

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 01-06-2018		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 30-Sep-2014 - 29-Mar-2018	
4. TITLE AND SUBTITLE Final Report: Asymmetric Electron Transfer Rates At Organic-Inorganic Hybrid Interfaces Via Self-Assembled Bilayers			5a. CONTRACT NUMBER W911NF-14-1-0660		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611102		
6. AUTHORS			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES Florida State University Sponsored Research Administration 874 Traditions Way, Third Floor Tallahassee, FL 32306 -4166			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 66413-MS-YIP.20		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:		17. LIMITATION OF ABSTRACT		15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU	UU		Kenneth Hanson
					19b. TELEPHONE NUMBER 850-645-0479

RPPR Final Report

as of 24-Jul-2018

Agency Code:

Proposal Number: 66413MSYIP

Agreement Number: W911NF-14-1-0660

INVESTIGATOR(S):

Name: Ph.D. Kenneth Hanson

Email: hanson@chem.fsu.edu

Phone Number: 8506450479

Principal: Y

Organization: **Florida State University**

Address: Sponsored Research Administration, Tallahassee, FL 323064166

Country: USA

DUNS Number: 790877419

EIN: 591961248

Report Date: 29-Mar-2018

Date Received: 01-Jun-2018

Final Report for Period Beginning 30-Sep-2014 and Ending 29-Mar-2018

Title: Asymmetric Electron Transfer Rates At Organic-Inorganic Hybrid Interfaces Via Self-Assembled Bilayers

Begin Performance Period: 30-Sep-2014

End Performance Period: 29-Mar-2018

Report Term: 0-Other

Submitted By: Ph.D. Kenneth Hanson

Email: hanson@chem.fsu.edu

Phone: (850) 645-0479

Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 4

STEM Participants: 5

Major Goals: The goal of this research is to influence electron transfer dynamics at an organic-inorganic interface in order to maximize the rate of electron transfer in one direction (forward electron transfer, FET) and suppress it in the reverse direction (back electron transfer, BET). As outlined in the original proposal these goals are to be achieved by 1) tuning the energy of the bridge so that FET and BET occur through two different mechanisms, fast incoherent hopping and slower coherent tunneling, respectively, and 2) to generate self-assembled bilayers containing asymmetric bridges that asymmetrically influence electron transfer rates between the active material and the metal oxide surface.

Accomplishments: The Hanson research group has introduced self-assembled bilayers as a simple, scalable, modular, and effective method for manipulating electron transfer at organic-inorganic interfaces. Our initial efforts involved altering the length of a photophysically and electrochemically inert bridging molecule (Figure 1a).[J. Phys. Chem. C 2015, 119, 3502] The length of the molecular bridge (i.e. distance between the dye and the semiconductor) did exponentially decrease FET (decreased J_{sc}) and BET (slowed recombination and increased V_{oc} , Figure 1b) indicating that the bridge and metal ion are acting as a tunneling barrier for electron transfer events.[ACS Appl. Mater. Interfaces 2015, 7, 27730] Unfortunately, the observed enhances in V_{oc} and FF are far outweighed by the significant decrease in J_{sc} and thus overall device performance decreases with increasing bridge length.

Following our proof-of-concept distance dependence studies we then shifted our focus to tuning the energy of the bridging molecule and metal ion. We demonstrated that CuII linking ions can have a profound effect on the excited-state dynamics in the bilayer film.[Phys. Chem. Chem. Phys. 2017, 19, 2679] To further elucidate the role of the metal ion in the assemblies, we incorporated several different cations, CdII, CuII, FeII, LaIII, MnII, SnIV, ZrIV and ZnII into the self-assembled bilayer films (Figure 3). Bilayers composed of CuII, FeII, and MnII exhibit significant excited state quenching. This reduces the injection yield but also, for CuII and MnII bilayers, significantly slows back electron transfer kinetics.[Langmuir 2017, 33, 9609] Ultrafast transient absorption measurements indicate that CuII, FeII, and MnII ions quench the excited state with a rate constant of $\sim 10^7$ s⁻¹ which is competitive with electron injection (109 s⁻¹). [J. Phys. Chem. C, 2018, 122, 9835] Collectively these metal ion studies are a major contribution in that we have notably slowed BET while still maintaining reasonably high FET, the primary objectives of this proposal. This scheme is analogous to the metal ion mediated electron transfer found in naturally occurring photosynthetic schemes and opens the door to a new structural handle, the metal ion, that can be used to tune electron transfer events at the interface.

We also introduced directionally controlled energy and electron transfer as an alternative means to tune electron transfer dynamics at the interface. This strategy requires a bilayer composed of two dyes, p1M and pN3 in Figure 4, whose energetics are appropriate for energy/electron transfer from the outside towards the surface.

