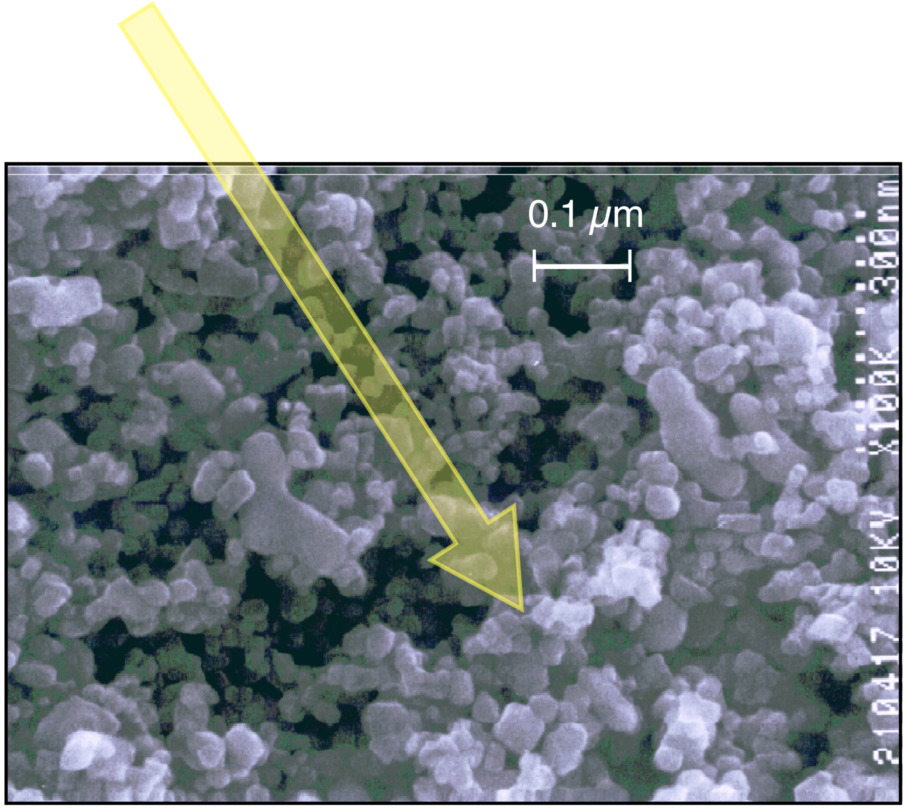
Mesoporous titanium dioxide | electrolyte bulk heterojunction

The term "bulk heterojunction" is used to describe a heterojunction composed of two different materials acting as electron- and a hole- transporters, respectively, which are mixed together in a bulk and thus containing several discrete interfaces.



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A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films

Brian O'Regan* & Michael Grätzel†

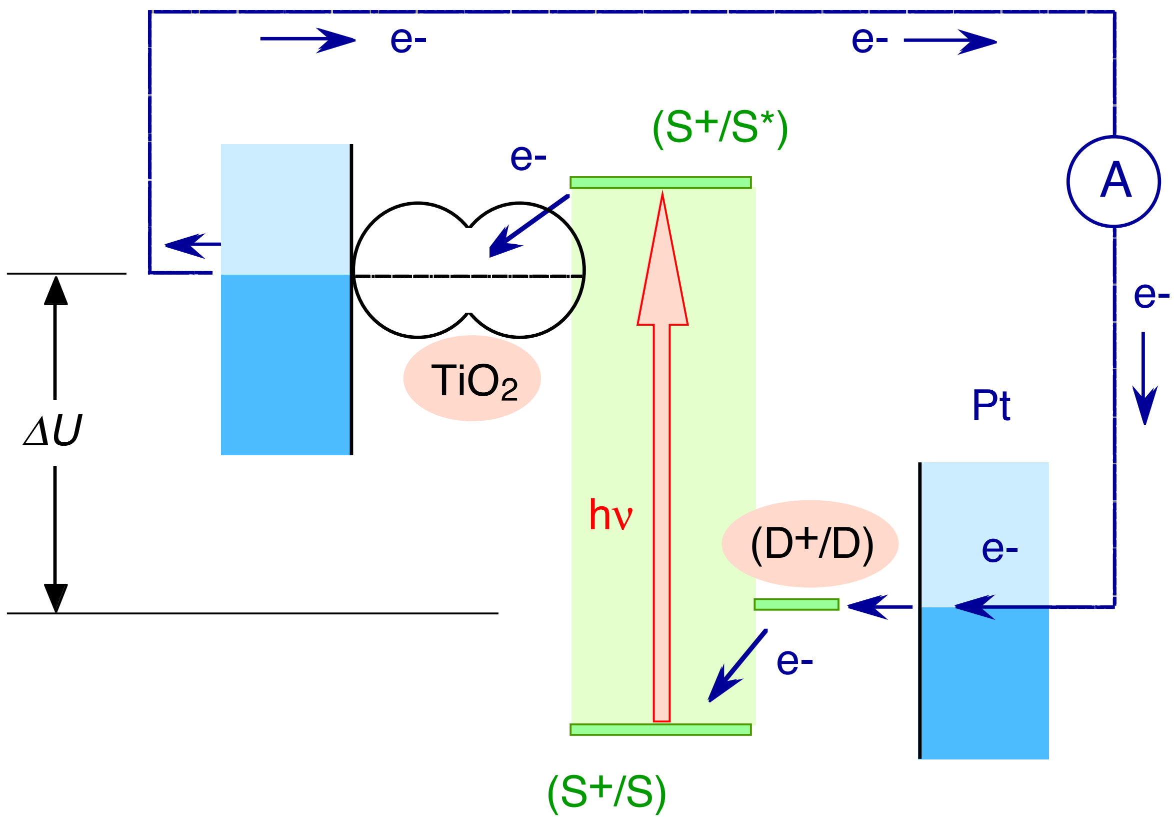
Institute of Physical Chemistry, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

