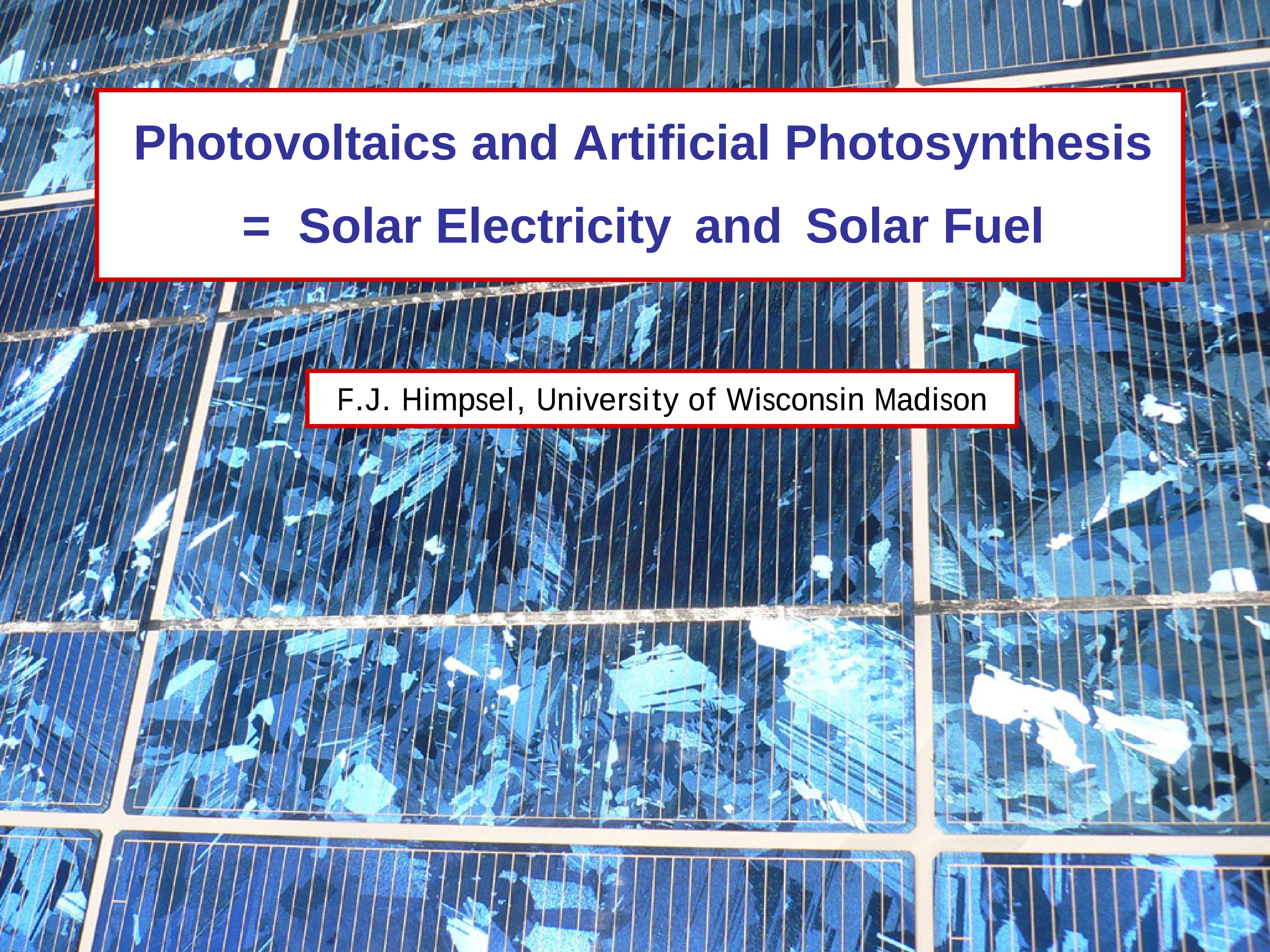
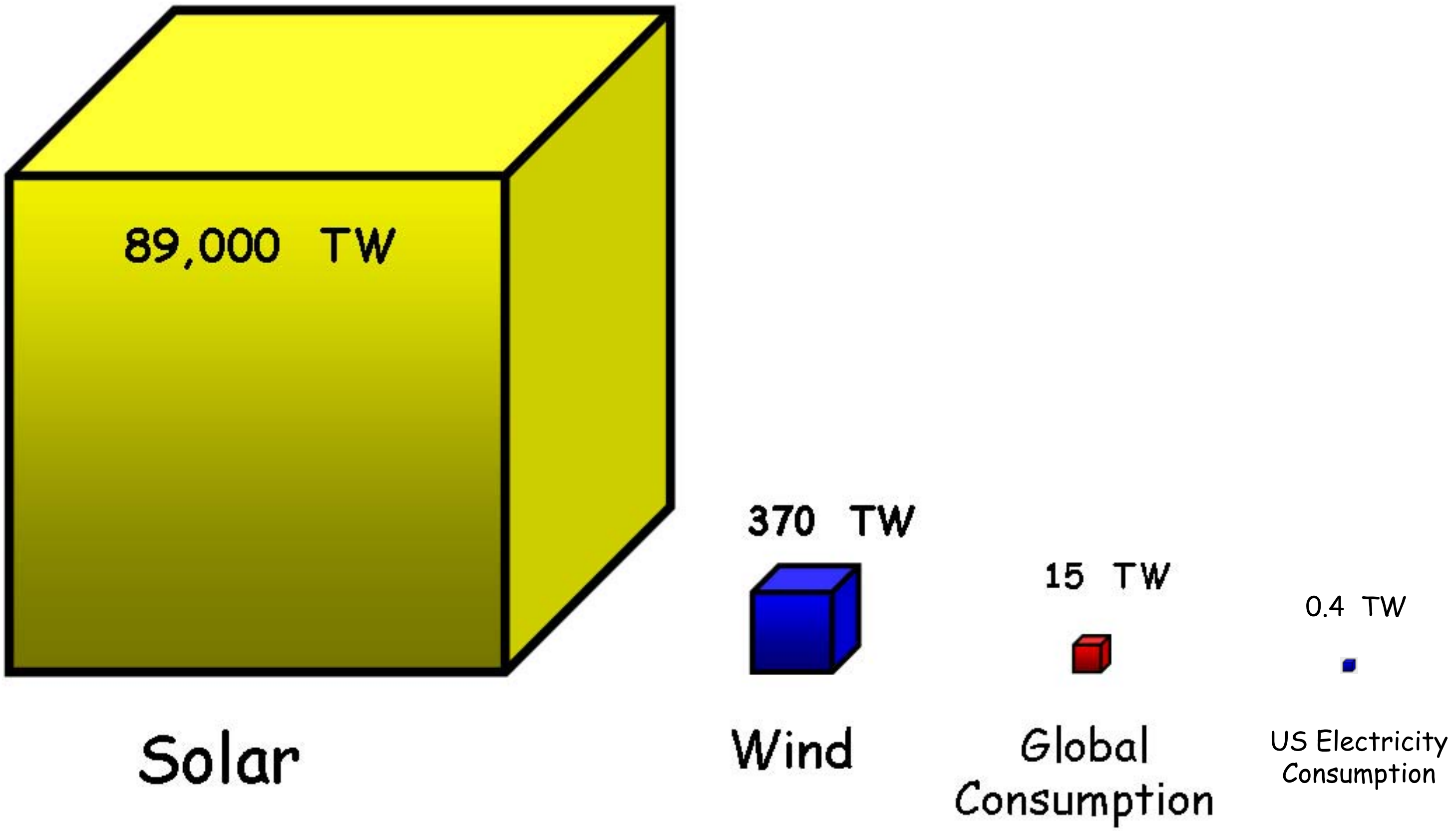


Photovoltaics and Artificial Photosynthesis

= Solar Electricity and Solar Fuel

F.J. Himpsel, University of Wisconsin Madison

Electricity from the Sun is an ideal source of energy (fully convertible)



100×100 km^2 of solar cells could produce all the electricity for the US.

The required area of solar cells

$1\ \text{kW/m}^2$	(Incident solar power)
$\times\ \frac{1}{4}$	(Useful daylight)
$\times\ 0.16$	(Efficiency of a solar cell)
$\times\ 10^{10}\ \text{m}^2$	($100\times100\ \text{km}^2$)

$= 0.4\ \text{TW}$

= Electric power consumed in the US

0.7 TW could be generated by all the rooftops in the US (NREL study).

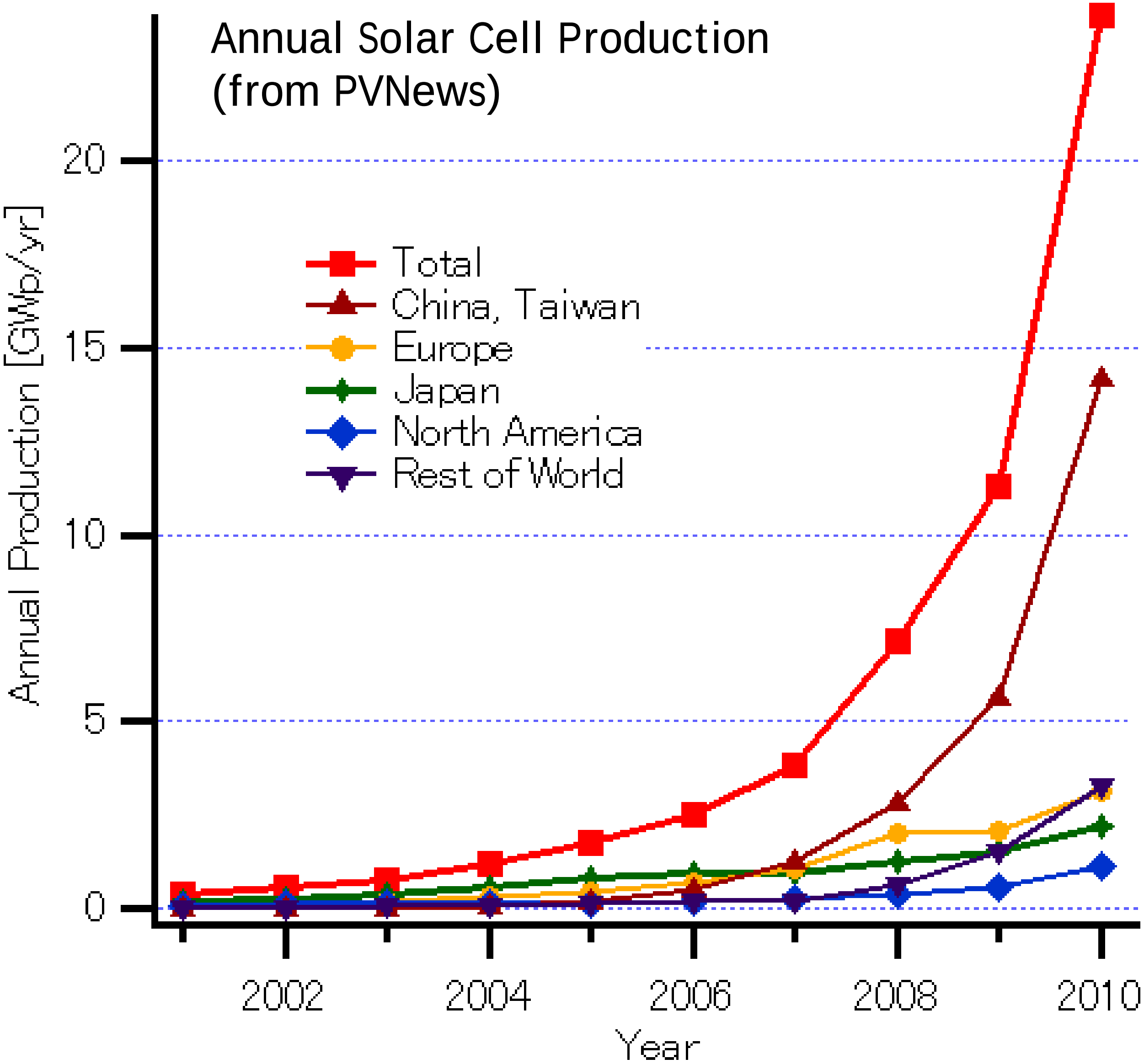
How much would it cost ?

