Eastern Regional Photosynthesis Conference

30th Anniversary

Chair: Nancy Y. Kiang
Co-Chair: Valter Zazubovich

Marine Biological Laboratory, Woods Hole, MA USA
April 12-14, 2013
On the cover: Absorbance spectra in vitro of chlorophylls a, b, d, and f. Figure generously contributed by Min Chen (The University of Sydney) and Robert Blankenship (Washington University in St. Louis)
Dear Colleagues,

It is a great pleasure to welcome you to the 30th Anniversary of the annual Eastern Regional Photosynthesis Conference at the Marine Biological Laboratory in beautiful Woods Hole, Massachusetts. ERPC is the longest-running regional conference on photosynthesis in the U.S., bringing together researchers from the U.S. East Coast every year for relaxing and intensive scientific exchange. The conference has a tradition of encouraging as much discussion as possible over meals together, poster receptions, and oral presentations that all attend. ERPC especially nurtures students and young scientists in a collegial, immersive learning environment.

Scientifically, the conference has expanded from a focus on understanding of the molecular mechanisms of natural photosynthesis, to include research on artificial photosynthesis and cutting-edge chemical and biological approaches to renewable energy. We are very pleased to have plenary speakers this year who reflect this range, probing fundamental science while maintaining a view toward sustainability: Bob Blankenship of Washington University in St. Louis, who is one of the originators of ERPC, will review light harvesting in natural photosynthesis; Jerry Meyer of John Hopkins University will address efficiency of solar energy conversion and electron transfer in dye-sensitized solar cells; and Joe Berry of the Carnegie Institution for Science will tie the molecular to the global scale, addressing the trends in photosynthetic productivity of our planet under human influences and climate change.

This conference would not be possible without the generosity of several sponsors, who are providing financial support for discounted student registrations, rental of the conference spaces, plenary speaker travel, student and post-doctoral scientist awards, and many other general expenses. We would like to express our gratitude to these sponsors, who are listed in this program book. Thanks also are due to Liz McCarthy of MBL, whose unflappable good cheer and efficiency make conference organizing a breeze. Thanks also to Christopher Shashkin at Columbia University for figuring out ways around various hurdles.

Looking forward to many fruitful discussions with you at ERPC's 30th Anniversary.

Nancy Kiang, Chair, ERPC30, Email: nyk2101@columbia.edu
Valter Zazubovits, Co-Chair, ERPC30, Email: vzazubov@alcor.concordia.ca
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30th Eastern Regional Photosynthesis Conference

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### Conference Schedule at a Glance

*LECTURES WILL BE HELD IN THE SPECK AUDITORIUM. POSTER SESSIONS WILL BE HELD AT THE SWOPE CENTER.*

**Friday: April 12th, 2013**

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
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</thead>
<tbody>
<tr>
<td>4 - 6 PM</td>
<td>ARRIVAL AND REGISTRATION (Swope Center Lobby)</td>
</tr>
<tr>
<td>4:00 PM</td>
<td>COCKTAILS (Meigs Room, Swope Center)</td>
</tr>
<tr>
<td>6:00 PM</td>
<td>DINNER (Swope Dining Hall)</td>
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<tr>
<td>7:15 PM</td>
<td>WELCOME AND OPENING REMARKS (Speck Auditorium)</td>
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<tr>
<td>7:30 PM</td>
<td>PLENARY LECTURE – Robert E. Blankenship (Washington University in St. Louis) (Speck Auditorium)</td>
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<tr>
<td>8:30 PM</td>
<td>SESSION 1 - LIGHT HARVESTING A - CONTRIBUTED PAPERS (Speck Auditorium)</td>
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<td>9:10 PM</td>
<td>POP-UP TALKS - 1 minute each (Speck Auditorium)</td>
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<td>9:20 PM</td>
<td>MIXER AND POSTER VIEWING (Meigs Room and Swope Lobby)</td>
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**Saturday: April 13, 2013**

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<th>Time</th>
<th>Event</th>
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<tr>
<td>7:00-8:00 AM</td>
<td>BREAKFAST (Swope Dining Hall)</td>
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<td>8:30 AM</td>
<td>SESSION 2 - LIGHT HARVESTING B - CONTRIBUTED PAPERS (Speck Auditorium)</td>
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<tr>
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<td>SESSION 3 - ELECTRON TRANSFER - CONTRIBUTED PAPERS (Speck Auditorium)</td>
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<td>10:00 AM</td>
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<td>10:15 AM</td>
<td>COFFEE BREAK</td>
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<td>SESSION 4 - PSI A - NATURAL AND THEORETICAL - CONTRIBUTED PAPERS (Speck Auditorium)</td>
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<td>4:00 PM</td>
<td>POSTER SESSION (Swope Lobby)</td>
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<td>COCKTAILS, POSTER SESSION CONTINUES (Meigs Room and Swope Lobby)</td>
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<td>6:00 PM</td>
<td>LOBSTER BOIL DINNER (Swope Dining Hall)</td>
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<td>PLENARY LECTURE – Gerald J. Meyer (Johns Hopkins University) (Speck Auditorium)</td>
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<td>SESSION 5 - ARTIFICIAL PHOTOSYNTHESIS - CONTRIBUTED PAPERS (Speck Auditorium)</td>
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<td>MIXER (The Captain Kidd Bar &amp; Restaurant)</td>
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<td>BARUCH ’60 AWARDS PRESENTATION AND CLOSING REMARKS (Speck Auditorium)</td>
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ERPC Detailed Conference Program

PLENARY SPEAKERS
Robert E. Blankenship (Washington University in St. Louis)
Gerald Meyer (Johns Hopkins University)
Joseph A. Berry (Carnegie Institution)

Code Key: N-Natural, A-Artificial, T-Theoretical

CONFERENCE SCHEDULE

Friday: April 12, 2013
4:00-6:00 PM ARRIVAL AND REGISTRATION
4:00 PM COCKTAILS
6:00 PM DINNER

7:15 PM WELCOME AND OPENING REMARKS
Chair: Nancy Kiang

7:30 PM PLENARY LECTURE: Robert E. Blankenship (Washington University in St. Louis) - 'Photosynthetic Antennas: The First Step in Biological Solar Energy Conversion'

8:30 PM SESSION I: LIGHT HARVESTING A: NATURAL AND THEORETICAL – CONTRIBUTED PAPERS.
Chair: Harry Frank
(20 minutes each)

8:30 PM Presentation N1: Joseph Tang, "Effects of Wavelengths and Intensities of Illumination on Green Photosynthetic Bacteria"
8:50 PM Presentation T1: Mehdi Najafi, "Unified Approach to Modeling Spectral Hole Burning and Single Molecule Spectroscopy Results in Photosynthetic Complexes Based on Rate Matrices"

9:10 PM Pop-Up Talks

9:20 PM MIXER AND POSTER VIEWING

Saturday: April 13, 2013

7:00-8:30 AM 7:00-8:00AM BREAKFAST

8:30 AM SESSION 2: LIGHT HARVESTING B: NATURAL PHOTOSYNTHESIS – CONTRIBUTED PAPERS.
Chair: John Golbeck

8:30 AM Presentation N2: Allen Derks, "The Push and Pull of NPQ in two Diatoms"
8:50 AM Presentation N3 (30 min): Fedor I. Kuzminov, "Studies of energy transfer and photoprotective energy dissipation in cyanobacteria using fluorescent non-linear spectroscopy and variable fluorescence techniques"

9:20 AM SESSION 3: ELECTRON TRANSFER: NATURAL PHOTOSYNTHESIS
Chair: Victor Batista

9:20 AM Presentation N4: Sam Mula, "Introduction of a Hydrogen Bond between Phylloquinone PhQA and a Threonine Side-chain OH Group in Photosystem I"
9:40 AM **Presentation N5-T**: Leslie Vogt, "Molecular model of atrazine binding in the QB site of Photosystem II"

10:00 AM GROUP PHOTO
10:15 AM COFFEE BREAK

10:30 AM **SESSION 4: PSII A: NATURAL AND THEORETICAL – CONTRIBUTED PAPERS**
Chair: Marilyn Gunner

10:30 AM **Presentation N6**: David Vineyard, "Natural variants of Photosystem II subunit D1 tune photochemical fitness to solar intensity"

10:50 AM **Presentation N7**: Ravi Pokhrel, "Probing the role of chloride in Photosystem II"

11:10 AM **Presentation N8**: Christopher Coates, "The Tuning of Proton-Coupled Electron Transfer Reactions in Solar Energy Conversion: A Comparison of the Redox-Active Tyrosine Residues of Photosystem II"

11:30 AM **Presentation T2**: Abdullah Mahboob, "Towards an artificial Photosystem II: Second generation of the E. coli BFR 'reaction center"

11:50 AM Pop-Up Talks

12:00 PM LUNCH

2:00-4:00 PM EXHIBITS AND FREE TIME

4:00-6:00 PM MIXER + POSTER SESSION

6:00 PM LOBSTER BOIL DINNER

7:30 PM **PLENARY LECTURE: Gerald J. Meyer (Johns Hopkins University) - Electron Transfer at Illuminated Molecular Semiconductor Interfaces**
Chair: Ron Koder

8:30 PM **SESSION 5: ARTIFICIAL PHOTOSYNTHESIS – CONTRIBUTED PAPERS.**
Chair: Art Van der Est

8:30 PM **Presentation A1**: Andrew Mutter, "Rational Design of a Zinc Phthalocyanine Binding Protein"

8:50 PM **Presentation A2**: John Harrold, "Photoelectron Generation by Rhodospirillum rubrum Chromatophores"

9:10 PM **Presentation A3**: Cooper French, "Moldulating Internal Electric Fields by Supercharging Exterior Hydrophilic Residues in a de novo Protein"

9:30 PM MIXER (The Captain Kidd Bar & Restaurant)

**Sunday: April 14, 2013**

7:00-8:30 AM BREAKFAST PRELIMINARY CHECK-OUT

9:00 AM **SESSION 6: PSII B: NATURAL AND ARTIFICIAL - CONTRIBUTED PAPERS**
Chair: Lakshmi (20/20 minutes)

9:00 AM **Presentation A4**: Sahr Khan, "Investigation of the $^{16}O/^{18}O$ Isotope Effect of Oxygen Evolution Catalyzed by $[\text{Mn(III/IV)}_2(-\text{O}_2)(\text{terpy})_2(\text{OH}_2)_2(\text{NO}_3)_3$"

