model for the adsorption of the molecule with respect to the underlying surface. Interestingly, the in-plane orientation of the m-ZnTCPP dye is aligned along the high symmetry directions of the surface. Along with imaging, local spectroscopy would be further studied and compared with the non-local techniques that are UPS and IPS.

Typically, STM techniques are well suited for relatively low dye concentrations. For higher coverage, the adsorbate orientation with respect to the surface will be probed using NEXAFS spectroscopy. Employing the dipole selection rules that govern NEXAFS transitions (as drawn in the Figure XX(a)) allow as a function of the electric field orientation (Figure xx(b)), the determination of the adsorbates orientation with respect to the sample surface. An example of such dichroic effects is shown in the Figure xx(c). NEXAFS spectra of a ZnTPP multilayer on a silicon surface, have been taken at the N 1s edge as a function of the polarized light incidence with respect to the surface, and reveal a clear stacking of the ZnTPP molecules parallel to the surface.

Moreover, do NEXAFS on different cores to probe different regions fo the molecule. Time resolved…?

investigate how functionalizing the phenyl ligands in the Zn-TPP molecule will influence intermolecular interaction when the molecule is anchored to the surface via a carboxylic acid group. The set of functionalized porphyrins we will use are illustrated in **Error! Reference source not found.** (a) and (b). These molecules have already been successfully synthesized in our group. **Error! Reference source not found.**(a) is a simple Zn-TPP molecule where one phenyl group has been functionalized with a carboxylic acid anchor group and is thus expected to be oriented with the plane of the porphyrin macrocycle perpendicular to the surface. The tendency for the phenyl groups to align perpendicular to the porphyrin macrocycle provides a small steric barrier to interaction of neighboring adsorbed molecules, but aggregation resulting in significant interaction is still possible. Functionalizing the phenyl groups with methyl ligands, as shown in **Error! Reference source not found.**(b) is expected to significantly decouple the porphyrin macrocycles on neighboring molecules, and result in an electronic structure more similar to isolated phorphyn macrocycles. Optical absorption studies performed in our group are consistent with this interpretation. [35]

We will perform a series of adsorption studies to determine the veracity of this interpretation. Our preliminary results on the functionalized Zn-TTP molecule of **Error! Reference source not found.**(a), described in Section IV.B3 above, were obtained from a surface sensitized by dipping into an ethanol solution containing this dye molecule. While the binding energy of the primary features observed in the photoemission spectrum of **Error! Reference source not found.**(a) are similar to those found for thick films of the Zn-TPP molecule, the relative intensities of these features is significantly different. We will compare these UPS and IPS results to spectra obtained when the molecule of **Error! Reference source not found.**(b) is adsorbed on the surface. With the reduced intermolecular interaction caused by the additional methyl groups, we expect the spectra to be much closer to that of the multilayer film. Furthermore, we will perform STM studies, similar to those shown in **Error! Reference source not found.** for the N3 molecule, to verify the adsorption geometry of the molecule and to search for evidence of molecular aggregation.

An alternative approach to influence the adsorbate geometry at the surface that we will also pursue is to change the terminal anchor group of the linker chain. A natural choice is to replace the carboxylic acid group with phosphoric acid, which is expected to bind much more strongly to the oxide. Stronger molecule-substrate bonding may mitigate aggregation caused by intermolecular interactions. Such a replacement on the N3 dye has resulted in poorer performance in DSSCs, most likely because it causes an undesired increase of the HOMO-LUMO gap. [28] [74] However, for the porphyrin-based molecules we will study here, the HOMO and LUMO levels have little weight on the linker group and therefore minimal impact on the gap or its location with respect to the substrate band edges is expected. Another possibility that we will pursue is to functionalize the anchoring phenyl ring with OH-groups, forming a catechol moiety. Catechol is known to be less sensitive to water contamination. Similar to phosphoric acid groups, and based on measurements we have obtained from the catechol/TiO_2 system, OH termination is expected to push the LUMO far up in CB. [71] Once again, however, these levels are decoupled from the relevant levels of the macrocycle. A potentially larger difference is that the OH-anchoring groups will be on neighboring carbons of the phenyl group, leading to a significantly different bonding geometry at the surface.