THE large-scale use of photovoltaic devices for electricity generation is prohibitively expensive at present: generation from existing commercial devices costs about ten times more than conventional methods[1]. Here we describe a photovoltaic cell, created from low- to medium-purity materials through low-cost processes, which exhibits a commercially realistic energy-conversion efficiency. The device is based on a 10-μm-thick, optically transparent film of titanium dioxide particles a few nanometres in size, coated with a monolayer of a charge-transfer dye to sensitize the film for light harvesting. Because of the high surface area of the semiconductor film and the ideal spectral characteristics of the dye, the device harvests a high proportion of the incident solar energy flux (46%) and shows exceptionally high efficiencies for the conversion of incident photons to electrical current (more than 80%). The overall light-to-electric energy conversion yield is 7.1–7.9% in simulated solar light and 12% in diffuse daylight. The large current densities (greater than 12 mA cm^{-2}) and exceptional stability (sustaining at least five million turnovers without decomposition), as well as the low cost, make practical applications feasible.

Solar energy conversion by photoelectrochemical cells has been intensively investigated[2-11]. Dye-sensitized cells differ from the conventional semiconductor devices in that they separate the function of light absorption from charge carrier transport. In the case of *n*-type materials, such as TiO_2, current is generated when a photon absorbed by a dye molecule gives rise to electron injection into the conduction band of the semiconductor, Fig. 1. To complete the circuit, the dye must be regenerated by

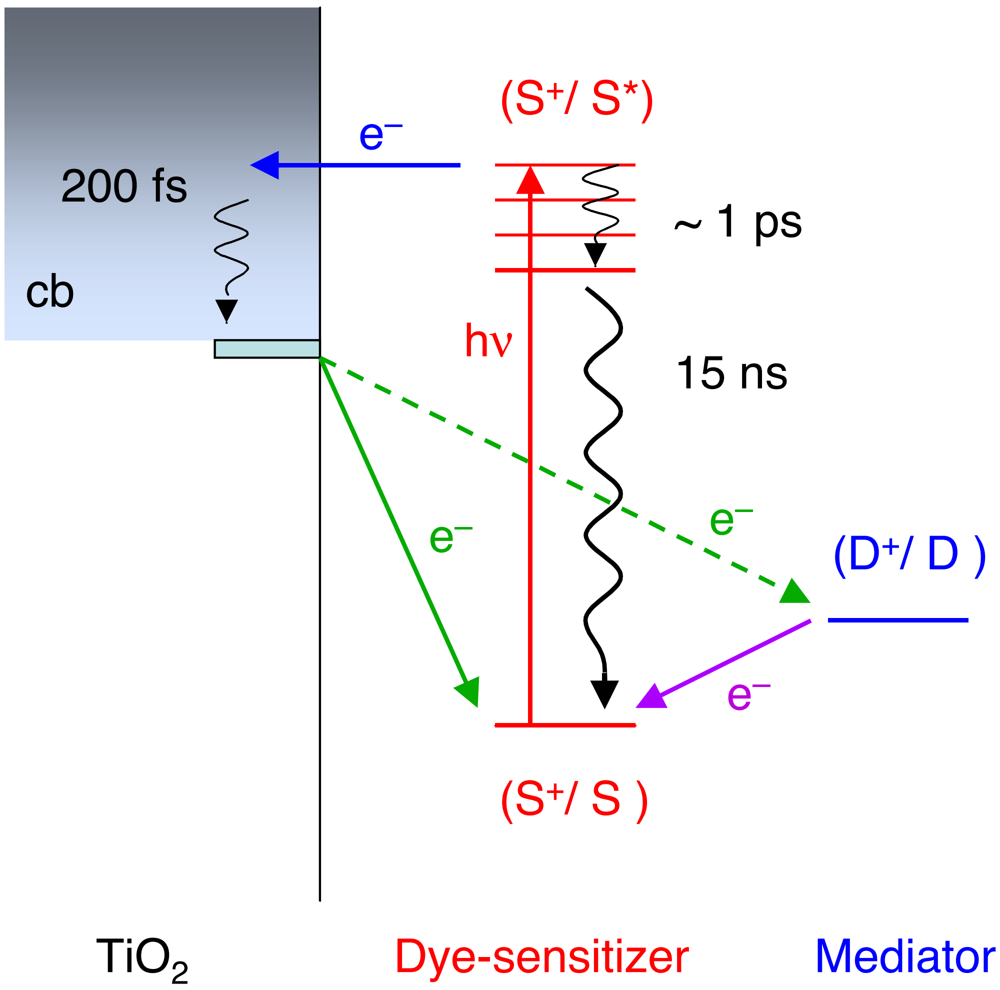
B. O'Regan & M. Grätzel, *Nature* **1991**, *353*, 737