9:20 AM **Presentation A5**: Kamil Woronowicz, "Enhanced Oxygen Evolution from Photosystem II Coupled to Chemically Modified Graphene"
<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
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<tr>
<td>9:40 AM</td>
<td><strong>Presentation N9</strong>: Sergei Miliksiyants, &quot;Electronic Structure of the OEC in the S2 State: A Comparative Study of Photosystem II and Related Dimanganese Model Systems by HYSCORE spectroscopy&quot;</td>
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<td>10:00 AM</td>
<td>COFFEE BREAK</td>
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<tr>
<td>10:30 AM</td>
<td><strong>PLENARY LECTURE</strong>: Joseph A. Berry (Carnegie Institution for Science) - 'Photosynthesis at Continental Scales' Chair: Gary Brudvig</td>
</tr>
<tr>
<td>11:30 AM</td>
<td><strong>BARUCH '60 STUDENT AWARDS PRESENTATION AND CLOSING</strong> Chair: Valter Zazubovits</td>
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All photosynthetic organisms contain a light-gathering antenna system, which functions to collect light and deliver energy to the photosynthetic reaction center, where electron transfer processes store chemical energy. There are a large number of different types of antenna complexes, which have almost certainly arisen multiple times during evolution to adapt organisms to particular photic environments. The antenna system that will be discussed in this talk is the chlorosome antenna and the associated FMO protein that is an intermediate in energy transfer between the chlorosome and the reaction center in green sulfur bacteria. This protein has been found to exhibit electronic quantum coherence effects, which may be important in its function. Advanced mass spectrometry methods have been used to determine the orientation of this protein in the intact photosystem, the cofactor composition of the native complex and how it interacts with the chlorosome and reaction center.
Recently an order of magnitude increase in solar energy conversion efficiencies from solar cells with molecular pigments has been realized. These solar cells are based upon mesoporous thin films of nanocrystalline (anatase) TiO$_2$ sensitized to visible light with inorganic coordination compounds that serve as dyes. Under simulated sunlight conditions, solar-to-electrical power conversion efficiencies in excess of 11.4% have been confirmed at certified laboratories. The sensitized materials have an enormous surface area, a long effective pathlength, and a high photoconductivity that affords both spectroscopic and photoelectrochemical characterization of interfacial charge transfer processes.

In this presentation an overview of dye-sensitized solar cells will be presented followed by more detailed experimental studies of interfacial electron transfer. Specific topics include excited state electron injection, interfacial charge recombination, and optimization of solar conversion efficiency. Examples of “supramolecular” compounds that perform more elaborate tasks at semiconductor interfaces will also be discussed. Particular emphasis will be placed on our ongoing studies of iodide oxidation which represents a key step for electrical power egneration and also provides a mechanism by which energy from the sun can be stored in chemical bonds.
The quantity of photosynthesis taking place on planet earth places an ultimate limit on the quantity and quality of life that can be supported - the global carrying capacity. The rapid growth of the human population has been made possible by appropriating an ever increasing fraction of earth’s productivity for human use (Vitousek et al, 1986). Over the short term this is may be a zero sum game, but it can be argued that some things humans have done such as improved agricultural practices and suppressing fires have increased productivity, while other things such as de-forestation, top soil loss and climate change may lead to decreasing global photosynthesis. As we contemplate a transition to a sustainable strategy for managing our planet’s resources, it is of importance to have an answer to questions such as: what is the photosynthetic productivity of earth? and is it changing? I will examine how and how well we know the answer to this question. Then I will introduce you to a newly demonstrated capacity to measure chlorophyll fluorescence from space (see Remote sensing of terrestrial chlorophyll fluorescence from space | SPIE Newsroom: SPIE). This provides an opportunity to measure a quantity that is intimately linked to the photosynthetic process, I think of this as a challenge for the photosynthesis research community. Can this be used to improve our estimates of photosynthesis?"
ORAL PRESENTATIONS - ABSTRACTS

Session 1 - LIGHT HARVESTING A - NATURAL AND THEORETICAL

Presentation N1 (Friday, 8:30 pm)

Probe Green Sulfur Bacteria in Response to Specific Light Frequencies
Tang, Joseph Kuo-Hsiang (Clark University) and Moataz Hannout (Clark University)

Green sulfur bacteria (GSBs) are suggested to be the best photon catcher in nature as they can perform photosynthesis under extreme low-light environments. GSBs harvest light using the chlorosome, which contains hundreds of thousands of bacteriochlorophylls (BChls) arranged in a high degree of ordered organization. To enhance our understanding how GSBs can perform photosynthesis under low-light environments in nature, we examine the Chlorobaculum [Cba.] tepidum cultures illuminated with far-red to near infrared (NIR) lights. Some interesting results have been obtained in our studies. First, cultures irradiated with 750 nm light (the Qy absorbance band of the chlorosome) grow better than cultures illuminated with 780, 800 and 850 nm lights. Second, to our surprise, cultures illuminated with 850 nm light (the absorbance band of the Cba. tepidum reaction center) exhibited decent growth and also synthesize the chlorosome. Third, cultures illuminated with 850 nm light exhibited red shift of the chlorosome absorption line compared with cultures irradiated with 750 nm light. We are currently investigating the chlorosome from cultures illuminated with specific light frequencies.

References

Presentation T1 (Friday, 8:50 pm)

Unified Approach to Modeling Spectral Hole Burning and Single Molecule Spectroscopy Results in Photosynthetic Complexes Based on Rate Matrices

Najafi, Mehdi (Concordia University, Montreal, PQ, CAN); Zazubovich, Valter (Concordia University, Montreal, PQ, CAN)

Abstract: We discuss developing and employing a new software to explore the pigment + protein energy landscape system via hole burning spectroscopy and, to certain extent, single molecule (single complex) spectroscopy. This model is based on multi-well energy landscape for the system using realistic values for barrier distributions and Monte Carlo-style approach. This is in contrast with earlier models, originally developed for glasses, and based on the two-level system concept. The changes of probabilities in each well upon cooling, burning, and thermocycling are followed and converted to spectral changes. The model covers spectral hole burning (in particular, non-photochemical hole burning, NPHB [1], hole recovery, and thermocycling [2]) and single molecule (or single complex) spectroscopy experiments [3], and we consider both tunneling and barrier hopping in both ground and excited states of a protein-chromophore system. The results of this simulation show that a) under realistic cooling conditions, the system is very far away from equilibrium (which is determined by Boltzman distribution at burn temperature); b) hole burning, recovery at fixed temperature (the same as burn temperature), and thermocycling results are in qualitative agreement with the experimental data; c) the system has spectral memory, meaning that burning and recovery of a burnt hole depends on the pre-burn condition which is in agreement with the experiment [5]. We also explored the effects of different protein energy landscapes (folding funnel-dominated and disorder-dominated) on the NPHB anti-hole shape and hole and anti-hole evolution. The qualitative and quantitative understanding of the properties of the protein energy landscapes and anti-hole shapes is specifically important for determining how light-induced site energy shifts (e.g. hole burning) alter the picture of excitonic interactions in PS complexes, and for modeling of their various resonant and non-resonant hole spectra [6, 7].

Non-photochemical quenching (NPQ) of chlorophyll fluorescence is a photo-protective response utilized by many photosynthetic organisms to thermally dissipate excess excitation energy. The NPQ mechanism in higher plants and diatoms involves a trans-thylakoid pH gradient triggered de-epoxidation/epoxidation of specific carotenoids (i.e. the xanthophyll cycle). Many diatom species are able to radically quench chlorophyll fluorescence when exposed to excess excitation pressure. Here we investigate differences in the induction and relaxation of fluorescence quenching between two diatom species (Nitzschia curvilineata (CCMP 555) and Navicula sp. (CCMP 2566)) under an assortment of irradiance and chemical treatments that affect the push towards and the pull away from NPQ. Fluorescence was measured with a PAM fluorometer during a dark-to-highlight-to-dark transition; variable fluorescence rise transients were kinetically analysed to additionally monitor electron flow. Nitzschia was able to perform NPQ at a magnitude of 3+ times that found in Navicula. Nitzschia also relaxed the quenching more both during and after highlight treatment. Evidence is given towards these differences being linked to electron flow within these species. Nitzschia was shown to have a higher PSII effective absorbance cross section and congruently seems to have a larger electron supply-to-sink ratio than Navicula under normal physiology conditions (NADPH is required for carotenoid epoxidation and the relaxation of NPQ). Manipulating the cellular redox state by either allowing the cultures to age or by adding exogenous electron acceptors predictably altered NPQ induction and relaxation. We speculate that species selected for habitats with highly variable light regimes (and performing a lot of NPQ) would have predisposed mechanisms to insure sufficient electron processing during large scale carotenoid inter-conversion.
Presentation N3 (Saturday, 8:50 am)

Studies of energy transfer and photoprotective energy dissipation in cyanobacteria using fluorescent non-linear spectroscopy and variable fluorescence techniques.

Kuzminov, Fedor I. (IMCS, Rutgers University, New Brunswick, NJ, USA); Karapetyan, Navasard (A.N.Bach Institute of Biochemistry, Russian Academy of Sciences, Moscow, RUS); Bolychevtseva, Yulia (A.N.Bach Institute of Biochemistry, Russian Academy of Sciences, Moscow, RUS); Elanskaya, Irina (Faculty of Biology, M.V.Lomonosov Moscow State University, Moscow, RUS); Fadeev, Victor (Faculty of Physics, M.V.Lomonosov Moscow State University, Moscow, RUS); Gorbunov, Maxim (IMCS, Rutgers University, New Brunswick, NJ, USA)

We use classical variable fluorescence techniques in combination with Non-Linear Laser Fluorimetry (NLLF) for diagnostics of photoenergetics in cyanobacteria. NLLF is based on analysis of photophysical parameters retrieved from a laser energy dependence of fluorophore’s fluorescence. These parameters include excitation cross-sections, the lifetimes of excited states and the rates of energy transfer, including the rate of singlet-singlet annihilation. Combination of NLLF and variable fluorescence techniques allowed us to study energy migration, kinetics of quenching center formation upon NPQ induction and subsequent quenching of excited states of light harvesting pigments. Here we report a model of exciton migration in PBS and a kinetic model of carotenoid-triggered non-photochemical quenching (NPQ) in cyanobacteria. We have determined molecular photophysical parameters of PBS chromophores (phycocyanin=PC, and allophycocyanin=APC) and of chlorophyll a (Chl) in quenched and non-quenched forms. Absence of changes in the excited state’s lifetimes and excitation cross-sections of both PC and Chl suggest that these pigments are not directly involved in the quenching process. On the other hand, changes in photophysical parameters of APC indicate direct energy transfer away from these pigments upon NPQ activation. Our results show that the NLLF provides important complementary information about energy migration processes on a sub-nanosecond and nanosecond time scales. According to our model, formation of the quenching center upon NPQ induction, which is triggered by special orange carotenoid-binding protein (OCP), is a multistep process. It includes both a stage of carotenoid light sensitization by blue-green light and light independent stages. This conclusion is based on several observations. Firstly, there is a dependence of NPQ induction rates from the intensity of actinic light and its saturation at high light intensities. Secondly, after pre-illumination of cyanobacteria with intense blue-green light for a short period of time the PBS fluorescence is quenched even after termination of a blue light illumination (so-called "dark" quenching). Thus, our data suggest the existence of at least one intermediate state between the initial (non-active) and quenching (active) states of the photoprotective system involved in NPQ. The mechanism of PBS quenching center formation involves, therefore, at least two stages: blue light induced transformation from the initial to intermediate state (both of which do not quench PBS fluorescence) and then light independent conversion to an active form.
Session 3 - ELECTRON TRANSFER: NATURAL PHOTOSYNTHESIS