$$
\begin{array}{ll}
\quad 1\ \$/\mathrm{W} & \text{(Price of solar cells per Watt)} \\
\times\ 0.4\ \mathrm{TW} & \text{(Electric power generated in the US)} \\
\hline
=\ 0.4\ \mathrm{T\$} & =\ 0.4\ \text{Trillion Dollars}
\end{array}
$$

Mechanical support structure adds significant costs.

But one can design buildings to provide the support.

Electricity from sunlight



Rapid growth in China.

Significant in Europe.

US is behind , but greatly improved in recent years.

Price comparison: Solar versus fossil energy

- **Solar energy is free, while fossil fuels need to be paid for.**
- **\$/kW versus \$/kWh**
- **Energy payback time matters for solar energy (1-4 years).**
- **Typical warranty is 25 years.**
- **The price of solar cells is less than 1/3 of the total cost. The rest is for support structure, converter, labor.**
- **Higher efficiency keeps support structure small.**

Forbes 1/02/2013 @ 12:13PM | 17,055 views

Warren Buffett In \$2 Billion Solar Deal

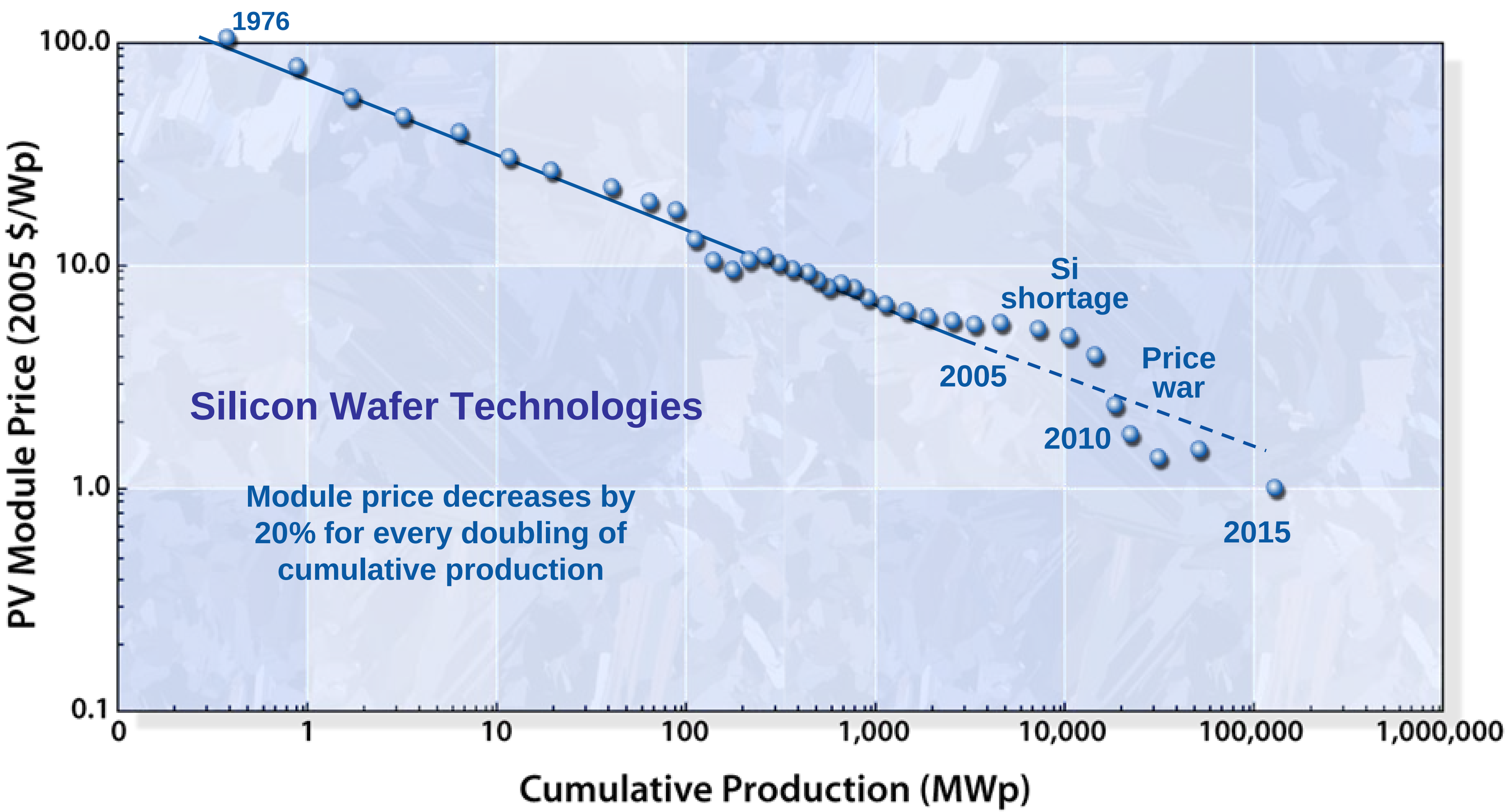
+ Comment Now + Follow Comments

Making a big bet on solar energy, Warren Buffett's MidAmerican Energy Holdings Company has acquired two SunPower solar photovoltaic power plant projects in California for between \$2 billion and \$2.5 billion, the companies said Wednesday.

First Solar Array (Photo credit: russf)

Silicon solar cells dominate, but progress is slow

(unlike Moore's law: no miniaturization, mainly volume)



NREL + IRENA

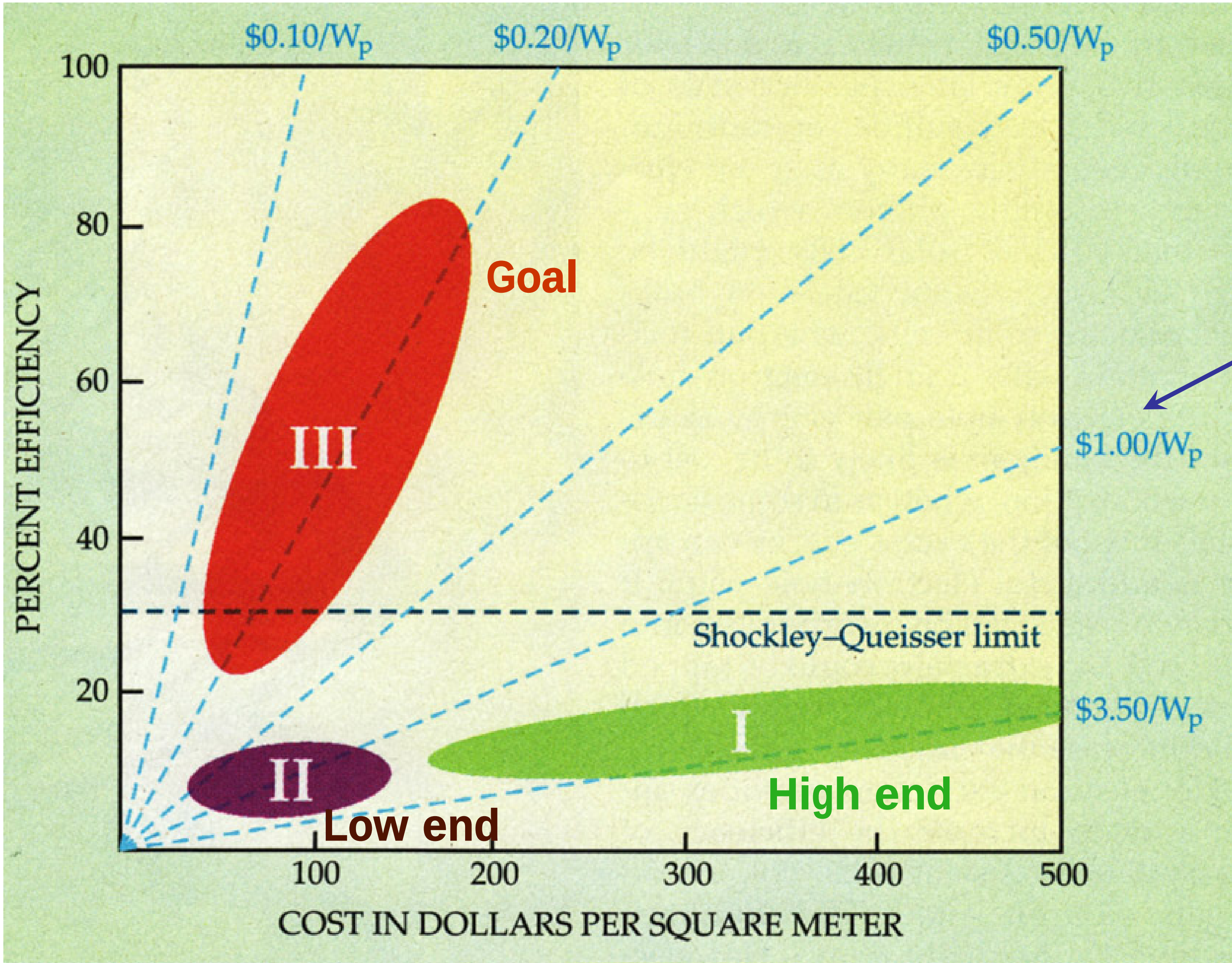
- **Si solar cells dominate, but:**
  Little room for improvement, twice the energy payback time
- **Try everything: Nanoparticles, molecules, polymers, perovskites, ...**
- **Less material, low temperature processing**
- **Print solar cells roll-to-roll, like newspaper**
- **Use existing support structures**

Maintain efficiency!

The rooftops in the US could generate all of our electricity.

