OMB No. 0925-0001 and 0925-0002 (Rev. 03/2020 Approved Through 02/28/2023)

BIOGRAPHICAL SKETCH

Provide the following information for the Senior/key personnel and other significant contributors.
Follow this format for each person. **DO NOT EXCEED FIVE PAGES.**

NAME: Gisriel, Christopher James

eRA COMMONS USER NAME (credential, e.g., agency login): CGISRIEL

POSITION TITLE: Postdoctoral Associate

EDUCATION/TRAINING *(Begin with baccalaureate or other initial professional education, such as nursing, include postdoctoral training and residency training if applicable. Add/delete rows as necessary.)*

INSTITUTION AND LOCATION	DEGREE (if applicable)	START DATE MM/YYYY	END DATE MM/YYYY	FIELD OF STUDY
Arizona State University	BS	06/2010	04/2013	Biochemistry
Arizona State University	PHD	08/2014	12/2017	Biochemistry
Arizona State University	Postdoc	01/2018	8/2019	Biochemistry
Yale University	Postdoc	10/2019	present	Chemistry

A. Personal Statement

The long-term goals of my research are to realize how light-driven oxidoreductases utilized by phototrophic organisms can be used to better understand protein assembly, especially the preparation of active sites containing inorganic metal clusters. I hope to exploit such an understanding to improve upon current technologies and develop new technologies for improving human health. The research proposed herein aims to meticulously dissect a light-activated metalloenzyme called Photosystem II.

After serving a tour of duty in Afghanistan with the U.S. Army, I began to recognize that I had a passion for understanding characteristics of the natural world invisible to the naked eye. This led me to an undergraduate degree program at Arizona State University where I learned about the usefulness of using light-activated proteins for elucidating molecular mechanisms. I gained experience in time-resolved spectroscopy and X-ray crystallography as a graduate student, publishing a first-author paper in *Science* that presented the structure of a new class of enzyme. I also met my present spouse in this laboratory, who was a medical school student and is now a resident physician at Yale New Haven Hospital in the Department of Pathology.

Upon gaining my Ph.D. in Biochemistry from Arizona State University, I was asked by Professor Petra Fromme, who was also at Arizona State University, take a postdoctoral position, leading a team of scientists in structural biology experiments using X-ray free electron lasers which I accepted. In the Fromme Lab, I designed and led high-profile experiments at the Stanford Linear Accelerator Center (Stanford, CA, US) and the European XFEL (Hamburg, Germany) resulting in a first-author publication in *Nature Communications* with 77 other co-authors from 22 different institutions.

I became interested in cryo-EM and solved a structure of a photoactive protein adapted to specialized light conditions, resulting in a first author publication in *Science Advances* and a subsequent first/corresponding author Perspective in *Nature – Communications Biology*. I joined the Brudvig Lab shortly after solving the structure because it had opportunities for me to apply more sophisticated methods of cryo-EM and to gain new expertise such as inorganic chemistry, electron paramagnetic resonance, and computational approaches. Professor Brudvig's pattern of excellent mentorship and community standing, and the environment that Yale cultivates for addressing fundamental biological questions, makes it an ideal site in which to transition toward independence. I will continue my postdoctoral training by elucidating the mechanism of metal cluster assembly in the photosystem II enzyme, and transition toward independence by broadening this scope, investigating the biogenesis of the protein that prepares the active site, both of which can be used as models for understanding metal cofactors and protein assembly in general.

B. Positions and Honors

Positions and Employment

2010 - 2013	Undergraduate Research Assistant, Arizona State University
2014 - 2017	Graduate Research Assistant, Arizona State University
2018 - 2019	Postdoctoral Research Associate, Arizona State University
2019 -	Postdoctoral Research Associate, Yale University

Other Experience and Professional Memberships

2018 -	Ad hoc reviewer for various reputable journals (Nature Communications, Nature Plants, eLife, Geobiology, IJMS, Free Radical Biology and Medicine, and Journal of the Royal Society Interface)
2018 -	BioXFEL Scholar
2017 -	Achievement Rewards for College Scientists (ARCS) Scholar
2017 - 2019	Gordon Research on Photosynthesis Seminar Chair