Presentation N4 (Saturday, 9:20 am)

Introduction of a Hydrogen Bond between Phylloquinone PhQA and a Threonine Side-chain OH Group in Photosystem I

Mula, Samuel (Brock University, St. Catharines, ON, CAN); McConnell, Michael (Arizona State University, USA); Ching, Amy (Brock University, USA); Zhao, Nan (Georgia State University, USA); Gordon, Heather (Brock University, USA); Hastings, Gary (Georgia State University, USA); Redding, Kevin (Arizona State University, USA); van der Est, Art (Brock University, CAN)

Photosystem 1 contains phylloquinone cofactors (PhQA and PhQB) responsible for mediating electron transfer between the chlorophyll-a molecule, A0, and the iron sulfur cluster, Fx. We have investigated the influence of the H-bond between the backbone nitrogen of amino acid residue PsaA-L722 and oxygen, O4, of PhQA on the electron transfer (ET) kinetics by mutating PsaA-L722 to threonine (Thr). Molecular dynamics simulations in conjunction with ONIOM electronic structure calculations predict the possibility of a second H-bond between the OH group of the Thr side chain and O4. Changes in the hyperfine splitting were observed in the transient EPR spectra of the radical pair P700+PhQA– in the mutant. These changes indicate the mutation causes increased spin density on the carbon atom adjacent to the methyl group of PhQA as would be expected if an additional H-bond to the OH group were formed. The hyperfine couplings predicted by the ONIOM calculations are in excellent agreement with the experimental spectra. Unexpectedly, the room temperature rate of ET from PhQA to Fx in the PsaA-L722T mutant was slightly greater than in the wild type. The second H-bond should increase the stability of the PhQA– radical and thus slow the forward ET. We hypothesize that the observed increased rate may be due to greater electronic coupling between the donor and acceptor. A change in the slope of the Arrhenius plot of the electron transfer rate occurs near the protein glass transition temperature (~200K). Although this change in slope can be reproduced by the Hopfield equation, we speculate that it is more likely the result of solvent dynamics being frozen out as opposed to quantum mechanical effects.
Molecular model of atrazine binding in the QB site of Photosystem II

Vogt, Leslie (Yale University, New Haven, CT, USA); Batista, Victor (Yale University, New Haven, CT, USA)

As one of the most widely applied herbicides, atrazine is used to control weeds in most of the sweet corn fields in the United States. This triazine-based herbicide binds the D1 protein of Photosystem II (PSII) in the site usually occupied by the second and final plastoquinone cofactor (QB) that is part of the electron transfer chain. By competing with QB for the binding site on the stromal side of the protein, atrazine effectively blocks the electron transfer from the first plastoquinone (QA) and promotes the formation of reactive intermediates that cause photodamage. Although the structure of atrazine in the quinone binding site has been determined for the bacterial reaction center (bRC), it has not been established how atrazine binds to the slightly larger site in PSII. Using molecular dynamics (MD) simulations, we show the set of hydrogen bonds that stabilize atrazine in the QB pocket, including interactions with a histidine ligand of the non-heme iron and with backbone atoms on the distal side. Using MD, we also probe the effect of the Ser264Ala mutation that has been shown to confer atrazine resistance in higher plants.
Presentation N6 (Saturday, 10:30 am)

Natural variants of Photosystem II subunit D1 tune photochemical fitness to solar intensity

Vinyard, David (Rutgers University, Piscataway, NJ, USA); Gimpel, Javier (University of California, San Diego, USA); Ananyev, Gennady (Rutgers University, USA); Cornejo, Mario (Rutgers University, USA); Golden, Susan (University of California, San Diego, USA); Mayfield, Stephen (University of California, San Diego, USA); Dismukes, Charles (Rutgers University, USA)

Photosystem II (PSII) is comprised of six core polypeptides that make up the minimal unit capable of performing the primary photochemistry of light-driven charge separation and water oxidation in all oxygenic phototrophs. The D1 subunit of this complex contains most of the ligating amino acid residues for the Mn$_4$Ca$_5$ core of the water-oxidizing complex (WOC). Most cyanobacteria have 3-5 copies of the psbA gene coding for at least two isoforms of D1, while algae and plants have only one isoform. Synechococcus elongatus PCC 7942 contains two D1 isoforms: D1:1 is expressed under low light conditions, and D1:2 is upregulated in high light or stress conditions. Using a heterologous psbA expression system in the green alga Chlamydomonas reinhardtii, we have measured growth rate, WOC cycle efficiency, and O$_2$ yield as a function of D1:1, D1:2, or the native algal D1 isoform. D1:1-PSII cells outcompete D1:2-PSII cells and accumulate more biomass in light-limiting conditions. On the other hand, D1:2-PSII cells easily outcompete D1:1-PSII cells at high light intensities. The native C.r.-PSII WOC cycles less efficiently at all light intensities and produces less O$_2$ than either cyanobacterial D1 isoform. D1:2-PSII makes more O$_2$ per saturating flash than D1:1-PSII, but exhibits lower WOC cycling efficiency at low light intensities due to a 40% faster charge recombination rate in the S3 state. These functional advantages of D1:1-PSII and D1:2-PSII at low and high light regimes, respectively, can be explained by differences in predicted redox potentials of PSII electron acceptors that control kinetic performance. Supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Photosynthetic Systems program (DE-FG02-10ER16195).
PROBING THE ROLE OF CHLORIDE IN PHOTOSYSTEM II
Pokhrel, Ravi (Yale University, New Haven, CT, USA)

The role of chloride in photosystem II (PSII), although probed extensively, is still unclear. Using structural information of PSII along with a careful comparison with other Cl$^{-}$-activated enzymes, we proposed a role of Cl$^{-}$ at the D2-K317 site in PSII.\textsuperscript{1} In our proposal, in the absence of Cl$^{-}$ at this site, a salt bridge forms between D2-K317 and D1-D61.\textsuperscript{1,2} To probe Cl$^{-}$ binding and activation properties at the D2-K317 site, we studied the effect of the D2-K317A mutation. Steady-state O$_2$ evolution measurements, performed in the presence and absence of Cl$^{-}$, show that the D2-K317A mutant is independent of Cl$^{-}$. This is consistent with loss of the Cl$^{-}$ requirement when the charged Lys residue is replaced by an uncharged residue that no longer binds to an essential carboxylate (D1-D61) in the absence Cl$^{-}$, analogous to observations in other Cl$^{-}$-activated enzymes. The structure of the OEC was probed using EPR spectroscopy. A g = 2 multiline S2-state signal, identical to the wild-type g = 2 multiline S2-state signal, was observed for the of PSII cores from D2-K317A. Flash-dependent yields of O$_2$ and the oxygen release kinetics in the S3$\rightarrow$[S4]$\rightarrow$S0 transition were measured for the D2-K317A cores and the wild-type cores using a bare platinum electrode. The miss factor for the D2-K317A cores was 22% compared to only 8% in the wild-type cores, and the O$_2$ release kinetics in the S3$\rightarrow$[S4]$\rightarrow$S0 transition was slower in the D2-K317A cores. These results collectively suggest that the proton transfer is inefficient in the D2-K317A cores, thereby giving rise to a higher miss factor and slower O$_2$ release during the S3$\rightarrow$[S4]$\rightarrow$S0 transition.

Presentation N8 (Saturday, 11:10 am)

The Tuning of Proton-Coupled Electron Transfer Reactions in Solar Energy Conversion: A Comparison of the Redox-Active Tyrosine Residues of Photosystem II

Coates, Christopher (Rensselaer Polytechnic Institute, Troy, NY, USA); Milikisiyants, Sergey (Rensselaer Polytechnic Institute, Troy, NY, USA); Lakshmi, K.V. (Rensselaer Polytechnic Institute, Troy, NY, USA)

In the Type II photosynthetic reaction center (RC), Photosystem II (PSII), proton-coupled electron transfer (PCET) reactions diminish the energetic penalty for the four electron transfers that are required in the oxidation of water to dioxygen. Thus, PCET greatly enhances the electrochemical driving force of the water oxidation reaction by coupling proton (PT) and electron transfer (ET) processes. The solar water oxidation reaction of PSII is facilitated by light-driven PCET reactions at the redox-active tyrosine cofactors. PSII contains two symmetric tyrosine residues, Y_Z and Y_D, within the heterodimeric polypeptide core. Although Y_Z and Y_D are chemically identical, the redox properties and reaction kinetics of these cofactors are very different. The function of these redox-active tyrosine residues is unique due in part to influences from the differing protein environments. While the recent high-resolution X-ray crystal structure has allowed for refinement of tyrosine interactions with its environment, the mechanism of PCET is not known. In the present study, we use 2D hyperfine sub-level correlation spectroscopy to investigate the PCET reactions at the Y_Z and Y_D residues of PSII.
Towards an artificial Photosystem II : Second generation of the E. coli BFR 'reaction center'

Mahboob, Abdullah (Brock University, St. Catharines, CAN); Vassil’ev, Sergej (Brock University, St. Catharines, CAN); Poddutoori, Prashanth (Brock University, St. Catharines, CAN); Bruce, Doug (Brock University, St. Catharines, CAN); van der Est, Art (Brock University, St. Catharines, CAN)

