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Approved for public release; distribution is unlimited.

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The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

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RPPR Final Report
as of 07-Apr-2023

Agency Code: 21XD

Proposal Number: 74109EM **Agreement Number: W911NF-19-1-0357**

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DUNS Number: 790877419 EIN: 591961248
Report Date: 04-Feb-2023 Date Received: 05-Apr-2023
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Title: Understanding and Controlling the Structure at Organic-Inorganic Interfaces for the Generation of Stimuli Responsive Multilayered Materials
Begin Performance Period: 05-Jun-2019 **End Performance Period:** 04-Nov-2022
Report Term: 0-Other
Submitted By: Kenneth Hanson Email: hanson@chem.fsu.edu
Phone: (850) 645-0479
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STEM Degrees: 2 **STEM Participants:** 2

Major Goals: The primary goals of this project are to use carefully designed molecular derivatives, metal linking ions, and self-assembly methods, along with a combination of Förster resonance energy transfer (FRET) and polarized attenuated total reflectance (ATR), to determine the parameters that dictate the structure (i.e. the relative distances and orientation) of the molecules in the self-assembled films. We will then use steady-state and time-resolved measurement techniques determine how the structure of the multilayer film dictates the properties of the interface. Additionally, we will incorporate stimuli responsive molecular motifs into the assemblies that will act as reversible molecular switches to externally control, using either optical or electrical stimuli, electron and energy transfer at the interface.

As outlined in the original proposal, these goals are to be achieved with the following specific aims:
1) Synthesize a series of donor, acceptor, and stimuli-responsive molecules and incorporate them into bilayer assemblies.
2) Determine the structure of the self-assembled bilayers using spectroscopic techniques.
3) Understand the structure-function relationships that dictate electron/energy transfer at the interface.
4) Generate stimuli responsive self-assembled multilayers that modulate energy and electron transfer at the interface.

Accomplishments: See attached document.

Training Opportunities: During the duration of this grant, this project has supported the partial effort of two postdocs (Dhruba Pattadar and Wendi Zhang) and several semesters of effort for six graduate students (Alex Robb, Ashley Arcidiacono, Noelle Watson, Grace McLeod, Suliman Ayad and Erica Knorr). These researchers received training/mentorship in all aspects of the research process including hypothesis generation, experimental design, and processing/interpreting/presenting results. They have become familiar with a wide range of experimental techniques including synthesis, spectroscopy, and device preparation/characterization. These researchers are also involved in all steps of the publication process including outlining the manuscript and generating publication quality figures. They are required to write the first draft, are involved in multiple revisions, and help facilitate the manuscript submission process. The postdoc and graduate students have also been in active communication via both email and our zoom meetings. Of particular note is that due to the unexpected departure of a postdoc at UA, an FSU graduate student, Ashley Arcidiacono, spent the summer of 2022 at UA completing the ATR measurements outlined in this proposal.

Although attendance at conferences was limited due to COVID-19 restrictions, Ashley Arcidiacono presented her work on aims 2 and 3 as a poster for the AIP Photonics in Chemical Physics Virtual Conference (Sept 26-28, 2022) and in person at the Spring ACS Meeting (March 20-24, 2022). More recently, all four graduate students and one undergraduate student who worked on this project were able to present their results at the 30th annual meeting of the Inter-American Photochemical Society. That resulted in 2 graduate poster awards for Erica Knorr (Aim 3) and Ashley Arcidiacono (Aim 2) and one undergraduate poster award for Sarah Lindbom (Aim 3).

Results Dissemination: In addition to the undergraduate presentations noted above, the PI has given several presentations related to this work:

2022, October 12
Milan, Italy; International Symposium on Singlet Fission and Photon Fusion, "TTA-UC Solar Cells: Understanding and Controlling the Structure of Metal Ion Linked Multilayer Photoanodes" (Invited Talk)

2022, August 4
Newport, Rhode Island; Gordon Research Conference on Electron Donor-Acceptor Interactions, "Understanding and Controlling Molecular Structure and Excited State Dynamics at Dye-Metal Oxide Interfaces" (Invited Talk)

2022, May 24
Cancun, Mexico; Fusion Frontiers in Photochem, "Impact of Structure On Energy and Electron Transfer At Molecular Multilayer-Metal Oxide Interfaces" (Invited Talk)

2022, April 8
University of South Carolina, Department of Chemistry, "Harnessing Molecular Photon Upconversion Using Self-Assembled Multilayers on Metal Oxide Surfaces" (Invited Talk)

2022, February 4
Villanova, Department of Chemistry, "Applied Molecular Photophysics: My 25-Year Journey in Color Chemistry" (Invited Talk)

2021, March 23
William Patterson Unviersity, Department of Chemistry, "Harnessing Molecular Photon Upconversion Using Self-Assembled Multilayers on Metal Oxide Surfaces" (Invited Talk)

2021, March 10
Madrid, Spain; NanoGE Conference, "Harnessing Molecular Photon Upconversion in Dye-Sensitized Solar Cells" (Invited Talk via Zoom)

2020, October 28
Florida Southern University, Department of Chemistry & Biochemistry, "Harnessing Molecular Photon Upconversion Using Self-Assembled Multilayers on Metal Oxide Surfaces" (Invited Talk via Zoom)

Even with travel/conference limitations, the internet continues to provide a platform to reach a global audience. For more than a decade, the PI has been heavily involved in generating and disseminating chemistry/science content online as a blogger for chemistry-blog.com, as a contributor/moderator on the Chemistry subreddit and—since starting as a faculty member—through the Hanson group twitter profile and website.