IV. C5: Exploring the role of the oxide substrate

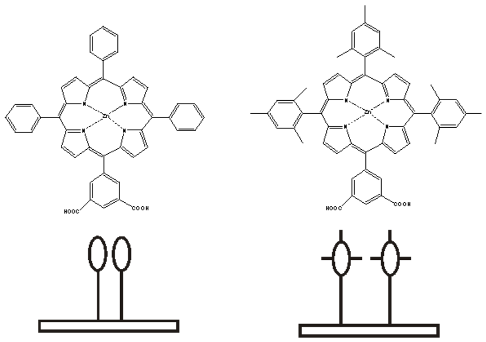
Our discussion so far has focused on modifying a series of TPP-based molecules as a means of controlling energy level alignment with the levels of an oxide substrate. However, it is also understand how the properties of the substrate influence this alignment as well. Our studies of the N3 dye on TiO_2 and ZnO found that the alignment of the HOMO level was similar on both oxides, but the LUMO feature was different in the two cases. This is likely the result of a wider range of bonding configurations on the ZnO surface as compared to TiO_2. The transferability of results we find on ideal substrates such as rutile TiO_2(110) to other oxide systems, with different and gaps and different heats of formation, is an important aspect to explore. Even in the context of a particular oxide, it is important to know whether nanoscale structures, which are more commonly used in practical situations, will exhibit the same trends we find for adsorption on ideal single crystal surfaces. To address this question, we will explore the properties of the molecules described in Sections IV.C1 – IV.C4 on single crystal rutile TiO_2(110) and ZnO(11-20). These studies will be followed by studies on commercially available (Degussa P25) anatase TiO_2 nanoparticles, as well as MOCVD-grown single crystal ZnO nanorods provided by Yicheng Lu at Rutgers, New Brunswick. As time allows, we will explore the extension of these studies to other oxides, particularly those with different band gaps. Epitaxial Al_2O_3 films grown on NiAl substrates will be an excellent starting point as it presents a well-characterized surface and is highly compatible with electron spectroscopic and scanning probe measurements.

STUFF NOT TO FORGET:::::

-Adsorption modes:
Molecule/Molecule interaction (loss of exciton) **UV-vis**,**STM**
Molecule orientation with respect to the surface **STM**, **NEXAFS**
Bonding interaction **FTIR, XPS, STM**

-Electronic structure determination:
Adsorbate characterization (chemical) **UV-vis, Electrochemistry, XPS, UPS-IPS, NEXAFS**
Energy alignment **XPS, UPS-IPS**
Provides input for theory to improve description of these systems **UPS-IPS, UV-vis**

-Electron transfer mechanisms:
Time resolved NEXAFS?



a) b)

Fig. 10: Schematic diagrams of ZnTPP and trimethyl-ZnTPP (Zn-TMTPP) porphyrin-derivative dyes to be used in the proposed research.

Complementary techniques

V. Educational and Outreach Activities

Our education and outreach activities will focus on photovoltaic applications of organic dyes similar to those studied in the research portion of this program, but readily found in everyday items such as berry juices. Due to dwindling fossil fuel reserves it is generally recognized that a transition to alternative energy sources will become absolutely necessary during this century. In addition to advancing the technology toward this transition, the research activities proposed here provide a unique opportunity to educate young people – the nation's future decision makers – about the importance, opportunities, and challenges of alternative and renewable energy technologies. Toward this important goal we will implement a new program to integrate advanced solar-cell science into high school and undergraduate science curricula. DSSC research-based activities are ideally suited for outreach and education at the high-school and undergraduate levels, since a working photovoltaic device can be constructed relatively simply by the students from inexpensive and nontoxic materials [75, 76]. Based on this idea, we will develop three hands-on experimental laboratory modules and a technical demonstration of nanotechnology in photovoltaic devices. These lab modules will be integrated into undergraduate laboratory courses of several physical sciences departments of Rutgers New Brunswick and Newark, aspects will be used as demonstrations in undergraduate lecture courses, while others will be tailored toward high-school science courses and K-12 outreach activities.