Photosystem II (PSII) of photosynthesis has the unique ability to photochemically oxidize water and evolve oxygen. Recently an engineered Bacterioferritin photochemical ‘reaction center’ (BFR-RC) using a zinc chlorin pigment (ZnCe$_6$) in place of the native heme has been proposed to oxidize a bound manganese ion through a tyrosine residue, thus mimicking two of the key reactions on the donor side of PSII. The redox potential of ZnCe$_6$ was determined in three organic solvents using Cyclic Voltammetry (CV) and Density Functional Theory (DFT) calculations. Based on the experimental value from CV measurements, as well as calculations showing shift due to the protein environment, the redox potential corresponding to the first oxidation of ZnCe$_6$ in BFR-RC was determined to be 640mV. The first oxidation of ZnCe$_6$ was found to be sufficient for the oxidation of the manganese cluster, but not sufficient to oxidize the tyrosine residue. The redox potential corresponding to the second oxidation; however, seems to be sufficient to oxidize tyrosine. Based on our calculations and experimental work, we propose that ZnCe$_6$ oxidizes the manganese cluster and tyrosine separately. In order to develop a second generation BFR reaction center, we proposed using phosphorus porphyrin pigment instead of ZnCe$_6$. The phosphorus pigment will be cross-linked to BFR-RC through two cysteine residues axially. Towards this goal, we have synthesized a series of sulfur-linked phosphorus pigments to examine their oxidation and optical properties. DFT calculations show that the sulfur-linked phosphorus porphyrins will have an oxidation potential near 1.3V. This oxidation potential is sufficient to oxidize tyrosine , as well as being close to that of P680.
Phthalocyanines have long been used as primary donor molecules in synthetic light-powered devices due to their superior properties when compared to natural light activated molecules such as chlorophylls. Their use in biological contexts, however, has been severely restricted due to their high degree of self-association, and its attendant photoquenching, in aqueous environments. To this end we report the rational redesign of a *de novo* four helix bundle di-heme binding protein into a heme and Zinc(II) phthalocyanine (ZnPC) dyad in which the ZnPC is electronically and photonically isolated. The redesign required transformation of the homodimeric protein into a single chain four helix bundle and the addition of a negatively charge sulphonate ion to the ZnPC macrocycle. Two different final constructs were tested, and differences in ZnPC binding affinity can be explained by steric interference from the newly added connecting loop. Singular binding of ZnPC was verified by absorption spectroscopy and magnetic circular dichroism spectroscopy. The engineering guidelines determined here, which enable the simple insertion of a monomeric ZnPC binding site into any artificial helical bundle, are a robust starting point for the creation of functional photoactive nanodevices.
Owing to the considerable current interest in replacing fossil fuels with solar radiation as a clean, renewable and secure energy source, light-driven electron transport in natural photosynthetic systems offers a valuable blueprint for conversion of sunlight to useful energy forms. In particular, intracytoplasmic membrane vesicles (chromatophores) from the purple bacterium Rhodospirillum rubrum provide a fully functional and robust photosynthetic apparatus, ideal for biophysical investigations of energy transduction and incorporation into biohybrid photoelectrochemical devices (1). These vesicular organelles, which arise by invagination of the cytoplasmic membrane, are the sites of the photochemical reaction centers and the light harvesting 1 (LH1) complex. The LH1 protein is responsible for collecting visible and near-IR radiant energy and funneling these excitations to the reaction center (RC) for conversion into a transmembrane charge separation. Here, we have investigated the morphology, fluorescence kinetics and photocurrent generation of chromatophores from Rsp. rubrum deposited directly onto gold surfaces in the absence of chemical surface modifications. Atomic force microscopy showed a significant coverage of the gold electrode surface by Rsp. rubrum chromatophores and revealed details about the distribution of the LH1-RC structures. By in situ fluorescence induction/relaxation measurements, a significant quantum yield of photochemistry was demonstrated in the photoactive films. Three relaxation times after induction were determined for the chromatophores in suspension and their average relaxation time was measured after immobilization on the surface of the electrodes. Chronoamperometric measurements showed that the assembled bioelectrodes were capable of generating sustained photocurrent under white light illumination at 220 mW/cm² with a maximum value of 1.5 μA/cm², which slowly declines in about one week. This study demonstrates the possibility of photoelectrochemical control of robust chromatophore preparations from Rsp. rubrum paving the way for future incorporation into solar cells.

Presentation A3 (Saturday, 9:10 pm)

Modulating Internal Electric Fields by Supercharging Exterior Hydrophilic Residues in a de novo Protein

French, Cooper (City College of New York, Queens, NY, USA); Everson, Ben (City College of New York, USA); Mutter, Andrew (City College of New York, USA); Zhang, Lei (City College of New York, USA); Koder, Ronald (City College of New York, USA)

De novo designed proteins offer insight into the function of natural proteins and have demonstrated potential as novel pharmaceutical and industrial agents in their own right. Researchers have successfully improved solubility and stability by “supercharging” the exterior residues of natural proteins. We explore the effects of moderate and extreme charge variations of a previously described hemoprotein. We demonstrate reliable tuning of the internal electrical field and midpoint potential of heme ligands by altering the exterior residue charges and overall charge of the protein. This ability provides further tools in design of charge separation and transfer systems. We also demonstrate the practicable limits of supercharging within our experimental system.
Investigation of the $^{16}\text{O}/^{18}\text{O}$ Isotope Effect of Oxygen Evolution Catalyzed by

$[\text{Mn(III/IV)}_{2}(-\text{O})_{2}(\text{terpy})_{2}(\text{OH}_{2})_{2})(\text{NO}_{3})_{3}$

*Khan, Sahr (USA); Ertem, Mehmed (USA); Pal, Rhitankar (USA); Batista, Victor (USA); Brudvig, Gary (USA)*

The complex $[\text{Mn(III/IV)}_{2}(-\text{O})_{2}(\text{terpy})_{2}(\text{OH}_{2})_{2})(\text{NO}_{3})_{3}$ (where terpy = 2,2':6'2"-terpyridine) is a functional model of the oxygen evolving complex (OEC) in Photosystem II (Limburg, J. et. Al., *J. Am. Chem. Soc.* 2001, 123, 423-430). It follows first order Michaelis-Menten kinetics and catalyzes oxygen production from water in the presence of chemical oxidants like Potassium Oxone®. In this study, the $^{16}\text{O}/^{18}\text{O}$ isotope composition associated with oxygen production with this complex during catalytic turnover is measured with a Thermo MAT 253 dual inlet mass spectrometer. The $^{16}\text{O}/^{18}\text{O}$ ratio of evolved dioxygen is then compared to the oxygen isotopic composition of natural abundance water and Potassium Oxone® to get a competitive kinetic isotope effect. The mechanism of oxygen evolution is obtained by comparing these results to kinetic isotope effects calculated by computational studies. These findings provide a benchmark for mechanisms associated with O-O bond formation and could help elucidate the mechanism of water splitting by the OEC during photosynthesis.
Enhanced Oxygen Evolution from Photosystem II Coupled to Chemically Modified Graphene

Harrold, John W. (Rutgers University, USA); Hirsh, Donald J. (The College of New Jersey, USA); Woronowicz, Kamil (Medgar Evers College of CUNY, Rutgers University, USA); Yamaguchi, Hisato (Rutgers University, USA); Gorbunov, Maxim Y. (Rutgers University, USA); Ananyev, Gennady (Rutgers University, USA); Rutherford, A. William (Imperial College, GBR); Dismukes, Charles (Rutgers University, USA); Chhowalla, Manish (Rutgers University, USA); Vittadello, Michele (Medgar Evers College of CUNY, Brooklyn, NY, USA)

Graphene oxide (GO) is an atomically thin nanosheet that is derived from the chemical exfoliation of graphite. The availability of oxygen functional groups on GO makes it a versatile bidimensional substrate for self-assembly of proteins giving rise to hybrid bio-conjugates via non-specific or specific molecular interactions. In this study we report the oriented self-assembly of photosystem II core complexes (PSII) on GO nanosheets that have been chemically modified with Ni\textsuperscript{2+} nitriloacetic acid coordination sites (GO-NiNTA), resulting in GO-NiNTA-PSII bio-conjugates in suspension.\textsuperscript{1} Using fluorescence kinetic studies we demonstrate that PSII linked to the GO-NiNTA resin exhibit a quantum yield of photochemistry as high as 0.74, which is slightly lower than native PSII in aqueous buffer at pH = 6.5. The resin has the capability of partially preserving the activity of PSII for a limited number of turnovers in the absence of redox mediators suggesting the possibility of direct electron transfer from PSII to GO. Oxygen evolution measurements indicate that immobilized PSII display twice the pulse oxygen yield of free PSII and an initial rate of > 7900 μmol O\textsubscript{2} / (mg Chl • h) under continuous illumination and assistance of ferricyanide. This unprecedented initial rate corresponds to an oxygen turnover time of 14 ms per PSII and a remarkable initial volumetric photocurrent density of 5.5 mA/mL. Our work shows that GO-NiNTA are biocompatible substrates for the functional assemblies of natural photosynthetic components and provide valuable structural elements for the design of bio-inspired and bio-hybrid electron transport chains.

Presentation N9 (Sunday, 9:40 am)

Electronic Structure of the OEC in the S2 State: A Comparative Study of Photosystem II and Related Dimanganese Model Systems by HYSCORE spectroscopy

Milikisivants, Sergey (Rensselaer Polytechnic Institute, Troy, NY, USA); Coates, Christopher (Rensselaer Polytechnic Institute, Troy, NY, USA); Chatterjee, Ruchira (Rensselaer Polytechnic Institute, Troy, NY, USA); Koua, Faisal (Okayama University, Okayama, JPN); Shen, Jian-Ren (Okayama University, Okayama, JPN); Lakshmi, KV (Rensselaer Polytechnic Institute, Troy, NY, USA)

The recent 1.9 Å resolution X-ray structure of Photosystem II (PSII) [Umena et al. Nature, 2011, 473, 55] provides a detailed molecular geometry of the Oxygen Evolving Complex (OEC) in its dark stable S1 state. Despite the remarkable breakthrough in the resolution achieved by the new crystal structure for the OEC in the S1 state, its structure in the higher oxidation states remain largely unknown. Another important problem yet to be solved is our limited knowledge about electronic structure of the Mn4Ca-oxo cluster.

Weak magnetic interactions between the paramagnetic tetra-manganese core and surrounding magnetic nuclei are very sensitive to both molecular geometry and electronic structure of the OEC. Two-dimensional hyperfine sublevel correlation (HYSCORE) spectroscopy is a particularly sensitive technique to resolve hyperfine interactions in multinuclear paramagnetic centers such as the OEC of PSII.