RPPR Final Report as of 24-Jul-2018

These DSSCs exhibits a 10% increase in J_{sc} , V_{oc} , and η over the monolayer devices due to increased incident photon-to-electron conversion efficiency across the entire visible spectrum. [ACS Appl. Mater. Interfaces, 2016, 8, 28633] In this bilayer film p1M is directly excited (1 in Figure 5), energy is transferred from p1M* to pN3 (2), an electron is injected from pN3* into TiO₂ (3), p1M to pN3+ electron transfer (4), and finally recombination (5). In the context of the goals of this proposal, this architecture effectively maintains high FET yield but slows BET.

One unexpected observation from this study was that simply coordinating the ZrIV metal ion to the first dye, without the second dye, decreased the J_{sc} but—remarkably—increased V_{oc} relative to the dye alone. In a follow-up study, we coordinated several different metal cations (CdII, CuII, FeII, LaIII, MnII, SnIV, ZrIV and ZnII) to the surface bound dye (Figure 6).[Inorg. Chem., 2017, 56, 11168] The metal ions decreased J_{sc} but increased the V_{oc} by upwards of 130 mV relative to the parent devices. We attributed the decrease in J_{sc} and increase in V_{oc} to the metal ion slowing dye regeneration and back electron transfer kinetics, respectively. This observation was particularly intrigued because it suggested that simply coordinating the metal ion to a surface bound dye helps inhibits BET but not FET.

In a related, but somewhat tangential project, our research group recently published a review article titled "Multimolecular assemblies on high surface area metal oxides and their role in interfacial energy and electron transfer" (Figure 7).[Chem. Soc. Rev. 2018, 47, 104] In the review we summarize current research efforts to control energy and electron transfer at organic-inorganic interfaces using multiple molecular species. The topic is directly relevant to this proposal. It highlights the utility of our self-assembled bilayer strategies and will hopefully solidify us as leaders in this area of research. As a side, this review was a byproduct of a graduate level writing course that was taught by the PI and a manuscript describing the class has recently been published.[J. Chem. Educ., 2018, 95, 810]

Goals Not Met

Our original proposal described the incorporation of molecular bridges 1-5 (Figure 8) into the bilayer film. Steady-state and time-resolved emission indicate that the films exhibit similar back electron transfer rates but with a trend of increasing injection yield/rate with lowered LUMO energies. While we can assume that molecules 1-5 have similar orientations relative to the surface, we cannot definitively say that is the case since we do not have structural information about the interface.

A second unmet goal involves the synthesis of asymmetric bridging molecules R0-2 (Figure 9). We have performed all of the synthetic steps towards R0-R2 except the last step involving the conversion of CN to COOH groups. All of the conditions we have attempted for this reaction (protecting groups and reagents) decomposes the molecule presumably by cleaving the PO₃R₂ group.

While re-evaluating our synthetic procedure we came up with an alternative strategy to generate asymmetric bridges, self-assembled tri-layers (Figure 10). This structure effectively achieves the same energetic scheme as with R0-R2 but each bridge can be independently synthesized effectively avoiding the synthetic difficulties mentioned above. Preliminary measurements indicate that FET is faster with the higher energy bridge on the outside as compared to near the surface. Unfortunately, as mentioned above, we have no structural information about the interface and thus cannot definitively attribute this behavior to the energetics of the bridge and not difference in structure between the multilayer films.

The lack of structural information about the interface is a problem that is actively being address via collaboration. We are working with Scott Saavedra at University of Arizona to perform attenuated total reflectance of the films to gain direct structural information about the molecular orientations relative to the surface. A proposal regarding this work is currently in preparation and we anticipate submission within the next two months.

Key Outcomes and Achievements

- 1) Introduced self-assembled bilayers as an effective means of manipulating electron transfer at organic-inorganic interfaces.
- 2) Demonstrated that the length of the molecular bridge can be used to slow both FET (lower J_{sc}) and BET (increased V_{oc}).
- 3) We showed that incorporating CuII, FeII, and MnII into the self-assembled bilayers dramatically slows BET and asymmetrically influence electron transfer dynamics at the interfaces.
- 4) We used fsTA to elucidate the mechanism of electron injection.
- 5) We introduced self-assembled bilayers of two different chromophores, effectively slowing BET while maintaining high electron injection yields.
- 6) We also demonstrated that simply coordinating the metal ion to a surface bound dye helps inhibits BET but not FET.
- 7) In total this work has resulted in 9 publications (cited >70 times) and one patent pending.
- 8) Two Ph.D.s and two undergraduate honors theses were generated as a result of this work.