The Hanson research group Twitter account has been active since July 2013 and has accumulated more than 1025 followers. Our primary contribution is our weekly photo (#picpickoftheweek) that captures research performed in our lab. The brightly colored nature of the work described here readily lends itself to beautiful photos including these example posts:

Metal oxide Prep/thin films:
https://twitter.com/HansonFSU/status/1563250995089395713
https://twitter.com/HansonFSU/status/1525135955929223169

Spectroscopy:
https://twitter.com/HansonFSU/status/1550579200230301701
https://twitter.com/HansonFSU/status/1431365141350785030

Chromophores:
https://twitter.com/HansonFSU/status/1527650061575929858
https://twitter.com/HansonFSU/status/1522704337407033346
https://twitter.com/HansonFSU/status/1504921654287286275
https://twitter.com/HansonFSU/status/1502403875059425282

Lastly, we create a video abstract to accompany every one of our corresponding author publications which we share via our publications (https://www.chem.fsu.edu/~hanson/) and Youtube (https://www.youtube.com/channel/UCkyMpoRcuTMrfD1kdPgYWkw/videos) pages.

A video abstract for our ARO supported articles can be viewed below.
J. Photochem Photobio: https://youtu.be/HBNued3xOeM
ACS AM&I: https://youtu.be/PguEk1LMJsQ
JPC: https://youtu.be/KYWTen8dAWE
J. Photochem Photobio: https://youtu.be/jvfTYIKND-o

The feedback has been overwhelmingly positive, so we intend to continue our online dissemination efforts with the manuscripts currently in preparation.

Honors and Awards: This project resulted in two graduate and one undergraduate poster awards at the 30th annual meeting of the Inter-American Photochemical Society.

Protocol Activity Status:

Technology Transfer: One patent was issued over the course of the project that is related to this work but was submitted during my previous ARO-YIP award period.

Hanson, K.; Wang, J. C.; Banerjee, T.; Ogunsolu, O.O. "Modulating Electron Transfer Dynamics at Hybrid Interfaces via Self-Assembled Bilayers" U.S. Pat. US 10916381B2 (2021).

PARTICIPANTS:

Participant Type: PD/PI
Participant: Kenneth Hanson
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Co PD/PI
Participant: S. Scott Saavedra
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Suliman Ayad
Person Months Worked: 4.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Ashley Arcidiacono
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Alex Robb
Person Months Worked: 8.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Noelle Watson
Person Months Worked: 8.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Grace McLeod
Person Months Worked: 4.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Erica Knorr
Person Months Worked: 8.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Dalton Miles
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Sarah Lindbom
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

ARTICLES:

RPPR Final Report
as of 07-Apr-2023

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of Photochemistry and Photobiology A: Chemistry
Publication Identifier Type: DOI Publication Identifier: 10.1016/j.jphotochem.2019.112291
Volume: 390 Issue: First Page #: 112291
Date Submitted: 5/27/20 12:00AM Date Published: 3/1/20 5:00AM
Publication Location:
Article Title: Metal ion linked multilayers on mesoporous substrates: Energy/electron transfer, photon upconversion, and more
Authors: Alex J. Robb, Erica S. Knorr, Noelle Watson, Kenneth Hanson
Keywords: multilayers, electron/energy transfer, upconversion, self-assembly, solar energy conversion
Abstract: Metal ion linked multilayers on mesoporous, semiconducting surfaces has recently emerged as a simple but effective strategy to facilitate photoinduced energy and electron transfer events at organic-inorganic interfaces. In this manuscript we recount our groups work in understanding, controlling, and harnessing photoinduced processes in these multilayer assemblies. This includes, 1) manipulating interfacial electron transfer rates at dye-semiconductor interfaces, 2) generating directional energy and electron cascade solar cells, and 3) facilitating and harnessing molecular photon upconversion via triplet-triplet annihilation. We then close with a brief summary of the progress to date, general limitations with the current films/work, and an outlook as to what the future may hold holds for these multilayer films.
Distribution Statement: 2-Distribution Limited to U.S. Government agencies only; report contains proprietary info
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: ACS Applied Materials & Interfaces
Publication Identifier Type: DOI Publication Identifier: 10.1021/acsami.0c07968
Volume: Issue: First Page #:
Date Submitted: 8/20/20 12:00AM Date Published: 7/30/20 4:00AM
Publication Location: United States
Article Title: Role of Metal Ion Linked Multilayer Thickness and Substrate Porosity in Surface Loading, Diffusion, and Solar Energy Conversion
Authors: Alex J. Robb, Dalton Miles, Sahan R. Salpage, Noelle Watson, Qingquan He, Qiang Wu, and Kenneth H
Keywords: metal ion linked, multilayer, dye-sensitized, solar cell, diffusion
Abstract: Metal ion linked multilayers offer an easily prepared and modular architecture for controlling energy and electron transfer events on nanoparticle, metal oxide films. However, unlike with planar electrodes, the mesoporous nature of the films inherently limits both the thickness of the multilayer and subsequent diffusion through the pores. Here we systematical investigated the role of TiO2 nanoparticle film porosity and metal ion linked multilayer thickness on surface loading, through-pore diffusion, and overall device performance. The porosity and multilayer thickness were controlled by varying in TiO2 sintering times and the number of ZnII linked layers of bridging molecules (B = p-terphenyl diphosphonic acid) between the metal oxide and the Ru(bpy)2((4,4?-PO3H2)2bpy)]Cl2 dye (RuP) in the TiO2-(Bn)-RuP films. Using ATR-IR and UV-Vis spectroscopy we observed that at least two molecular layers (i.e. TiO2-B2 or TiO2-B1-RuP) could be formed on all films but subsequent loading was dependen
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Journal: The Journal of Physical Chemistry C
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.jpcc.0c08715
Volume: 124 Issue: 43 First Page #: 23597
Date Submitted: 11/3/20 12:00AM Date Published: 10/1/20 4:00AM
Publication Location:
Article Title: Examining the Influence of Bilayer Structure on Energy Transfer and Molecular Photon Upconversion in Metal Ion Linked Multilayers
Authors: Ashley Arcidiacono, Yan Zhou, Wendi Zhang, Jeffrey O. Ellison, Suliman Ayad, Erica S. Knorr, Autumn
Keywords: multilayer, energy transfer, upconversion, metal ion linked
Abstract: Metal ion linked multilayers are a unique motif to spatially control and geometrically restrict molecules on a metal oxide surface, which is of interest in a number of promising applications. Here we use a bilayer composed of a metal oxide surface, an anthracene annihilator molecule, Zn(II) linking ion, and porphyrin sensitizers to probe the influence of the position of the metal ion binding site on energy transfer, photon upconversion, and photocurrent generation. Despite being energetically similar, varying the position of the carboxy metal ion binding group (i.e., ortho, meta, para) of the Pt(II) tetraphenyl porphyrin sensitizer had a large impact on energy transfer rates and upconverted photocurrent that can be attributed to differences in their geometries. From polarized attenuated total reflectance measurements of the bilayers on ITO, we found that the orientation of the first layer (anthracene) was largely unperturbed by subsequent layers. However, the tilt angle of the porphyr
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of Photochemistry and Photobiology
Publication Identifier Type: DOI Publication Identifier: 10.1016/j.jpap.2021.100088
Volume: Issue: First Page #:
Date Submitted: 8/28/22 12:00AM Date Published:
Publication Location:
Article Title: Inhibited Interlayer Electron Transfer in Metal Ion Linked Multilayers on Mesoporous Metal Oxide Films
Authors: Ashley Arcidiacono, Alex J. Robb, Rafael A. Masitas, Sahan R. Salpage, Grace M. McLeod, Jiaqi Chen,
Keywords: metal ion linked, multilayer, dye-sensitized, electron transfer, electron donor
Abstract: The incorporation of dye-electron donor motifs on metal oxide surfaces is a common strategy to increase dye regeneration rate, slow recombination, and improve overall dye-sensitized device performance. Here we used zinc ion linked multilayer assembly of a dye (N3) and a cobalt polypyridyl electron donor (Co) on TiO2 as an alternative to traditional covalently linked dye-donor systems. The formation of the TiO2-N3-Zn-Co multilayer was monitored using UV-Vis and ATR-IR and we introduced inductively coupled plasma mass spectrometry as a means of quantifying the surface loading of spectroscopically obscured molecules like Co. Interestingly, and contrary to the original intent, the addition of Co electron donor impeded the dye-sensitized device in nearly every performance metric. Transient absorption measurements indicate that both excited state quenching of N3 by Co and Co to N3+ electron transfer are slower than the intrinsic excited state decay and recombination, respectively. We sugges
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Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Physical Chemistry C
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.jpcc.2c08632
Volume: 127 Issue: 5 First Page #: 2705
Date Submitted: 3/23/23 12:00AM Date Published: 1/1/23 5:00AM
Publication Location:
Article Title: Molecular Orientation of -PO3H2 and -COOH Functionalized Dyes on TiO2, Al2O3, ZrO2, and ITO: A Comparative Study.
Authors: Dhruba Pattadar, Lianqing Zheng, Alex J. Robb, Drake Beery, Wei Yang, Kenneth Hanson, S. Scott Sa
Keywords: electron transfer, orientation, ATR, metal oxide
Abstract: Modifying metal oxides (MOx) with organic monolayers is widely employed to tailor interfacial properties in organic electronic devices and dye-sensitized solar cells. The effects of modification are frequently assessed by performing experiments on model monolayer|MOx interfaces, where an “inert” MOx (e.g., Al2O3) is used as a control for an “active” MOx (e.g., TiO2). An underlying assumption in these studies is that the inert and active monolayer|MOx structures are similar. This assumption was examined here. Using UV–vis attenuated total reflection spectroscopy, we measured the mean tilt angle of 4,4?-(anthracene-9,10-diyl)bis(4,1-phenylene) diphosphonic acid (A1P) adsorbed on indium tin oxide (ITO), TiO2, ZrO2, and Al2O3. When the surface roughness of the MOx substrate and the surface coverage (?) of the A1P film were constant, the orientation of A1P was the same. 4,4?-(Anthracene-9,10-diyl)bis(4,1-phenylene)dicarboxylic acid (A1C) was adsorbed on the same set of MOx substrates.
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Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 4-Under Review
Journal: Analytical Chemistry
Publication Identifier Type: Publication Identifier:
Volume: Issue: First Page #:
Date Submitted: 3/23/23 12:00AM Date Published:
Publication Location:
Article Title: Molecular Orientation and Energy Transfer Dynamics of a Metal Oxide Bound Self-Assembled Trilayer
Authors: Dhruba Pattadar, Ashley Arcidiacono, Drake Beery, Kenneth Hanson, S. Scott Saavedra
Keywords: metal oxide, electron transfer, trilayer, orientation
Abstract: Self-assembly of molecular multilayers via metal ion linkages has become an important strategy for interfacial engineering of metalloid and metal oxide (MOx) substrates, with applications in numerous areas, including energy harvesting, catalysis, and chemical sensing. An important aspect for rational design of these multilayers is knowledge of molecular structure-function relationships. For example, in a multilayer composed of different chromophores in each layer, the molecular orientation of each layer, both relative to the adjacent layers and the substrate, dictates the efficiency of vectoral energy and electron transfer. Here we describe an approach using UV-vis attenuated total reflection (ATR) spectroscopy to determine the mean dipole tilt angle of chromophores in each layer in a metal-ion linked trilayer self-assembled on indium-tin oxide. We also perform transient absorption spectroscopy to monitor interlay energy transfer dynamics in order to relate structure to function. In
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 4-Under Review
Journal: ACS Applied Optical Materials
Publication Identifier Type: Publication Identifier:
Volume: Issue: First Page #:
Date Submitted: 3/23/23 12:00AM Date Published:
Publication Location:
Article Title: Metal Ion-Linked Molecular Multilayers on Inorganic Substrates: Structure and Applications
Authors: Ashley Arcidiacono, Kenneth Hanson
Keywords: metal ion-linked, multilayers, structure, orientation