The mesoporous TiO_2 photoanode in DSSCs is made of typically 10-15 nm-radius nanocrystalline particles, whose dimensions are smaller than the typical Debye length characterizing this material. As a conseqence, no space charge layer is form inside the particles and no electric field is formed at the oxide/ adsorbed dye layer interface that could help separating photogenerated charges. The prevention of the carriers recombination (back electron transfer) must then rely on the kinetic competition between the various forward and back electron transfer processes (see next page).



SC = TiO_2
S = redox dye-sensitizer
D = redox mediator

Kinetic competition between ET processes in DSSC



Photoexcitation:

$$S\,|\,SC \overset{h\nu}{\rightleftarrows} S^*|\,SC$$

Charge injection:

$$S^*|SC \longrightarrow e^- (SC) + S^+|SC$$

35 fs - 15 ps

Dye regeneration:

$$S^+|SC + D \longrightarrow S|SC + D^+$$

0.1 - 30 μs

Charge recombination:

$$S^+|\,SC + e^- \longrightarrow S\,|\,SC$$

0.2 - 0.8 ms

Dark current:

$$D^+ + e^- \longrightarrow D$$

10 ms

Dye-sensitized nanocrystalline solar cells (DSSC)

DSSC Basics:

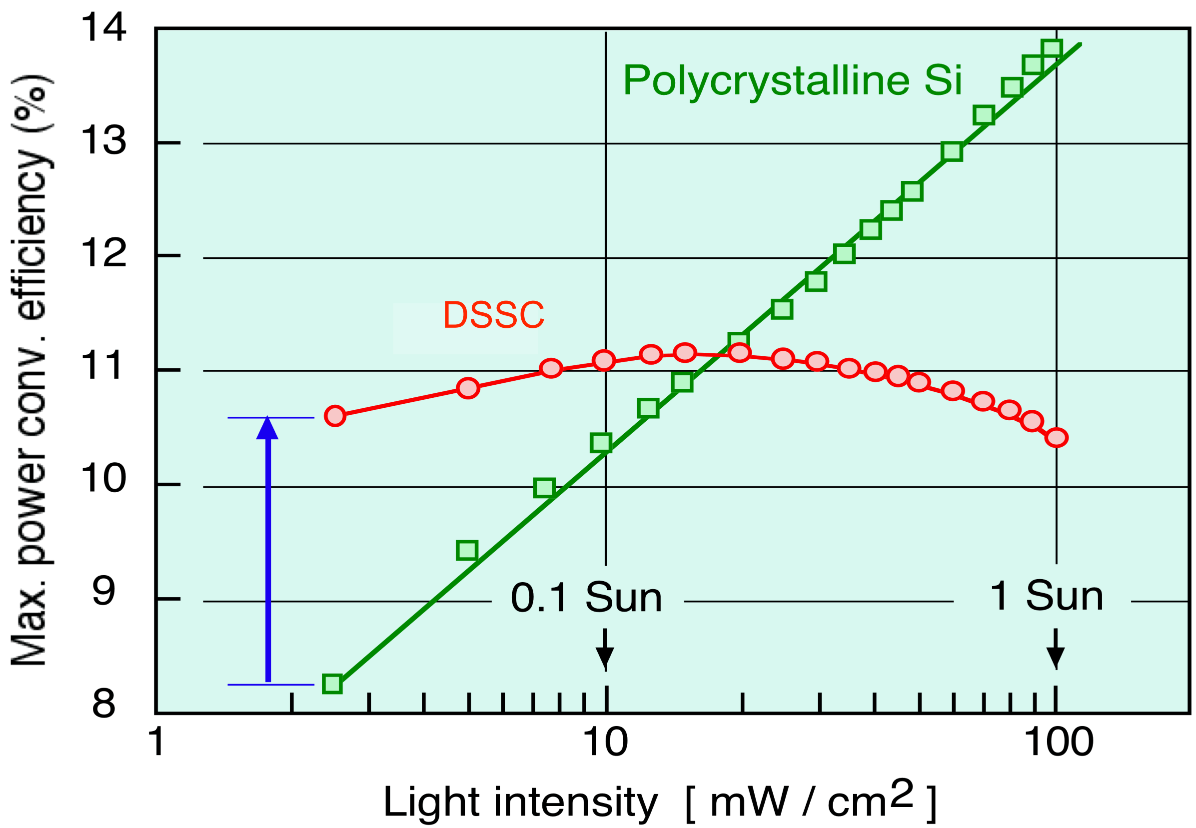
- Cell efficiency = 10-12%
- Module efficiency = 6-9%
- 0.3 year payback period
  (32 kWh/m^2) / [(1700 kWh/m$^2 \cdot$ yr) * 0.06]

