

Final Technical Report

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Title: Membrane-organized Chemical Photoredox Systems

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Executive summary—

This project involved basic research into ways in which integrated photochemical systems could be used to drive economically and/or environmentally desirable reactions (e.g., H₂ formation or CO₂ reduction) using direct solar energy. Emphasis in these studies was placed upon: (1) exploring the influence of microphase compartmentation in controlling chemical reactivity to promote formation of desirable products and block deleterious side-reactions that hampered system performance in the absence of these organizing components; (2) developing minimal photofuel systems that can address issues concerning technological feasibility utilizing readily available and self-assembling components; and (3) characterizing molecular mechanisms of reaction of essential catalysts (primarily those that would allow use of water as a sacrificial reactant).

Our research in areas 1 and 2 generally falls within a discipline known as biomimetic chemistry, in which duplication of bioenergetics principles are attempted using materials that are much simpler and more robust than their biological counterparts. Most of our work (much of which has been pioneering) has made use of ultrathin closed bilayer membranes that can compartmentalize selected reactants within their interior space and otherwise control the 3-dimensional topographic organization of reaction components through combined electrostatic and hydrophobic forces. In this work, we have developed unique asymmetric membrane-organized assemblies that utilize organic pseudobases known as pyrylium ions as combined photosensitizers and transmembrane redox relays, essentially combining several functions into a single compound. The absorption bands of the pyrylium ions can be tuned from the near-uv to near-ir regions through suitable derivatization and their photoexcited states are strongly oxidizing, hence capable of driving water oxidation. Moreover, we have shown that they can rapidly transport charge across closed bilayer membranes via an electroneutral e⁻/OH⁻ antiport mechanism that allows the carrier to cycle indefinitely without encountering rate-retarding polarization effects. This latter feature is highly desirable for high flux applications such as production of solar fuels. Recent research has focused upon means to couple these photoinitiated transmembrane reactions to drive catalyzed water oxidation and reduction to generate fuels. We have not yet achieved the ultimate goal of highly efficient water oxidation, but by the end of the funded period, had developed several photosystems based upon these principles that are capable of sustained photoproduction of H₂ using visible light.

Development of catalysts for water oxidation is widely considered to be crucial to advancement of the technology of direct solar photoconversion to produce fuels or to effect meaningful bioremediation. Our research on *water oxidation* (area 3) has been directed at understanding mechanisms of catalysis by *cis,cis*-(bpy)₂Ru(OH₂)₂O⁴⁺ and related polyimine complexes, which are relatively well-defined molecular catalysts. Using a variety of physical techniques (many of which were first adapted to this type of study in my laboratory), we have: (i) identified the redox state of the complex ion that is catalytically active; (ii) shown using ¹⁸O isotopic labeling that there are two reaction pathways, both of which involve participation of solvent H₂O; and (iii) detected and characterized by advanced EPR, a real-time mass spectrometric, pulse radiolysis, and resonance Raman spectroscopies new species which may be key intermediates in the catalytic cycle. In the course of pursuing these studies, we have introduced to the field

new techniques and approaches that are now being used by others as they pursue development of superior catalysts.

Narrative summary of project, including comparisons of accomplishments and goals—

As noted in the Executive Summary, the primary purpose of this research was to use biomimetic approaches to elucidate organizing principles governing reactions important to solar photoconversion processes. Secondary objectives were to develop systems that could serve as models useful in driving technology in these areas. Our focal areas were microphase systems (primarily vesicles and micelles) as regulatory organelles, around which we organized components of photoreactive systems that were potentially capable of splitting water. At the outset of these studies, mechanisms of chemical catalysis of water oxidation were very poorly understood, necessitating that we also investigate these reactions as well. The primary goals were very broad—devise something that works and evaluate the underlying reactivity principles. We had very exciting initial results adapting pyrylium ions as agents that could drive primary photochemical processes and simultaneously shuttle electrons across closed bilayer membranes in an electroneutral fashion, specifically by acting as an e^-/OH^- antiport through hydrolytic ring-opening and closing cycles. These reactions were fast (occurred on millisecond timescales) and had overall photochemical quantum yield approaching unity (the theoretical limit). However, when we modified the pyrylium ions to shift the absorption bands toward the near-infrared region (necessary to efficiently harvest solar energy) and lower their reduction potential (necessary to catalytically reduce protons to H_2 in neutral media), the photoyields dropped off precipitously. Similarly, coupling the transmembrane redox process to O_2 photoproduction was ineffective. These problems were ultimately identified as relating to the effect of substituent derivatization upon the pseudobase ring-opening and closing reactions that were essential to transmembrane cycling of redox equivalents. Specifically, the substituents that shifted the optical absorption bands and lowered redox potentials also stabilized the ring-closed form of the dye, causing the rates of the cycling between the isomeric forms to decrease below acceptable levels. Although it seems evident that these particular compounds will not be useful in practical applications, we were able to demonstrate H_2 photoproduction in similar vesicular and micellar constructs, and insights obtained have led to development of alternative systems utilizing self-assembling surfactants including N-alkylcyanopyridinium ions as photosensitizers that appear in initial experiments to be superior to the pyrylium-based systems. Although the grant has formally ended, this work was initiated during its active phase and I intend to continue this study as opportunity allows.