Nanoparticle ink on metal foil

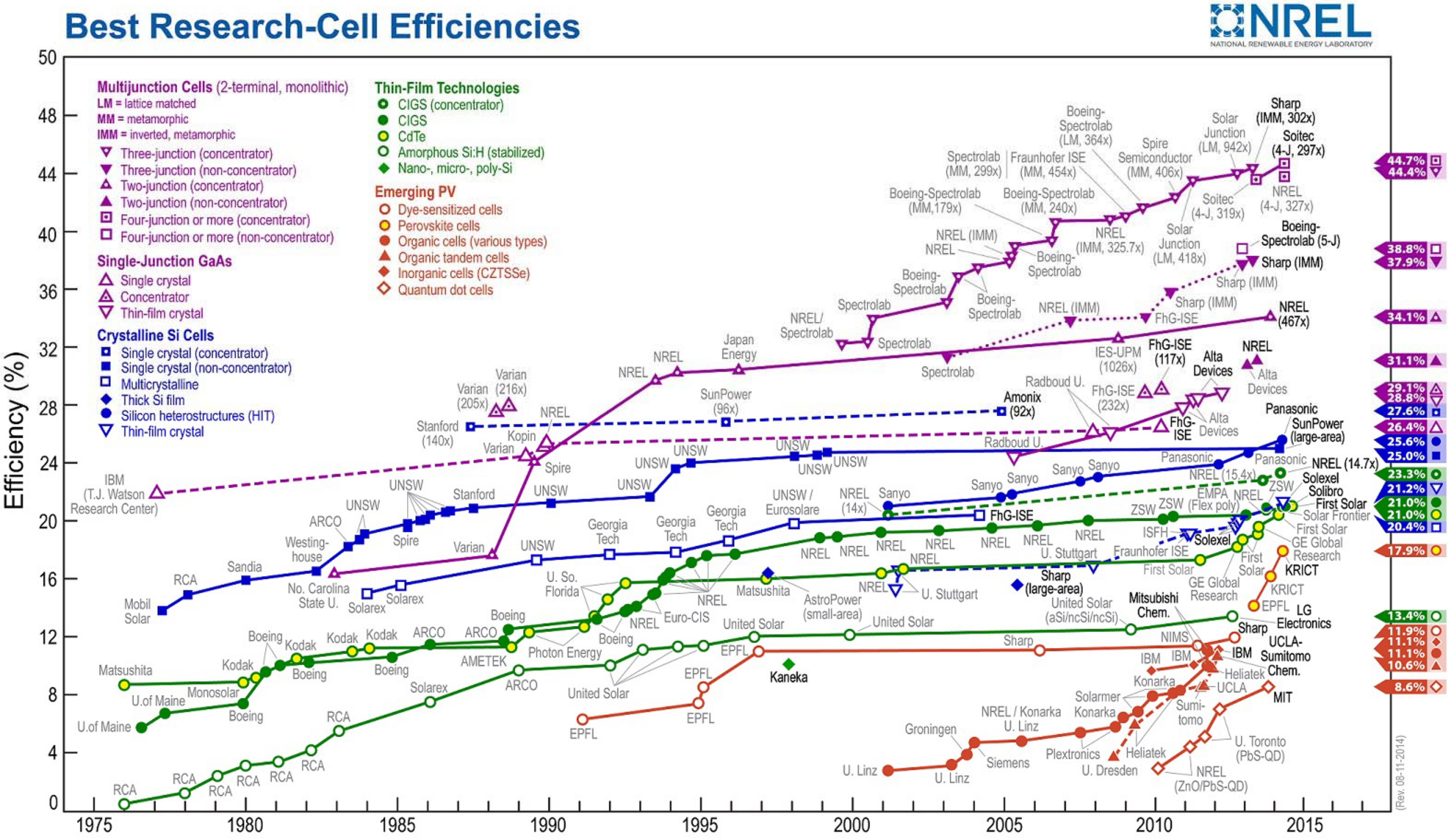
Cost versus efficiency



1 $/W

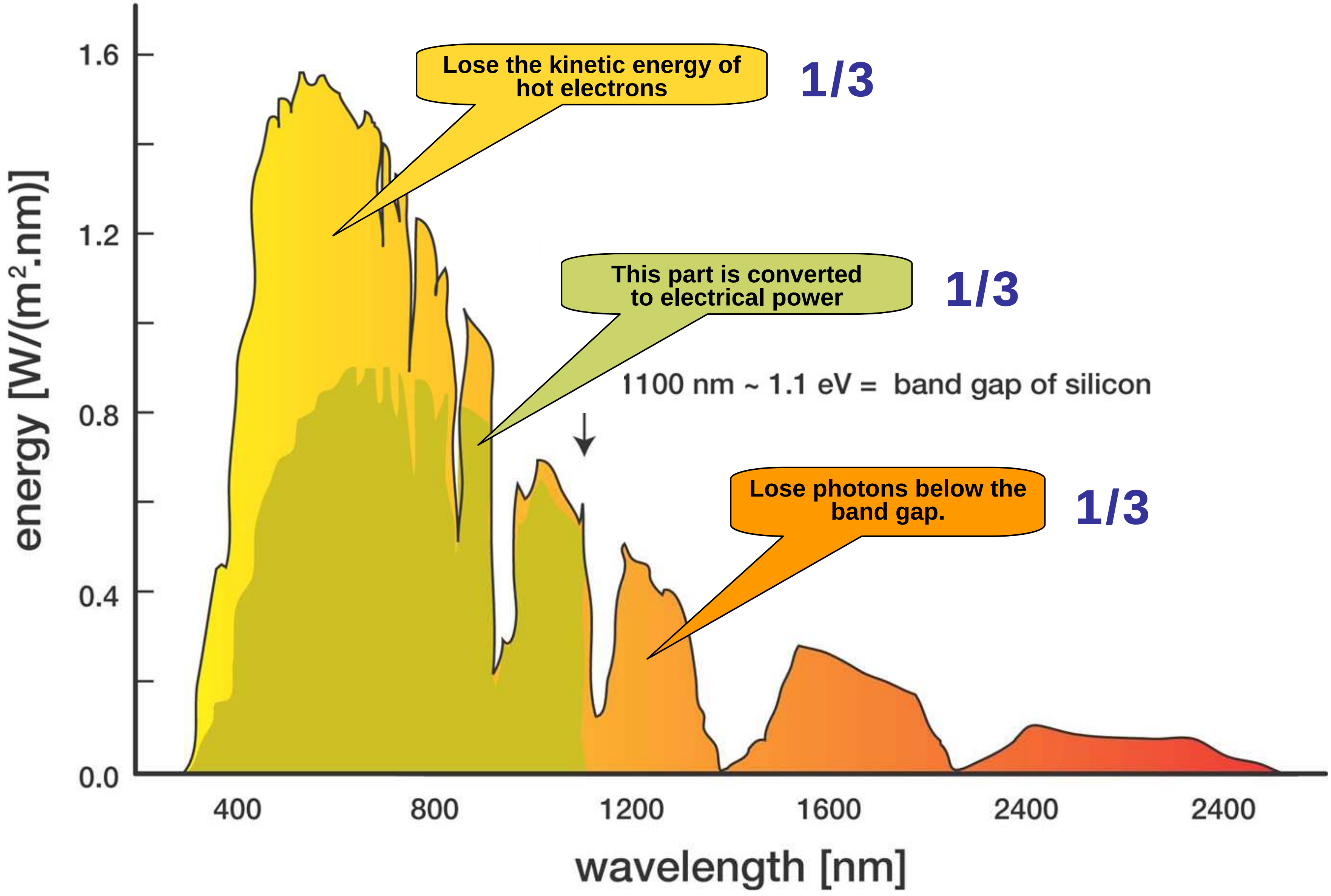
Low end designs are more cost-effective (less $/W).

Physics Today,
March 2007, p. 37



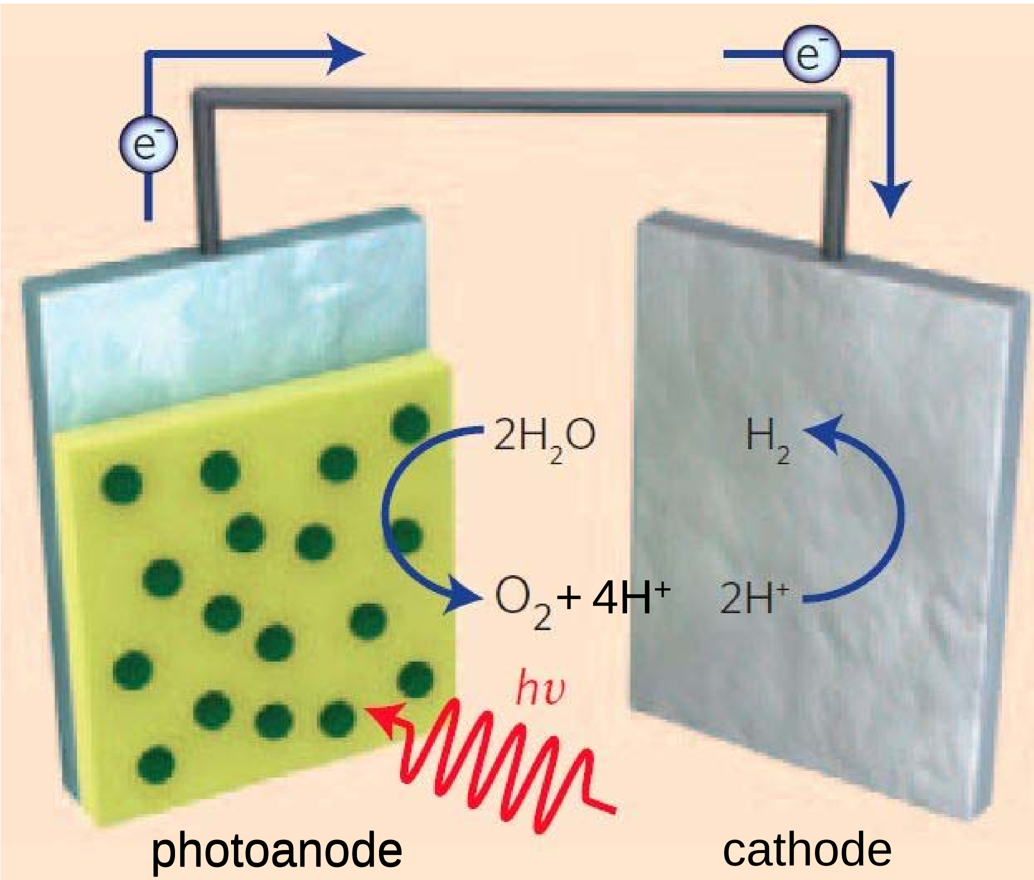
Best Research-Cell Efficiencies
NREL
NATIONAL RENEWABLE ENERGY LABORATORY
Efficiency (%)
Multijunction Cells (2-terminal, monolithic)
LM = lattice matched
MM = metamorphic
IMM = inverted, metamorphic
Three-junction (concentrator)
Three-junction (non-concentrator)
Two-junction (concentrator)
Two-junction (non-concentrator)
Four-junction or more (concentrator)
Four-junction or more (non-concentrator)
Single-Junction GaAs
Single crystal
Concentrator
Thin-film crystal
Crystalline Si Cells
Single crystal (concentrator)
Single crystal (non-concentrator)
Multicrystalline
Thick Si film
Silicon heterostructures (HIT)
Thin-film crystal
Thin-Film Technologies
CIGS (concentrator)
CIGS
CdTe
Amorphous Si:H (stabilized)
Nano-, micro-, poly-Si
Emerging PV
Dye-sensitized cells
Perovskite cells
Organic cells (various types)
Organic tandem cells
Inorganic cells (CZTSSe)
Quantum dot cells
44.7%
44.4%
38.8%
37.9%
34.1%
31.1%
29.1%
28.8%
27.6%
26.4%
25.6%
25.0%
23.3%
21.2%
21.0%
21.0%
20.4%
17.9%
13.4%
11.9%
11.1%
11.1%
10.6%
8.6%
(Rev. 08-11-2014)