Abstract: Metal ion-linked multilayers have emerged as a simple and modular means of assembling molecular components on an inorganic substrate. The choice of molecules, based on their excited state energies and redox potentials, has enabled the directional control of energy and electron transfer events for application in electrochromics, solar energy harvesting, molecular rectifiers, photocatalysis, and more. Here we recount the more than 35-year journey of metal ion-linked multilayers and their transition from planar to mesoporous substrates and from homogeneous to heterogeneous multilayers. This includes showcasing the vast range of components (i.e., substrates, metal ions, and molecules), structural insights, and applications. We also highlight current limitations in our knowledge of and ability to control of these systems which must be overcome to realize the full potential of metal ion-linked multilayers.

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Acknowledged Federal Support: **Y**

WEBSITES:

URL: https://youtu.be/jvfTYlKND-o
Date Received: 27-Aug-2021
Title: Video Abstract: Metal Ion Linked Multilayers on Mesoporous Substrates
Description: This video is a presentation summary of our Journal of Photochemistry and Photobiology A: Chemistry article titled, "Metal Ion Linked Multilayers on Mesoporous Substrates: Energy/Electron Transfer, Photon Upconversion, and More" narrated by first author Alex Robb.
URL: https://youtu.be/PguEk1LMJsQ
Date Received: 27-Aug-2021
Title: Video Abstract: Role of Metal Ion Linked Multilayer Thickness and Substrate Porosity
Description: This video is a presentation summary of the data presented in our ACS Applied Materials and Interfaces article titled, "Role of Metal Ion Linked Multilayer Thickness and Substrate Porosity on Surface Loading, Diffusion, and Solar Energy Conversion" narrated by first author Alex Robb.
URL: https://youtu.be/KYWTen8dAWE
Date Received: 27-Aug-2021
Title: Video Abstract: Influence of Structure on Energy Transfer & Molecular Photon UC in Metal Ion Linked Multilayers
Description: This video is a presentation summary of the data presented in our Journal of Physical Chemistry C article titled, "Examining the Influence of Bilayer Structure on Energy Transfer and Molecular Photon Upconversion in Metal Ion Linked Multilayers" narrated by first author Ashley Arcidiacono.
URL: https://youtu.be/HBNued3xOeM
Date Received: 23-Mar-2023
Title: Video Abstract: Inhibited Interlayer Electron Transfer in Metal Ion Linked Multilayers on Meso Metal Oxide Films
Description: This video summarizes our article written in Journal of Photochemistry and Photobiology titled, "Inhibited Interlayer Electron Transfer in Metal Ion Linked Multilayers on Mesoporous Metal Oxide Films" narrated by first author Ashley Arcidiacono.

PATENTS:

Intellectual Property Type: Patent Date Received: **08-Sep-2021**
Patent Title: Modulating Electron Transfer Dynamics at Hybrid Interfaces via Self-Assembled Bilayers
Patent Abstract:
Patent Number: 10916381B2
Patent Country: USA
Application Date: 14-Jul-2015 Application Status: 3
Date Issued: 09-Feb-2021

Intellectual Property Type: Patent Date Received: **08-Sep-2021**
Patent Title: Modulating Electron Transfer Dynamics at Hybrid Interfaces via Self-Assembled Bilayers
Patent Abstract:
Patent Number: 10916381B2
Patent Country: USA
Application Date: 14-Jul-2015 Application Status: 3
Date Issued: 09-Feb-2021

Partners

,

I certify that the information in the report is complete and accurate:
Signature: Kenneth Hanson
Signature Date: 4/5/23 3:56PM

Abstract

The rate, efficiency, and direction of energy and electron transfer at organic-inorganic interfaces is critical for their application in bioelectronics, solar energy conversion, electrocatalysis, sensing, and more. There is typically a barrier to electronic communication across these hybrid interfaces but self-assembly of molecular multilayers has emerged as a simple and modular means of gaining unprecedented control over interfacial energy and electron transfer events. While tuning the energetics of the molecular assemblies has proven successful thus far, the lack of structural knowledge and architectural control of these interfaces has limited our ability to unlock the full potential of self-assembled interfaces.

To remedy this shortcoming, this proposal outlines a three-year program with the objective of using carefully designed molecular derivatives, metal linking ions, and self-assembly methods, along with a combination of Förster resonance energy transfer and polarized attenuated total reflectance, to determine the parameters that dictate the structure (i.e. the relative distances and orientation) of the molecules in the self-assembled films. We will then use steady-state and time-resolved measurement techniques determine how the structure of the multilayer film dictates the properties of the interface. Additionally, we will incorporate stimuli responsive molecular motifs into the assemblies that will act as reversible molecular switch to externally control, using either optical or electrical stimuli, electron and energy transfer at the interface.