Our water oxidation research was initiated at a time when there was very little interest among the scientific community in this topic. However, it soon became evident that to achieve any technological objective in direct solar photoconversion a cheap, inexhaustible supply of electrons (reducing equivalents) would be required, and the only *bona fide* molecular water oxidation catalysts that were known were basically a series of dinuclear ruthenium diimine complexes. Using techniques that were new to the field (EPR, resonance Raman, real time mass spectrometric and, more recently, advanced EPR pulse radiolysis, and DFT computational analyses) we were able to identify the

catalytically active oxidation state, characterize several redox intermediates, and map pathways for water oxidation in these complexes. One major achievement was the elucidation of one of these pathways as involving reaction of a highly oxidized ruthenyl (Ru=O) ion as an immediate precursor of O-O bond formation. This same metal-oxo construct is now recognized as the key intermediate in a wide variety of metal-catalyzed water oxidation reactions. Our studies also revealed that another pathway for water oxidation exists, one that curiously did not involve the Ru-coordinated oxo atom, i.e., Ru=O. A number of studies made in our laboratory suggest that non-innocent participation of the bipyridine ligands may be involved, and I have written speculative mechanisms illustrating how that might occur. Although our recent data are consistent with this possibility, we were unable to obtain definitive information on the existence of any of the hypothetical intermediates. Apart from our inability to identify this pathway, the major objectives of the study were realized and the scientific community has and will continue to benefit from application of the several unique methods that we have adapted to study of these reactions.

The products developed under the award consist entirely of peer-reviewed scientific publications, which are organized by topic and listed below in reverse chronological order. They report in detail the nature of our experiments, methodologies used/developed, and our findings.

Publications—

A. Organized photochemical systems—

- [1] L. Zhu, R. F. Khairutdinov, J. L. Cape, and J. K. Hurst: “Photoregulated transmembrane charge separation by linked spiropyran-anthraquinone molecules” *J. Am. Chem. Soc.* **2006**, *128*, 825-835.
- [2] M.-Q. Zhu, L. Zhu, J. J. Han, W. Wu, J. K. Hurst and A. D. Q. Li: “Spiropyran-based photochromic polymer nanoparticles with optically switchable luminescence” *J. Am. Chem. Soc.* **2006**, *128*, 4303-4309.
- [3] L. Zhu, W. Wu, M.-Q. Zhu, J. J. Han, J. K. Hurst and A. D. Q. Li: “Reversibly photoswitchable dual-color fluorescent nanoparticles as new tools for live-cell imaging” *J. Am. Chem. Soc.* **2007**, *129*, 3524-3526.
- [4] S. Liang, L. Zhu, and J. K. Hurst, “Cyclic transmembrane charge separation mediated by low-potential pyrylium ions”, *Langmuir* **2012**, *28*, 12171-12181.
- [5] S. Tabatabaei, S. Liang, J. A. Brozik, and J. K. Hurst, “Enhancement of dye-mediated H₂ photoproduction by sodium dodecyl sulfate”, work in progress.

B. Water oxidation catalysis—

- [6] J. K. Hurst, J. L. Cape, A. E. Clark, S. Das and C. Qin: “Mechanisms of water oxidation catalyzed by ruthenium diimine complexes” *Inorg. Chem.* **2008**, *47*, 1753-1764.

- [7] J. L. Cape & J. K. Hurst: "Detection and mechanistic relevance of transient ligand radicals formed during $[\text{Ru}(\text{bpy})_2(\text{OH}_2)]_2\text{O}^{4+}$ -catalyzed water oxidation" *J. Am. Chem. Soc.* **2008**, *130*, 827-829.
- [8] J. L. Cape, S. V. Lymar, T. Lightbody, and J. K. Hurst: "Characterization of intermediary redox states of the water oxidation catalyst, $[\text{Ru}(\text{bpy})_2(\text{OH}_2)]_2\text{O}^{4+}$ " *Inorg. Chem.* **2009**, *48*, 4400-4410.
- [9] J. L. Cape, W. F. Siems, and J. K. Hurst: "Pathways of water oxidation catalyzed by ruthenium "blue dimers" characterized by ^{18}O -isotopic labeling", *Inorg. Chem.* **2009** *48*, 8729-8735.
- [10] J. K. Hurst: "In pursuit of water oxidation catalysts for solar fuel production", *Science* **2010**, *328*, 315-31.
- [11] A. Ozkanlar, J. L. Cape, J. K. Hurst, and A. E. Clark: "Covalent hydration reactions in model monomeric Ru 2,2'-bipyridine complexes: thermodynamic favorability as a function of metal oxidation and overall spin states", *Inorg. Chem.* **2011**, *50*, 8177-8187
- [12] A. E. Clark and J. K. Hurst: "Mechanisms of water oxidation catalyzed by ruthenium coordination complexes", *Prog. Inorg. Chem.* **2012**, *57*, 1-52.
- [13] J. A. Stull, J. L. McHale, F. J. Knorr, S. V. Lymar, and J. K. Hurst: "Anomalous reactivity of ceric ammonium nitrate in ruthenium "blue dimer"-catalyzed water oxidation" *J. Am. Chem. Soc.* **2012**, *134*, 19973-19976.
- [14] J. A. Stull, T. A. Stich, J. K. Hurst, and R. D. Britt: "Electron paramagnetic resonance analysis of a transient species formed during water oxidation catalyzed by the complex ion, $[(\text{bpy})_2\text{Ru}(\text{OH}_2)_2]\text{O}^{4+}$ ", *Inorg. Chem.* **2013**, *52*, 4578-4586.
- [15] D. E. Polansky, J. K. Hurst, and S. V. Lymar: "Application of pulse radiolysis to mechanistic investigations of water oxidation catalysis" *Eur. J. Inorg. Chem.* **2014**, *2014*, 619-634.
- [16] J. K. Hurst, M. Roemeling, and S. V. Lymar: "Persulfate oxidation of the "blue dimer" ($\text{cis,cis}-[\text{Ru}(\text{bpy})_2(\text{OH}_2)]_2\text{O}^{4+}$)" *J. Phys. Chem.* **2014**, manuscript in preparation.