RPPR Final Report as of 24-Jul-2018

Training Opportunities: The research described here has been pursued primarily by two graduate students (Tola Ogunsolu and Jamie Wang) and three undergraduate student (Kyle Violette, Ian Murphy, Alex Braun). These students receive training/mentorship in all aspects of the research process including hypothesis generation, experimental design, as well as processing, interpreting, and presenting results. Students performing this research become familiar with a wide range of experimental techniques including synthesis, electrochemistry, spectroscopy, and device characterization. Students 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.

We also emphasize the importance of giving high quality oral and poster presentations. In addition to the regular presentations in group meeting and as required by the FSU graduate curriculum, the students have had the opportunity to attend and present at several conferences (13 posters, 6 oral presentations) as noted below. A remarkable total of 4 poster awards have been received by students presenting this research. Additionally, all students in the Hanson Research Group regularly attend FSU department of chemistry seminars that cover topics including materials science, physical chemistry, inorganic chemistry, and others. We believe that the research opportunities in our program provide excellent training for the next generation of innovators in alternative energy research.

Invited presentations by PI:

2) 2018, March 21 New Orleans, Louisiana; Spring 2018 National ACS Meeting, PCET PhotoCatalysis with Inorganic Molecules & Materials, "Modulating electron transfer dynamics at dye-semiconductor interfaces via self-assembled bilayers" (Invited Talk)

1) 2017, November 9 Charlotte, North Carolina, "Modulating Electron Transfer Dynamics at Dye-Semiconductor Interfaces via Self-Assembled Bilayers" (Invited Talk)

Oral presentations by Students:

6) 2018, April 20 FSU Graduate Women in Science Seminar Series, Tallahassee, FL. Omotola Ogunsolu "Solar Cells; Let the Sun pay your bill!"

5) 2017, March 31 First Annual James S. Brooks Symposium, Tallahassee, FL. Omotola O. Ogunsolu "Maximizing Light Absorption in Dye-Sensitized Solar Cells Using Self-Assembled Bilayers" (Oral)*

4) 2016, November 8-11 43rd Annual NOBCCHE Conference, Raleigh, NC. Omotola O. Ogunsolu "Controlling Electron Transfer in Dye-Sensitized Solar Cells Using Self-Assembled Bilayers" (Oral)*

3) 2016, May 5-7 ACS Florida Annual Meeting and Exposition, Palm Harbor, Florida; Jamie Wang "Asymmetrically Influencing Electron Transfer Dynamics at Dye-Semiconductor Interfaces"

2) 2015, December 6-10 African Materials Research Society Conference (AMRS), Accra, Ghana; Omotola O. Ogunsolu "Inhibiting Interfacial Recombination Events In Dye-Sensitized Solar Cells Using Self-Assembled Bilayers"

1) 2015, May 7-10 ACS Florida Annual Meeting and Exposition, Palm Harbor, Florida; Jamie Wang "Modulating Electron Transfer Dynamics via Self-Assembled Bilayers at Dye-Semiconductor Interfaces"

Poster presentations by Students:

13) 2018, March 18-22 255th ACS National Meeting & Exposition, New Orleans, LA. Jamie C. Wang "Energy Dependent Electron Transfer Dynamics at Dye-Bridge-Semiconductor Interface"

12) 2017, July 22-28 Gordon Research Conference (GRC) on Photochemistry, Lewiston, ME. Jamie C. Wang "Exploring the Non-Innocent Nature of the Linking Ions on Self-Assembled Bilayer Films"

11) 2017, Jan 2-5 Inter-American Photochemical Society Meeting (I-APS), Sarasota, FL. Jamie C. Wang, "Influence of Metal Linking Ions on the Stability, Photophysical and Electrochemical Properties of Self-Assembled Bilayer Films"

10) 2016, May 5-7 ACS Florida Annual Meeting and Exposition, Palm Harbor, Florida; Kyle Violette "Elucidating the Role of Metal Linking Ions in Self-Assembled Bilayers" (1st place undergrad poster)

