Designing Materials for Solar Energy Conversion

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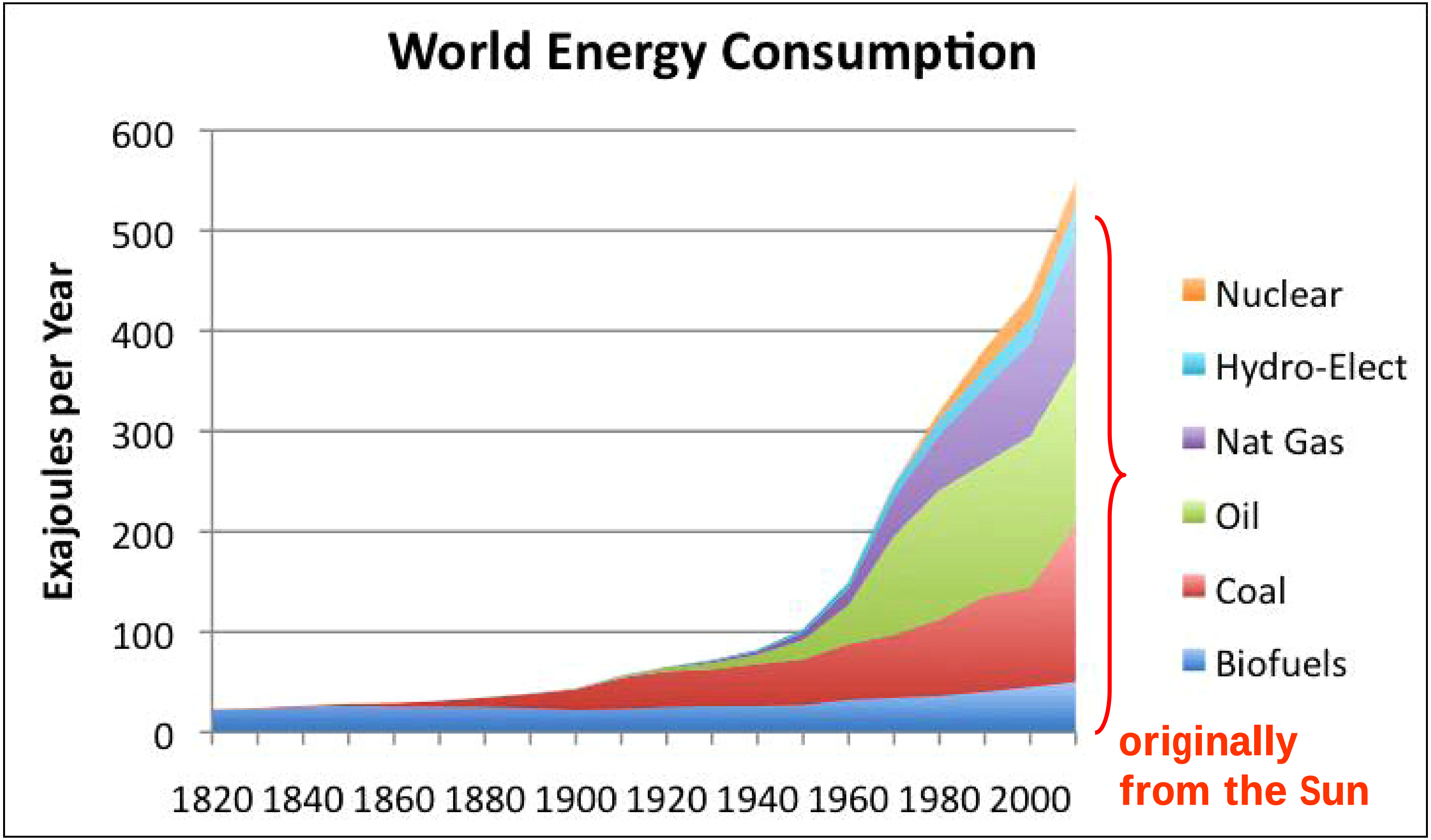
Where will our energy come from?



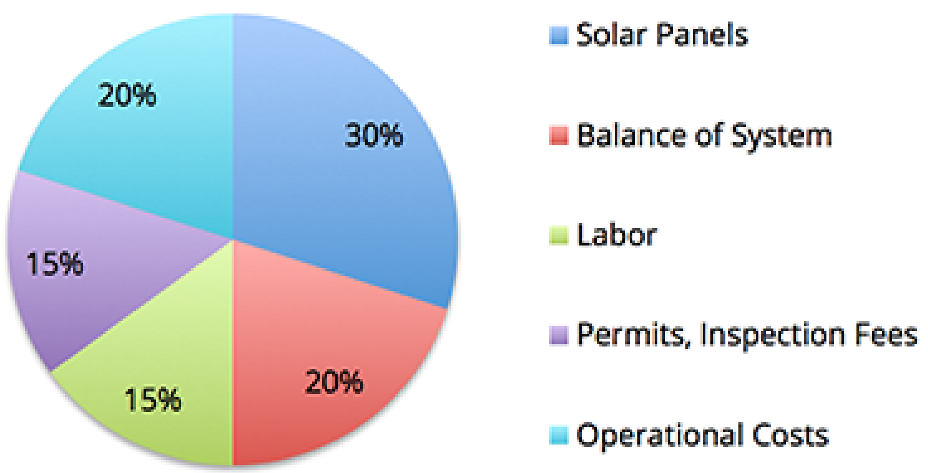
100×100 miles^2 of solar cells could produce all the electricity for the US .

