

# SCIENCE WHITE PAPER

FOR DISCUSSION  
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TITLE: UTILIZATION OF NEW MEXICO'S  
ABUNDANT SOLAR NATURAL RESOURCE TO  
CONSERVE WATER AND IMPROVE THE  
ENVIRONMENT

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Utilization of New Mexico's Abundant Solar Natural Resource to Conserve Water and Improve the Environment: Contributing P.I.'s Prof. Michael Heagy (NMT), Prof. Marty Kirk (UNM), Prof. John Grey (UNM), Prof. Yang Qin (UNM), Prof. Jeremy Smith (NMSU), Arcadius Krivoshein (NMHU)

**Abstract:** Global energy consumption is projected to double between the years 2001 and 2050.<sup>1</sup> While there are sufficient proven reserves of coal, gas and oil to meet these energy needs for several centuries, the CO<sub>2</sub> emissions produced by burning these fossil fuels are projected to result in global climate change. Multiple solutions to this energy problem are centered on the use of solar energy as the driving force for new energy technologies. Given New Mexico's natural resource of abundant sunshine 250 days/year or approximately 6000 hours/year, this white paper focuses on the use of solar energy for (1) CO<sub>2</sub> mitigation and conversion to methanol via dye doped ZnS nanocomposites (2) Electrocatalytic water oxidation by manganese pyridinophane complexes and (3) Fundamental studies of organic photovoltaic's, polymer solar cell, or organic optoelectric devices. Each of these research areas is expected to contribute substantially to the Energy, Water and Environment components in the proposed NM EPSCoR Nexus.

## **I. Solar energy used to improve the Environment: Chemical mitigation of CO<sub>2</sub> via dye doped ZnS nanocomposites**

### **A. Introduction**

One potential approach to reducing atmospheric CO<sub>2</sub> linked to global climate change is the trapping and subsequent photoinduced conversion to a value-added product without the use of additional CO<sub>2</sub> generating power sources. This approach, referred to as "chemical carbon mitigation" can lead to methanol as an end product; a potentially useful and important bulk chemical.<sup>1,2</sup> The "methanol economy" has been highlighted as an alternative to the "hydrogen economy" and championed by Chemistry Nobel laureate Prof. George A. Olah as a renewable and readily transportable fuel compared to hydrogen.<sup>3</sup> Recently, added significance has been imbued to this field of research as evidenced by the number of reviews dedicated to turning carbon dioxide into fuel. Homogenous photosensitizer systems with metal cocatalysts and semiconductor colloids have been observed to produce only CO and formic acid.<sup>4</sup> The advantage of these systems is their incorporation of light-driven strategies to photocatalyze the reduction of CO<sub>2</sub>, however, their ability to complete the full 6e<sup>-</sup> reduction to methanol falls short at formic acid or is compromised by system instability and provides low yields of methanol.

### **B. Specific Aims**

Since the preliminary work of Yoneyama *et al.* featuring the unique combination of both biocatalytic and microcrystalline semiconductor systems, the advent of dye-sensitized nanoparticulate semiconductor technology enabling a reduced band-gap for ZnS has been reported.<sup>8</sup> Lower band-gap capabilities have been made possible with the use of donor-acceptor dyes appended to ZnS nanoparticles. Lower-band gap semiconductors should therefore translate into visible light photoexcitation properties. In addition, nanoparticle catalysts are expected to vastly increase the number of reaction sites with concomitant increase in CO<sub>2</sub> reduction. Hence, the key aims of this proposal center on the use of ambient solar energy for the photochemical reduction of CO<sub>2</sub> to methanol. Given the large scope of the CO<sub>2</sub> to methanol process and the technical difficulty of a six-electron reduction in total, our investigations are divided into key steps of this process.

(1) Improved inorganic semiconductor ZnS in nanoparticle size to effect the reduction of CO<sub>2</sub>.

(2) Development of organic dyes that augment the performance of this semiconductor by lowering the band-gap so that visible light energy can be utilized in the process.