Honors

2012	Wayne W. Luchsinger Chemistry Scholarship recipient, ASU
2017	Richard Malkin Award recipient, Western Photosynthesis Conference
2017	Johnston Endowment Scholar award recipient, ARCS Foundation
2017	College of Liberal Arts and Sciences CLAS Leader, ASU
2017	College of Liberal Arts and Sciences Graduate Excellence Award, ASU
2017	College of Liberal Arts and Sciences Outstanding Graduate, ASU
2017	Summa Cum Laude (Ph.D. Biochemistry), ASU

C. Contribution to Science

1. **Early Career:** Heliobacteria are photoheterotrophic Firmicutes that produce large amounts of hydrogen gas. Understanding the fundamental aspects of their light-driven metabolism can be exploited for use in biophotovoltaic cells. To provide a basis for such applied work, members of my group and our collaborators from the Pennsylvania State University characterized electron transfer from the photosystem enzyme to downstream soluble electron acceptors, and we worked in collaboration with the lab of Anne Jones at ASU to compose an electrode surface that could transfer electrons to the cell, driving drive hydrogen gas formation.

a. Ferlez, B. *, Cowgill, J., Dong, W., **Gisriel, C.**, Lin, S., Flores, M., Walters, K., Cetnar, D., Redding, K.†, & Golbeck, J.† (2016). Thermodynamics of the electron acceptors in *Heliobacterium modesticaldum*: An exemplar of an early homodimeric type I photosynthetic reaction center. *Biochemistry*, *55*(16), 2358-2370. (doi: https://doi.org/10.1021/acs.biochem.5b01320) PMID: 27033441

b. Herrera-Theut, K. A.*, **Gisriel, C.**, Laureanti, J., Orf, G., Baker, P., Jones, A. K., & Redding, K.† (2017). Evaluating the role of a multi-heme cytochrome c in electron transfer from an electrode surface to *Heliobacterium modesticaldum*. *The FASEB Journal*, *31*, 913.13-913.13.

2. **Graduate Career:** Phototrophy evolved ~3.5 billion years ago in an anoxygenic environment, from which all modern phototrophs evolved, such as plants and cyanobacteria that perform oxygenic photosynthesis. One extant family of phototroph, anoxygenic bacteria called Heliobacteria, contain a simple oxygen-intolerant photosystem thought to be similar to an ancient ancestor of all modern photosystems. At ASU, I solved the first structure of this fourth class of reaction center protein complexes and provided evolutionary insight into phototrophy.
    a. **Gisriel, C.***, Sarrou, I., Ferlez, B., Golbeck, J., Redding, K., & Fromme, R.† (2017). Structure of a symmetric photosynthetic reaction center–photosystem. *Science*, *357* (6355), 1021-1025. (doi: https://doi.org/10.1126/science.aan5611) PMID: 28751471
    b. Orf, G.*****, **Gisriel, C.***, & Redding, K.† (2018). Evolution of photosynthetic reaction centers: insights from the structure of the heliobacterial reaction center. *Photosynthesis Research*, *138* (1), 11-37. (doi: https://doi.org/10.1007/s11120-018-0503-2) PMID: 29603081

3. **Postdoctoral Career (a):** While traditional X-ray crystallography is the most well-established and widely-used technique used for structural biology, it is often limited by the fact that X-ray damage alters the protein structure, calling into question whether the observed structure is biologically relevant. Serial femtosecond crystallography, however, uses X-ray Free Electron Lasers (XFEL) to delivery fast and intense laser pulses to individual crystals, producing a damage-free diffraction pattern from each of many crystals to comprise a full data set. Unfortunately, only a few XFEL facilities exist to date, and beamtime is in high demand, unable to be procured by most researchers. This bottleneck can be partially alleviated by faster data collection as exemplified by the European XFEL's ability to collect data at megahertz repetition rates. To show that this technique can be used to solve structures of large membrane protein complexes that exhibit valuable biological characteristics, I led a team of individuals in solving the first serial femtosecond crystallography structure of photosystem I at the European XFEL.
    a. **Gisriel, C.***, Coe, J.*, Letrun, R., Yefanov, O. M., Luna-Chavez, C., Stander, N. E., Lisova, S., Mariani, V., Kuhn, M., Aplin, S., Grant, T. D., Dörner, K., Sato, T., Echelmeier, A., Cruz Villarreal, J., Hunter, M. S., Wiedorn, M. O., Knoska, J., Mazalova, V., Roy-Chowdhury, S., Yang, J.-H., Jones, A., Bean, R., Bielecki, J., Kim, Y., Mills, G., Weinhausen, B., Meza, J. D., Al-Qudami, N., Bajt, S., Brehm, G., Botha, S., Boukhelef, D., Brockhauser, S., Bruce, B. D., Coleman, M. A., Danilevski, C., Discianno, E., Dobson, Z., Fangohr, H., Martin-Garcia, J. M., Gevorkov, Y., Hauf, S., Hosseinizadeh, A., Januschek, F., Ketawala, G. K., Kupitz, C., Maia, L., Manetti, M., Messerschmidt, M., Michelat, T., Mondal, J., Ourmazd, A., Previtali, G., Sarrou, I., Schön, S., Schwander, P., Shelby, M. L., Silenzi, A., Sztuk-Dambietz, J., Szuba, J., Turcato, M., White, T. A., Wrona, K., Xu, C., Abdellatif, M. H., Zook, J. D., Spence, J. C. H., Chapman, H. N., Barty, A., Kirian, R. A., Frank, M., Ros, A., Schmidt, M., Fromme, R., Mancuso, A. P., Fromme, P.†, & Zatsepin, N. A.† (2019). Membrane protein megahertz crystallography at the