RPPR Final Report
as of 24-Jul-2018

- 9) 2016, May 5-7 ACS Florida Annual Meeting and Exposition, Palm Harbor, Florida; Omotola O. Ogunsolu "Energy and Electron Transfer Cascade Self-Assembled Bilayers for Application in DSSCs"
- 8) 2015, October 9-10 Florida Inorganic/Material Symposium (FIMS), Gainesville, FL. Ian Murphy "Self-assembled Bilayer Dye Sensitized Solar Cell" (1st place undergrad poster)
- 7) 2015, October 9-10 Florida Inorganic/Material Symposium (FIMS), Gainesville, FL. Jamie C. Wang "Asymmetrically Influencing Electron Transfer Dynamics at Dye-Semiconductor Interfaces" (1st place grad poster)
- 6) 2015, October 9-10 Florida Inorganic/Material Symposium (FIMS), Gainesville, FL. Omotola O. Ogunsolu "Inhibiting Interfacial Recombination Events In Dye-Sensitized Solar Cells Using Self-Assembled Bilayers"
- 5) 2015, Jan 15-16 Southeast Ultrafast Conference (SEUEFC), Tallahassee, FL. Jamie Wang "Modulating Electron Transfer Dynamics at Dye-Semiconductor Interfaces via Self-Assembled Bilayers"
- 4) 2015, Jan 1-4 Inter-American Photochemical Society Meeting (IAPS), Sarasota, FL. Jamie Wang "Modulating Electron Transfer Dynamics at Dye-Semiconductor Interfaces via Self-Assembled Bilayers"
- 3) 2014, Oct 10 Natural Science Graduate Symposium (NSGS), Tallahassee, FL. Jamie Wang "Modulating Electron Transfer Dynamics at Dye-Semiconductor Interfaces via Self-Assembled Bilayers"
- 2) 2014, Oct 3-4 Florida Inorganic/Material Symposium (FIMS), Gainesville, FL. Jamie Wang "Modulating Electron Transfer Dynamics at Dye-Semiconductor Interfaces via Self-Assembled Bilayers" (Runner-up for best poster)
- 1) 2014, Aug 03-07 Gordon Research Conference- Donor Acceptor Electrons Interaction, Newport, RI. Jamie Wang "Modulating Electron Transfer Dynamics at Dye-Semiconductor Interfaces via Self-Assembled Bilayers"

RPPR Final Report

as of 24-Jul-2018

Results Dissemination: In addition to our publications and presentations listed above we have established two successful, ongoing activities to share our research and science with the general public through our 1) online effort and 2) Ask a Scientist event. Feedback for these efforts has been overwhelmingly positive and we intend to continue on a regular basis.

Online Efforts.

The internet provides 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.

Additionally, my research group creates a video abstract for every one of our corresponding author publications. Luckily, this is easy thanks to the efforts of the late Harry Kroto whose FSU/GEOSET studio initiative provides a simple mechanism for recording PowerPoint presentations with both video of the presenter and the slides in simulcast. Here is a list of links of the video abstracts that are currently available (4 additional videos are pending).

- <https://www.youtube.com/watch?v=LZXbhW8g9jY>
- <http://mediasite.capd.fsu.edu/Mediasite/Play/3115ddc471724477a28fcc19a28a37011d>
- <http://mediasite.capd.fsu.edu/Mediasite/Play/35f84e947f1d4d17b492e3510fd7b4ce1d>
- <http://mediasite.capd.fsu.edu/Mediasite/Play/c991c4a718104ddf9d84a0d462112df51d>
- <http://mediasite.capd.fsu.edu/Mediasite/Play/1a25d2392e7549a7953eec77536094961d>

Ask a Scientist.

While our online effort allows us to reach a large, science-seeking audience, Ask a Scientist allows us to achieve another goal: bridging the gap between the science lab and the general population through regular one-on-one interactions. Towards this goal, the PI conceived of and established an outreach activity called Ask A Scientist which is held at Tallahassee's once-a-month, community-wide First Friday event. First Friday is an eclectic mix of artists, musicians, hobbyists, chefs, and—for the last two years—scientists who set up tents and exhibits in Railroad Square park on the first Friday of every month. First Friday is visited by 5,000-10,000 people each month and is continuing to grow. The audience is composed of children and adults with a range of social, demographic, economic, ages, and political backgrounds as diverse as Tallahassee itself. At each Ask A Scientist event, I invite 4-5 scientists—predominantly FSU faculty—from across disciplines like chemistry, physics, engineering, psychology, oceanography and biology (~40 volunteers to date) to stand by a tent and sign proclaiming Ask a Scientist. What follows is ~3 hours of science discussions with anyone who passes by.

Honors and Awards: 2018 Florida State University Undergraduate Teaching Award

2018 Chemical Society Reviews Emerging Investigator

2017 Journal of Materials Chemistry A Emerging Investigator

2016 AAAS Early Career Award for Public Engagement with Science (Top 5 Finalist)

2016 "Emerging Investigators in Inorganic Photochemistry and Photophysics"

Inorganic Chemistry, DOI: 10.1021/acs.inorgchem.6b02830.

2015 Selected as 1 of 50 "Not to miss" presentations at the Fall National ACS Meeting,

Meeting of the American chemical Society

National

Protocol Activity Status:

Technology Transfer: Our ultrafast transient absorption measurements were performed in collaboration with Milan Sykora at Los Alamos National Laboratory. Jamie Wang, and FSU graduate student, spent 3 months at Los Alamos performing the measurements and processing the data. The data from the visit has contributed to at least two manuscripts with a third in preparation.

