innovation

The Spectrum of
Clean Energy Innovation

Fundamental Science

Market-Relevant Research

Systems Integration

Testing and Validation

Commercialization

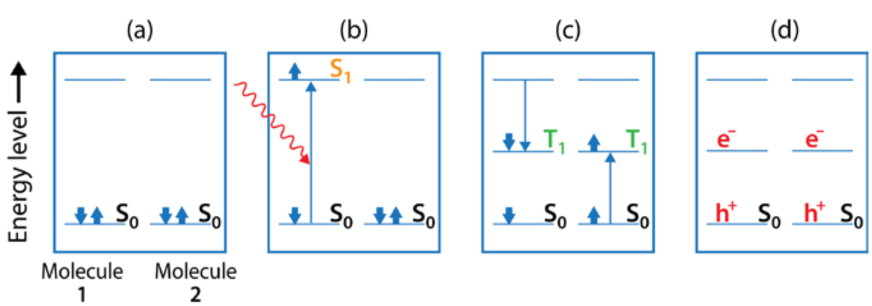
Deployment

Singlet Fission Holds Two-for-One Potential in Solar Cells

Consumers like two-for-one deals. So do scientists at the National Renewable Energy Laboratory (NREL), who are working on innovative concepts for highly efficient solar cells in collaboration with scientists at the University of Colorado at Boulder (CU) and Northwestern University. NREL scientists have confirmed the first molecular compound specifically designed to exhibit multiple-exciton generation through singlet fission—in effect, producing two electrons for every one photon absorbed by the compound.

But what exactly *is* this process? A singlet refers to a pair of electrons in an atom that are spinning in opposite directions. And fission implies splitting. So singlet fission indicates the dividing up of the energy in singlet electrons. But more specifically, the process, illustrated in the figure below, includes the following steps:

- A molecule of a special material, described in the next section, is illuminated by high-energy photons of light.
- This energy excites the electrons from their low-energy ground state (S_0) to an excited high-energy singlet state (S_1).
- As the singlet "relaxes," some of its energy is transferred to a neighboring molecule with electrons in the ground state.
- The result is two molecules that each contain a triplet state (T_1)—where the electrons are spinning in the same direction—at an energy level between the ground state and high-energy singlet state.
- Each triplet generates one electron and one "hole," a vacancy left by the electron that behaves like a positively charged particle. Each electron-hole pair can potentially contribute to a solar cell's photocurrent.



The basics of singlet fission: (a) Two neighboring organic molecules in their unexcited ground states S_0 (thick arrows indicate direction of electron spin); (b) A high-energy photon excites the first molecule, creating a singlet state S_1; (c) The first molecule relaxes to a lower-energy triplet state T_1 and transfers energy to the second coupled molecule, which is excited to a triplet state; (d) The two T_1 states each generate a free electron (e^-) and hole (h^+). Hence, one high-energy photon produces two electron-hole pairs—a two-for-one transaction. Illustration by Al Hicks, NREL

Through deep technical expertise and an unmatched breadth of capabilities, NREL leads an integrated approach across the spectrum of renewable energy innovation. From scientific discovery to accelerating market deployment, NREL works in partnership with private industry to drive the transformation of our nation's energy systems.

This case study illustrates NREL's innovations in Fundamental Science through Market-Relevant Research

NATIONAL RENEWABLE ENERGY LABORATORY

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

The bottom line is that one high-energy photon can produce two electron-hole pairs if the energy of one excited singlet can be split into two lower-energy triplets. This process is unlike the typical solar cell scenario, where one photon leads to one electron-hole pair and the photon energy in excess of the bandgap energy is lost as wasted heat. In contrast, singlet fission produces the "two-for-one" possibility in a solar cell, which can boost the cell's power conversion efficiency.

Evolution of a disruptive concept

The singlet-fission phenomenon has been known for more than three decades. But a 2006 NREL publication finally got scientists to consider it seriously as a light-harvesting scheme. This work led to an extensive search by NREL researchers and collaborators, guided by quantum mechanics, for appropriate candidate materials. An outcome has been the elucidation of two design principles having promising results.