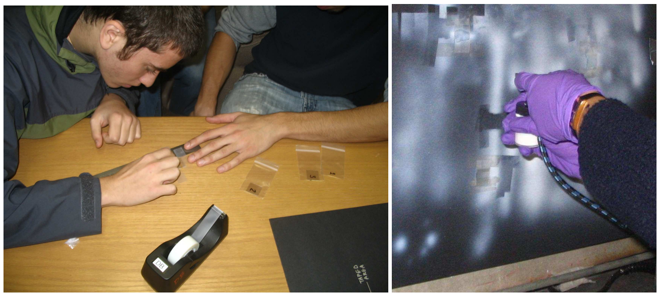


Fig. 11: Undergraduate students involved in making DSSC's this semester. Students apply tape to define the active layer area (left) and spray on a titania-nanoparticle suspension (right).

Undergraduate Education: For the lab modules, FTO coated glass slides will be provided as electrodes. The students will coat one of the electrode surfaces with TiO_2 sol-gel colloidal solution, and sensitize the TiO_2 nanoparticles with natural flavonoid dyes (anthocyamine) by dipping in blackberry juice. Upon adding a droplet of electrolyte and clamping the two electrode slides together with paper clips, a working solar cell is obtained.

We are already in the process of bringing this kind of solar cell into the classroom this semester in the Materials Science and Engineering department at RU-New Brunswick. The students are using a simple spray coating process with commercially available powders to build working solar cells. Fig. 12 shows students in the process of making DSSC's. Deliberate variations in the coating thickness, sample geometry, and electrolyte used are being tested by various student teams in the class. Future examples of valid class participation projects include varying the dye concentration to look at the importance of dye coverage on the titania surface, comparing different dyes, and changing the heat treatment/sintering conditions of the titania to understand the importance of microstructure.

K-12 Education: The high school lab module will be developed and integrated into high-school curricula in collaboration with two high school science teachers who are also our research collaborators, Dr. A. Rajagopal at South Brunswick High School, and Dr. A. Danese of Morristown High School.

In addition to hands-on lab experiences for the students, the lab modules will be used as a basis for classroom demonstrations that will be used to compliment existing outreach activities within Rutgers, illustrated in Fig. 13. The outreach activities have been developed to address specific demographic deficiencies in science & engineering [77-82]. The PV demonstration will be used in the following outreach activities aimed at increasing the participation of women and minorities in technical disciplines:

- TEEM (The Engineering Experience for Minorities), a residential program for African-American, Latino and Native American high school juniors. During the residential program the students have the opportunity to attend lectures and tour departments. It is proposed that the PV demonstration be used during the department tours to illustrate the importance of nanotechnology and renewable energy.

- TARGET (The Academy at Rutgers for Girls in Engineering and Technology). This is a series of lectures and experimental demonstrations intended to introduce girls to the exciting World of Engineering and Technology. The PV demonstration will be used in support of lectures on technology and the environment.
- The New Jersey Governor's School of Engineering and Technology for high achieving students across New Jersey. This is an opportunity for outstanding high school students to work directly with professors and their research students over a 10 week summer period. It is proposed that two or more of these high school students work with our team on the fabrication and characterization of titania based PV devices.
- Nanodays. Each year Rutgers runs open-house events where high school students and teachers can participate in a series of lectures, demonstrations and departmental tours highlighting nanotechnology. Specifically, Nanodays emphasize the current and future importance of nanoscale devices and phenomena in everyday situations. The titania PV demonstration will be an ideal example of how nanotechnology can help reduce the problems of fossil fuel dependency.

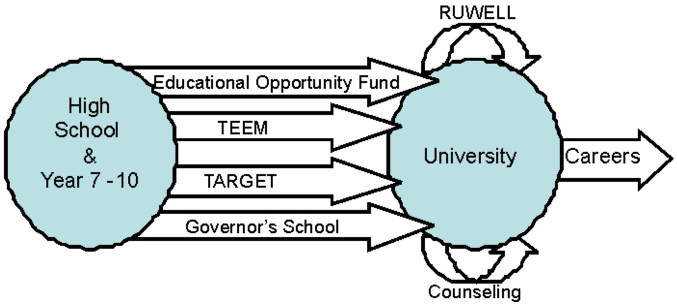


Fig. 12: The solar cell demonstration will be integrated into a wide range of outreach and student support programs at Rutgers (see text for details).

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