Patent Pending:

Hanson, K.; Wang, J. C.; Banerjee, T.; Ogunsolu, O.O. "Modulating Electron Transfer Dynamics at Hybrid Interfaces via Self-Assembled Bilayers" U.S. Pat. Appl. Publ. (2016), WO 2016018609.

PARTICIPANTS:

Participant Type: Graduate Student (research assistant)

Participant: Jamie C. Wang

RPPR Final Report
as of 24-Jul-2018

Person Months Worked: 6.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Omotola Ogunsolu

Person Months Worked: 6.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student

Participant: Ian Murphy

Person Months Worked: 2.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student

Participant: Kyle Violette

Person Months Worked: 2.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student

Participant: Alex Braun

Person Months Worked: 2.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

ARTICLES:

RPPR Final Report as of 24-Jul-2018

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Langmuir

Publication Identifier Type: DOI

Publication Identifier: 10.1021/acs.langmuir.7b01964

Volume: 33

Issue: 38

First Page #: 9609

Date Submitted: 10/9/17 12:00AM

Date Published: 9/1/17 4:00AM

Publication Location:

Article Title: Self-Assembled Bilayers on Nanocrystalline Metal Oxides: Exploring the Non-Innocent Nature of the Linking Ions

Authors: Jamie C. Wang, Kyle Violette, Omotola O. Ogunsolu, Seda Cekli, Eric Lambers, Hadi M. Fares, Kenneth

Keywords: Metal ion, electron transfer, self-assembly

Abstract: Self-assembled bilayers on nanocrystalline metal oxide films are an increasingly popular strategy for modulating electron and energy transfer at dye–semiconductor interfaces. A majority of the work to date has relied on ZrII and ZnIV linking ions to assemble the films. In this report, we demonstrate that several different cations (CdII, CuII, FeII, LaIII, MnII, and SnIV) are not only effective in generating the bilayer assemblies but also have a profound influence on the stability and photophysical properties of the films. Bilayer films with ZrIV ions exhibited the highest photostability on both TiO₂ and ZrO₂. Despite the metal ions having a minimal influence on the absorption/emission energies and oxidation potentials of the dye, bilayers composed of CuII, FeII, and MnII exhibit significant excited-state quenching. The excited-state quenching decreases the electron injection yield but also, for CuII and MnII bilayers, significantly slows the back electron transfer kinetics.

Distribution Statement: 1-Approved for public release; distribution is unlimited.

Acknowledged Federal Support: Y

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Inorganic Chemistry

Publication Identifier Type: DOI

Publication Identifier: 10.1021/acs.inorgchem.7b01531

Volume: 56

Issue: 18

First Page #: 11168

Date Submitted: 10/9/17 12:00AM

Date Published: 9/1/17 4:00AM

Publication Location:

Article Title: Increasing the Open-Circuit Voltage of Dye-Sensitized Solar Cells via Metal-Ion Coordination

Authors: Omotola O. Ogunsolu, Jamie C. Wang, Kenneth Hanson

Keywords: metal ion, electron transfer, open-circuit voltage, hybrid interface

Abstract: Considerable efforts are dedicated to increasing the open-circuit voltage (Voc) of dye-sensitized solar cells (DSSCs) by slowing charge recombination dynamics using atomic layer deposition, alkyl-substituted dyes, coadsorbents, and other strategies. In this report, we introduce metal-ion coordination to a metal oxide bound dye as an alternative means of increasing Voc. Metal-ion coordination has minimal influence on the photophysical and electrochemical properties of the N3 dye, but presumably because of increased steric hindrance at the interface, it slows charge recombination kinetics and increases Voc by upwards of 130 mV relative to the parent N3 DSSC. With respect to the nature of the metal ion, the trend in decreasing short-circuit current (Jsc) and increasing Voc correlates with the charge of the coordinated metal ion (MIV ? MIII ? MII). We attribute this trend to electrostatic interactions between the metal cation and I– or I3–, with the more highly charged cations maintaining

Distribution Statement: 1-Approved for public release; distribution is unlimited.