- The first is that singlet fission should release or absorb negligible energy: the energy difference represented by the distance from S_1 down to T_1 should be about equal to the distance from S_0 up to T_1. At least two classes of organic compounds meet this principle, and NREL and CU researchers have most recently focused on the "biradicaloid" class, a group of compounds with two highly reactive areas, which lead to unusual physical properties. In particular, the biradicaloid material DPIBF, or 1,3-diphenylisobenzofuran, essentially has a perfect ratio of singlet-to-triplet excitation energies of 2 to 1. This means that photons with energy at least twice that of DPIBF's bandgap energy can produce two positive and two negative charges, and can therefore potentially double the electrical current of a solar cell.
- The second principle establishes that the best geometry between neighboring planes of DPIBF molecules is a staggered stacking of the molecules.

Using spectroscopy to analyze a DPIBF thin film, scientists measured the yield of triplets per each photon to be 200% (±30%) at a temperature of 77 K. This value represents nearly perfect efficiency, with two triplets created per one absorbed photon, and validates the theory behind the two design principles.

Thermodynamic modeling indicates that a simple multilayered solar cell based on singlet fission could increase the photovoltaic power conversion efficiency by more than 43% above the Shockley-Queisser limit (the maximum theoretical limit for a single absorber layer with no solar concentration or multiplication). The resulting conversion efficiency would be about 46%.

Taking the concept to the next level

The results in singlet-fission research represent an advance by NREL in basic science. But it will take much applied research to find ways to leverage this effect in a commercial solar cell. Using spectroscopy, singlet fission has been demonstrated to be efficient under the right circumstances. But challenges ahead include understanding how the process functions in a wider range of compounds and how to incorporate these organic molecules into devices.

Consequently, at least several more years of research will be needed to push these sorts of singlet-fission cells closer to prime time. Specifically, researchers need to identify optimal materials to use, and then develop these materials within actual solar devices, with the goal of collecting the electrons produced by the triplet states. The effort will be intense, but the result is that more of the sun's energy will be available to generate solar electricity and produce solar fuels. This is a key step toward making solar electricity and fuels more efficient and cost competitive as a conventional power source.

Advancing Third-Generation Solar Cells

The singlet-fission process extends NREL's work from the mid 1970s on concepts now generally referred to as "third-generation" approaches of solar photon conversion. Early work focused on hot-carrier conversion, which is a process in solar cells that increases solar conversion efficiency by using more of the sun's energy, rather than losing it as heat. Then, in 2000, an NREL research team suggested multiple-exciton generation (MEG) in quantum dots, which are semiconductor nanocrystals—lead selenide, for example—that can produce more than one electron-hole pair or exciton from one high-energy photon. Singlet fission is the molecular analog of MEG in inorganic quantum dots.

New NREL result—published in the December 16, 2011, edition of *Science*—is the first report of MEG in an operating quantum dot solar cell, manifested as an external quantum efficiency (EQE) greater than 100% that was measured at low light intensity. EQE is a percentage defined as the number of electrons flowing per second in the external circuit of a solar cell, divided by the number of photons per second of a specific energy (or wavelength) that enter the solar cell. No prior solar cells have ever exhibited EQEs above 100% at any wavelength of the solar spectrum.

Researchers at NREL achieved the peak EQE value of 114% with a layered cell having the following structure from top to bottom: an antireflection-coated glass with a thin layer of a transparent conductor, a nanostructured zinc oxide layer, a quantum dot of lead selenide (treated with ethanedithiol and hydrazine), and a thin layer of gold as the back electrode.

National Renewable Energy Laboratory

15013 Denver West Parkway
Golden, CO 80401
303-275-3000 • www.nrel.gov

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

NREL/FS-6A42-53605 • April 2012

Printed with a renewable-source ink on paper containing at least 50% wastepaper, including 10% post consumer waste.