Efficiency limit: 33% for a single junction (Shockley/Queisser)

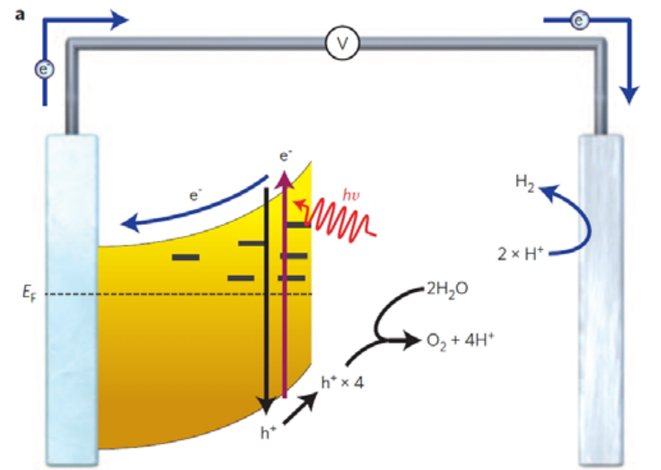


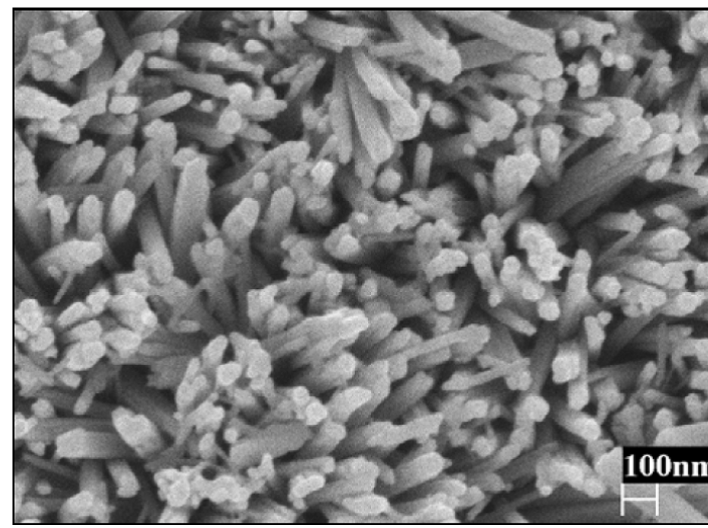
Fuel from sunlight via artificial photosynthesis

Water splitting



Tachibana, Vayssieres, Durrant,
Nature Photonics **6**, 511 (2012)

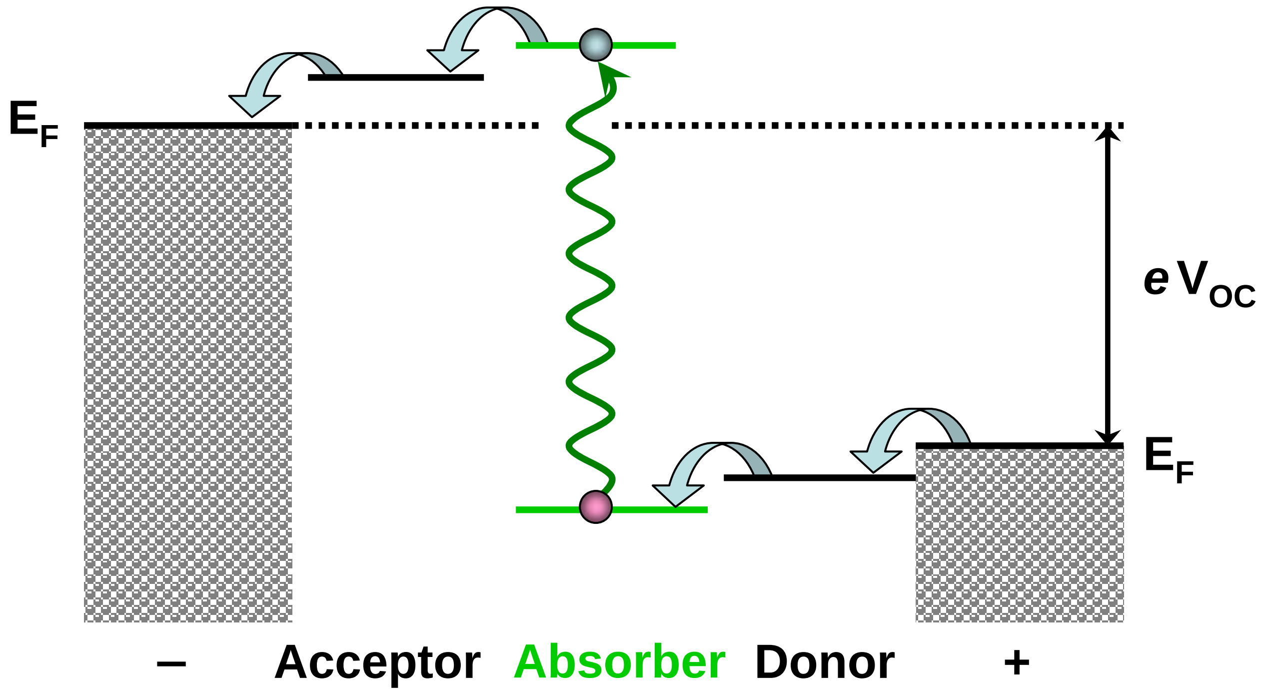




Efficient carrier transport by single crystal Fe_2O_3 nanorod photoanode (Vayssieres)

Design a solar cell from scratch.

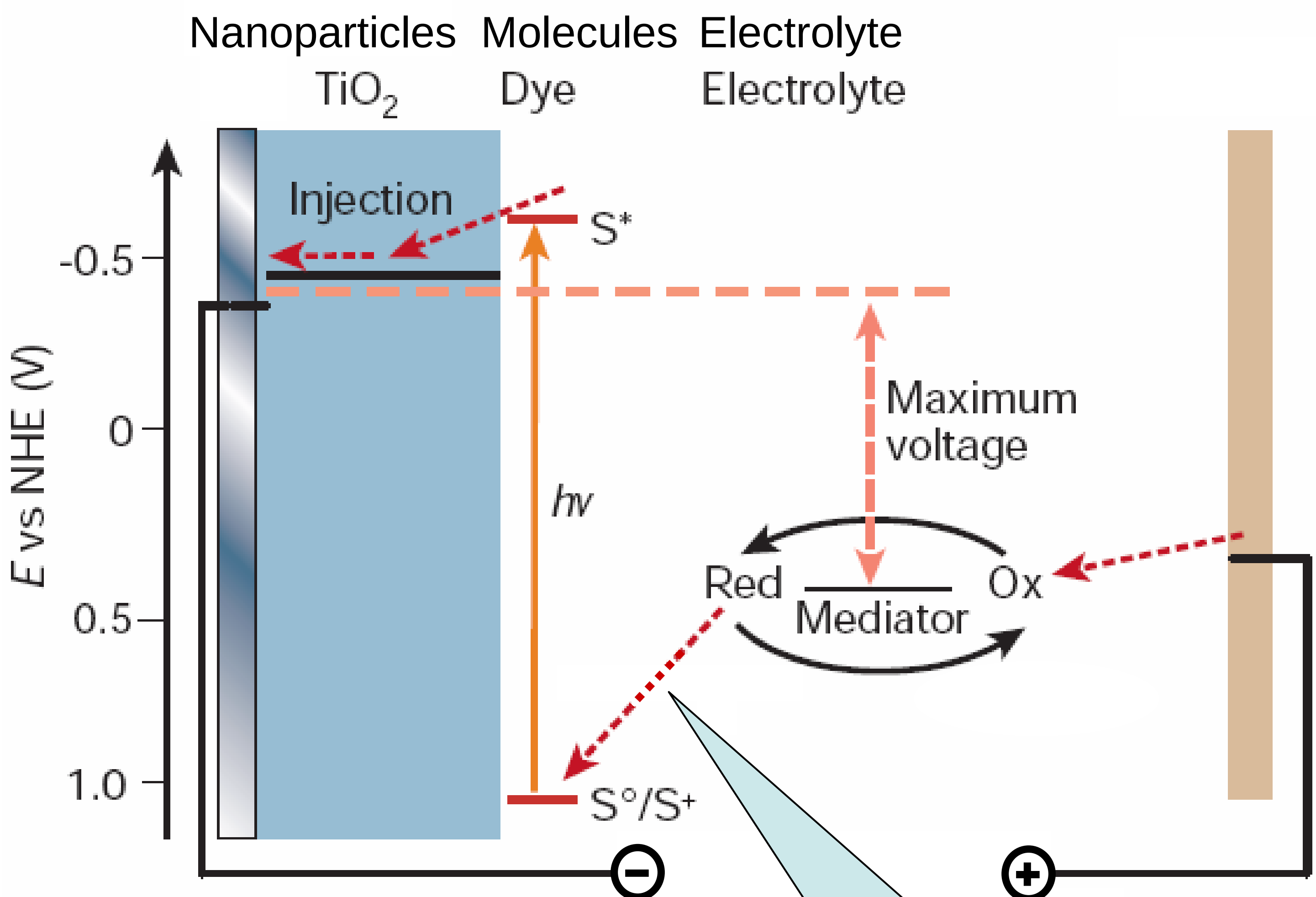
Have 4 energy levels, 3 materials to play with.