Advantages of DSSC:

- Much less sensitive to angle of incidence (good in diffuse light)
- Can be designed for operation at very low light levels
- Efficiency is optimal at low light intensity of scattered light
- Wide range of optimal temperatures
- Much less sensitive to partial shading
- Manufacturing is cheap and easy, needs only commonly available processing equipment
- Significantly lower embodied energy than other solar cells

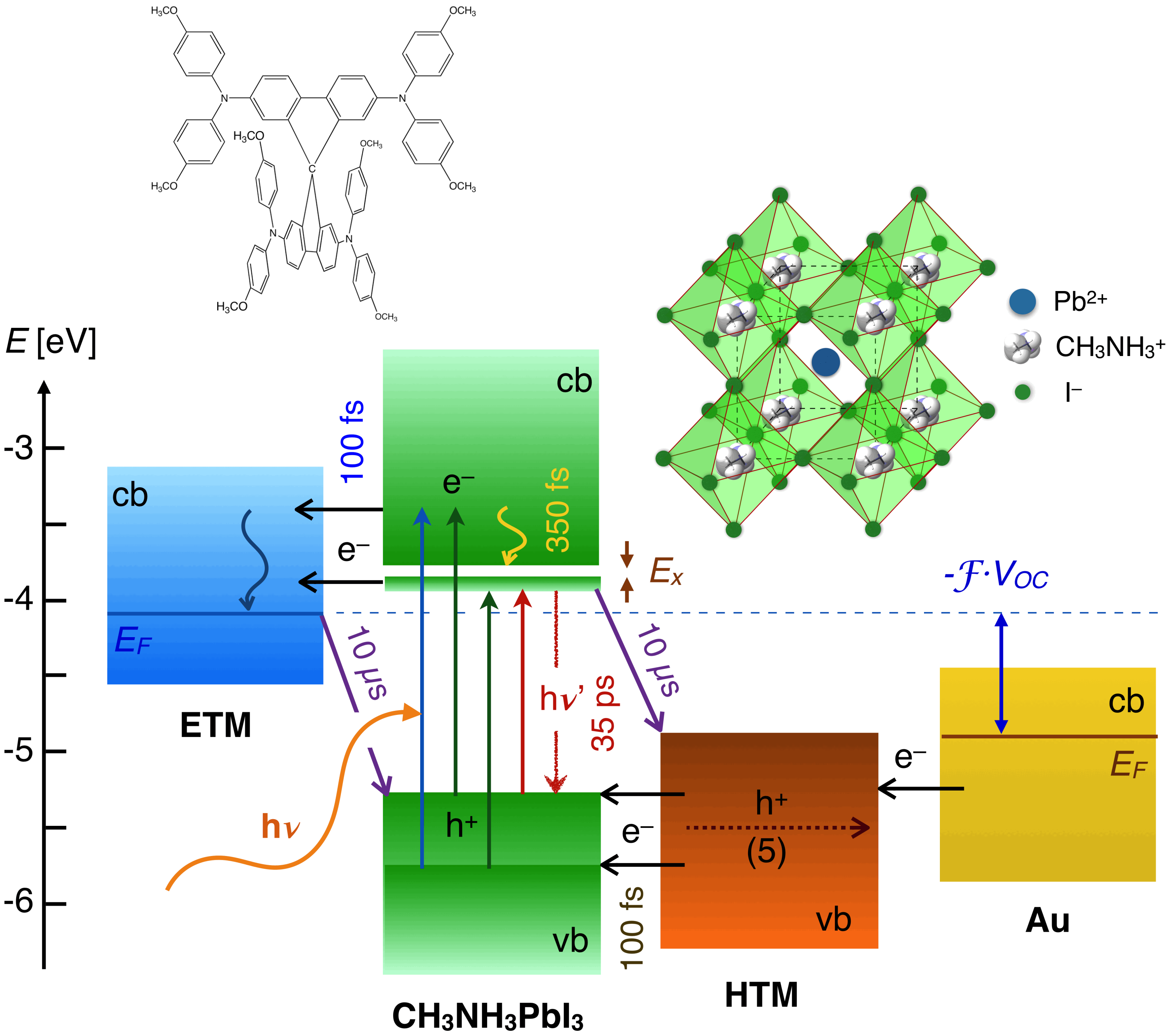
DSSC vs Si cells under low light intensity