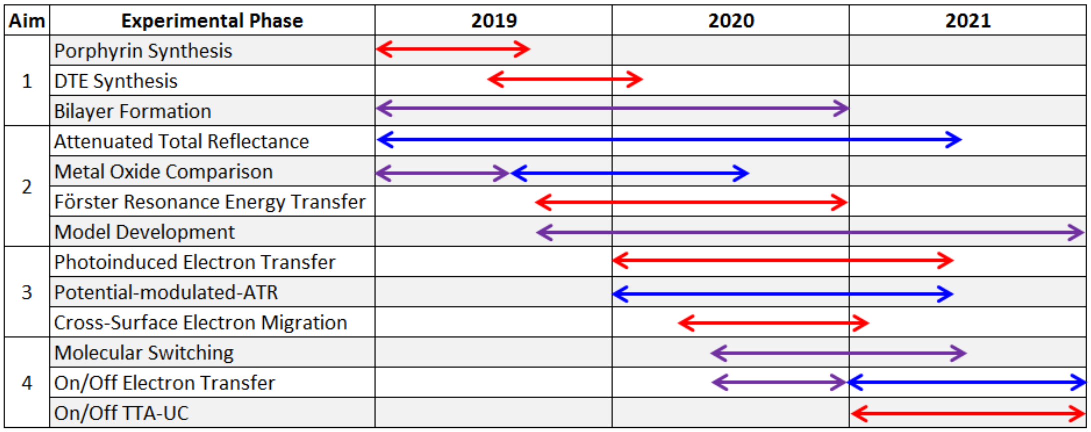
Collectively, this work will elucidate the role of the metal ion and molecular structure in dictating the structure of the self-assembled bilayer as well as how that structure influences the electrochemical and photophysical properties of the interface. This contribution is significant because this structure-property knowledge can be used to design new interfaces with exquisite control over energy and electron transfer at hybrid interfaces. In addition to improving the performance of electrocatalysts, photodetectors, and other applications mentioned above, the generation of interfaces that exhibit structural changes under external stimulation opens the door to new applications for self-assembled hybrid interfaces including non-linear optics, electrochromic windows, logic gates, read-write arrays, and more. Thus, these insights have broad implications for increasing both fundamental knowledge and utility of hybrid interfaces. Equally important is that we will have introduced two new strategies, Förster resonance energy transfer and polarized attenuated total reflectance, to characterize the structure of assemblies at multimolecular interfaces.

Objectives

The primary goals of this project are to use carefully designed molecular derivatives, metal linking ions, and self-assembly methods, along with a combination of Förster resonance energy transfer (FRET) and polarized attenuated total reflectance (ATR), to determine the parameters that dictate the structure (i.e. the relative distances and orientation) of the molecules in the self-assembled films. We will then use steady-state and time-resolved measurement techniques determine how the structure of the multilayer film dictates the properties of the interface. Additionally, we will incorporate stimuli responsive molecular motifs into the assemblies that will act as reversible molecular switches to externally control, using either optical or electrical stimuli, electron and energy transfer at the interface.

As outlined in the original proposal, these goals are to be achieved with the following specific objectiveswith the originally proposed timeline shown below:

1) Synthesize a series of donor, acceptor, and stimuli-responsive molecules and incorporate them into bilayer assemblies.
2) Determine the structure of the self-assembled bilayers using spectroscopic techniques.
3) Understand the structure-function relationships that dictate electron/energy transfer at the interface.
4) Generate stimuli responsive self-assembled multilayers that modulate energy and electron transfer at the interface.



Aim	Experimental Phase	2019	2020	2021
1	Porphyrin Synthesis	←→		
	DTE Synthesis	←—	—→	
	Bilayer Formation	←—	—→	
2	Attenuated Total Reflectance	←—	——	—→
	Metal Oxide Comparison	←→←—	—→	
	Förster Resonance Energy Transfer	←—	—→	
	Model Development	←—	——	—→
3	Photoinduced Electron Transfer		←—	—→
	Potential-modulated-ATR		←—	—→
	Cross-Surface Electron Migration		←—	—→
4	Molecular Switching		←—	—→
	On/Off Electron Transfer		←→	←→
	On/Off TTA-UC			←→

Findings

<u>Significant results summary.</u>

1) Manuscripts: 5 published, 2 submitted, 4 actively being written
2) All target molecules have been synthesized.
3) ATR can be used to determine the structure on multilayers.
4) Binding group and surface don't impact binding angle of first layer.
5) Both linking ion and binding group position can tune second layer orientation.
6) Structure impact both energy and electron transfer.
7) Energy transfer and structure are similar on planar and mesoporous oxides.
8) Multilayers are an effective means of generating stimuli responsive surfaces.

The significant results for the duration of this project are summarized below and are partitioned by the specific aims in the original proposal.

Aim 1) Synthesize a series of donor, acceptor, and stimuli-responsive molecules and incorporate them into bilayer assemblies.

All of the molecules of interest for this project are shown in Figure 1, have been synthesized and we have completed the goals of this aim.

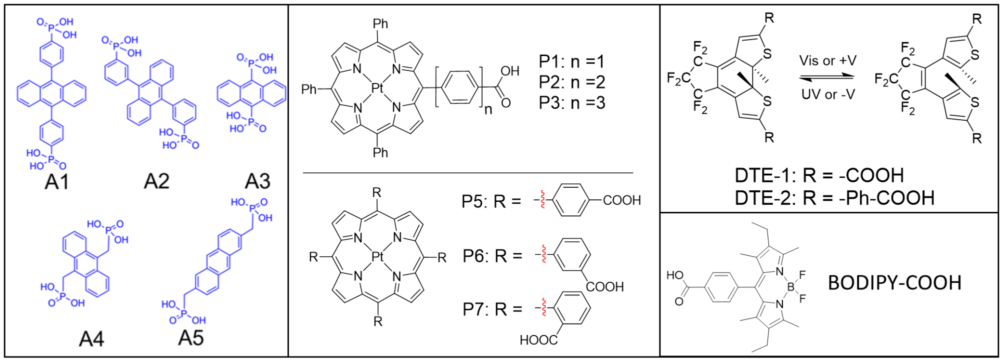


Figure 1. Molecular structures of the anthracene (A1-5) and porphyrin (P1-3, 5-7) derivatives and the open (o) and closed (c) forms of DTE-1/2.

