

New Directions for Efficient Solar Water Splitting Based on Two Photosystems and Singlet Fission Chromophores

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Objectives

The objective of this HFI project is to conduct the basic science that will lead to the discovery and ultimate development of photoconversion approaches that can produce hydrogen via H₂O splitting at costs competitive with or less than their present cost derived from steam reforming of natural gas. This will require a system with very high conversion efficiencies (>32%) coupled with very low capital costs (<\$200/m²). We focus on solar water splitting using two coupled photosystems (a photocathode and a photoanode), analogous to what occurs in biological photosynthesis, but where one of the photoelectrodes exhibits efficient photogenerated electron-hole pair multiplication via singlet fission (SF), a process that produces two triplet states from a singlet state. Thermodynamic calculations show that such coupled photosystems have the highest possible theoretical conversion efficiencies, exceeding those of single photoelectrode cells by ~50%, and that only one photoelectrode needs to undergo SF.

Technical Barriers

SF in the photoanode or photocathode must be very efficient, and for a tandem cell with both photoelectrodes in series optically and electrically, the SF chromophore should have its first excited singlet state at ~2 eV and its lowest triplet state at ~1 eV. The second photoelectrode should have a bandgap of ~1 eV and the energetic alignment of the two photoelectrodes must allow appropriate recombination of an electron and hole from the photoanode and photocathode, respectively, to maintain charge balance. In one optimum configuration the two chromophores at the

photoanode and photocathode need to be electronically coupled to nanocrystalline electron-conducting and hole-conducting supports. The system must also be photostable and avoid photocorrosion of both photoelectrodes; one approach is to isolate the surfaces of the photoelectrodes from contact with water.

Abstract

The research objective of this HFI program is to conduct the basic science that will lead to the discovery and ultimate development of photoconversion approaches that can produce hydrogen via H₂O splitting at costs competitive with or less than their present cost derived from steam reforming of natural gas. This will require a system with very high conversion efficiencies (>32%), coupled with very low capital costs (< \$200/m²). We will focus on solar water splitting using two coupled photosystems (a photocathode and a photoanode), analogous to what occurs in biological photosynthesis, but where one of the photoelectrodes is based on a molecular chromophore that exhibits efficient singlet fission (SF), a photophysical process wherein two triplet states are created from the first excited singlet state produced by absorption of a single photon. We have demonstrated a 200% QY of triplet states formed from the first excited singlet state via SF in molecular crystals of diphenylisobenzofuran (DPIBF). Thermodynamic calculations show that such coupled photosystems have the highest possible theoretical conversion efficiencies, exceeding those of single photoelectrode water-splitting cells by 50%. The system is also expected to have significantly enhanced conversion efficiency (> 20% increase depending on overvoltage) when concentrated solar power is used; this effect will be experimentally investigated for the first time.

Progress Report

Thermodynamics

Our research shows clearly that the use of two photosystems produces much higher theoretical conversion efficiencies (by a factor of ~50%) for solar water splitting at all values of the total cell overpotential compared to cells with just one photoelectrode. These results are summarized in Figure 1. The lower lines show the maximum efficiency for a single photoelectrode cell as a function of the total cell overvoltage for H₂O splitting, and the upper lines show the efficiency dependence on overvoltage for a double-electrode tandem cell with different types of the two photoelectrodes. SF/M1 is the result when one photoelectrode produces SF and the second generates just 1 e⁻/photon. SF/M2 has one electrode producing SF and the second producing 2 e⁻/