In this study, we apply HYSCORE spectroscopy to measure 1H and 14N hyperfine couplings in the S2 state of the OEC. In order to relate the obtained experimental data to the electronic and geometric structure of the OEC, spectroscopic properties of several model systems have been additionally characterized in details by HYSCORE. We use two synthetic compounds namely, [H2O(terpy)MnIII(m-O)2MnIV(terpy)OH2](NO3)3 (terpy = 2,2’:6’,2”-terpyridine) and [(bipy)2MnIII(m-O)2MnIV(bipy)2](ClO4)3 (bipy = 2,2’-bipyridine) as well as seproxidized (MnIII-MnIV) form of Manganese Catalase as a comparison systems for the OEC. Based on experimental data we obtained for the OEC and dimanganese model systems we draw important conclusions with respect to the electronic structure as well as molecular geometry of the OEC in the S2 state.
Ziegler, Jessica (Rensselaer Polytechnic Institute, Troy, NY, USA); Coates, Christopher (Rensselaer Polytechnic Institute, Troy, NY, USA); Milikisiyants, Sergey (Rensselaer Polytechnic Institute, Troy, NY, USA); Lakshmi, K.V. (Rensselaer Polytechnic Institute, Troy, NY, USA)

P21: Spectrally-dependent energy-storage efficiency in the Chl d cyanobacterium, Acaryochloris marina
Mielke, Steven (Rockefeller University, New York, NY, USA); Kiang, Nancy (NASA GISS, USA); Blankenship, Robert (Washington University, St. Louis, USA); Mauzerall, David (Rockefeller University, USA)

P22: Investigating the role of natural variations in the D1 subunit of Photosystem II on the efficiency and kinetics of photoassembly
Sun, Jennifer S. (Rutgers, The State University of New Jersey, Morganville, NJ, USA); Vinyard, David (USA); Ananyev, Gennady (USA); Gimpel, Javier (USA); Mayfield, Stephen (USA); Dismukes, Gerard (USA)

P23: Non-functional chlorophyll complexes and photosystem I fluorescence emission in C3 and C4 leaves
Peterson, Richard B. (The Connecticut Agricultural Experiment Station, New Haven, CT, USA); Oja, Vello (University of Tartu, Tartu, EST); Eichelmann, Hillar (University of Tartu, Tartu, EST); Bichele, Irina (University of Tartu, Tartu, EST); Laisk, Agu (University of Tartu, Tartu, EST)

P24: The Effect of Sr2+ Substitution on Structure of Oxygen Evolving Complex of Photosystem II Studied by 1H HYSCORE Spectroscopy
Milikisiyants, Sergey (Rensselaer Polytechnic Institute, Troy, NY, USA); Coates, Christopher (Rensselaer Polytechnic Institute, Troy, NY, USA); Chatterjee, Ruchira (Rensselaer Polytechnic Institute, Troy, NY, USA); Koua, Faisal (Okayama University, Okayama, JPN); Shen, Jian-Ren (Okayama University, Okayama, JPN); Lakshmi, K. V. (Rensselaer Polytechnic Institute, Troy, NY, USA)
Coates, Christopher (Rensselaer Polytechnic Institute, Troy, NY, USA); Ziegler, Jessica (Rensselaer Polytechnic Institute, Troy, NY, USA); Manz, Katherine (Rensselaer Polytechnic Institute, Troy, NY, USA); Good, Jacob (Rensselaer Polytechnic Institute, Troy, NY, USA); Chatterjee, Ruchira (Rensselaer Polytechnic Institute, Troy, NY, USA); Hao, Sijie (Pennsylvania State University, University Park, PA, USA); Golbeck, John (Pennsylvania State University, University Park, PA, USA); Lakshmi, K. V. (Rensselaer Polytechnic Institute, Troy, NY, USA)

P26: The Effect of Protein Aggregation on the Spectroscopic Properties and Excited State Kinetics of the LHCII Pigment-Protein Complex from Green Plants
Magdaong, Nikki (University of Connecticut, Storrs, CT, USA); Enriquez, Miriam (University of Connecticut, Storrs, CT, USA); LaFountain, Amy (University of Connecticut, Storrs, CT, USA); Rafka, Lauren (University of Connecticut, Storrs, CT, USA); Frank, Harry (University of Connecticut, Storrs, CT, USA)

P27: Photosystem II Fluorescence Quenching During Desiccation
Schaven, Kristin (Brock University, St. Catharines, ON, CAN); Bruce, Doug (USA); Vassiliev, Sergei (CAN); Cardon, Zoe (Marine Biological Laboratory, Woods Hole, MA, USA)

P28: Electrostatic Effects on Proton-Coupled Electron Transfer in Oxomanganese Complexes Inspired by the Oxygen-Evolving Complex of Photosystem II
Amin, Muhamed (USA); Vogt, Leslie (USA); Vassiliev, Serguei (USA); Rivalta, Ivan (USA); M. Sultan, Mohammad (USA); Bruce, Doug (USA); W. Brudvig, Gary (USA); S. Batista, Victor (USA); Gunner, Marilyn (USA)

P29: Protein Film Voltammetry and Co-factor Electron Transfer Dynamics in Spinach Photosystem II Core Complex
Zhang, Yun (University of Connecticut, Storrs, CT, USA); Magdaong, Nikki (University of Connecticut, Storrs, CT, USA); Frank, Harry A. (University of Connecticut, Storrs, CT, USA); Rusling, James F. (University of Connecticut, Storrs, CT, USA)

P30: Carbon metabolism of anaerobic anoxygenic phototrophs and aerobic anoxygenic phototrophs: Roseobacter denitrificans, Rhodobacter capsulatus and Rhodobacter sphaeroides
Wang, Yaya (Clark University, Worcester, MA, USA); Zare, Farrokh (USA); Cipi, Blerina (USA); Lika, Gloria (USA); Tang, Joseph (USA)
P31: Illuminate The Green Sulfur Bacterium *Chlorobaculum tepidum* With Far Red To Near Infrared Light
*Zare, Farrokh* (Clark university, worcester, MA, USA); *Hannout, Moataz* (Clark university, worcester, MA, USA); *tang, joseph* (Clark university, worcester, MA, USA)

P32: Immobilization of Photosystem II Core Complexes on Chemically Modified Titanium(IV) Oxide Surfaces
*Hull, Dominic O.* (Medgar Evers College of CUNY, USA); *Harrold, John W.* (Rutgers University, USA); *Fraser, Ryan* (Midwood High School, USA); *Rutherford, A. William* (Imperial College, GBR); *Falkowski, Paul G.* (Rutgers University, USA); *Vittadello, Michele* (Medgar Evers College of CUNY, Brooklyn, NY, USA)

P33: Hemoprotein Design Using Minimal Sequence Information
*Everson, Bernard H.* (City College of New York, Brooklyn, NY, USA); *French, Cooper* (City College of New York, USA); *Mutter, Andrew* (City College of New York, USA); *Nanda, Vikas* (UMDNJ and the Center for Advanced Biotechnology and Medicine, USA); *Koder, Ronald* (City College of New York, USA)

P34: The effects of the distributions of excitation energy transfer rates on the nonresonant spectral holes in trimeric photosynthetic protein complexes: the study of Fenna-Matthews-Olsen protein
*Herascu, Nicoleta* (Concordia University, Montreal, PQ, CAN); Prof. *Zazubovits, Valter* (Concordia University, CAN); Prof. *Jankowiak, Ryszard* (Kansas State University, USA)

P35: Insights into the S0 state of Oxygen Evolving Complex within PS-II and kinetic isotope effects calculations in biomimetic oxo-manganese catalysts
*Pal, Rhitankar* (USA); *Negre, Christian* (USA); *Ertem, Mehmed Zahid* (USA); *Vogt, Leslie* (USA)

P36: The Virtual Planetary Laboratory Biological Pigments Database
*Kiang, Nancy Y.* (Columbia University, New York, NY, USA)

Ziegler, Jessica (Rensselaer Polytechnic Institute, Troy, NY, USA); Coates, Christopher (Rensselaer Polytechnic Institute, Troy, NY, USA); Milikisyants, Sergey (Rensselaer Polytechnic Institute, Troy, NY, USA); Lakshmi, K.V. (Rensselaer Polytechnic Institute, Troy, NY, USA)

The light-driven process of photosynthesis oxidizes water to molecular oxygen in the following charge-transfer reaction: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4e^- + 4\text{H}^+$. The four-electron water oxidation reaction is catalyzed by a tetranuclear manganese-calcium-oxo ($\text{Mn}_4\text{Ca-oxo}$) cluster in the Oxygen-Evolving Complex (OEC) of Photosystem II (PSII). In order to mimic the function of the $\text{Mn}_4\text{Ca-oxo}$ cluster, we have synthesized mixed-valence dimanganese ($\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$) di-$\mu$-oxo complexes with a variety of substituted terpyridine ligands. We have determined the X-ray crystal structures of the dimanganese ($\text{III}/\text{IV}$) di-$\mu$-oxo complexes that confirm the presence of bound substrate water molecules. We characterize the electronic the complexes by UV-Vis spectroscopy, electrospray mass spectrometry, infrared spectroscopy, EPR spectroscopy and oxygen-evolution assays. In detailing the structure and function of these complexes, we develop a clearer understanding of the catalytic activity of the $\text{Mn}_4\text{Ca-oxo}$ cluster in the OEC of PSII.
Spectrally-dependent energy-storage efficiency in the Chl d cyanobacterium, *Acaryochloris marina*

*Mielke, Steven* (Rockefeller University, New York, NY, USA); *Kiang, Nancy Y.* (NASA GISS, USA); *Blankenship, Robert* (Washington University, St. Louis, USA); *Mauzerall, David* (Rockefeller University, USA)

We present photoacoustic measurements of the wavelength-dependent energy-storage efficiency in two cyanobacteria: *Acaryochloris marina*—the only oxygenic phototroph known to employ Chl d in primary photochemistry—and *Synechococcus leopoliensis*, a common Chl a species. The high accuracy and spectral resolution of the data allow modeling of the observed efficiency that yields key information, including: (1) the PSI and PSII trap wavelengths (obtained, for the first time, directly from energy measurements); (2) the PSI- and PSII-specific efficiencies; and (3) the degree to which uphill energy transfer contributes to storage at wavelengths longer than those of the traps. Results are consistent with previous work; e.g., the directly observed trap wavelengths are near those inferred from spectroscopic studies. The value for PSII in *A. marina*—723 ± 3 nm—is in close agreement with previously reported spectroscopic values, supporting the view that the primary electron-donor is a Chl d molecule at the accessory (ChlD1) site. Comparison of results from *A. marina* with those from *S. leopoliensis* demonstrates that energy storage in *A. marina* is not thermodynamically limited by its use of far-red (< ~750-nm) photons. We also present recently obtained data confirming a significant dip in the observed efficiency of *A. marina* near 725 nm. This feature may be associated with the underlying structure of photosystem-specific absorption. Further refinement of the analysis procedure will enable this novel implementation of photoacoustics to provide fast, reliable access to a range of essential photosynthetic quantities and processes.