Small energy drop: Large voltage
Large energy drop: Large current

Want both

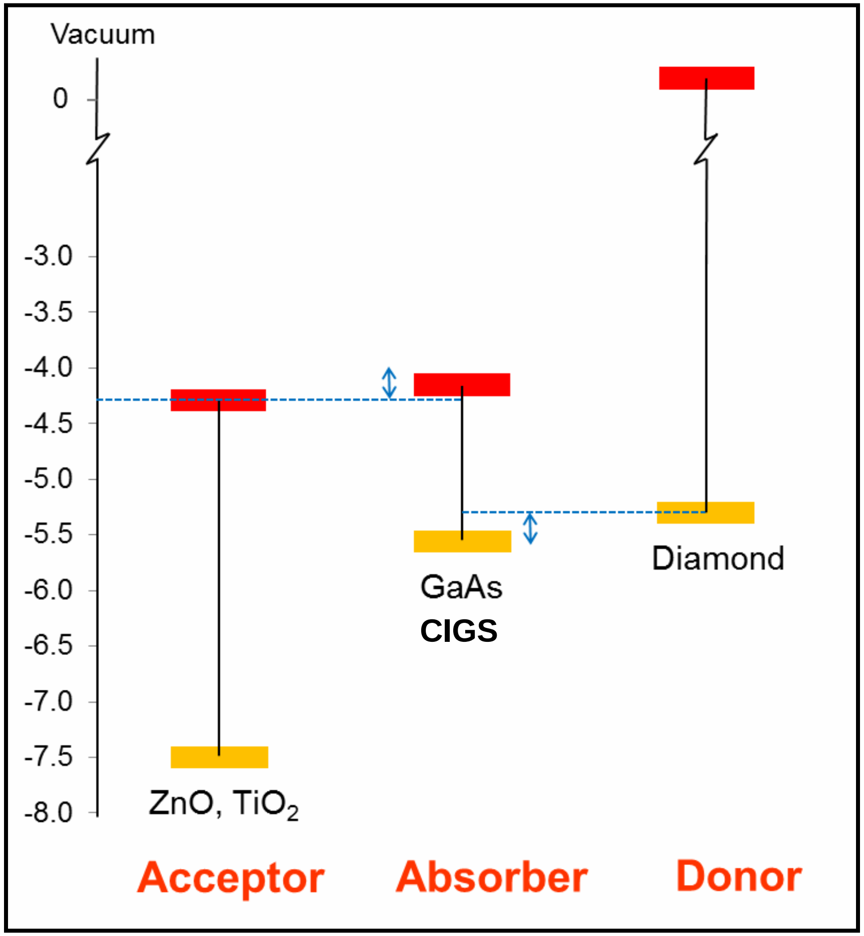
Dye-sensitized solar cells combine 3 types of materials

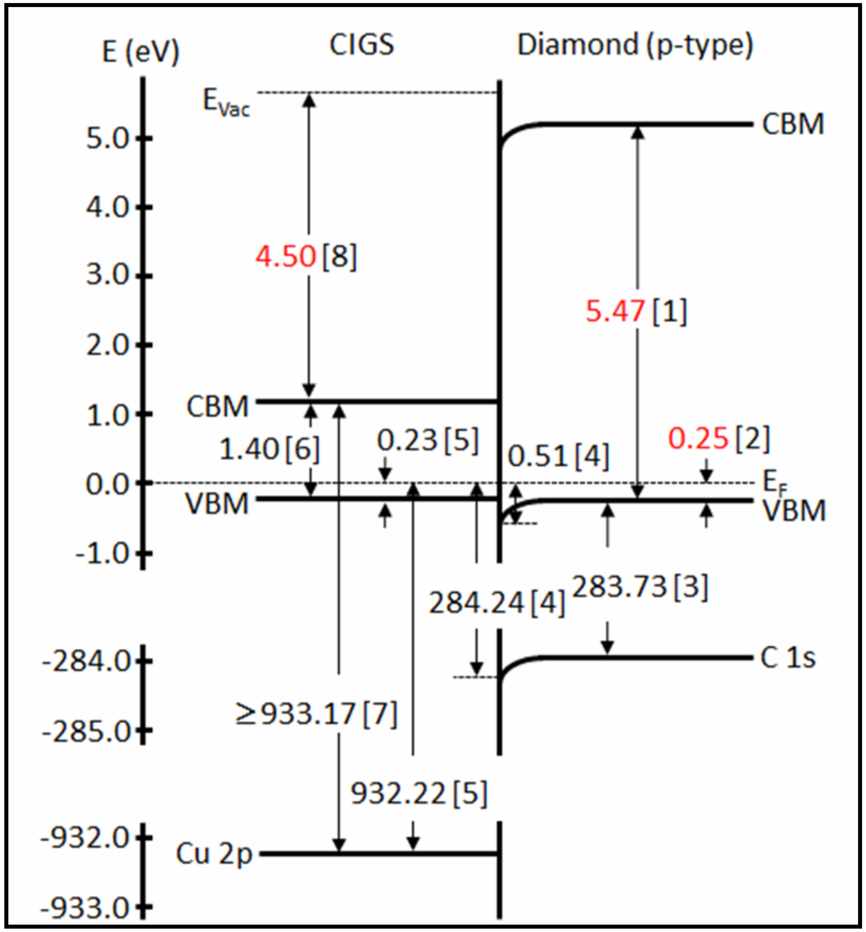


Lose half the voltage on the donor side.

Grätzel, Nature **414**, 338 (2001)
and J. Phys. Chem. C **112** (2008)

Combine semiconductors with tailored band offsets



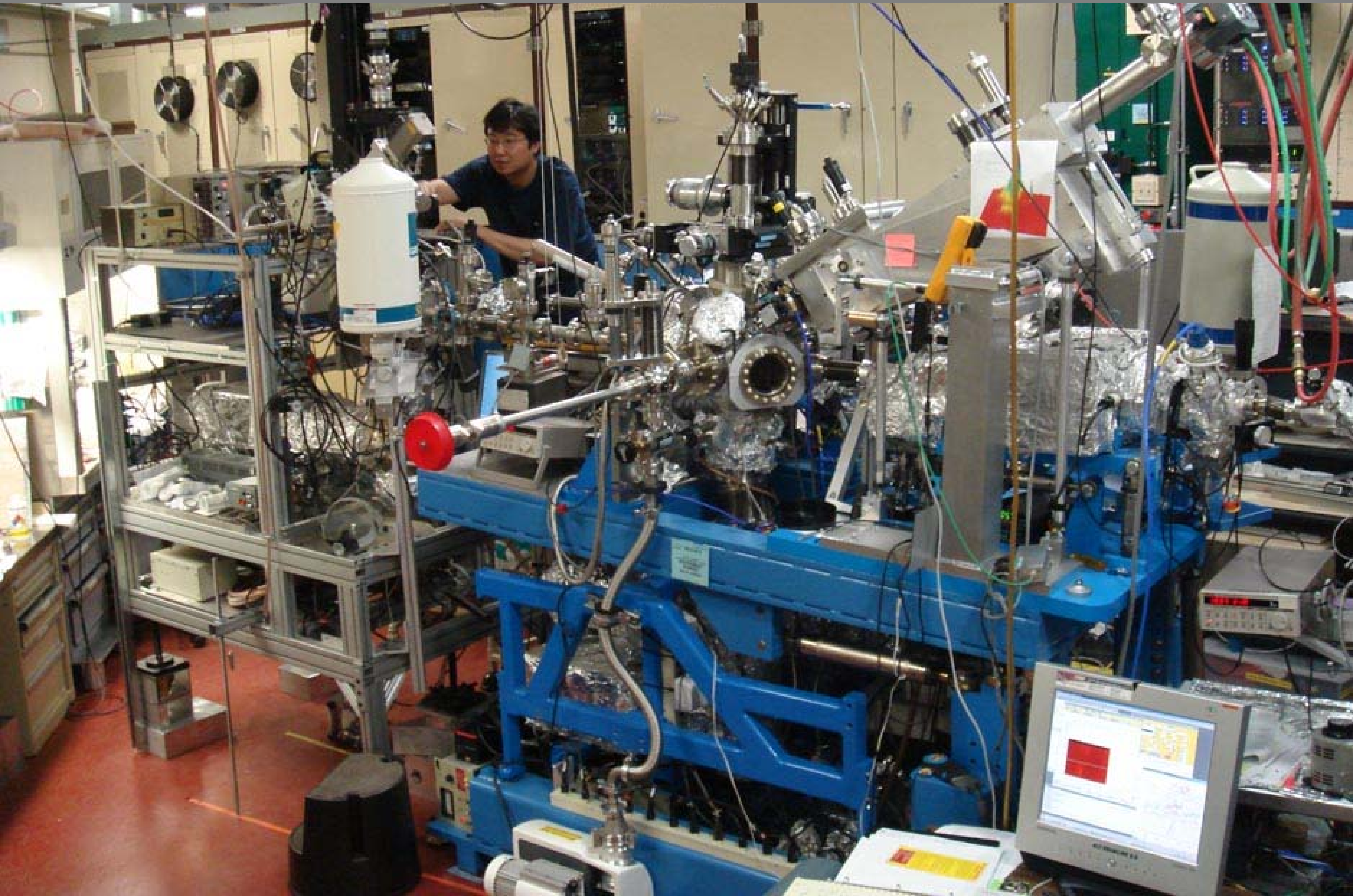


Diamond film as inert, transparent electron donor

Energy levels from XAS, XPS, UPS, optical spectroscopy

Kapilashrami et al., J. Appl.Phys. **116**, 143702 (2014).

Two end stations at an undulator beamline (BL8 at the ALS)