European XFEL. *Nature Communications*, *10* (1), 5021. (doi: https://dx.doi.org/10.1038%2Fs41467-019-12955-3) PMCID: PMC6828683

4. **Postdoctoral Career (b):** The ability for some photosynthetic bacteria to make use of lower-energy far-red light is a novel characteristic whose understanding could lead to more robust crops. These bacteria alter their photosystem proteins, switching-out certain subunits to replace some chlorophyll *a* molecules with chlorophyll *f* or *d*, enabling them to use the lower-energy light for photochemistry. To uncover the molecular basis of this phenomenon in the photosystem I enzyme, I solved its single-particle cryo-EM structure, participated in spectroscopy experiments that characterized energy transfer through the complex, and wrote a perspective to guide the field in how to improve tetrapyrrole assignments in cryo-EM maps.
    a. **Gisriel, C.***, Shen, G., Kurashov, V., Ho, M-Y., Zhang, S., Williams, D., Golbeck, J., Fromme, P., & Bryant, D.† (2019). The structure of Photosystem I acclimated to far-red light illuminates an ecologically important acclimation process in photosynthesis. *Science Advances, 6* (6). (doi: https://doi.org/10.1126/sciadv.aay6415) PMCID: PMC7393486
    b. **Gisriel, C.*†**, Wang, J., Brudvig, G., & Bryant, D. (2020). Opportunities and challenges for assigning cofactors in cryo-EM density maps of chlorophyll-containing proteins. *Communications Biology*, *3* (408). (doi: https://doi.org/10.1038/s42003-020-01139-1) PMCID: PMC7393486
    c. Tros, M.*, Mascoli, V., Shen, G., Ho, M-Y., Bersanini, L., **Gisriel, C.**, Bryant, D., & Croce, R.† (2021) Breaking the red-limit: Efficient trapping of long-wavelength excitations in chlorophyll *f*-containing Photosystem I. *Chem* (In press)

5. **Postdoctoral Career (c):** Photosystem II catalyzes water oxidation, producing all the oxygen in the atmosphere as a byproduct. To cope with oxidative damage while maintaining the active site cofactor, the cell constantly repairs the enzyme, making the system of interest in understanding biogenesis of metalloenzymes. To understand the structure of Photosystem II in a state of disassembly, I solved the single-particle cryo-EM structure of the inactivated enzyme showing unique characteristics of the apo-active site.
    a. **Gisriel, C.***, Zhou, K., Huang, H-L., Debus, R., Xiong, Y., & Brudvig, G.† (2020). Cryo-EM structure of monomeric photosystem II from *Synechocystis* sp. PCC 6803 lacking the water-oxidation complex. *Joule, 4* (10) 2131-2148. (doi: https://doi.org/10.1126/sciadv.aay6415) PMCID: PMC7393486

*represents first author(s), †represents corresponding author

Complete List of Published Work in My Bibliography:
https://www.ncbi.nlm.nih.gov/myncbi/1HYFc8Tx1jWUrm/bibliography/public/

D. Additional Information: Research Support

Independent Research Support

YEAR	SOURCE
2017 - 2018	Achievement Rewards for College Students (ARCS)
2019 - 2020	Brown Postdoctoral Fellowship for Plant Sciences, Yale University

BIOGRAPHICAL SKETCH

Provide the following information for the Senior/key personnel and other significant contributors.
Follow this format for each person. **DO NOT EXCEED FIVE PAGES.**