Investigating the role of natural variations in the D1 subunit of Photosystem II on the efficiency and kinetics of photoassembly

Sun, Jennifer S. (Rutgers, The State University of New Jersey, Morganville, NJ, USA); Vinyard, David (USA); Ananyev, Gennady (USA); Gimpel, Javier (USA); Mayfield, Stephen (USA); Dismukes, Gerard (USA)

The efficiency of oxygenic photosynthesis is limited by light-induced damage of the Photosystem II (PSII) complex due to damage of its D1 subunit, called photoinactivation. Repair occurs by replacement of a new D1 polypeptide, and photo-induced reassembly of the Mn4CaO5 water-oxidizing complex (WOC) from free inorganic cofactors (Mn2+, Ca2+, HCO3-, H2O), through a process known as photoassembly. While algae and higher plants possess only one isoform of the D1 subunit, the cyanobacterium Synechococcus elongatus PCC 7942 contains two D1 isoforms: D1:1, which is expressed under low light conditions, and D1:2, which is expressed under high light or stress conditions. These cyanobacterial D1 isoforms were previously heterologously expressed in a strain of the green alga Chlamydomonas reinhardtii lacking its native D1-encoding genes. In this study, we measured the rates and yield of WOC photoassembly in PSII reaction centers containing D1:1, D1:2, or the native algal D1 isoform. At slow single turnover flash frequencies (“low light”), D1:1-apo-WOC-PSII has an approximately 20% faster rate of photoassembly compared to D1:2-apo-WOC-PSII, consistent with other data demonstrating slower charge recombination and a growth advantage at low light intensities (Vinyard et al, 2013). However, the maximal photoassembly yield achieved after several hundred flashes is >2-fold higher when the D1:2 isoform is present vs. D1:1, indicating a higher quantum yield. These results are consistent with the hypothesis that D1:2-PSII has a greater quantum yield of primary charge separation due to a less positive Pheo/Pheo- midpoint potential, while D1:1-PSII has slower [P680+QA-] recombination rate, due to a more positive QA/QA-midpoint potential.
Non-functional chlorophyll complexes and photosystem I fluorescence emission in C3 and C4 leaves

Peterson, Richard B. (The Connecticut Agricultural Experiment Station, New Haven, CT, USA); Oja, Vello (University of Tartu, Tartu, EST); Eichelmann, Hillar (University of Tartu, Tartu, EST); Bichele, Irina (University of Tartu, Tartu, EST); Laisk, Agu (University of Tartu, Tartu, EST)

Photosystem I (PSI) emits low and invariant fluorescence at room temperature comprising about 30% of $F_o$ in C3 plants and about 50% in C4 plants. We characterized invariant emission in developing leaves of Zea mays (maize, C4) and Helianthus annuus (sunflower, C3). Emission spectra of mature leaves showed that the $F_m/F_o$ was maximal and typically ≥ 10.5 suggesting that PSI does not fluoresce at 680 nm. This formed a basis for derivation of the entire PSI emission spectrum. Minimum ($F_o$) and maximum ($F_m$) fluorescence yields were simultaneously obtained at 680 and 750 nm from room temperature fluorescence induction transients excited with 595-nm light using dark-adapted (12 h) leaves of differing developmental state. Compared to fully mature leaves, immature leaf tissue from both maize and sunflower showed lower $F_m/F_o$ ratios at 680 nm suggesting occurrence of chlorophyll a-containing precursor complexes that lack variable fluorescence. A procedure was devised to separately quantify emission from PSI and the aggregate non-functional complexes. Once corrected for the non-functional complex emission, PSI emission was close to 50% of $F_o$ at all positions along the expanding maize leaf consistent with reported expression of O$_2$-insensitive (C4) photosynthesis in all green tissues. Assessment of the PSII/PSI ratio based on optical measurements and on chlorophyll a and b contents enabled us to correlate a specific pool of chlorophyll a to the non-functional complexes signal. We suggest that fluorescing PSII components occur in immature maize bundle sheath cells (BSC) yet do not assemble into functional units due to chlorophyll b deficiency and moreover are subject to reorganization/turnover culminating in the virtual absence of PSII in the BSC of mature leaf tissue.
The Effect of Sr2+ Substitution on Structure of Oxygen Evolving Complex of Photosystem II Studied by 1H HYSCORE Spectroscopy

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The mechanism of water oxidation by photosystem II (PSII) is of fundamental interest and is the object of extensive studies both in the past and present. In PSII, the solar water oxidation reaction occurs in the oxygen evolving complex (OEC). The OEC consists of a tetra-nuclear manganese calcium-oxo (Mn4Ca-oxo) cluster surrounded by amino acid residues. During the catalytic cycle the OEC goes through five different oxidation states S0 - S4. The recent 1.9 Å resolution X-ray structure of the OEC in the S1 state indicates that the Ca2+ ion forms a distorted cubane structure with three Mn ions, while the fourth Mn ion is "dangler". Despite the remarkable breakthrough in the determination of the structure of the S1 state, the mechanism of water oxidation is yet to be unraveled. The role of Ca2+ ion in the catalytic reaction of the OEC remains one of the most interesting questions that is yet to be answered. The structural and functional differences induced by metal ion substitution could provide valuable insight into the role of Ca2+ ion for catalysis of water oxidation in the OEC. The only divalent ion capable of restoring catalytic activity after substitution of Ca2+ ion is Sr2+ ion, however, the catalytic turnover is significantly slow upon Ca2+/Sr2+ substitution. In this study, we apply two-dimensional (2D) hyperfine sub-level correlation (HYSCORE) spectroscopy to probe the structural changes in the OEC in the S2 state induced by Sr2+ substitution. Since hyperfine interactions are highly sensitive to any perturbation of the electronic and geometric structure of paramagnetic centers, comparison of the 2D HYSCORE spectra of Sr2+/Ca2+ substituted PSII allows us to draw important conclusions with respect to structural changes induced by metal ion replacement.
Quinones are essential electron carriers in photosynthesis and cellular respiration, the biological processes that sustain life. The diverse redox potentials of quinones lend them great versatility in these essential processes. The redox potentials of quinones are controlled by substituent effects and by ‘smart matrix effects’, namely, the interactions with the surrounding protein environments. In the present study, a series of 1,4-naphthoquinone models are examined via cyclic voltammetry to provide relative redox potentials. In parallel, CW and pulsed EPR methods are used to directly determine the electronic properties of each naphthoquinone in aprotic and protic environments. The shifts in the redox potential of the quinones are found to be dependent on the nature of the substituent group and the number of substituent groups on the quinone molecule. Further, we establish a direct correlation between the nature of the substituent group and the change in electronic properties of the naphtho-semiquinone by analysis of the isotropic and anisotropic components of the electron-nuclear hyperfine interactions observed by CW and pulsed EPR studies, respectively. Examination of an extensive library of model quinones in both aprotic and protic solvents indicates that hydrogen-bonding interactions consistently accentuate the effects of the substituent groups of the naphthoquinones. This study provides direct support for the tuning and control of quinone cofactors in biological solar energy transduction through interactions with the surrounding protein matrix.
Photosynthetic organisms contain pigment-protein complexes that capture light energy and channel it to the reaction center to drive the photosynthetic light reactions. Energy absorbed by chlorophyll but not used for this purpose must be deactivated so that it does not cause destruction of the photosynthetic apparatus. This photoprotection process is known as nonphotochemical quenching. One hypothesized mechanism is that quenching of excess excited states of chlorophyll occurs by way of aggregation of the membrane-bound, light-harvesting pigment-protein complexes. The present work explores this issue by a spectroscopic analysis of aggregated and unaggregated LHCII complexes from green plants. Steady-state and time-resolved absorption and fluorescence spectroscopic experiments were carried out at room and cryogenic temperatures on monomeric and trimeric LHCII complexes isolated from spinach chloroplasts to examine the effect of aggregation on the spectroscopic properties and dynamics of the protein bound chlorophyll and carotenoid pigments.
Chlorolichens are able to recover photosynthetic ability after prolonged desiccation due to the presence of a fast-lifetime, long-wavelength quencher energetically coupled to PSII. In the desiccated state, this quencher protects PSII by safely dissipating absorbed light energy as heat. Upon rehydration, the quenching state is quickly reversible allowing photosynthesis to proceed. Time-resolved and steady state fluorescence spectroscopy of desiccated lichens have identified a distinct "quenching" spectral signature, a fast decay component with both short (680nm) and long wavelength (750nm) contributions. The purpose of this study was to compare the desiccation recovery abilities and spectral signatures of lichens to two isolated desert dwelling algae (*Chlorella* sp., Class *Trebouxiophyceae*; and *Scenedesmus* sp., Class *Chlorophyceae*), and their closely related aquatic species. Both desert algae quickly recover photosynthetic activity upon rehydration following desiccation for 60 days. However their fluorescence quenching display different spectroscopic signatures. *Chlorella* sp. have "quenching" signatures closely resembling those identified in the lichen, but to a lower extent, suggesting lichen symbiosis enhances a natural recovery mechanism. *Scenedesmus* sp. recovers just as well, but there is a lack of the lichen "quenching" signature, suggesting that *Scenedesmus* sp. uses a different mechanism for desiccation protection.
The influence of electrostatic interactions on the free energy of proton-coupled-electron-transfer (PCET) in biomimetic oxomanganese complexes inspired by the oxygen-evolving complex (OEC) of photosystem II (PSII), are investigated. The reported study introduces an enhanced Multi-Conformer Continuum Electrostatics (MCCE) model, parameterized at the density functional theory (DFT) level with a classical valence model for the oxomanganese core. The calculated pK_a's and oxidation midpoint potentials (E_m) match experimental values for eight complexes indicating that purely electrostatic contributions account for most of the observed couplings between deprotonation and oxidation state transitions. We focus on pK_a's of terminal water ligands in [Mn(II/III)(H_2O)_6]^{2+/3+} (1), [Mn(III)(P)(H_2O)_2]^3- (2, P = 5,10,15,20- tetrakis (2,6-dichloro-3-sulfonatophenyl) porphyrinato), [Mn(IV,IV)_2(µ-O)_2(terpy)_2(H_2O)_2]^{4+} (3, terpy = 2,2':6',2''-terpyridine) and [Mn_3(IV,IV,IV)(µ-O)_4(phen)_4(H_2O)_2]^{4+} (4, phen = 1,10-phenanthroline) and the pK_a's of µ-oxo bridges and Mn Em's in [Mn_2(µ-O)_2(bpy)_4]^{2+} (5, bpy = 2,2'-bipyridyl), [Mn_2(µ-O)_2(salpn)_2] (6, salpn = N,N'-bis(salicylidene)-1,3-propanediamine), [Mn_2(µ-O)_2(3,5-di(Cl)-salpn)_2] (7) and [Mn_2(µ-O)_2(3,5-di(NO_2)-salpn)_2] (8) which are most relevant to PCET mechanisms. The analysis of complexes 6-8 highlights the strong coupling between electron and proton transfers, with any Mn oxidation lowering the pK_a of an oxo bridge by 10.5±0.9 pH units. The model also accounts for changes in the E_m due to ligand substituents, such as those in complexes 6-8, due to the electron withdrawing Cl (7) and NO_2 (8). The reported study provides the foundation for analysis of electrostatic effects in other oxomanganese complexes and metalloenzymes, where PCET plays a fundamental role in redox-leveling mechanisms.
Protein Film Voltammetry and Co-factor Electron Transfer Dynamics in Spinach Photosystem II Core Complex