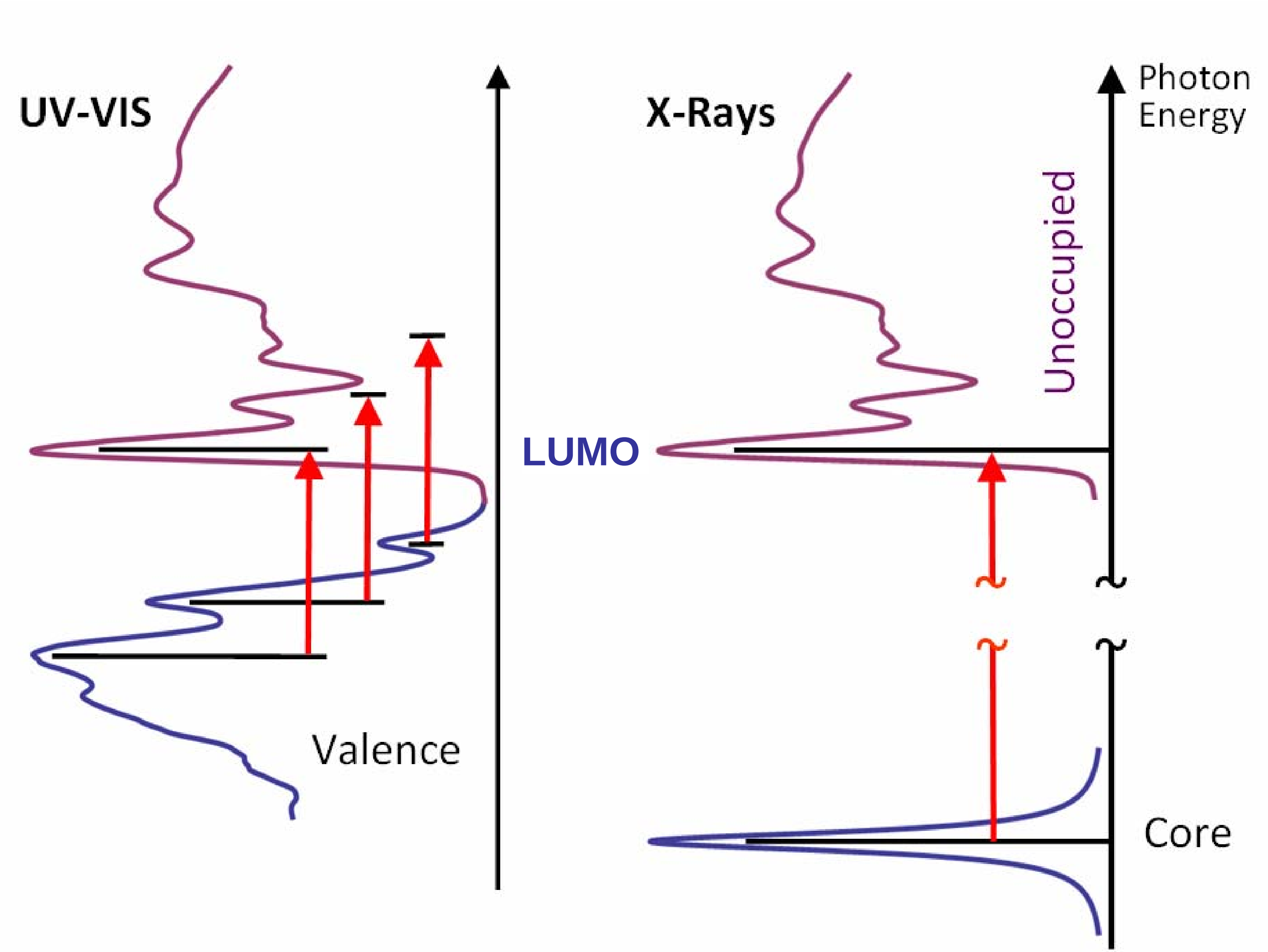


Need a tunable, polarized source of soft X-rays

Swiss Light Source

Shanghai Light Source

Absorption spectroscopy

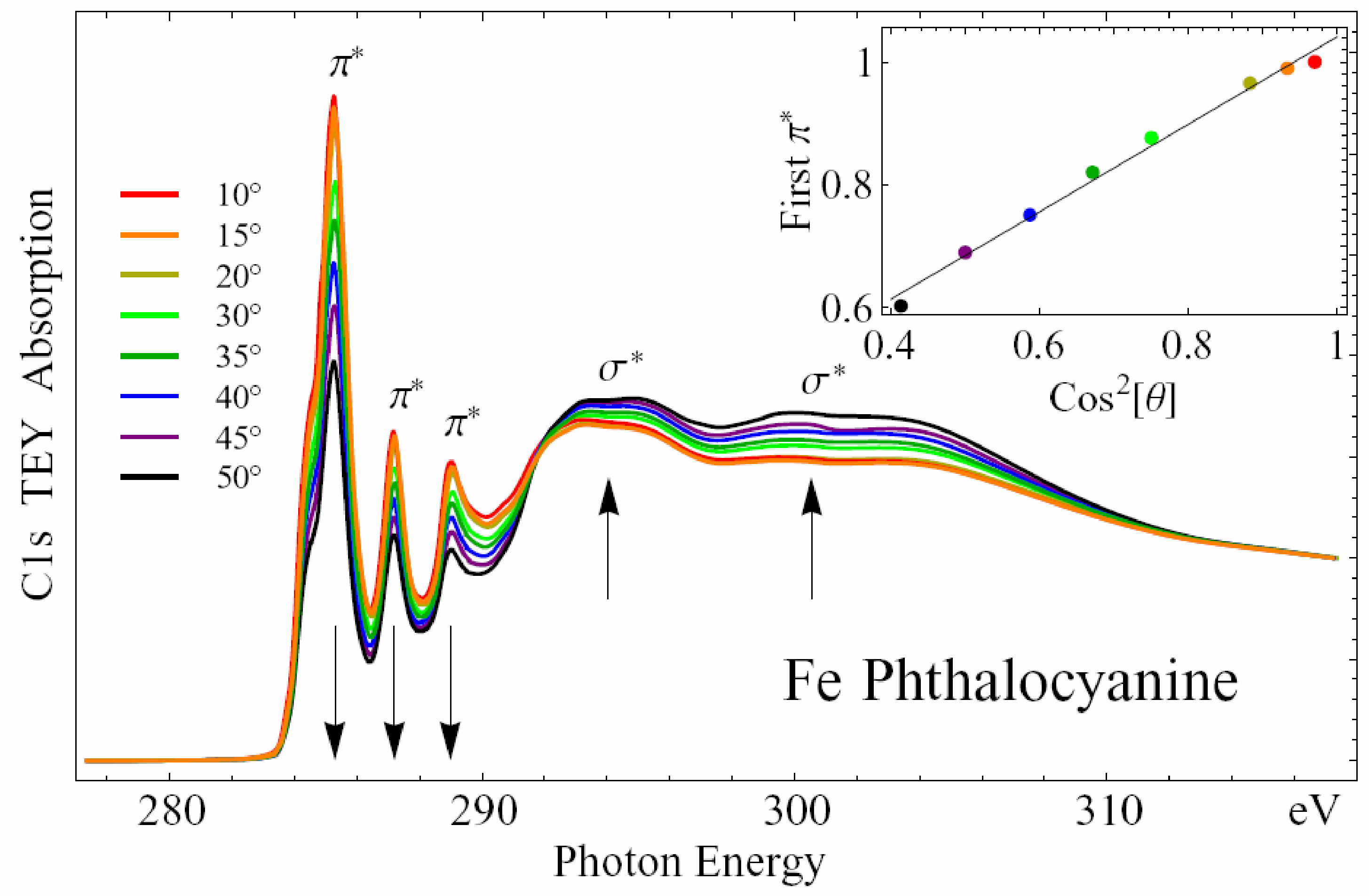


ambiguous **unique, element-specific**

Polarization dependence $\Rightarrow$ Orbital orientation

$\cos^2\theta$ dipole pattern with a maximum when the polarization vector is parallel to the orientation of the 2p orbital

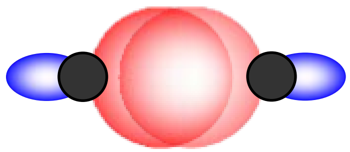
Transitions from the C1s core level to C2p valence orbitals



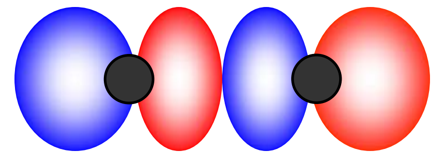
Cook et al., J. Chem. Phys. **131**, 194701 (2009).

σ- and π- bonds

σ-bond:

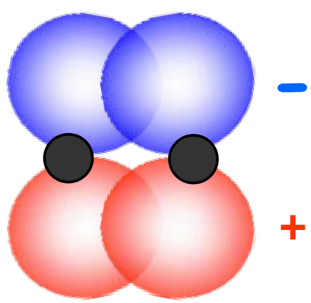


σ orbital



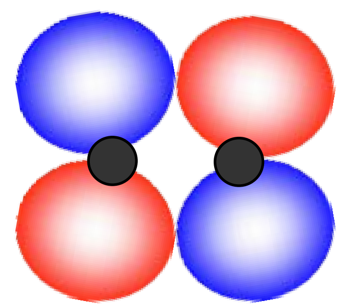
σ^* orbital

π-bond:



π-orbital

(bonding)



π^*-orbital

(antibonding)

Different projections of the density of states

Filled states:

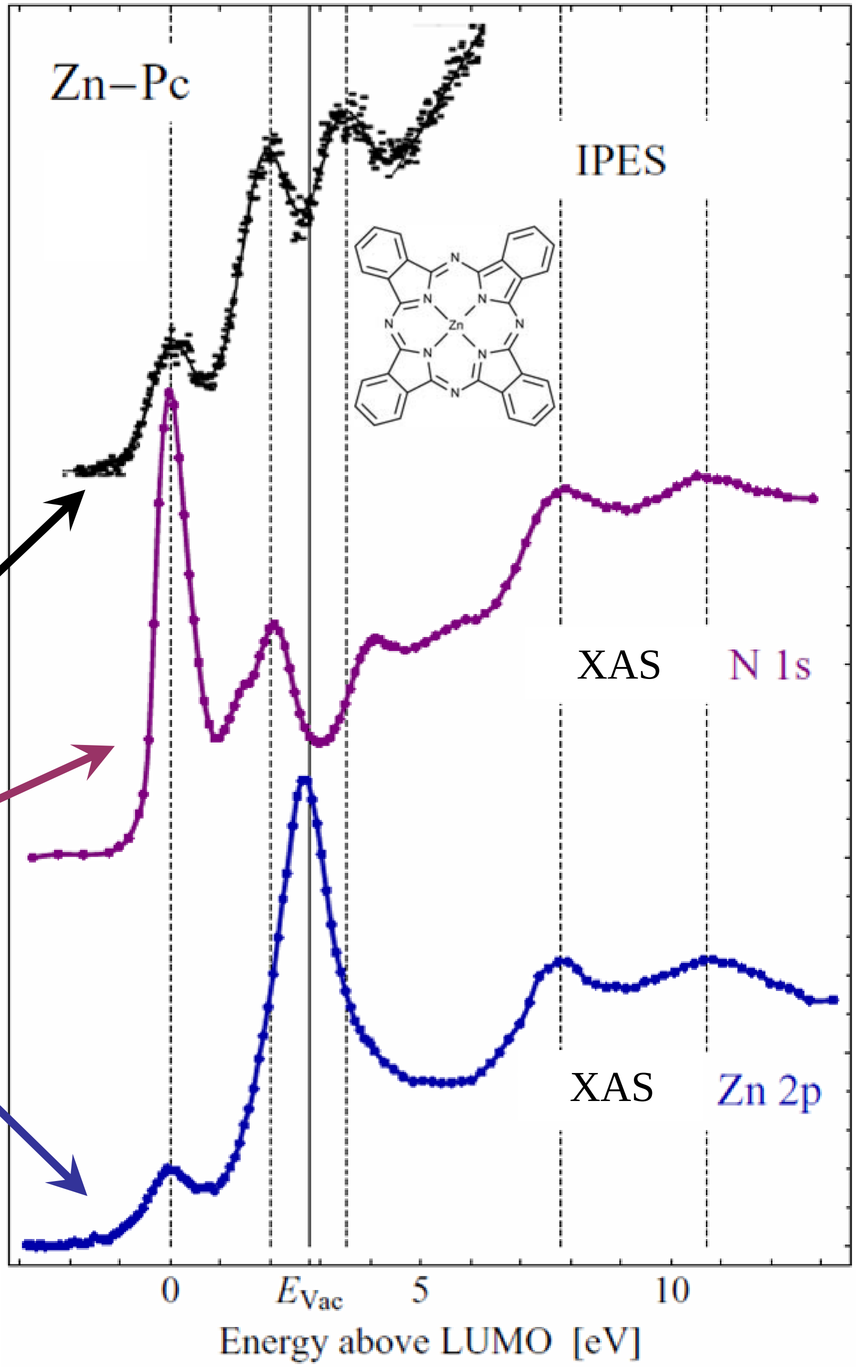
Photoemission: UPS, XPS

X-ray emission spectr.: XES

Empty states:

Inverse photoemission: IPES

X-ray absorption spectr.: XAS



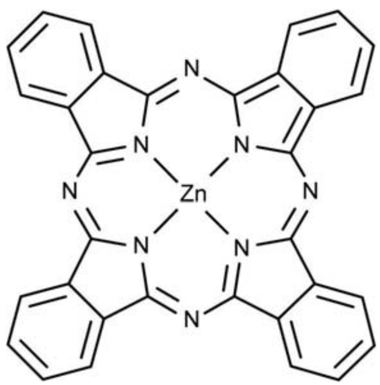
XAS: Cook et al., J. Chem. Phys. **134**, 204707 (2011).