NAME: Brudvig, Gary Wayne

eRA COMMONS USER NAME (credential, e.g., agency login): GBRUDVIG

POSITION TITLE: Benjamin Silliman Professor of Chemistry, Professor of Molecular Biophysics and Biochemistry (MB&B), Director of the Yale Energy Sciences Institute

EDUCATION/TRAINING *(Begin with baccalaureate or other initial professional education, such as nursing, include postdoctoral training and residency training if applicable. Add/delete rows as necessary.)*

INSTITUTION AND LOCATION	DEGREE *(if applicable)*	Completion Date MM/YYYY	FIELD OF STUDY
University of Minnesota, Minneapolis	B.S.	1976	Chemistry
California Institute of Technology	Ph.D.	1981	Chemistry
University of California, Berkeley	Postdoc	1980-1982	Chemistry

A. Personal Statement

As additionally described in the mentor section of the application herein, during my 38 years on the faculty at Yale University, I have advised 55 PhD students, 36 postdoctoral scholars, 14 MS students and 70 undergraduate researchers. These research scholars have all gone on to successful careers in a diverse range of fields including academia, biotech and pharmaceutical companies, law and medicine. Many hold faculty positions at academic institutions including: Michigan State Univ., Arizona St. Univ., Univ. of Massachusetts-Amherst, Washington Univ., Rensselaer Polytechnic Institute, Univ. of London, Nanyang Technological Univ., Singapore, National Chung Cheng University, Taiwan, National Chung Hsing University, Taiwan, Northeast Normal University, China, Nanjing Agricultural University, China, Louisiana St. Univ., Univ. of Kentucky, Univ. of Kansas, Univ. of Connecticut, Univ. of New Hampshire, Univ. of Cincinnati, North Dakota State Univ., Lewis & Clark College, Centre College and The College of New Jersey. My current research group includes 10 PhD students and 4 postdocs.

My research has been continuously supported during my 38 years at Yale by grants from a variety of federal agencies and foundations including the NIH, DOE, NSF and USDA. My research group is currently funded by the DOE, NSF and the TomKat Foundation.

Currently, I am the Benjamin Silliman Professor of Chemistry, with a secondary appointment as Professor of Molecular Biophysics and Biochemistry (MB&B), at Yale University and I direct the Energy Sciences Institute on Yale’s West Campus. Our research involves study of the chemistry of solar energy conversion in natural photosynthesis, especially research aimed at determining the molecular mechanism of photosynthetic oxygen evolution by photosystem II, and work to develop artificial bioinspired systems for solar fuel production. Research carried out by our group in the Energy Sciences Institute involves the design, synthesis, characterization and application of organic photosensitizers and inorganic catalysts for use in photoelectrochemical applications for artificial photosynthesis.

At Yale, I have served in a number of administrative positions in which I worked to enhance training and mentoring, and to promote inclusive and supportive scientific research environments. I served for 6 years as

Director of Graduate Studies in the Department of Chemistry. During this time, I promoted graduate mentoring by establishing annual meetings of all Chemistry graduate students with their faculty committee. I also served for 9+ years as Chair of the Department of Chemistry. As Department Chair, I attended three NIH-sponsored workshops in Washington, DC on promoting gender diversity, racial diversity and inclusivity of handicapped trainees and brought back information to my department to increase awareness of these topics. In addition, I served as Director of the NIH-supported Biophysics Training Program at Yale University from 1999 to 2006. As Director, I strived to promote mentorship and to increase the number of underrepresented minorities in the training program.

B. Positions and Honors

Positions and Employment

1975	Student Aide, Argonne National Laboratory
1976-80	National Institutes of Health Predoctoral Trainee, Caltech
1980-82	Miller Postdoctoral Fellow, University of California, Berkeley
1982-87	Assistant Professor of Chemistry, Yale University
1987-91	Associate Professor of Chemistry, Yale University
1991-present	Professor of Chemistry, Yale University (Chair, 2003-2009 and 2015-2018)
2003-present	Professor of Molecular Biophysics and Biochemistry, Yale University
2012-present	Founding Director, Energy Sciences Institute, Yale University