Aim 2) Determine the structure of the self-assembled bilayers using spectroscopic techniques.

and

Aim 3) Understand the structure-function relationships that dictate electron/energy transfer at the interface.

Because the structure and function of these multilayers are inherently tied together, we summarize the progress on both below.

Manuscript 1.

ACS App. Mater. Interfaces, **2020**, 12, 38003–38011 (https://doi.org/10.1021/acsami.0c07968)

As a prelude to structural studies, we systematically investigated the cooperative influence of nanoparticle film porosity and metal ion-linked multilayer thickness (Figure 2). From the dye loading, rough estimates indicate that in a film with 34 nm average pore diameter, the maximum multilayer film thickness is on the order of 4.6−6 nm, which decreases with decreasing pore size. These results show that care must be taken to balance multilayer thickness and substrate porosity.

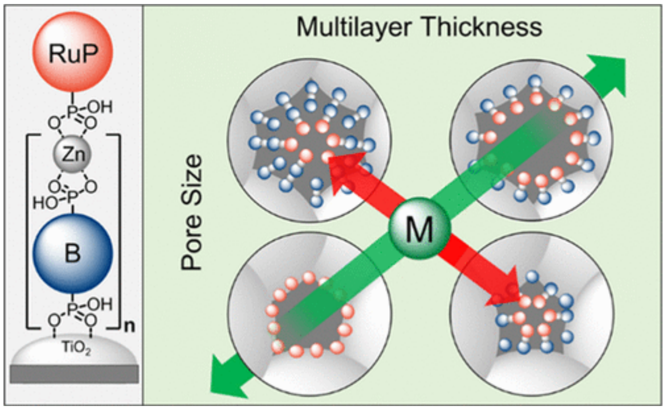


Figure 2. Graphical depiction of the decreased loading and through pore diffusion of the mediator with decreased pore size and increased multilayer thickness.

Manuscript 2.

J. Phys. Chem. C 2023, 127, 2705–2715. (https://doi.org/10.1021/acs.jpcc.2c08632)

We investigated the impact of binding group and metal oxide on the orientation of a monolayer. Interestingly we found that phosphonated (A1P) and carboxylated (A1C) complexes on TiO_2, ITO, ZrO_2, and Al_2O_3 (Figure 2) all exhibited a similar orientation (20˚) and agree well with the prediction from molecular dynamics simulations. These results suggest that the molecular packing, not the surface binding, dictates the tilt angle of the densely packed monolayer and that structurally it is valid to compare between different metal oxides for electrochemical (ITO), spectroscopic (ZrO_2), and device measurements (TiO_2).

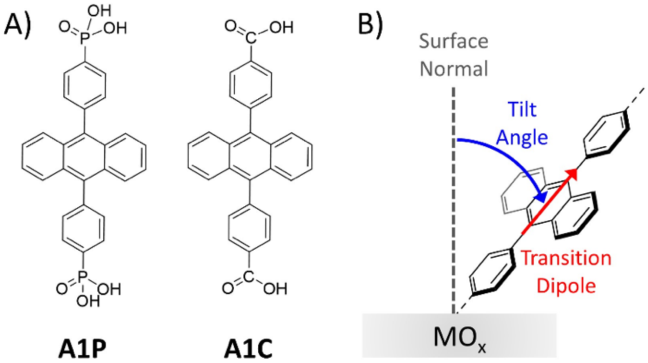


Figure 3. (A) Structures of A1P and A1C. (B) Schematic of the diphenyl anthracene core of A1P and A1C adsorbed on a MOx substrate, showing the position of the absorption transition dipole and the tilt angle measured using ATR.

Manuscript 3.

Draft in the hands of collaborators. (Submission by June)

We the investigated the role of the metal ion (Zn vs. Zr vs. La) structure and dynamics of an anthracene (**A**) porphyrin (**P**) ion linked self-assembled bilayer (Figure 4). While Zr and Zn linked layers exhibited similar structure and dynamics, La linked layers exhibited a 10° more tilted orientation which manifested as a slowed energy transfer rate. This result indicates that the nature of the metal ion can be used to control the structure and properties of the multilayers.

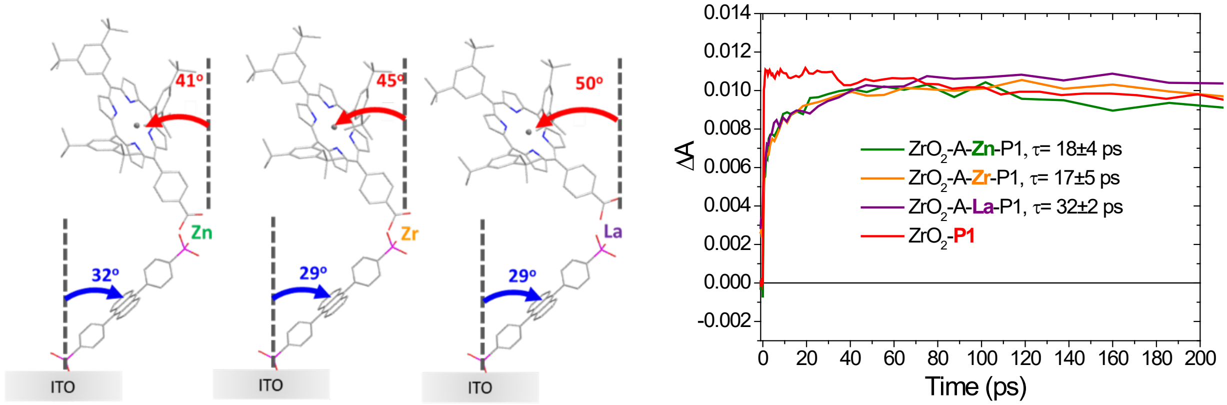


Figure 4. Depiction of the mean tilt angles of anthracene (**A**) and porphyrin (**P1**) in **A**-M-**P1** bilayers, linked by Zn, Zr, and La (left), and single wavelength kinetics monitoring the rise of **P1** excited states via **A** to **P1** energy transfer (right).