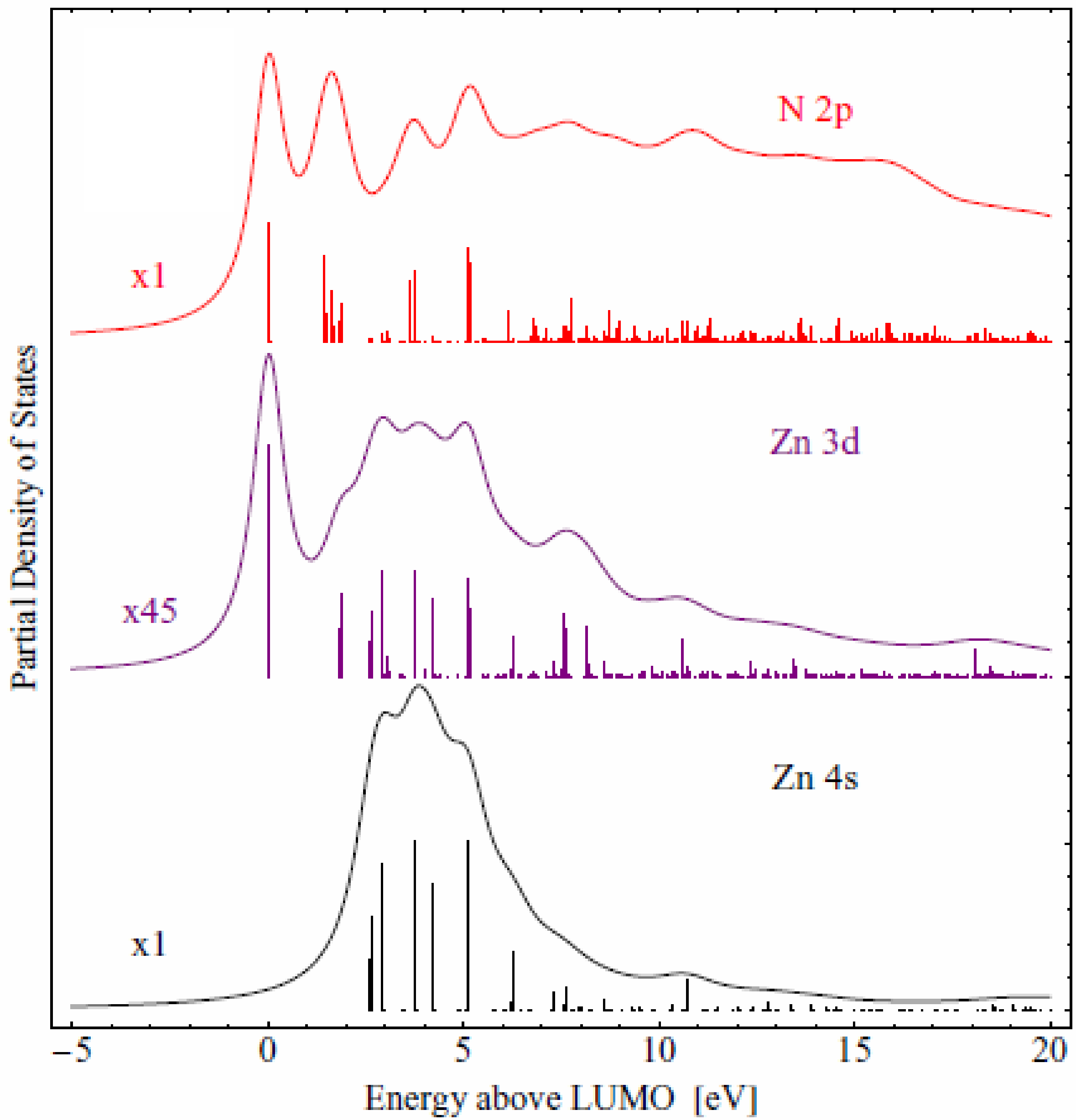
IPES: Gao and Kahn, Org. Electron. **3**, 53 (2002).

Calculated projections of the density of states

Levels get very dense at higher energy.

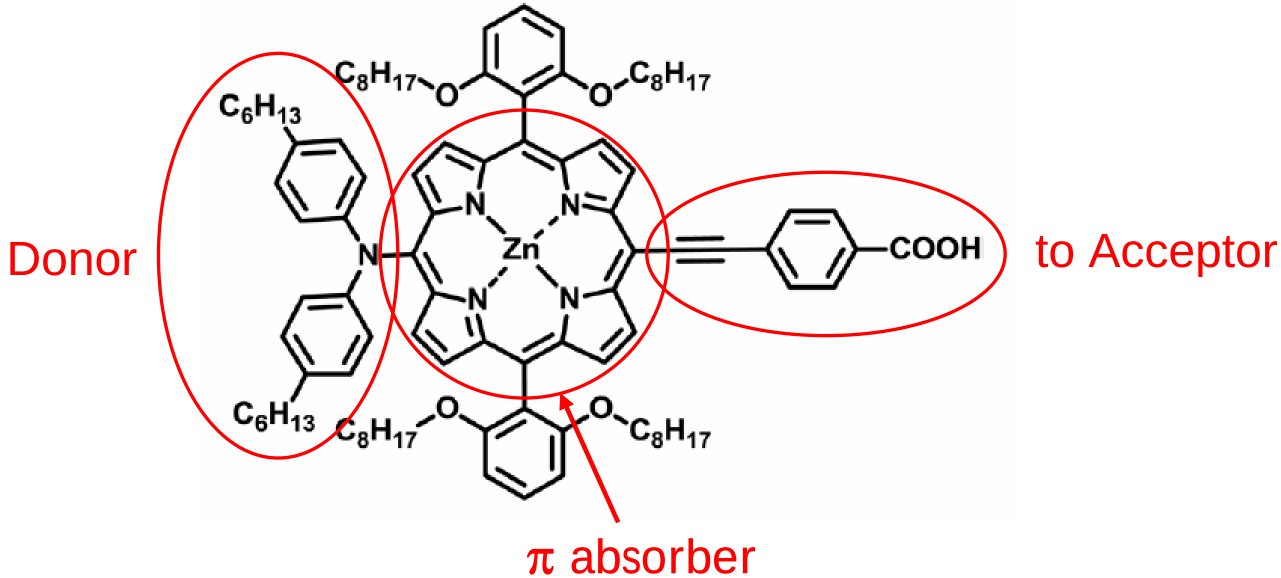
Focus on the LUMO.





Cook et al., J. Chem. Phys. **134**, 204707 (2011).

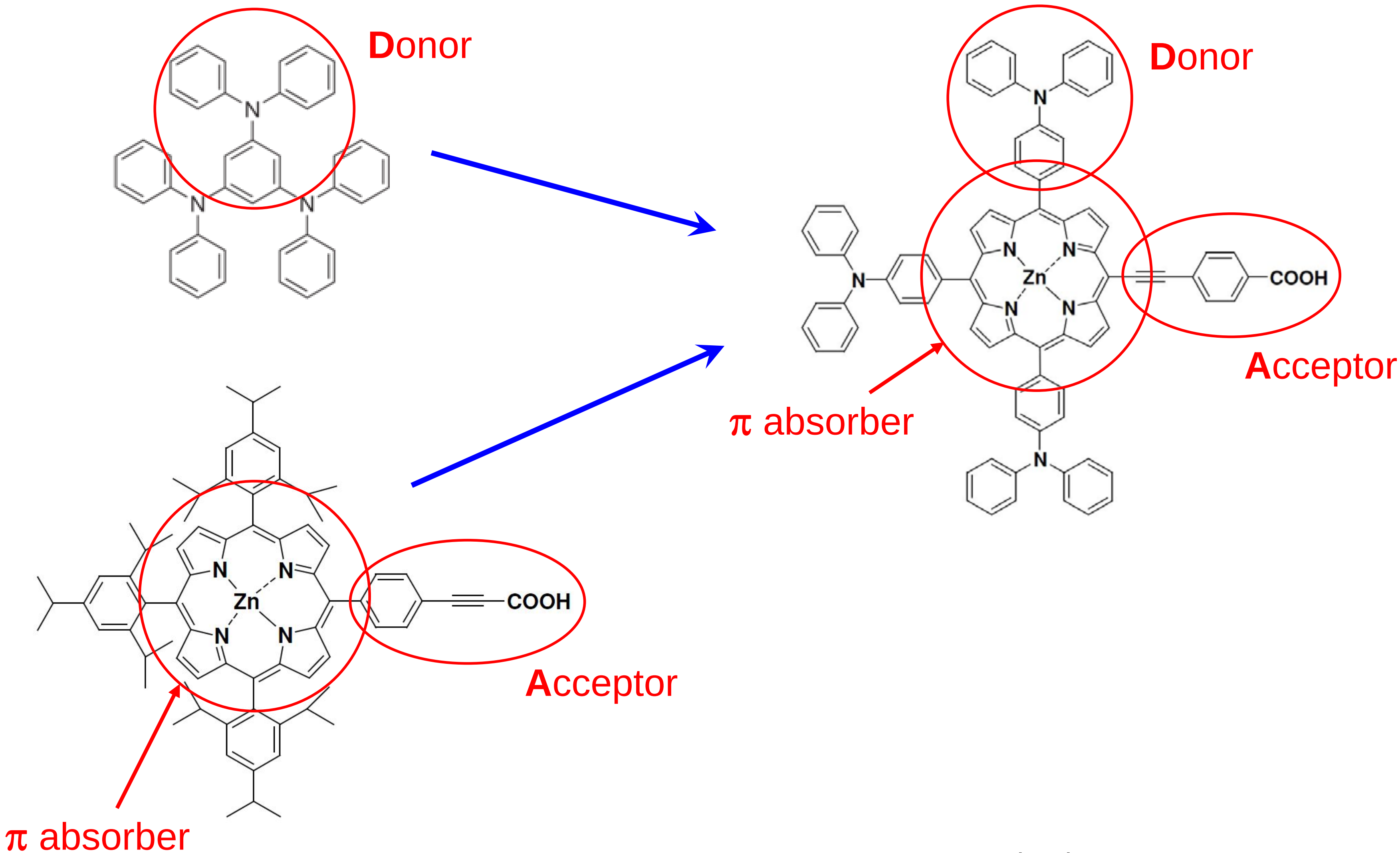
Combine the 3 components of a solar cell in one molecule with atomic perfection



Set record efficiency for dye-sensitized solar cells (12.3%)

Grätzel group: Yella et al. Science **334**, 629 (2011).