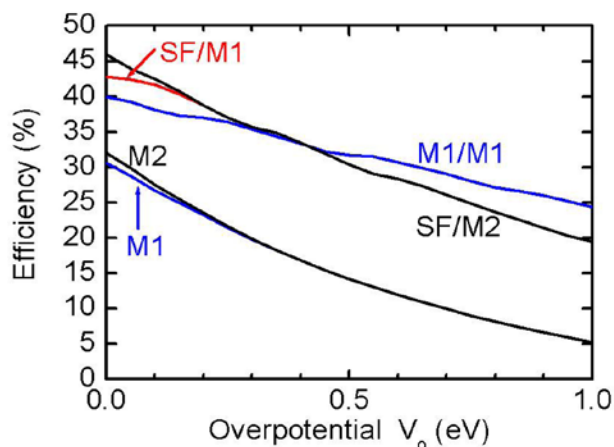


FIGURE 1. Maximum thermodynamic water-splitting conversion vs. total cell overvoltage for cells with single photoelectrodes (M1 and M2, bottom curves) and cells with two photoelectrodes (SF/M1, M1/M1, and SF/M2(SF), top curves). Definitions of the M1, M2, and SF characteristics are described in the text and shown in Fig. 2.

photon after the photoexcitation equals twice the bandgap (E_g) energy; for our purposed here M2 is the same as SF. Finally, M1/M1 is a conventional electrode system in which both electrodes produce $1 e^-$ /photon. For SF, the molecular bandgap is defined as the triplet state energy, which is close to one-half the first excited singlet state energy, because it is the triplet energy at which the photogenerated electrons are emitted. Thus, SF is analogous to an indirect-bandgap semiconductor in which the lowest energy transition is forbidden. Figure 2 shows the QY characteristics as a function of photon energy normalized to the bandgap (E_{photon}/E_g) that defines M1, M2 (SF), Mmax, SF (L3 is a linear characteristic that is not considered here.)

Singlet Fission

We report the first designed molecular system that exhibits perfect SF efficiency, producing two triplet states from an excited singlet state of the molecule (1,3-diphenylisobenzofuran (DPIBF)—Figure 3). Our experiments indicated a quantum yield at 77K of 200% for the creation of the two triplets in DPIBF. Both molecular design principles and broader concepts of coupling chromophores into functional networks were key advances that produced 200% QYs via SF. The compound DPIBF was identified as a promising candidate by using theory to direct a search for chromophores likely to have a desirable ratio of singlet and triplet excitation energies, the latter being difficult to measure experimentally. Recent theory led to the discovery that the natural geometry that the molecules adopt while packing into crystals, a staggered stacked sandwich type orientation, was optimum for SF.

Thin polycrystalline films of DPIBF were made by subliming the compound in vacuum onto substrates. When done correctly, the films showed strong spectroscopic signatures indicating a high yield of triplets. In order to

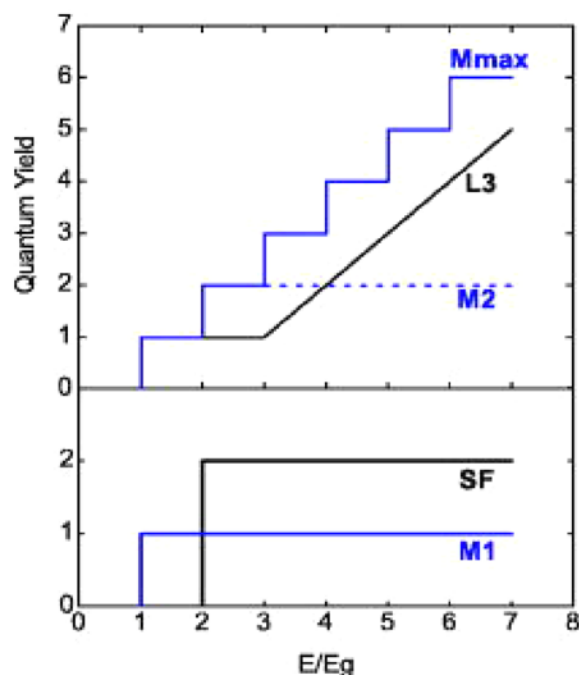


FIGURE 2. Characteristics of the QY vs. (photon energy/bandgap) that define M1, M2, Mmax, and SF. Characteristics labeled L(n) apply to the behavior of quantum dots and are not considered in this proposal.