Manuscript 4.

J. Phys. Chem. C 2020, 43, 23597-23610. (https://doi.org/10.1021/acs.jpcc.0c08715)

Using ATR and MD simulation we demonstrated that the position of the metal ion binding group (i.e., o-, m-, or p-) can be used to impact the orientation of the second layer molecules as shown in Figure 5. There were three major contributions from this report: 1) that ATR could be used to determine the orientation of two chromophores, 2) that when correcting for surface roughness, the angles determined by ATR and MD simulation were nearly identical, 3) that the binding group could be used to control the second layer which impacted the energy transfer dynamics and device performance.

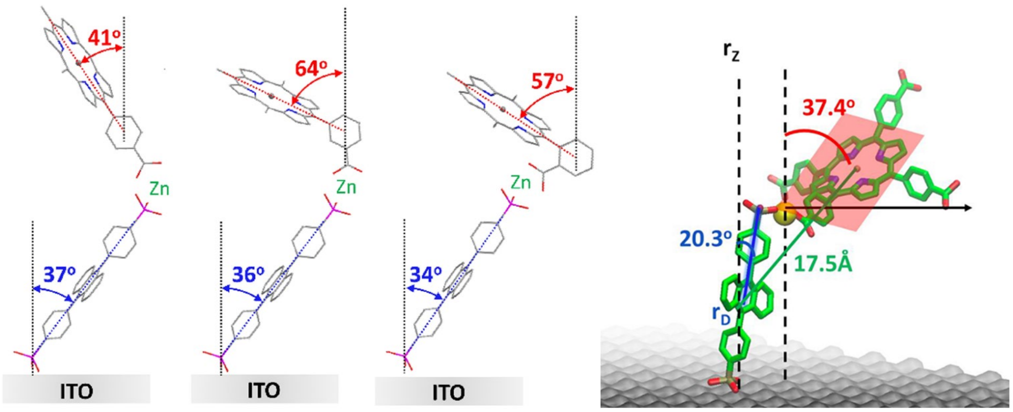


Figure 5. Schematic depictions of the mean orientation of A-Zn-P bilayer films on ITO from ATR (left) and MD simulations (right).

Manuscript 5:

J. Photochem. Photobio. 2022, 9,100088. (https://doi.org/10.1016/j.jpap.2021.100088)

The above work focused on controlling energy transfer but we also demonstrated that we can influence electron transfer as well. As an example, we showed that **Co** to **N3**$^+$ electron transfer readily occurs in solution but the geometric restriction imposed by the multilayer architecture effectively slows interlayer electron transfer (Figure 6). This knowledge may enable unique opportunities in long distance spin/magnetic moment communication between complexes for use in QIS, for example.

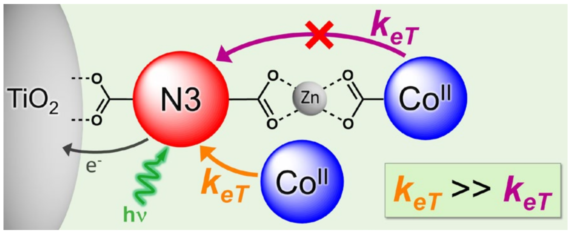


Figure 6. Schematic representation of TiO$_2$-**N3**-Zn-**Co** bilayer with inhibited and allowed electron transfer events shown in purple and orange, respectively.

Manuscript 6.

Analytical Chemistry (Under review)

With knowledge of the first and second layer in hand (*vida supra*), we sought to determine the structure of a trilayer film using ATR (Figure 7). This work demonstrated, for the first time, that the structure of a three-component film can be determined using ATR. Using transient absorption, we observed ultrafast, third to second layer energy transfer (3×10^{11} s^{-1}) that occurred at unity efficiency which is attributed to the close proximity of the species. This is why, at least in part, this trilayer is the record holding film for harnessing triplet-triplet annihilation in an upconversion solar cell.

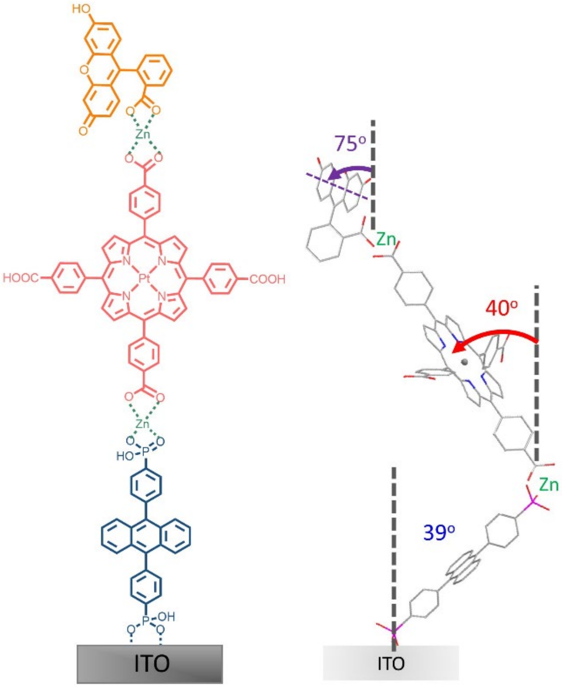


Figure 7. Schematic representation of the ITO-**A**-Zn-**P** -Zn-**F** trilayer (left) and tilt angle as determined by ATR (right).

Manuscript 7.