As illustrated in the figure below, the overall catalytic cycle involves photodriven excitation of ZnS by chromophore dye absorbed onto the ZnS surface. The valence band of ZnS potentially resides at the appropriate energy to be involved in both CO<sub>2</sub> reduction as well as reduction of enzyme cofactor PQQ. This cofactor regenerates the enzyme, methanol dehydrogenase, for final conversion of formic acid (HCOOH) to methanol.<sup>7</sup> Finally, the additional byproduct, acetone is formed via oxidation of isopropyl alcohol. This red/ox pathway allows for the ZnS semiconductor to be regenerated to its photoactive state.

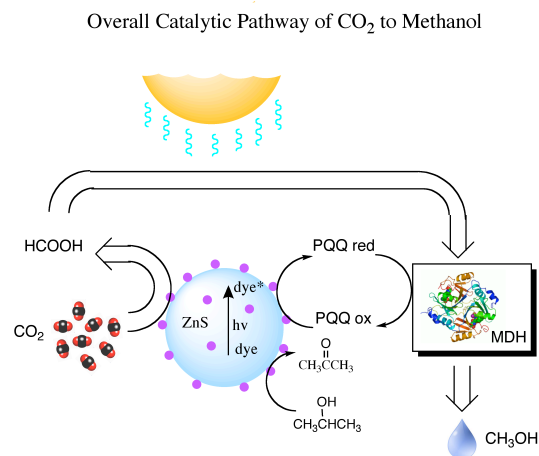
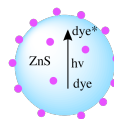


Fig. 1. Schematic illustration of photoinduced reduction of carbon dioxide using ZnS/NP and methanol dehydrogenase (MDH).



### C. Dye-Doped Composite ZnS Nanoparticles

Organic-inorganic nanoparticles, mixed at the molecular level or near-molecular level, have attracted considerable attention because of their large potential applications in the field of optics,<sup>13</sup> electronics,<sup>14</sup> mechanics,<sup>15</sup> and photoconductors.<sup>16</sup> The hybridization of organic and inorganic semiconductors has permitted not only a wide-range array of emitter and carrier transport materials, but also a new approach to construct high-performance electroluminescent devices. Thus nanometer-scale organic-inorganic composite materials have been shown to possess high photoluminescence efficiency of organic materials and high carrier density with low resistivity of inorganic semiconductors. Zinc sulfide has been shown to display a dramatic increase in luminescence intensity and a distinct change in emission wavelength when doped with charge-transfer dyes. Relative to pure ZnS nanoparticles, which absorb in a narrow wavelength region centered at 325 nm, Yang, *et al.* have shown these composites absorb over a broad range in the optical spectrum from 300 nm to 650 nm.<sup>8</sup> For the purpose of initiating this project and based on the success of the published dye systems used with ZnS, plans currently include synthesis of dyes characterized by enhanced charge-transfer properties. Such systems are predicated on a dialkylamino-donor/pyridinium-acceptor group platform.

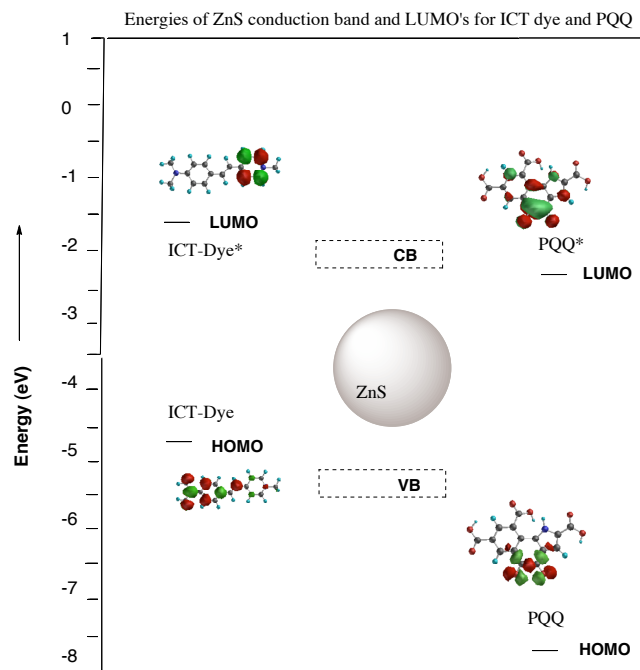


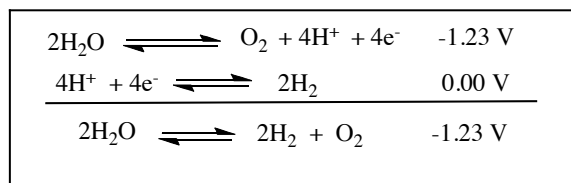
Figure 2. Unified energy level map of requisite chromophores with respect to ZnS CB.