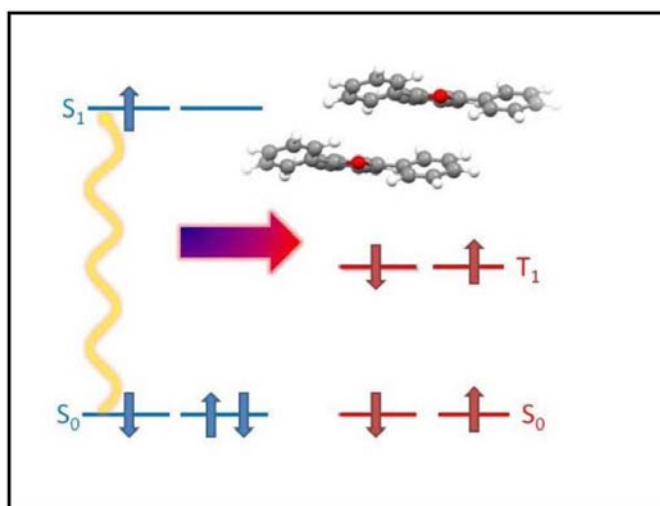


FIGURE 3. Depiction of the singlet fission process by which single absorbed photon creates an excited singlet state that evolves into two triplet states. Electron transfer can then occur from the two triplet states to produce two electrons per absorbed photon in a solar cell device. The molecules shown are DPIBF in a staggered stacking orientation known from its crystal structure.

quantify the yield, ultrafast laser experiments were performed to accurately measure the initial populations of photoexcited singlet states and their time evolution into triplets on a picosecond time scale. A careful analysis of the data led to yields approaching 200% and an increase in the triplet formation rate of more than ten thousand compared with

the isolated DPIBF molecule. Both observations support the notion that efficient singlet fission is occurring and that the design criteria set forth may be quite general.

Nanocrystalline Hole Conductors

One objective of the research was to develop porous hole-conducting nanocrystalline semiconductor supports to capture photogenerated holes from the ground state of optically excited chromophores (e.g., QDs and molecular dyes) and transport them to the hole-collecting substrate, which contacted a dark catalytic anode to drive water oxidation. Toward that end, we developed synthetic protocols for preparing inverse opal nanocrystalline films as hole conductors. Ordered polystyrene (PS) bead films were prepared as templates for directing the growth of ordered porous semiconducting materials. We developed a methodology to deposit 3–4- μm -thick films of 300-, 400-, and 500-nm PS beads arranged in a hexagonal close-packed array with periodic porosity. These PS templates were used to prepare CdSe inverse opals by electrochemical deposition. The resulting structures displayed significant light absorption over a wide portion of the near-infrared region. The unexpected enhanced light absorption in this spectral region was shown to result from a disordered pore structure and a high refractive index contrast present in the CdSe inverse opal architecture. Similar PS templates were used recently to prepare Cu–CuO core-shell inverse opals. Both of the copper oxides are intrinsically p-type with respective bandgaps of 1.4 eV for CuO and 2.1 eV for Cu_2O . An examination of the photonic bandgap of Cu_2O shows that it shifts from 680 to 895 nm when the pore size is increased from 300 to 400 nm. Transmission electron microscopy (TEM) and X-ray energy dispersive spectroscopy (EDS) measurements of the Cu–Cu_xO inverse opal electrodes showed a continuous Cu core surrounded by a 20-nm-thick oxide wall (Figure 4). We found that the Cu–CuO core-shell structures were about 15-fold more conductive than cupric oxide inverse opal electrode. The fact that adding a metal core to a poor conductor, such as the CuO, improved its electrical conductivity suggests that a similar approach might be useful for improving the conductivity of other poorly conducting p-type and n-type materials. We also prepared nanocrystalline films of ZnSe and ZnTe nanocrystals that were suitable for studying dye-sensitized hole injection and transport. Films comprising these nanocrystals with thicknesses of 2–3 μm were prepared by spin coating from concentrated solutions followed by thermal or amine-based chemical treatments to remove an initial surface layer of electrically insulating oleate ligands.