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Direct protein film voltammetry (PFV) was used to investigate the redox properties of the Photosystem II (PSII) core complex from spinach. The complex had high oxygen evolving capacity and was incorporated into lipid and polyclon films. Three well-defined reversible pairs of reduction and oxidation voltammetric peaks were observed at 4°C in the dark. PFV results were similar in both types of films, indicating that the environment of the PSII-bound cofactors were not influenced by film type. The peaks were assigned to chlorophyll a (Chl a) (E_m = -0.47 V, all vs, NHE, at pH 6), quinones (-0.12 V), and the manganese (Mn) cluster (E_m= 0.18 V). Midpoint potentials of these peaks differed to various extents from previous redox titration data and may be influenced by electrode double-layer effects. Mn-depleted PSII did not show the 0.18 V peak, supporting the assignment to the Mn cluster in PSII. PFV of the iron heme protein cytochrome b-559 (Cyt b-559), a PSII component, gave a partly reversible peak pair at 0.004 V that did not have a potential similar to any peaks of PSII. The closest peak in PSII to 0.004 V is the 0.18 V peak that was found to be associated with a 2 electron process, and thus inconsistent with iron heme protein voltammetry. This suggests that redox reactions involving the cyt b-559 component are not observed in these experiments. The -0.47 V peak had similar peak potential and peak potential-pH dependence to that found for purified Chl-a incorporated into DMPC films. Heterogeneous electron transfer (hET) rate constants were estimated by theoretical fitting and digital simulations for the -0.47 V and 0.18 V peaks. Data for the Chl a peaks were best fit to a one-electron model, while the peak assigned to the Mn cluster was best fit by a two-electron/one proton model.
Carbon metabolism of anaerobic anoxygenic phototrophs and aerobic anoxygenic photo-phototrophs: *Roseobacter denitrificans*, *Rhodobacter capsulatus* and *Rhodobacter sphaeroides*

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We report the central carbon metabolism, including carbohydrate and acetate metabolism, for aerobic anoxygenic phototrophic bacterium *Roseobacter denitrificans* and anaerobic phototrophic *Rhodobacter capsulatus* and *Rhodobacter sphaeroides*. All three bacteria can grow aerobically in darkness. It has been reported that *Rsb. denitrificans* can produce purple pigment in darkness and low-light intensity can prevent this bacterium from pigment production.

Also, *Rsb. denitrificans* can grow aerobically in light whereas *Rba. capsulatus* and *Rba. sphaeroides* can only grow anaerobically in light. In contrast to *Rba. capsulatus* and *Rba. sphaeroides*, carbohydrate metabolism and central carbon metabolism in *Rsb. denitrificans* have not been completely understood. Here, we study the metabolism of *Rsb. denitrificans* and compare to *Rba. capsulatus* and *Rba. sphaeroides*. We feed these three bacteria with different carbon sources, including glucose, fructose, acetate (with and without bicarbonate) and then we collect samples at different time points for examining expression levels of specific genes involved in central carbon metabolism. Biomass, nutrition uptake, photosynthetic pigments amount were also recorded.
Illuminate The Green Sulfur Bacterium Chlorobaculum tepidum With Far Red To Near Infrared Light

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Chlorobaculum tepidum (formly Chlorobium tepidum), a member of Chlorobiaceae family, is an anaerobic phototrophic, thermophilic bacterium and it is a model organism of green sulfur bacteria. C. tepidum was isolated from New Zealand hot springs. The C. tepidum can fix CO₂ under low light-intensity and convert CO₂ into biomass. To enhance our understanding how C. tepidum can perform photosynthesis under low-light environments, we presented the first report on the green photosynthetic bacteria illuminated with specific wavelengths. C. tepidum cultures are illuminated with far-red to near infrared (NIR) lights, i.e., 750nm, 780nm, 800nm and 850 nm. Some interesting results have been revealed in our studies. First, the culture grown well with these specific wavelengths and cultures illuminated with 750 nm light grow better than cultures illuminated with white light. Second, cultures illuminated with 850 nm light still synthesize the chlorosome. As green photosynthetic bacteria are known to regulate the biogenesis of the chlorosome relative to light intensities, we are currently investigating the cultures grown by varying illuminated wavelengths and light intensities, as well as characterizing the chlorosome from those cultures.
The investigation of photosynthesis is of great interest from a fundamental point of view but also as a blueprint for energy storage and generation applications. The immobilization of photosynthetic proteins as self-assembled monolayers provides a platform for electron transfer kinetics studies.\(^1\) The orientation of histidine-tagged proteins onto TiO\(_2\) poses a non-trivial challenge with respect to the chemical modification of the metal oxide surface and the stabilization of the proteins. Here, we immobilize Photosystem II core complexes (PSII), isolated from Thermosynechococcus elongatus, His-tagged at the carbon terminus of the CP47 domain onto a titanium(IV) oxide surface. We developed a strategy for surface modification using a combination of organosilanes, a succinimide coupling agent and a Nickel(II) ion - nitrilotriacetic acid (Ni-NTA) coordination complexes. The modified surfaces before and after PSII immobilization were characterized by Fourier Transform Infrared Spectroscopy Attenuated Total Reflectance (FT-IR-ATR). The medium infrared spectra provided vibrational evidence for the stepwise surface modification and binding of the PSII on the titanium(IV) oxide surface. The vibrational assignment was confirmed by Gaussian decomposition. Further characterization of PSII tethered to TiO\(_2\) was carried out using a non-invasive fluorescence technique in order to assess the remaining photosynthetic activity of PSII. The quantum yield of photochemistry was 0.59 for immobilized PSII as opposed to 0.81 for PSII in suspension. There are no significant differences in the observed fluorescence relaxation times (t) in free PSII and immobilized PSII. This latter result indicates that there is no spontaneous electron transfer from PSII to chemically modified TiO\(_2\), possibly due to the resistance of the chemically modified interface. The value of the functional absorption cross-section interpolated across the visible spectrum (365-750 nm) is 35.7 Å/q. Using this value we estimate that the theoretical current density could be as high as 61 μA/cm\(^2\).

Hemoprotein Design Using Minimal Sequence Information

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We present a simple method for the design of cofactor binding proteins which utilizes a low degree of primary sequence specificity. Starting with a bioinformatically derived helical porphyrin-binding consensus sequence, we generate a ‘wire-frame’ model of an idealized four alpha-helix bundle which contains both the target cofactor and the consensus amino acids on both ligating helices. We then use the model to determine the level of solvent exposure of each remaining unspecified side chain, using database-derived helical side-chain frequencies to randomly select these remaining side chain identities. Evaluation of this method using a ten member library demonstrated that additional sequence information, in the nonligand pair of helices, was required to create a cavity for cofactor binding. Our results allow us to estimate that there are $10^{54}$ sequences which should fold into a four-helix bundle and bind one or more porphyrin cofactors. These data demonstrate that, at least in the case of helical bundle proteins, functional sequence space is much too large for evolution to explore.
THE EFFECTS OF THE DISTRIBUTIONS OF EXCITATION ENERGY TRANSFER RATES ON THE NONRESONANT SPECTRAL HOLES IN TRIMERIC PHOTOSYNTHETIC PROTEIN COMPLEXES: THE STUDY OF FENNA-MATTHEWS-OLSEN PROTEIN

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The model describing the effects of the homogeneous line widths (or lifetime) distributions on the resonant hole burning spectra (SHB) in photosynthetic chlorophyll-protein complexes has been reported recently [1]. The model has been successfully applied to simulate the evolution of resonant spectral holes in several photosynthetic complexes, where either excitation energy transfer occurs between two pigments with quasi-degenerate absorption bands, or where the distributions were independently known otherwise. Here we report extending our previous model of SHB to a system of three pigments with identical degenerate lowest-energy states connected by EET. We have also introduced some novel capabilities, allowing for more accurate modeling of the non-resonantly burned spectral holes (the lower-energy satellite holes burned via downhill EET), and the pseudo-phonon side band (PSB) of the hole spectrum. Moreover, the SHB software was improved to simultaneously calculate a comprehensive set of spectra (absorption, emission, hole-burned and/or fluorescence line narrowing). As the lowest-energy absorption band in trimeric Fenna-Matthews-Olsen (FMO) complex [2] is contributed by three pigments (one pigment per monomer) connected by relatively slow EET [3] we have chosen to test our new SHB model by fitting several non-resonant spectral holes burned into the lowest-energy state of FMO protein from Chlorobium tepidum. As we will show, our model captures all important features of the spectra evolution.

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Insights into the S0 state of Oxygen Evolving Complex within PS-II and kinetic isotope effects calculations in biomimetic oxo-manganese catalysts
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Photosystem-II (PS-II) found in the thylakoid membrane of all the higher plants, algae and cyanobacteria, is one of the most efficient biological oxidant, which harvests solar energy and promotes the generation of molecular O$_2$ from the water molecules. The catalytic core within PS II contains a metal oxide cluster with the formula CaMn$_4$O$_5$. The ability of this cluster to stepwise oxidize the Mn atoms (also known as the Kok cycle) through light driven electron transport mechanism and release protons through the Chloride ion channels makes it a remarkable water splitting enzyme whose efficiency is unmatched by any artificial catalyst.

By using a combined Monte-Carlo/Quantum Mechanics Molecular Mechanics (QMMM) approach coupled with Extended X-ray Absorption Fine Structure simulations (EXAFS), we propose the structure for the S0 state of the Oxygen-Evolving Complex (OEC) in photosystem II. In addition to the geometry of the CaMn$_4$O$_5$ cluster, charges on individual Mn atoms and the protonation state of a µ-oxo bridge at the S0 state are determined. Following our previous work on the structure determination of the dark-stable S1 state, we also propose the mechanism of transition from the S0 to the S1 state of the OEC. Our study reveals that one Mn atom gets oxidized and a bridging oxo (O5) deprotonates during the S0 to S1 transition.