In preparation. (Submission by the start of May)

One of the fundamental questions regarding the energy transfer dynamics in the films is if the energy and electron transfer occurs within an assembly (k_{IA} in Figure 8) or between unlinked species in each layer (k_{IL}). To differentiate between the two, we monitored energy transfer dynamics while diluting our first layer with a non-linked and photophysically inert molecule (Grey in Figure 8). Both forward and back energy transfer were found to be independent on the dilution, strongly supporting that inter-assembly energy transfer is the dominate communication pathway between the multilayers.

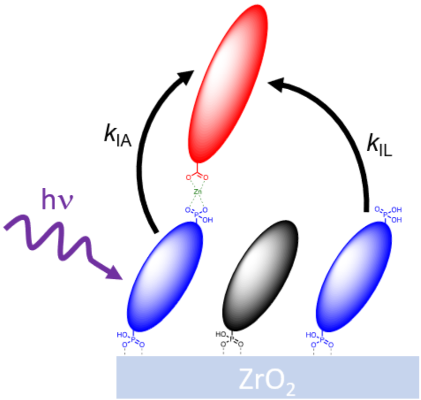


Figure 8. Schematic representation of possible inter-assembly (k_{IA}) and interlayer (k_{IL}) energy transfer in a bilayer composed of a donor (A, blue), acceptor (P, red), and an inter spacer molecule (grey).

Manuscript 8.

Manuscript in preparation. (Submission by July)

With inter-assembly established as the dominant energy transfer mechanism, we were then able to use the distance between the layers to determine the intermolecular angle as depicted in Figure 9. Forward and back energy transfer rates were found to be the same on both planar and mesoporous oxides indicating that the planar surfaces can serve as a structural surrogate for the mesoporous films. From ATR measurements we found the tilt angle of A remains relatively constant (~30°) the tilt angle decreases in the order P1 (50±1) < P2 (36±2) < P3 (22±4). These angles can then be correlated with energy transfer rates to provide structure-property insights into the multilayer.

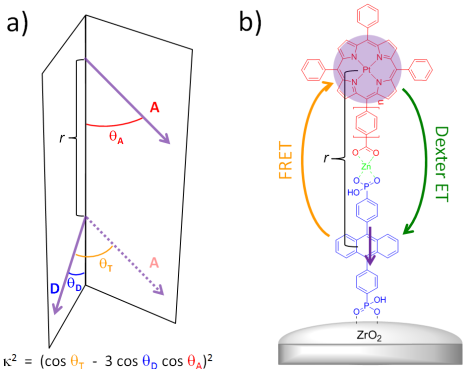


Figure 9. a) Depiction of the angle between transition dipole moments for donor (A) and acceptor (P, n=1-3). b) Schematic representation of the bilayer film depicting FRET, Dexter energy transfer, distance (*r*), and dipole moment/plane (purple).

Manuscript 9 and 10.

Complementing the experimental work described above, we have written two review articles:

1) Summarizes our groups progress in studying metal ion linked multilayers.
J. Photochem. Photobiol. A, 2019, 390, 112291.
(https://doi.org/10.1016/j.jphotochem.2019.112291)

2) A comprehensive review article recounting all work on metal ion-linked multilayers since their inception in 1988.
ACS Appl. Opt. Mater. (Under review).

Aim 4) Generate stimuli responsive self-assembled multilayers that modulate energy and electron transfer at the interface.

Manuscript 11.

Manuscript in preparation. (Submission by the end of May)

With our photo switching molecule in hand, we have generated multilayer films on ZrO2 (Figure 10). Under 600 nm and 365 nm excitation, the films undergo reversible photoswitching that is readily observable via the color change (Figure 11 top). The reversibility (Figure 11 bottom) dramatically increases when adding a metal ion and a second molecule (i.e., CDCA). These results demonstrate the feasibility of using metal ion-linked multilayers in stimuli responsive interfaces. This manuscript is actively in preparation.

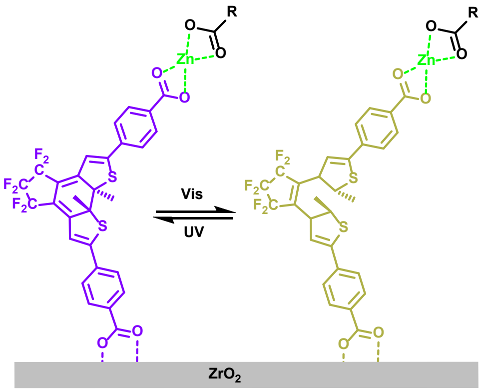


Figure 10. Schematic depiction of the reversible light induced switching of the DTE molecule on a ZrO_2 surface.

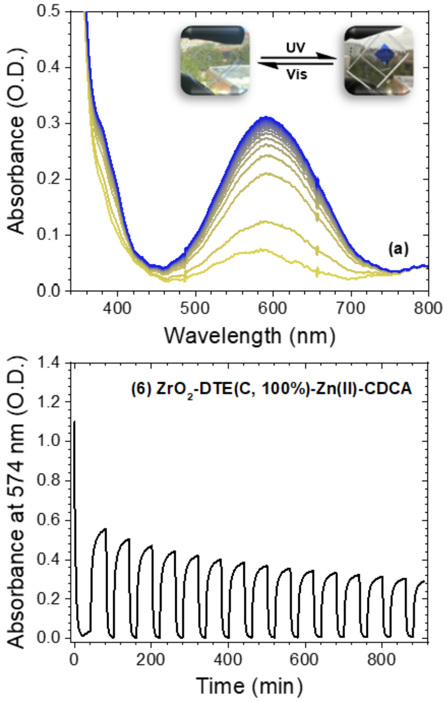


Figure 11. Full spectra (top) and single wavelength (bottom) monitoring of the photoswitching process under 365 and 600 nm light cycles. Inset: a photo of the photochromic response.