Acknowledged Federal Support: Y

RPPR Final Report as of 24-Jul-2018

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.8b02387

Volume: 122

Issue: 18

First Page #: 9835

Date Submitted: 5/24/18 12:00AM

Date Published: 4/1/18 12:00AM

Publication Location:

Article Title: Elucidating the Role of the Metal Linking Ion on the Excited State Dynamics of Self-Assembled Bilayers

Authors: Jamie C. Wang, Omotola O. Ogunsolu, Milan Sykora, Kenneth Hanson

Keywords: electron transfer, dye-semiconductor, electron injection, quenching

Abstract: Metal ion-linked, self-assembled multilayers on nanocrystalline metal oxide surfaces have recently emerged as an effective strategy for manipulating energy and electron transfer dynamics at organic–inorganic interfaces. The choice of metal ion can have a large impact on the stability, loading concentration, and other properties of the films. Here we report our investigation into the role of the linking ion on the subnanosecond excited state dynamics in the bilayer films (TiO₂–B–M–RuP). While metal linkers like CdII, LaII, SnIV, ZnII, and ZrIV are photochemically inert, paramagnetic linking ions such as CuII, FeII, and MnII quench the excited state of the dye with a rate constant on the order of 10⁸ s⁻¹. The absence of new spectral features in the transient absorption spectrum suggests that energy transfer, and not electron transfer, is responsible for the excited state quenching. On TiO₂, the electron injection rate for TiO₂–B–M–RuP is an order of magnitude slower ($?1 \times 10^9$ s⁻¹) than

Distribution Statement: 1-Approved for public release; distribution is unlimited.

Acknowledged Federal Support: **Y**

DISSERTATIONS:

Publication Type: Thesis or Dissertation

Institution: Florida State University

Date Received: 27-Jul-2016

Completion Date: 11/9/15 11:44PM

Title: Self-Assembled Bilayers in Dye-Sensitized Solar Cells

Authors: Ian Murphy

Acknowledged Federal Support: **N**

Publication Type: Thesis or Dissertation

Institution: Florida State University

Date Received: 24-Jan-2017

Completion Date: 9/23/16 10:08PM

Title: A Systematic Study of the Effect of the Metal Linking Ion within a Layer-By-Layer Structured Dye Sensitized Solar Cell

Authors: Kyle Violette

Acknowledged Federal Support: **Y**

Publication Type: Thesis or Dissertation

Institution: Florida State University

Date Received: 24-May-2018

Completion Date: 5/5/18 6:55PM

Title: Modulating Electron Transfer at Dye-Semiconductor Interfaces

Authors: Jamie C. Wang

Acknowledged Federal Support: **Y**

RPPR Final Report
as of 24-Jul-2018

Publication Type: Thesis or Dissertation

Institution: Florida State University

Date Received: 24-May-2018

Completion Date: 5/5/18 4:00AM

Title: MANIPULATING ENERGY AND ELECTRON TRANSFER ACROSS HYBRID ORGANIC-INORGANIC INTERFACES IN DYE-SENSITIZED SOLAR CELLS

Authors: Omotola O. Ogunsolu

Acknowledged Federal Support: Y

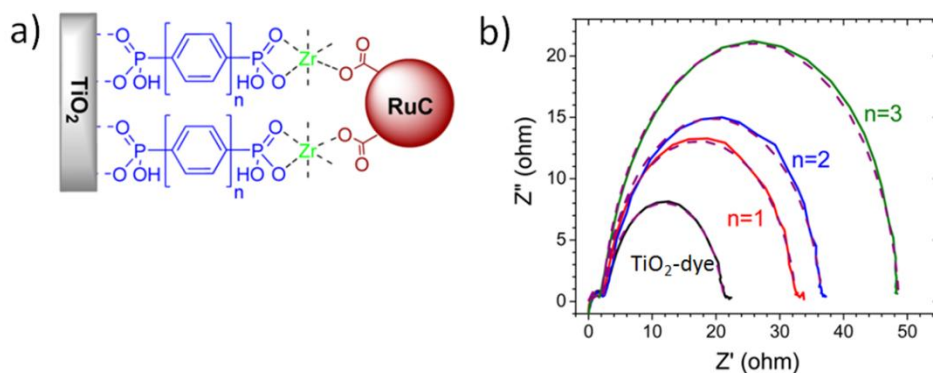


Figure 1. a) Schematic representation of the bilayer film assembly with bridges having $n=1, 2,$ or 3 phenyl groups. b) Nyquist Plot for cells composed of TiO_2 -dye and TiO_2 -(n)-Zr-dye.