## II. Electrocatalytic Water Oxidation by Manganese Pyridinophane Complexes: A Solution to the Nighttime Solar Energy Problem.

### A. Introduction

A common criticism of solar energy is directed toward the problem of nocturnal energy demand. One possible solution to this energy problem is the development of an artificial photosynthetic process for the production of  $H_2$ , a high energy fuel that does not produce  $CO_2$ . The proposed photosynthetic process converts solar energy into electrical energy, which is used to power the electrochemical splitting of water, oxidizing it to  $O_2$  at the anode and reducing it to  $H_2$  at the cathode (Scheme 1). This is a multielectron process that requires a minimum potential of 1.23 V (vs. SHE) under standard conditions and at pH 0 (Scheme 1). This potential is dependant on pH and increases to 1.64 V at pH 7. The multiple electron transfers and elementary reaction steps in the water splitting reaction result in a considerable kinetic barrier. In practice, this means that an overpotential is required to drive the reaction, reducing the overall energy efficiency. Electrocatalysts can reduce the overpotential and improve the Faradaic efficiency by reducing activation barriers and providing alternate reaction pathways that avoid high energy intermediates. While some catalysts can reduce water to  $H_2$  at zero overpotential, a similarly effective electrocatalyst for water oxidation has not been developed.

Scheme 1



## B. Homogeneous electrocatalysis

A significant advantage of homogeneous catalysts is that they are amenable to mechanistic investigations and catalyst tuning. The majority of complexes that function as homogeneous water oxidation catalysts are based on platinum group metals, particularly ruthenium and iridium. The expense and rarity of these metals is a considerable disadvantage to using these catalysts for long term energy solutions, and provides a strong incentive for developing water oxidation catalysts based on inexpensive and abundant first row transition metals.<sup>18</sup> In this regard it is significant that nature's photosynthetic machinery uses a manganese cluster (the water oxidizing complex of Photosystem II) to oxidize water to O<sub>2</sub>.<sup>19</sup> Despite this precedent, the development of homogeneous water oxidation catalysts based on first row metals is still in its infancy. Well-defined manganese complexes will be used as catalysts for electrolytic water oxidation. In contrast to the majority of homogenous water oxidation catalysts, the proposed catalysts are based on an earth-abundant and inexpensive metal. The complexes will be supported by the readily prepared and easily modified pyridinophane macrocycles, Py<sub>2</sub>(NR)<sub>2</sub>. Similarly to complexes of related open-chain aminopyridine ligands, electrochemical oxidation of [Py<sub>2</sub>(NR)<sub>2</sub>]MnII(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup> complexes under basic conditions will afford higher valent manganese oxo intermediates. The electronic structure of the molecules will be studied using a combined spectroscopic approach involving magnetic circular dichroism (MCD), variable-temperature, variable field MCD (VTH-MCD), electronic absorption, and multifrequency electron paramagnetic resonance (EPR) spectroscopies. Such spectroscopic work will be key in providing the necessary feedback into synthetic modifications of the pyridinophane macrocycle. Synthetic modifications of the pyridinophane molecule will be used to direct the reactivity of the [Mn=O] unit towards intermolecular O-O bond formation. Specifically, the pyridinophane macrocycle will be tailored to (1) prevent the formation of unreactive [MnIV(m-O)<sub>2</sub>MnIV] dimers; (2) prevent intramolecular ligand oxidation and subsequent catalyst decomposition; (3) facilitate the coupled electron/proton transfer events required to form [Mn=O] intermediates; and (4) promote nucleophilic OH-/H<sub>2</sub>O attack at the [Mn=O] unit. Catalytically active complexes will be identified and characterized by electrochemical methods and multiple spectroscopic techniques. In particular, cyclic voltammetry and coulometry experiments will be used to identify catalytically active complexes, characterize their electrochemical behavior and quantify their catalytic performance. Electrochemical methods will also be used to identify catalyst structure/activity relationships and direct synthetic efforts towards improving catalyst performance. Spectroscopic studies on important high-valent Mn=O species will be performed in order to determine how the pyridinophane macrocycle affects the relative electro-nucleophilicity of the terminal oxo ligand. The flexible molecular design is compatible with the longer term goals of attaching catalysts to electrode surfaces and incorporating them into photochemical devices.