Electron-hole recombination in Si and GaAs homojunction cells takes place essentially upon prior trapping of carriers. If the density of photogenerated carriers is low compared to the trap density (under low light intensity), recombination is very effective and the conversion efficiency thus tends to 0. Under high light intensities, trap states are filled up by the first carriers and recombination is minimized. As a result, conversion yields for such systems are generally higher under strong light irradiation.



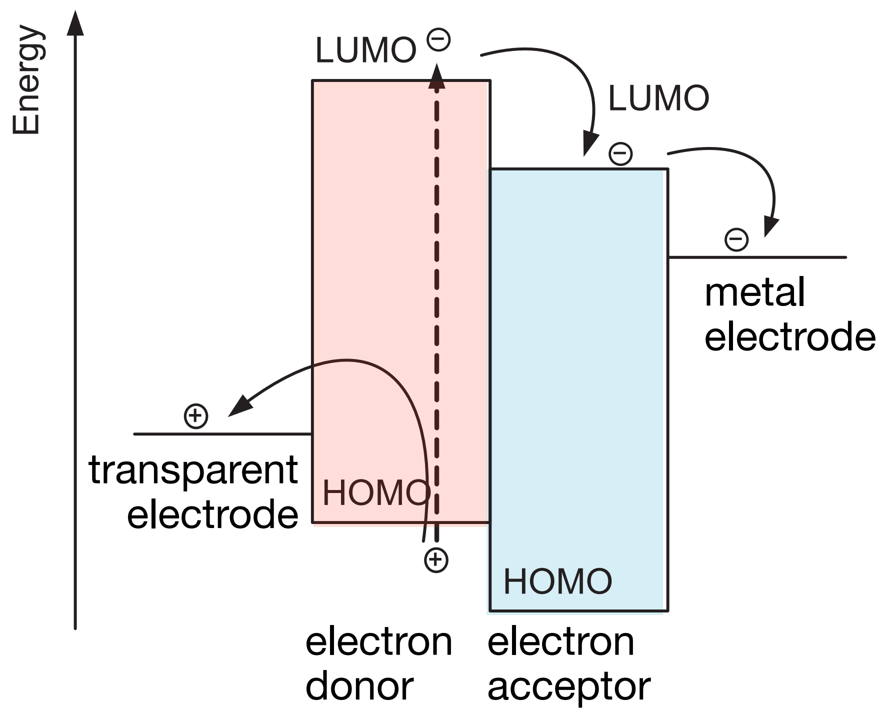
Efficiency of DSSC under high light intensities is often limited by the conduction of the hole transporting material (ion transport in the electrolyte). Their conversion efficiency tends then to be maximum under moderate incident light intensity (1/10 Sun).

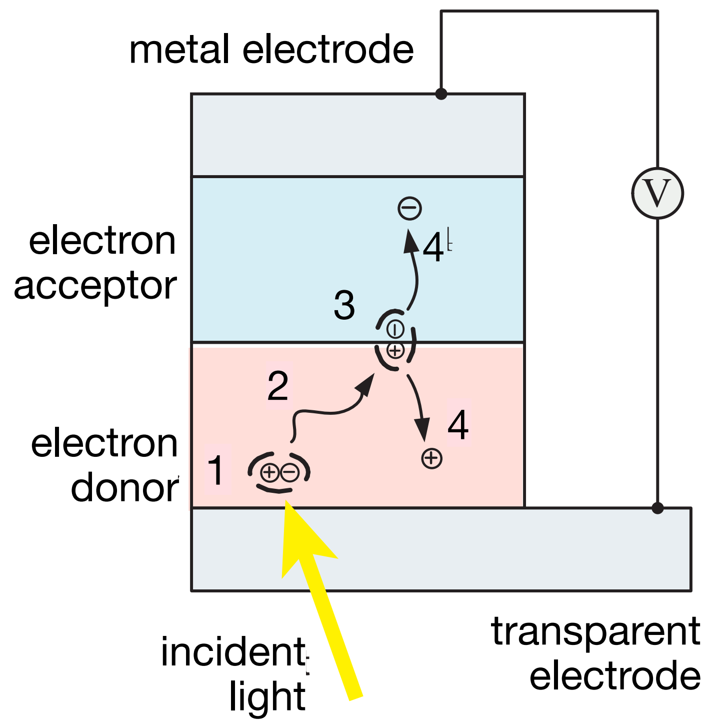
Solid-state double donor-acceptor heterojunction photovoltaic cells