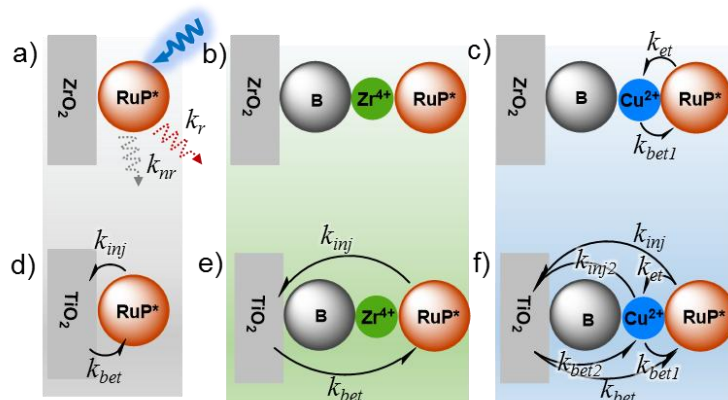


Figure 2. Excited state dynamics for the mono- and bilayers on ZrO_2 (a, b, and c) and TiO_2 (d, e, and f). k_r and k_{nr} are active in all films but are omitted for clarity.

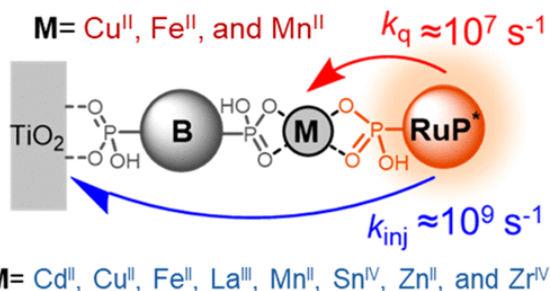


Figure 3. Schematic representation of the bilayer film and the influence of the metal ion on excited state quenching (k_q) and electron injection (k_{inj}).

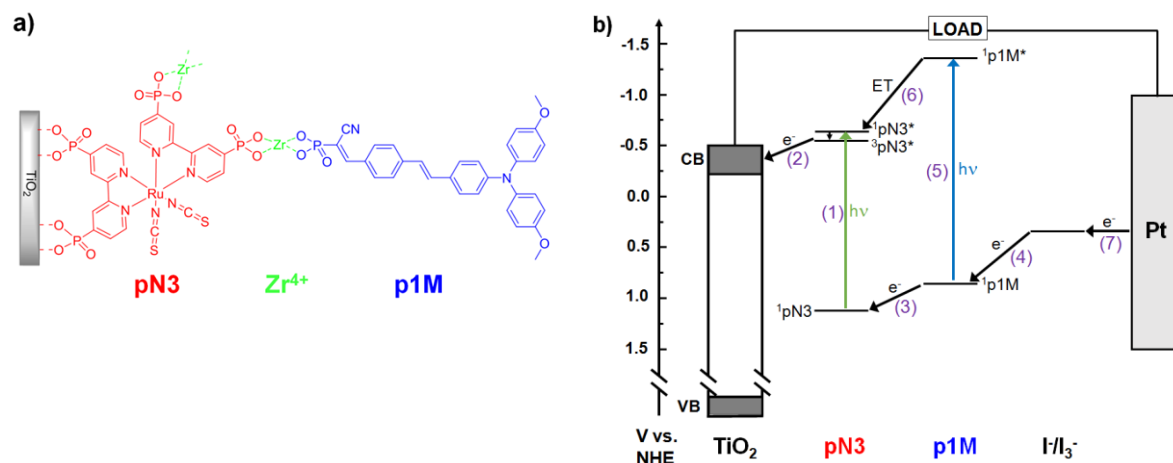


Figure 4. a) Schematic representation of the bilayer film assembly composed of **pN3** and **p1M** dyes. b) Electronic transitions and relative energetics for **pN3**, **p1M**, I^-/I_3^- and the conduction band energy of TiO_2 .

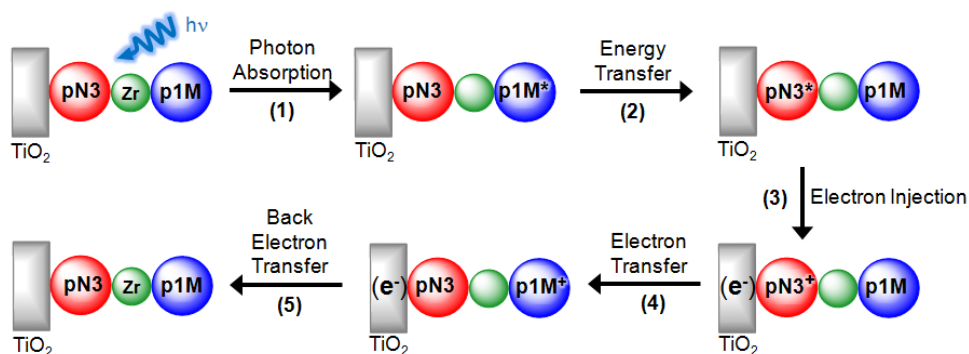


Figure 5. Proposed energy and electron transfer events in TiO_2 -**pN3**-Zr-**p1M**.