## III. Fundamental studies of organic photovoltaic's, polymer cells, or organic optoelectronic devices

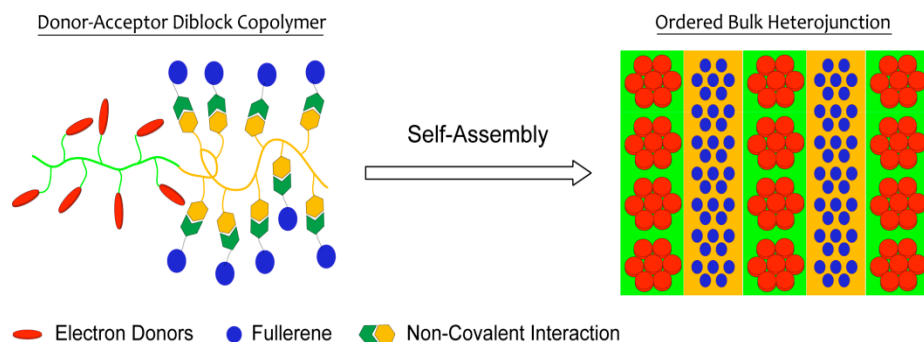
Bulk heterojunctions (BHJs) in organic photovoltaics (OPVs) have been obtained through blending electron donating and accepting materials. BHJs have been extensively studied and optimized to a seemingly efficiency limit for device performance. Such morphologies result from uncontrolled random phase separation and are thermodynamically unstable. In order to further improve OPV performance, a stable and precisely controlled morphology needs to be realized. Regarding the performance characteristics, a stable and precisely controlled morphology needs to be realized. Regarding performance characteristics of polymeric solar cells and general organic optoelectronic devices, perhaps

the most serious limiting factor in their performance is the trapping of mobile charge carriers by low energy sites, structural defects and impurities. Even ultrapure processing conditions under inert environments are not sufficient to guarantee the absence of trap species and the factors that control trap formation are now under intense study for a variety of polymer functional forms. Interestingly, it is commonly assumed that ordered regions of the polymer component are essential for good charge transport whereas disordered regions can trap charge thus reducing current generation. However, recent work in other conjugated organic materials (i.e. pentacene field-effect transistors) has suggested that instead disordered regions are actually trapping charge on ordered regions due to the energetic barriers that exist between these regions.

## B. Bulk Heterojunctions

We propose to achieve such ordered and thermodynamically stable BHJs from a single polymer system using self-assembly strategies. As shown in Scheme 2, diblock copolymers having disk-like liquid crystalline (LC) electron donors (i.e. phthalocyanine metal complexes) attached to one block (i.e. polystyrenes) and fullerene electron acceptors to the other (i.e. polyacrylates) are prepared. Controlled free radical polymerization (CFRP) techniques are the method of choice since they tolerate a wide range of functional groups. Direct polymerization of fullerene monomers is generally very difficult due to limited solubility and possible crossover linking. Post-polymerization modification is thus chosen for the attachment of fullerene through non-covalent interactions (i.e. complementary hydrogen bonding). This strategy allows for fine-tuning of the fullerene loading percentage without synthetic difficulties and