Organic photovoltaics (OPV)

Donor-acceptor bilayer cells

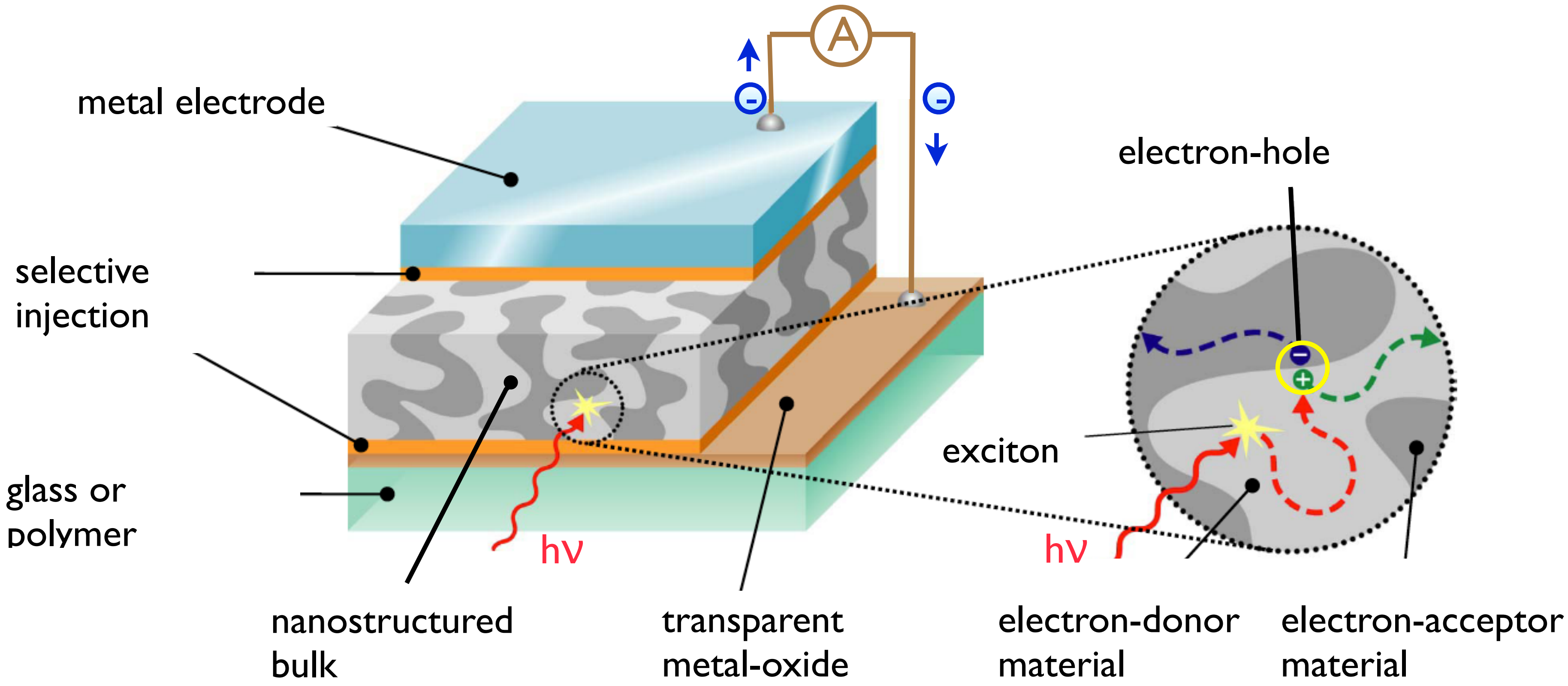




C. W. Tang
Appl. Phys. Lett. **1986**, *48*, 183

1) Exciton formation ; 2) Exciton diffusion
3) Charge separation ; 4) Charge transport