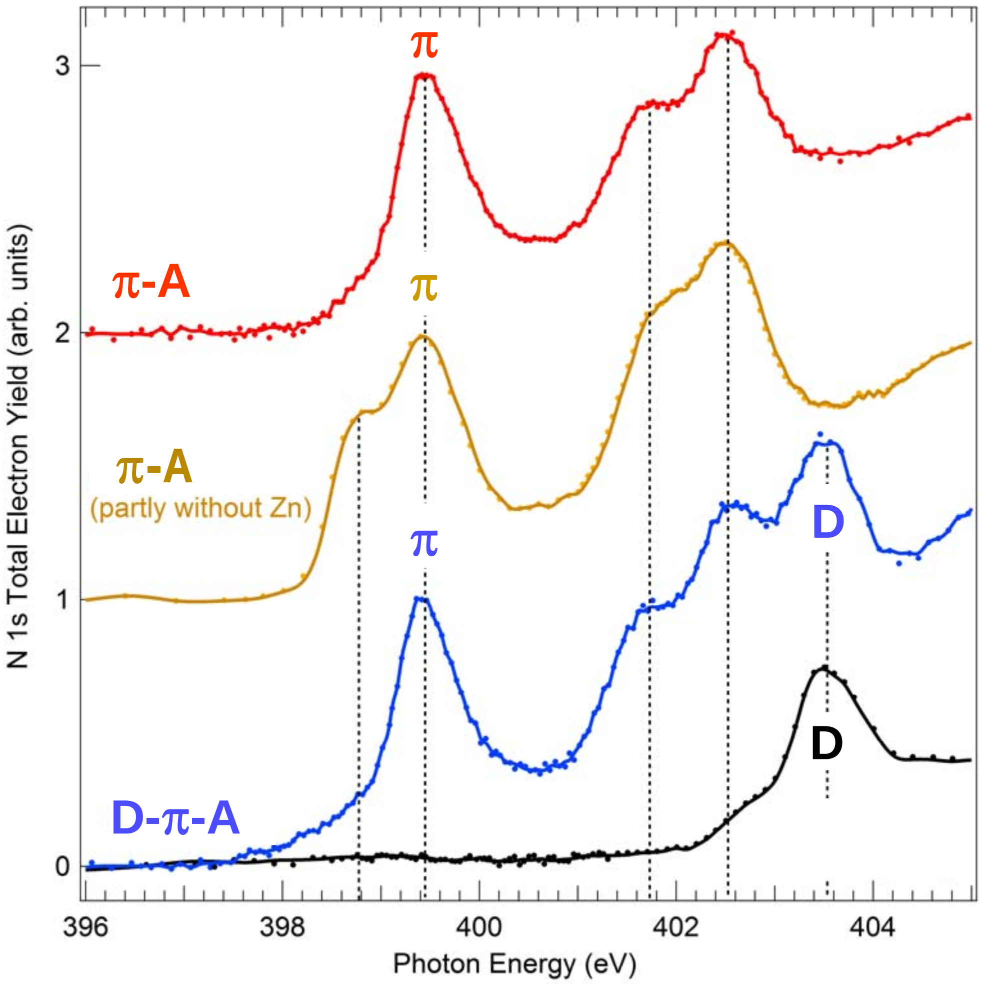
Probe the components individually



Custom synthesis:

Ragoussi et al., Eur. J. Org. Chem., Vol. 2013, p. 2832 (2013).

Identify specific atoms by their core levels and orbitals



This led to improved synthesis.

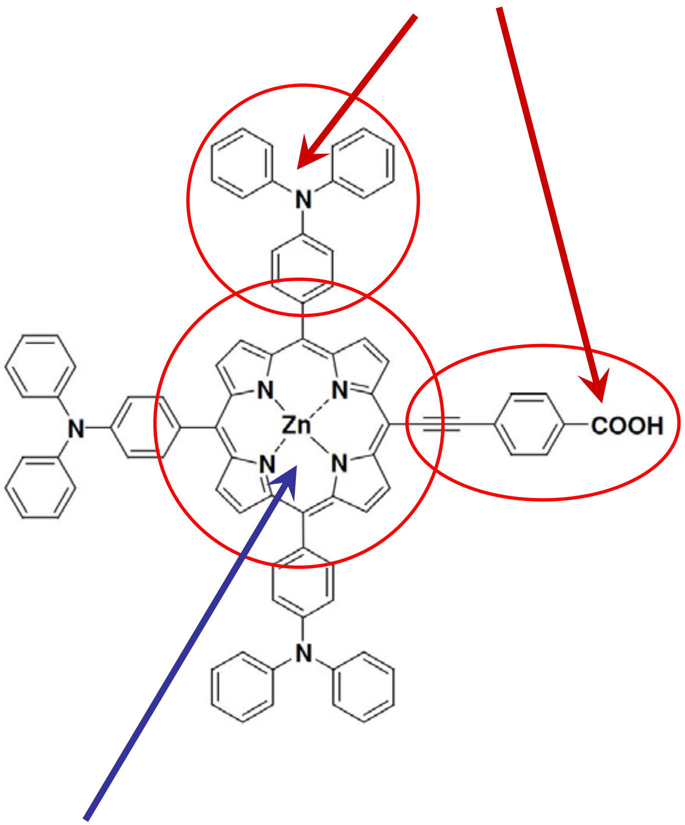
Weak point in the synthesis identified by theory (missing Zn atom).

Zegkinoglou et al., J. Phys. Chem. C **117**, 13357 (2013).

Beyond energy levels: time-resolution
Carrier lifetime vs. charge transfer rate

A dream experiment in photovoltaics and photoelectrochemistry

Probe the carriers on their way out with soft X-rays.

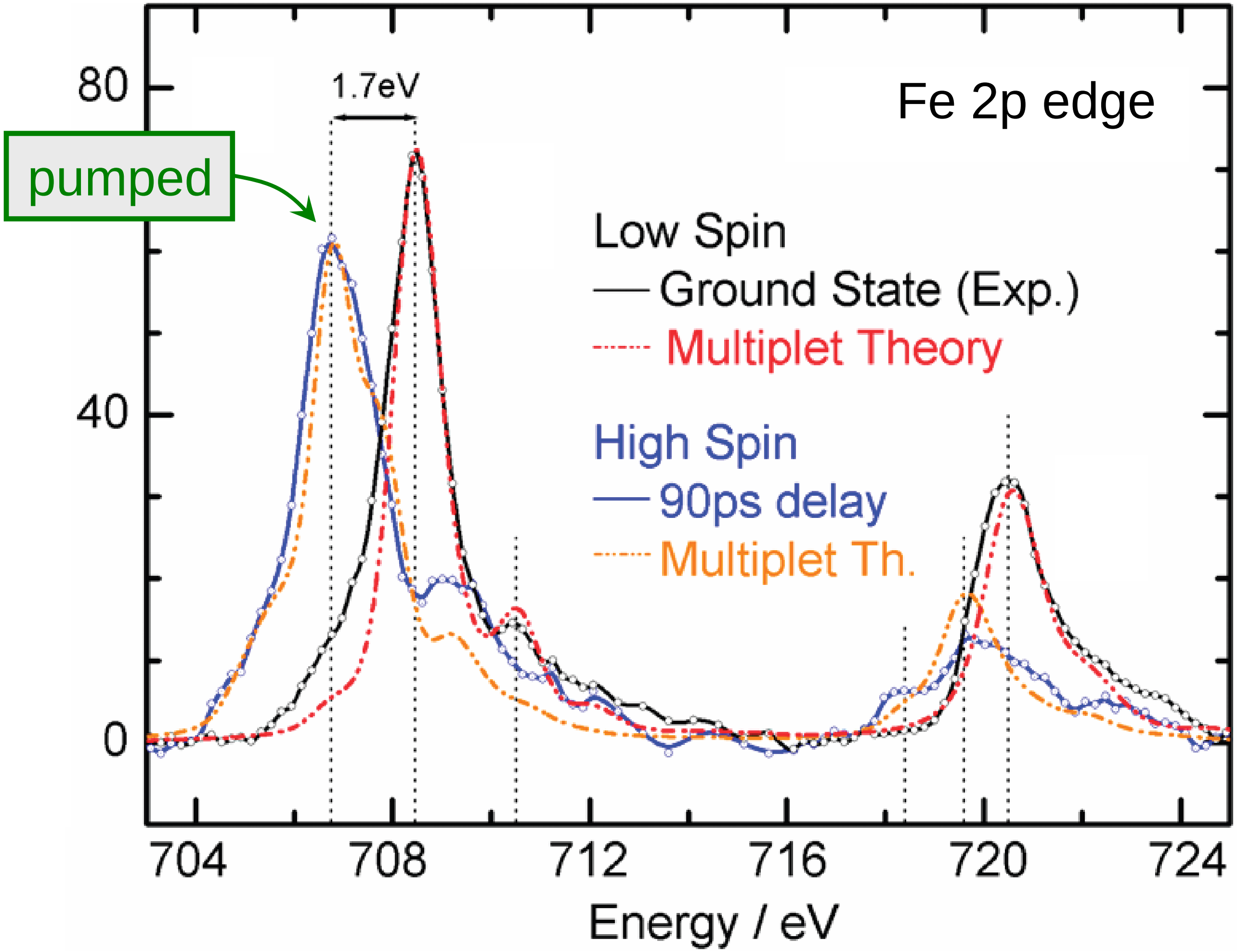


The lifetimes of the charge carriers affect the photocurrent dramatically.
When and where are the carriers lost?
(inside a molecule, across a device)

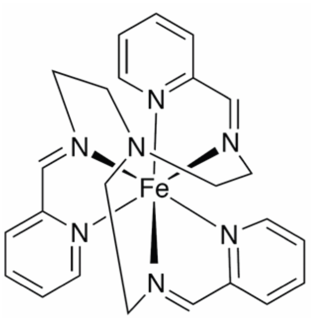
Pump the center with visible.

"Heroic" experiments

Need an X-ray laser to make such experiments accessible.



Detect an excitation at a specific atom in a molecule.



Huse et al., JACS **132**, 6809 (2010)

Summary: pros and cons of solar energy

No fuel cost.	Avoid paying hostile suppliers.
Available everywhere.	Avoid shortages, fluctuating oil price.
Does not pollute.	Avoid smog, mercury, fracking, …
Can be decentralized.	Independence is a great incentive.

Up-front investment.	
Energy storage overnight.	Make solar fuel during the day (possibly PV-assisted water splitting), run fuel cell at night (Bloom box).