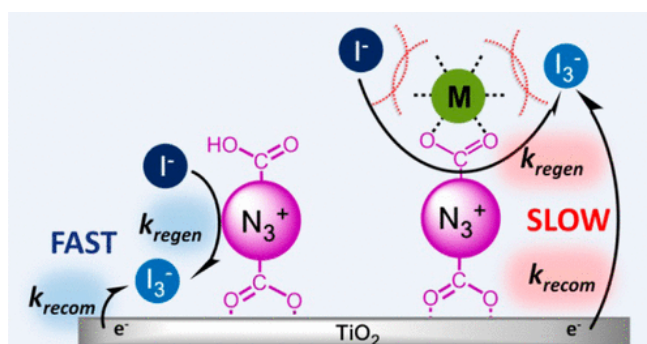


Figure 6. Schematic representation of N3 dye with metal ion ($M = Cd^{II}, Cu^{II}, Fe^{II}, La^{III}, Mn^{II}, Sn^{IV}, Zn^{II}, Zr^{IV}$) coordination and its influence on regeneration and recombination.

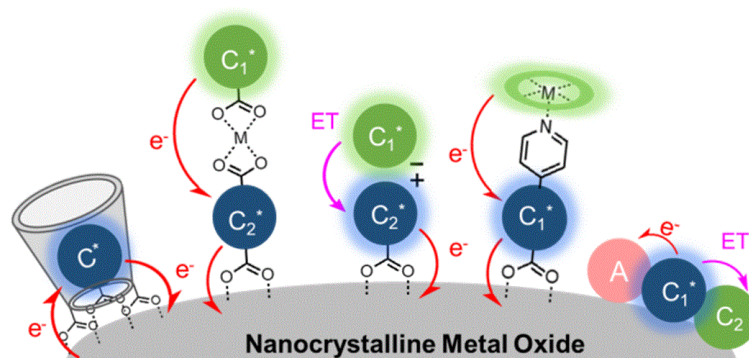


Figure 7. Multimolecular assembly strategies for controlling energy and electron transfer at organic-inorganic interfaces.

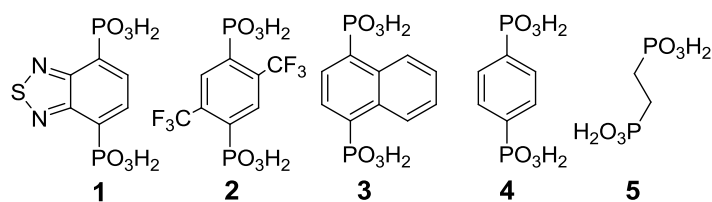


Figure 8. Synthesized bridging molecules with varying LUMO energies.

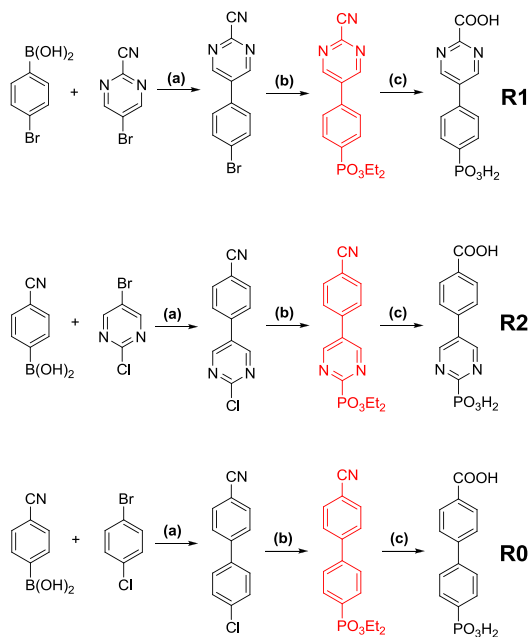


Figure 9. Synthetic scheme for asymmetric bridges **R1**, **R2** and **R0**. a) $Pd(PPh_3)_4$, K_2CO_3 , dry Toluene, N_2 , $110^\circ C$. b) $P(OEt)_3$, $NiBr_2$. c) HCl , $100^\circ C$.

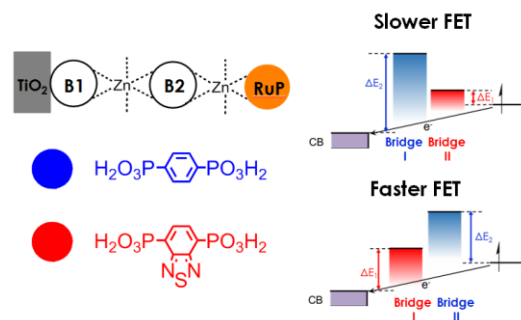


Figure 10. Qualitative energy level diagram for self-assembled trilayers composed of 1 and 4.