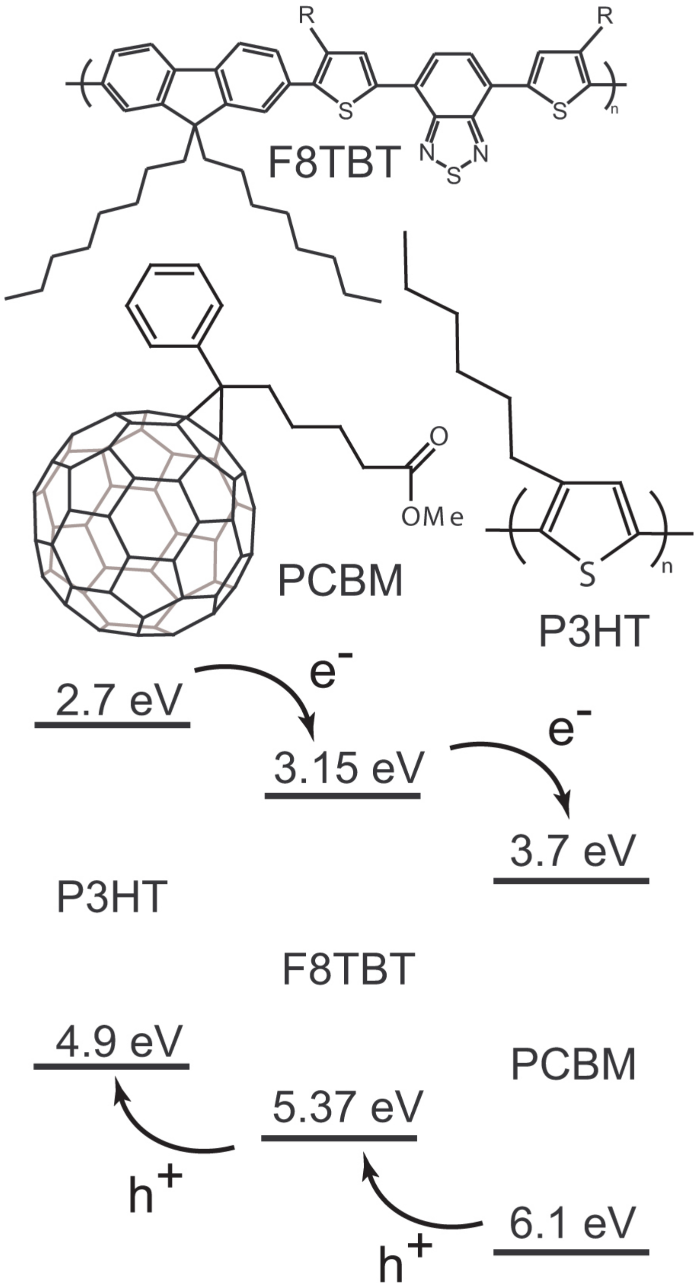
Organic donor-acceptor bulk heterojunction

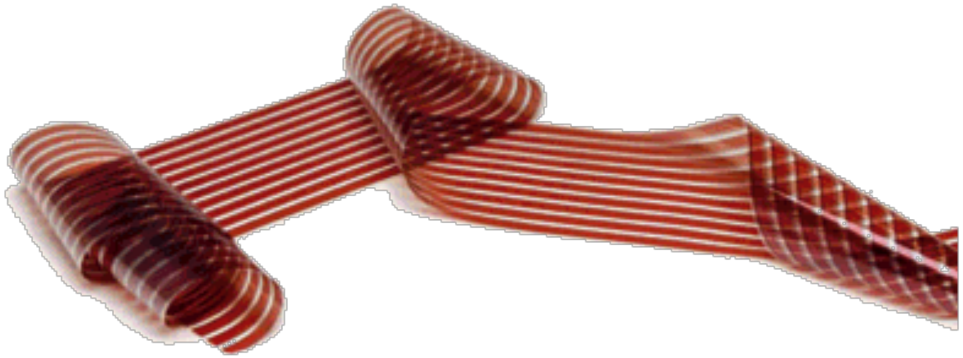


Electron-donor material combines three functions:

1) light absorption, 2) exciton conduction, and 3) hole transport

Conjugated polymer ('plastic') solar cells

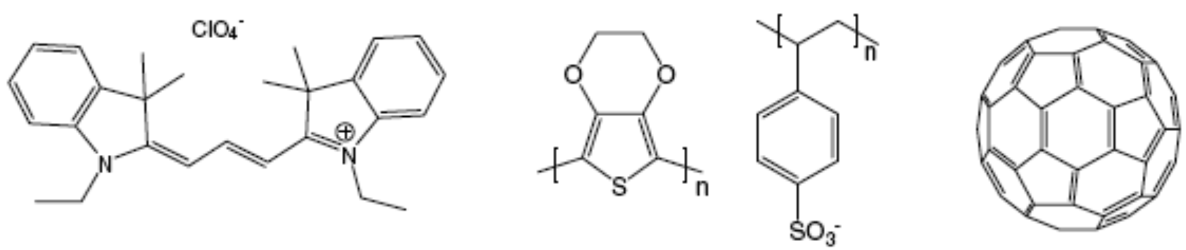


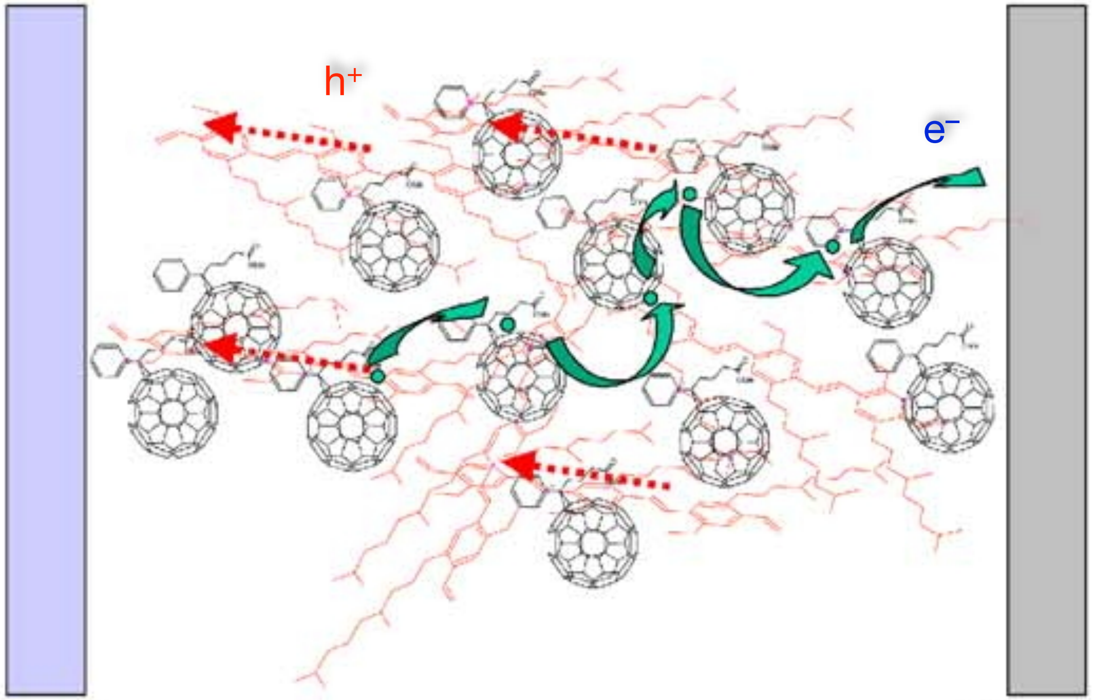


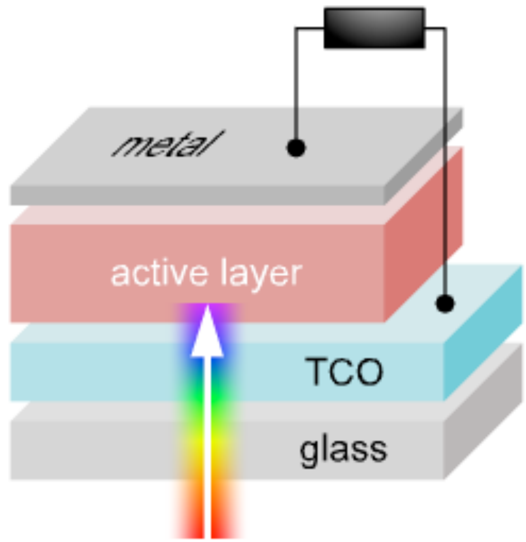
Conjugated polymers are excellent candidates for use in low-cost electronics and photovoltaics. Polymer-based solar cells have reached power conversion efficiencies of 6% in recent reports. Deposition of organics by screen printing, doctor blading, inkjet printing, and spray deposition is possible because these materials can be made soluble. These techniques are required for the high-throughput roll-to-roll processing that will drive the cost of polymer-based PV down to a point where it can compete with current grid electricity. Additionally, these deposition techniques all take place at low temperature, which allows devices to be fabricated on plastic substrates for flexible devices.

Small molecule-based OPV

Cy5 PEDOT:PSS C_{60}







F. A. De Castro et al.
Phys. Chem. Chem. Phys.
2009, *11*, 8886-8894

Convergence of 1st, 2nd and 3rd generation photovoltaic technologies

p-n junction: Si, GaAs(1G)
Thin-film CIGS, CdTe (2G)

OPV : polymer,
small molecule-based (3G)

DSSC : liquid electrolyte,
solid HTM-based (3G)