Scheme 1. Project Overview



solubility issues. Self-assembly of such copolymers can potentially lead to ordered and thermodynamically stable phase separation with domain sizes on the nanometer scale. LC electron donors and acceptors self-organize, within corresponding

domains, into ordered structures that afford high charge mobility and spatially separated transportations of positive and negative charges. The electronic properties of our bulk heterojunction materials will be determined by a combination of electrochemical and optical spectroscopic methods. The latter measurements will be important for determining bandgaps in these materials as a function of the donor and acceptor. Charge transfer character will be determined using photoluminescence measurements and EPR spectroscopy. EPR spectroscopy has been shown to be an important technique for understanding the nature of charge carriers in organic polymer bulk heterojunctions. As such, multifrequency EPR will be very useful in understanding the mobility and nature of polarons, anion radicals, and polaron-radical pairs, etc. generated under variable-temperature photoillumination conditions. The use of paramagnetic phthalocyanine metal complexes as donors is of particular interest due to their planar structure and extensive  $\pi$ -delocalization. We will use a combination of VTVH and NIR-UV-VIS MCD spectroscopies to probe the detailed electronic and magnetic structure of the metallophthalocyanine donor in these

copolymer bulk heterojunction materials.

The VTVH MCD technique will be used as an optical probe of chromophore magnetization. More specifically the VTVH MCD studies will address the optical polarization of the phthalocyanine donor chromophore and will allow for a specific determination of metallophthalocyanin spin-Hamiltonian parameters in a complimentary manner to EPR spectroscopy. In summary, these copolymers can serve as a single-component active layer in OPVs, significantly simplifying fabrication processes, and potentially fulfill the basic requirements for device optimization; enhanced light absorption, ordered morphology for maximum exciton dissociation and minimum charge recombination, and high conductivity for efficient charge collection. The magnetic and spectroscopic studies on materials will provide detailed insight into donor-acceptor behavior in ordered bulk heterojunctions.

### **C. Structural studies of organic charge transfer materials**

The goal of proposed research is to find an approach for understanding structural characteristics of organic charge transfer materials on molecular, supramolecular, and crystalline levels. Such an understanding is expected to help in design of novel materials for solar cells, semiconductors, etc. The importance of studies of molecular and crystal structure, supramolecular organization and electronic peculiarities of semiconductor charge transfer (CT) organic materials is provoked by a wide area of their potential applications such as solar cells, lighting devices, flexible screens, etc. In literature it was demonstrated that high charge mobility of organic materials with  $\pi$ -electron conjugated systems is directly related to their supramolecular and/or crystalline organization. In this project we plan to focus on crystal structure organization of organic CT materials on both geometrical and electronic levels and on evaluation of important intermolecular interactions that lead to manifestation of their CT properties. Two complementary techniques will be applied in this study: high-resolution X-ray diffraction analysis that allows for experimental characterization of charge density distribution in crystals and quantum chemical computations. Both methods will permit for evaluation of intermolecular interactions in crystals, including analysis of the nature and energetic characteristics, in particular, obtained directly from X-ray diffraction data, using analysis of the electron density topology, that is a new approach in the study of crystalline CT materials. The results obtained by will be used for a search of prospective organic materials with supramolecular organization beneficial for creation of CT organic materials with higher efficiency (such as cost-effective, easy-to-deploy, organic-based solar panels that are particularly attractive for rural states, such as New Mexico). Among the compounds studied we will use in the beginning known CT materials (tetrathiafulvalenes (TTF) and their derivatives, in particular DT-TTF), acenes (tetracene, pentacene) and some other to evaluate a workability of our approach, as well as other CT compounds like acenes derivatives and their  $\pi$ -complexes, and other compounds which crystal structure is governed by intermolecular stacking interactions and hydrogen bonds. A special attention will be paid to the growth of single crystals of acceptable quality. The DFT approach will be used for calculation molecular geometry and charge-transport properties. For periodical plane-wave crystal calculations the appropriate Perdew-Burke-Ernzerhof (PBE) functional will be used.

### **D. Concluding statements**

In closing, it should be emphasized that sections II and III highlight technologies that explore organic photovoltaics OPVs as an alternative to conventional silicon or inorganic solar cells systems. Implicit to

the use of solar energy is the understanding that less reliance on fossil fuels is realized and hence the high volumes of produced water used to extract petroleum reserves.

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