Other Experience and Professional Memberships

Chair, Eastern Regional Photosynthesis Conference, 1985, 2020
Chair, Gordon Research Conference on Biophysical Aspects of Photosynthesis, 2000
Chair, Gordon Research Conference on Solar Fuels, 2018
Executive Committee, Bioenergetics Subgroup of the Biophysical Society, 1994-1997
Editorial Board Member: *Photosynth. Res.*,1986-1995; *American Scientist*, 1989-1990; *Biospectroscopy*, 1994-2003; *Current Chemical Biology*, 2006-2017; Oxford University Press, 2009-2019; *Nanotechnology*, 2011-present; *CRC Press*, 2011-present; World Scientific Publishers, 2014-present; *Biochemistry*, 2017-present; *Nano Futures*, 2017-present; *Inorganics*, 2018-present; *Sci*, 2018-present
Faculty Member, F1000Prime, 2018-present
Associate Editor, *Biochemistry*, 2000-2016
Member, NIH Physical Biochemistry Study Section, 2000-2004
DOE Review Panels: Biological Energy Research Program, 1985; Energy Biosciences Program, 1993; SISGR Program, 2009; Solar Photochemistry Program, 2011; Early Career Research Program, 2015; Physical Biosciences Program, 2016, 2019; Office of Science Graduate Student Research Program, 2017
Lawrence Berkeley National Laboratory, Structural Biology Division Review Committee, 1997
Lawrence Berkeley National Laboratory, Physical Biosciences Division Review Committee (Chair), 2004, 2005
USDA Review Panel, Competitive Research Grants Program, 1987
NIH Special Study Sections: Program Project/Research Resource Reviews, 1992, '93, '97, '98
NIH Study Sections, ad hoc member: Metallobiochemistry, 1995; Physical Biochemistry, 1995, '96, '99;
Molecular & Cellular Biophysics, 1996; Small Instrumentation Grants, 1993, '96; Fellowships, 2002, '08
External reviewer: Dept. of Chemistry, Univ. of Albany, 2005; Dept. of Chemistry & Biochemistry, Arizona St. Univ., 2006, 2013; Dept. of Chemistry, Emory Univ., 2010; Dept. of Chemistry, Johns Hopkins Univ., 2011; Dept. of Chemistry, Dartmouth College, 2020
Scientific Advisory Committee, The Institute of Chemistry, Academia Sinica, 2017-present

Honors

1975	Phi Beta Kappa Honor Society
1976	Award of the American Institute of Chemistry for Outstanding Chemistry Student
1980	Herbert Newby McCoy Award for Outstanding Research in Chemistry
1982	Camille and Henry Dreyfus Newly Appointed Faculty Fellowship
1983	Searle Scholar
1985	Camille and Henry Dreyfus Teacher-Scholar
1986	Alfred P. Sloan Research Fellow

1989 Milton Harris, ‘29 Ph.D., Associate Professor of Chemistry, Yale University
1995 Elected Fellow of the American Association for the Advancement of Science
1997 Distinguished Alumni Award, Mounds View High School, Minnesota
1998 R. T. Major Lecture, University of Connecticut
2002 Watkins Lecture, Wichita State University
2005 Sunney I. Chan Lecture, Institute of Chemistry, Academia Sinica, Taipei, Taiwan
2008 Eugene Higgins Professorship, Yale University
2008 Baker Lecture, Cornell University
2011 Benjamin Silliman Professorship, Yale University
2012 Harry C. Allen Lecture, Clark University
2016 Sunney and Irene Chan Lecture, Hong Kong Polytechnic University
2016 Outstanding Achievement Award, University of Minnesota
2019 Elected member, Connecticut Academy of Science and Engineering (CASE)

C. Contributions to Science

1. Our group has contributed much of the work leading to the current understanding of water oxidation by photosystem II. We proposed the first molecular mechanism for O—O bond formation in photosystem II; this mechanism, based on our characterization of the O_2-evolving complex together with inorganic coordination chemistry, was included in a number of textbooks, including Stryer's "Biochemistry". We demonstrated that Ca^{2+} is part of the O_2-evolving complex and functions as a Lewis acid in the water-oxidation chemistry of photosystem II; subsequent crystallographic analyses confirmed that Ca^{2+} is part of the Mn_4CaO_5 catalytic core of the O_2-evolving complex and placed Ca^{2+} appropriately to activate water as a nucleophile, as we proposed. This connected our proposed mechanism for O—O bond formation involving nucleophilic attack of Ca^{2+}-bound water on an electrophilic Mn-bound oxo with the cuboidal model of the O_2-evolving complex proposed in the 3.5 Å X-ray crystal structure of photosystem II. We wrote a highly-cited review providing a critical analysis of proposed mechanisms, including the mechanism involving nucleophilic attack of water bound to Ca^{2+} on an electrophilic terminal oxo bound to high-valent Mn that our group has championed. These are found in the following publications:

- "Mechanism for Photosynthetic O_2 Evolution", Gary W. Brudvig and Robert H. Crabtree (1986) *Proc. Natl. Acad. Sci. USA 83*, 4586-4588.
- "Quantifying the Ion Selectivity of the Ca^{2+} Site in Photosystem II: Evidence for Direct Involvement of Ca^{2+} in O_2 Formation", John S. Vrettos, Daniel A. Stone and Gary W. Brudvig (2001) *Biochemistry 40*, 7937-7945.
- "Structure-Based Mechanism of Photosynthetic Water Oxidation", James P. McEvoy and Gary W. Brudvig (2004) *Phys. Chem. Chem. Phys. 6*, 4754-4763.
- "Water-Splitting Chemistry of Photosystem II", James P. McEvoy and Gary W. Brudvig (2006) *Chem. Rev. 106*, 4455-4483.

2. Our group has characterized electron transfer in photosystem II and contributed much of the work that led to the current understanding of this system. One study quantified the conditions for controlled advancement of the O_2-evolving complex by variation of the illumination temperature that enabled generation of the intermediate oxidation states of the O_2-evolving complex in high yield for spectroscopic investigation. We also demonstrated that cytochrome b_{559} is photooxidized in a secondary electron-transfer side path via an accessory chlorophyll that we named chlorophyll-Z; this chlorophyll was later resolved in the crystal structure of PSII and our name for it has been adopted by the field; our proposal that cytochrome b_{559} functions in photoprotection clarified the role of this enigmatic component of photosystem II and our proposed mechanism of action is now generally accepted. Also, by using site-directed mutagenesis and EPR spectroscopy, it is demonstrated that tyrosine-161 of the D1 protein of photosystem II is the electron-transfer intermediate, formerly known as redox cofactor Z and now Tyr-Z, that connects the charge-separation in the photosystem II reaction center involving P680 to the O_2-evolving complex. We identified conditions under which a carotenoid in photosystem II is reversibly photooxidized in high-yield in side-path electron transfer; the reversible oxidation of carotenoids in photosystem II is a unique reaction in a biological system and of significant interest as an example of a molecular wire connecting redox cofactors. These are found in the following publications:

- "Electron Transfer in Photosystem II at Cryogenic Temperatures", Julio C. de Paula, Jennifer B. Innes and Gary W. Brudvig (1985) *Biochemistry 24*, 8114-8120.
- "Cytochrome b_{559} May Function to Protect Photosystem II from Photoinhibition", Lynmarie K. Thompson and Gary W. Brudvig (1988) *Biochemistry 27*, 6653-6658.
- "Directed Alteration of the D1 Polypeptide of Photosystem II: Evidence that Tyr-161 is the Redox Component, Z, Connecting the Oxygen-Evolving Complex to the Primary Electron Donor, P680", James G. Metz, Peter J. Nixon, Matthias Rögner, Gary W. Brudvig and Bruce A. Diner (1989) *Biochemistry 28*, 6960-6969.
- "Characterization of Carotenoid and Chlorophyll Photooxidation in Photosystem II", Cara A. Tracewell, Agnes Cua, David H. Stewart, David F. Bocian and Gary W. Brudvig (2001) *Biochemistry 40*, 193-203.

3. Our group has developed many of the most active and robust synthetic molecular water-oxidation catalysts that are of great current interest for solar water-splitting applications. The Mn-terpy dimer reported by us remains the most active homogeneous Mn-based water-oxidation catalyst and has had a major impact in efforts to develop water-oxidation catalysts based on first-row transition metals for applications in solar energy conversion processes. We reported that organometallic Ir complexes are highly active for water oxidation catalysis initiated a new direction for homogeneous water-oxidation catalysis. We also reported a new method for probing homogeneous vs. heterogeneous catalysis based on simultaneous mass analysis and cyclic voltammetry using an electrochemical quartz crystal nanobalance. These are found in the following publications:

- "A Functional Model for O—O Bond Formation by the O_2-Evolving Complex in Photosystem II", Julian Limburg, John S. Vrettos, Louise M. Liable-Sands, Arnold L. Rheingold, Robert H. Crabtree and Gary W. Brudvig (1999) *Science 283*, 1524-1527.
- "Highly Active and Robust Cp* Iridium Complexes for Catalytic Water Oxidation", Jonathan F. Hull, David Balcells, James D. Blakemore, Christopher D. Incarvito, Odile Eisenstein, Gary W. Brudvig and Robert H. Crabtree (2009) *J. Am. Chem. Soc. 131*, 8730-8731.
- "Distinguishing Homogeneous from Heterogeneous Catalysis in Electrode-Driven Water Oxidation with Molecular Iridium Catalysts", Nathan D. Schley, James D. Blakemore, Navaneetha K. Subbaiyan, Christopher D. Incarvito, Francis D'Souza, Robert H. Crabtree and Gary W. Brudvig (2011) *J. Am. Chem. Soc. 133*, 10473-10481.

4. Our group developed methods based on saturation-recovery EPR spectroscopy for determination of long-range distances between paramagnetic centers in biomacromolecules. Specifically, we developed a new application of pulsed EPR based on our home-built instrumentation and demonstrated its use for long-range distance measurements in proteins; long-range distance measurements by EPR are now of major importance in protein structure-function studies and our method is gaining renewed interest as a technique that can be applied at both cryogenic and physiological temperature, whereas other pulsed EPR methods can only be carried out at cryogenic temperatures. This was shown in the following publication:

- "Using Saturation-Recovery EPR to Measure Distances in Proteins: Applications to Photosystem II", Donald J. Hirsh, Warren F. Beck, Jennifer B. Innes and Gary W. Brudvig (1992) *Biochemistry 31*, 532-541.

5. Our group in collaboration with the group of Victor Batista has developed computational models of the O_2-evolving complex in photosystem II that connect experimental spectroscopic data to mechanistic and structural models of the active site of this enzyme. This QM/MM study extended the 3.5 Å X-ray crystal structure of photosystem II with chemically sensible models of the O_2-evolving complex in the S_0-S_4 states and support for a mechanism of O—O bond formation involving nucleophilic attack of a Ca^{2+}-bound water on a Mn^{4+}-oxyl radical species:

- "Quantum Mechanics/Molecular Mechanics Study of the Catalytic Cycle of Water Splitting in Photosystem II", Eduardo M. Sproviero, José A. Gascón, James P. McEvoy, Gary W. Brudvig and Victor S. Batista (2008) *J. Am. Chem. Soc. 130*, 3428-3442.

D. Additional Information: Research Support and/or Scholastic Performance

<u>Current Grant Support</u>

"Structure-Function Studies of Photosystem II"
Principal Investigator: Gary W. Brudvig

Agency: Department of Energy; Grant No. DE-FG02-05ER15646; Period: April 1, 2005 to June 30, 2023
The specific aims of this project are to use biophysical and computational methods to investigate the water-oxidation chemistry and electron-transfer reactions of photosystem II in conjunction with studies of biomimetic inorganic oxomanganese model complexes.

"Photocatalytic Assemblies for Solar Fuel Production"
Principal Investigator: Gary W. Brudvig
Co-Principal Investigators: Victor Batista and Robert Crabtree
Agency: Department of Energy; Grant No. DE-FG02-07ER15909; Period: September 1, 2007 to February 28, 2023
The specific aims of this project are to develop and investigate systems for photocatalytic water oxidation using photosensitizers and catalysts attached to the surface of metal oxide nanoparticles.

"Terahertz Spectroelectrochemical Methods to Study Semiconductors, 2D Materials, and Metal Organic Frameworks (MOFs)"
Principal Investigator: Gary W. Brudvig
Agency: NSF; Grant No. CHE-1954453; Period: September 1, 2020 to August 31, 2023
The specific aim of this project is to develop electrochemical platforms to enable THz spectroscopic studies of charge transport as a function of applied potential in semiconducting materials.

"Dinuclear Heterogeneous Catalysts (DHCs) as a new Platform for Selective Oxidation of CO and Methane (CH_4)"
Principal Investigator: Dunwei Wang
Co-Principal Investigators: Gary W. Brudvig, Victor Batista and Xiaoqing Pan
Agency: NSF; Grant No. CHE 1955237; Period: June 1, 2020 to May 31, 2023
The specific aim of my portion of this project is to develop molecular catalyst precursors to be deposited on metal oxide surfaces and used for heterogeneous catalysis of methane and CO oxidation.