Future Directions

1,3-Diphenylisobenzofuran (1), cibalaktrot (2), and pentacene (3) are all compounds that fulfill the important relations $E(S_1) \geq 2E(T_1)$ and $E(T_2) > E(S_1)$ for efficient SF (see Figure 5). We will expand our efforts from (1) to also investigate (2) and (3). We will study complete water

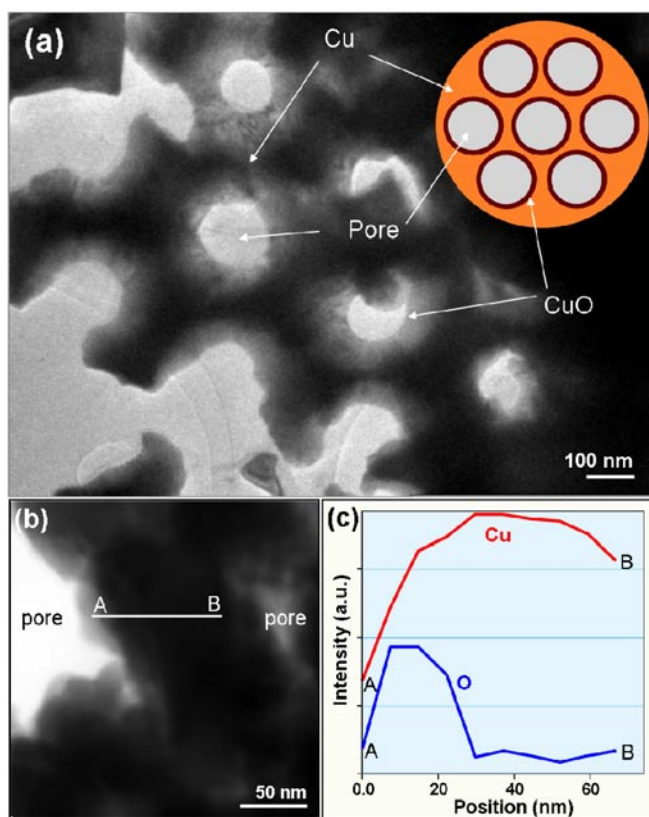


FIGURE 4. TEM images of Cu–CuO inverse opal nanowire mesh electrode with (a) low-magnification view, (b) higher-magnification view, and (c) the EDS cross-sectional line scan from point A to B in (b), highlighting the distribution profile of Cu and O across the core-shell nanowire mesh region.

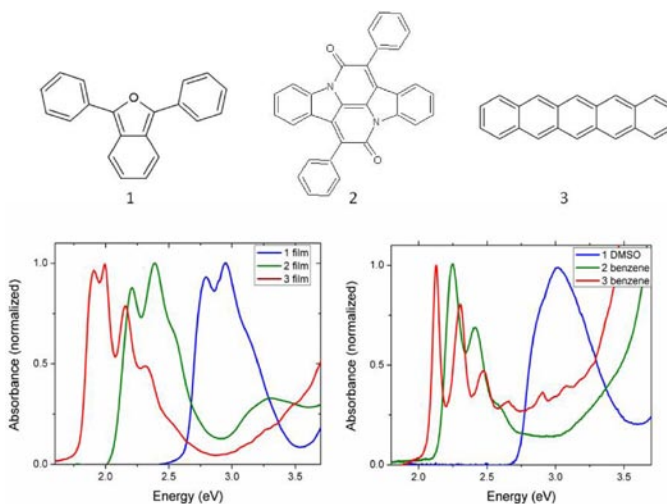


FIGURE 5. Molecular structures of monomeric SF compounds and their absorption spectra in film (lower left) and solution (lower right).

splitting cells with two photoelectrodes, one of which exhibits efficient SF at the cathode. We will optimize new hole conducting nanocrystalline supports for the anodic

photoelectrode and investigate new hole-injecting dyes. We will study the effects of solar concentration on cell performance, which is predicted to greatly increase the water splitting efficiency based on initial thermodynamic calculations.

Publication list (including patents) acknowledging the DOE grant or contract

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