Understanding the redox mechanism that operates in the biomimetic oxo-manganese catalysts can provide fundamental insights into the functional role of the OEC cluster within the PS-II. Thereby reproducing the isotope effects ($^{16}$O/$^{18}$O) observed due to Oxygen evolution under the experimental conditions will provide a benchmark for all the predicted theoretical models of these catalysts. Our current study revealed the kinetic and equilibrium isotope substitution effects on the Mn-terpy dimer [((H$_2$O)(terpy)MnIII(m-O)$_2$MnIV(H$_2$O)(terpy))] catalyst, where terpy = 2,2’:6-2’-terpyridine. Our calculated values are in close proximity with experimental data that yields a comprehensive understanding of the reaction cycle.
The Virtual Planetary Laboratory (VPL) is a team of scientists in the NASA Astrobiology Institute (NAI) who are interested in how to determine if planets orbiting other stars exhibit signs of life, "biosignatures." They focus on how to interpret and model the spectral signatures of planets as will be seen by space telescopes. The researchers are spread throughout many different university and NASA institutions and include astronomers, planetary scientists, geochemists, microbiologists, biochemists, biogeochemists, and more in highly interdisciplinary research.

Photosynthesis arose early in the Earth’s history and produces thus far the only known nearly unequivocal signs of life that can be seen at the planetary scale: atmospheric oxygen and the reflectance signature of vegetation. Therefore, photosynthetic biosignatures are a primary target in the astronomical search for life on exoplanets. The diversity of photosynthesis on Earth provides clues to how this successful life process might manifest itself differently when adapted to the spectral radiation of a parent star very different from our Sun, filtered through an atmosphere subject to different biogenic gas fluxes and photochemistry.

To foster further research into planetary biosignatures, VPL has made available to the scientific community the VPL Spectral Database, which includes data sets of molecular line lists, stellar spectra, and now the VPL Biological Pigments Database. The latter includes contributions by many scientists of absorbance spectra of biological pigments, with metadata of contributor names and publications, and significant features of the data. Data sets include different chlorophylls, bacteriochlorophylls, carotenoids, screening compounds for UV protection, and more continue to be added.

The VPL Biological Pigments Database is available at:

http://vplapps.astro.washington.edu/pigments

If you would like to contribute your data, please contact Nancy.Y.Kiang@nasa.gov
INDEX

A

Amin, Muhamed (USA) .......................................................... 28
Ananyev, Gennady (Rutgers University, USA) ...................... 10, 18
Ananyev, Gennady (USA) ...................................................... 22

B

Baird, James (Medgar Evers College of CUNY, USA) ..........15
Batista, Victor (USA) .......................................................... 17
Batista, Victor (Yale University, New Haven, CT, USA) .......9
Berry, Joseph A. (Carnegie Inst. for Science, Stanford, CA, USA) .......................................................... 2
Bichele, Irina (University of Tartu, Tartu, EST) .................23
Blankenship, Robert (Washington University in St. Louis, St. Louis, MO, USA) ...................................................... 1
Blankenship, Robert (Washington University, St. Louis, USA) .......................................................... 2
Bolychevtseva, Yulia (A.N.Bach Institute of Biochemistry, Russian Academy of Sciences, Moscow, RUS) ..........6
Bruce, Doug (Brock University, CAN) ................................ 7
Bruce, Doug (Brock University, St. Catharines, CAN) .........13
Bruce, Doug (USA) ............................................................. 27, 28
Brudvig, Gary (USA) .......................................................... 17

C

Cardon, Zoe (Marine Biological Laboratory, Woods Hole, MA, USA) .......................................................... 27
Chatterjee, Ruchira (Rensselaer Polytechnic Institute, Troy, NY, USA) .......................................................... 19, 24, 25
Chhowalla, Manish (Rutgers University, USA) ....................18
Ching, Amy (Brock University, USA) .................................... 8
Cipi, Blerina (USA) ............................................................. 30
Coates, Christopher (Rensselaer Polytechnic Institute, Troy, NY, USA) .......................................................... 19, 20, 24
Coates, Christopher (Rensselaer Polytechnic Institute, Troy, NY, USA) .......................................................... 12
Coates, Christopher (Rensselaer Polytechnic Institute, Troy, NY, USA) .......................................................... 25
Cornejo, Mario (Rutgers University, USA) .........................10

D

Derks, Allen (Brock University, St. Catharines, ON, CAN) ...7
Dismukes, Charles (Rutgers University, USA) ......................10, 18
Dismukes, Gerard (USA) ...................................................... 22

E

Eichelmann, Hillar (University of Tartu, Tartu, EST) ...........23
Elanskaya, Irina (Faculty of Biology, M.V.Lomonosov Moscow State University, Moscow, RUS) ...................... 6
Enciriquez, Miriam (University of Connecticut, Storrs, CT, USA) .......................................................... 26
Ertm, Mehmed (USA) .......................................................... 17
Ertm, Mehmed Zahid (USA) ............................................... 35
Eversen, Ben (City College of New York, USA) ..................16
Eversen, Bernard H. (City College of New York, Brooklyn, NY, USA) .......................................................... 33

F

Fadeev, Victor (Faculty of Physics, M.V.Lomonosov Moscow State University, Moscow, RUS) ...................... 6
Falkowski, Paul G. (Rutgers University, USA) ....................15, 32
Frank, Harry (University of Connecticut, Storrs, CT, USA) .26
Frank, Harry A. (University of Connecticut, Storrs, CT, USA) .......................................................... 29
Fraser, Ryan (Midwood High School, USA) .......................32
French, Cooper (City College of New York, Queens, NY, USA) .......................................................... 16
French, Cooper (City College of New York, USA) ..............33

G

Gimpel, Javier (University of California, San Diego, USA) ...10
Gimpel, Javier (USA) .......................................................... 22
Golbeck, John (Pennsylvania State University, University Park, PA, USA) .......................................................... 25
Golden, Susan (University of California, San Diego, USA) .10
Good, Jacob (Rensselaer Polytechnic Institute, Troy, NY, USA) .......................................................... 25
Gorbunov, Maxim (IMCS, Rutgers University, New Brunswick, NJ, USA) .......................................................... 6
Gorbunov, Maxim Y. (Rutgers University, USA) ..................18
Gordon, Heather (Brock University, USA) .......................... 8
Gunner, Marilyn (USA) ...................................................... 28

H

Hannout, Moataz (Clark University, USA) ........................... 4
Hannout, Moataz (Clark university, worcester, MA, USA) ...31
Hao, Siie (Pennsylvania State University, University Park, PA, USA) .......................................................... 25
Harold, John W. (Rutgers University, USA) ...................... 32
Harold, John W. (Rutgers University, USA) ......................15, 18
Hastings, Gary (Georgia State University, USA) .............. 8
Herascu, Nicoleta (Concordia University, Montreal, PQ, CAN) .......................................................... 34
Hirsh, Donald J. (The College of New Jersey, USA) ..........18
Hull, Dominic O. (Medgar Evers College of CUNY, USA) ...32

K

Karapetyan, Navasard (A.N.Bach Institute of Biochemistry, Russian Academy of Sciences, Moscow, RUS) ..........6
Khan, Sahr (USA) ............................................................. 17
Kiang, Nancy (NASA GISS, USA) ...................................... 21
Kiang, Nancy Y. (Columbia University, New York, NY, USA) .......................................................... 36
Koder, Ronald (CCNY Physics, New York, NY, USA) .......14
Koder, Ronald (City College of New York, USA) ..............16, 33
Koua, Faisal (Okayama University, Okayama, JPN) ..........19, 24
Kuzminov, Fedor I. (IMCS, Rutgers University, New Brunswick, NJ, USA) .......................................................... 6

L

LaFountain, Amy (University of Connecticut, Storrs, CT, USA) .......................................................... 26
Laisk, Agu (University of Tartu, Tartu, EST) ......................23
Pal, Rhitankar (USA) ......................................................... 17
Pal, Rhitankar (USA) ......................................................... 35
Peterson, Richard B. (The Connecticut Agricultural
Experiment Station, New Haven, CT, USA) ................. 23
Podduotoori, Prashanth (Brock University, St. Catharines, CAN) ......................................................... 13
Pokhrel, Ravi (Yale University, New Haven, CT, USA) ....... 11
Prof. Jankowiak, Ryszard (Kansas State University, USA) 28
Prof. Zazubovits, Valter (Concordia University, CAN) ...... 34

R

Rafka, Lauren (University of Connecticut, Storrs, CT, USA) ... 26
Redding, Kevin (Arizona State University, USA) ............... 8
Rivalta, Ivan (USA) .......................................................... 28
Rusling, James F. (University of Connecticut, Storrs, CT, USA) ................. 29
Rutherford, A. William (Imperial College, GBR) ............. 18, 32

S

S. Batista, Victor (USA) ..................................................... 28
Schaven, Kristin (Brock University, St. Catharines, ON, CAN) ......................................................... 27
Shen, Jian-Ren (Okayama University, Okayama, JPN) 19, 24
Sun, Jennifer S. (Rutgers, The State University of New Jersey, Morganville, NJ, USA) ......................... 22

T

tang, joseph (Clark university, worcester, MA, USA) ....... 31
Tang, Joseph (USA) .......................................................... 30
Tang, Joseph Kuo-Hsiang (Clark University, Worcester, MA, USA) ......................................................... 4

V

van der Est, Art (Brock University, CAN) .......................... 8
van der Est, Art (Brock University, St. Catharines, CAN) 13
Vassil’ev, Sergej (Brock University, St. Catharines, CAN) 13
Vassiliev, Sergei (CAN) ..................................................... 27
Vassiliev, Serguei (USA) ................................................... 28
Vinyard, David (Rutgers University, Piscataway, NJ, USA) 10
Vinyard, David (USA) ...................................................... 22
Vittadello, Michele (Medgar Evers College of CUNY, Brooklyn, NY, USA) ........................................... 15, 18, 32
Vogt, Leslie (USA) .......................................................... 28, 35
Vogt, Leslie (Yale University, New Haven, CT, USA) ....... 9

W

W. Brudvig, Gary (USA) ................................................... 28
wang, yaya (clark university, worcester, MA, USA) ......... 30
Woronowicz, Kamil (Medgar Evers College of CUNY, Rutgers University, USA) ........................................ 18
Woronowicz, Kamil (Medgar Evers College of CUNY, USA) ......................................................... 15

Y

Yamaguchi, Hisato (Rutgers University, USA) ................. 18

Z

Zare, Farrokh (Clark university, worcester, MA, USA) ....... 31
Zare, Farrokh (USA) ......................................................... 30
Zazubovich, Valter (Concordia University, Montreal, PQ, CAN) ......................................................... 5
Zhang, Lei (City College of New York, USA) .................... 16
Zhang, Yun (University of Connecticut, Storrs, CT, USA) 29
Zhao, Nan (Georgia State University, USA) ...................... 8
Ziegler, Jessica (Rensselaer Polytechnic Institute, Troy, NY, USA) ......................................................... 25
Ziegler, Jessica (Rensselaer Polytechnic Institute, Troy, NY, USA) ......................................................... 20
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