$1\ \text{kW/m}^2$	Incident solar power
$\times\ 1/4$	Useful daylight
$\times\ 0.20$	Efficiency of a solar cell
$\times\ 2.6 \cdot 10^{10}\ \text{m}^2$	100×100 miles^2
$=\ 1.3\ \text{TW}$	
$\approx\ 1\ \text{TW}$	Electric power generated in the US

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

How much would it cost ?

	0.5 $/W	Price of solar panels per Watt
×	1 TW	Electric power generated in the US
=	0.5 T$	≈ annual US defense budget



Solar panels are only a fraction of the cost. Need to work on the remainder.

Economics of solar versus fossil energy

- **Solar energy is free, fuels are not: $/kW vs. $/kWh**

  Figure of merit for solar is energy payback time (1-4 years).

  Want long life span (25 years for Si)

- **Today the price of solar cells is only ≈¼ of the total cost. The rest is for support structure, labor, red tape, ...**

  Higher efficiency ⇒ smaller panels ⇒ reduced costs

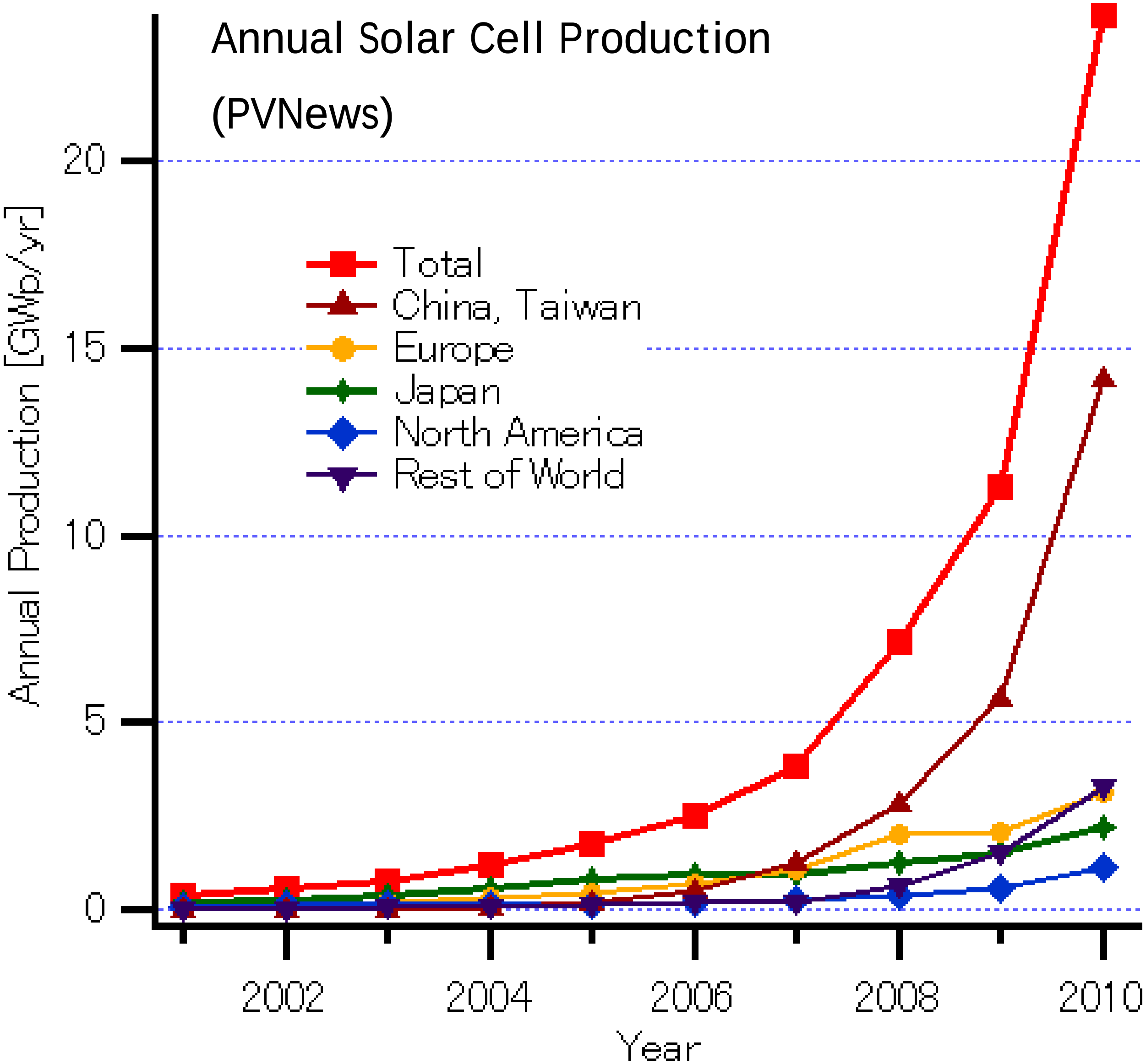
  Design solar cell support into buildings

  Reduce legal, financial hurdles (Solar City)

On June 8, 2014 Warren Buffett revealed that **Berkshire Hathaway Inc**'s (NYSE: BRK-B) subsidiary MidAmerican Energy (now renamed Berkshire Hathaway Energy) has invested $15 billion into solar and wind projects. Buffett added, "there's another $15 billion ready to go, as far as I'm concerned." ... three major solar investments totaling $6.02 billion.

The Motley Fool

Solar cell production rises quickly, but from a small base

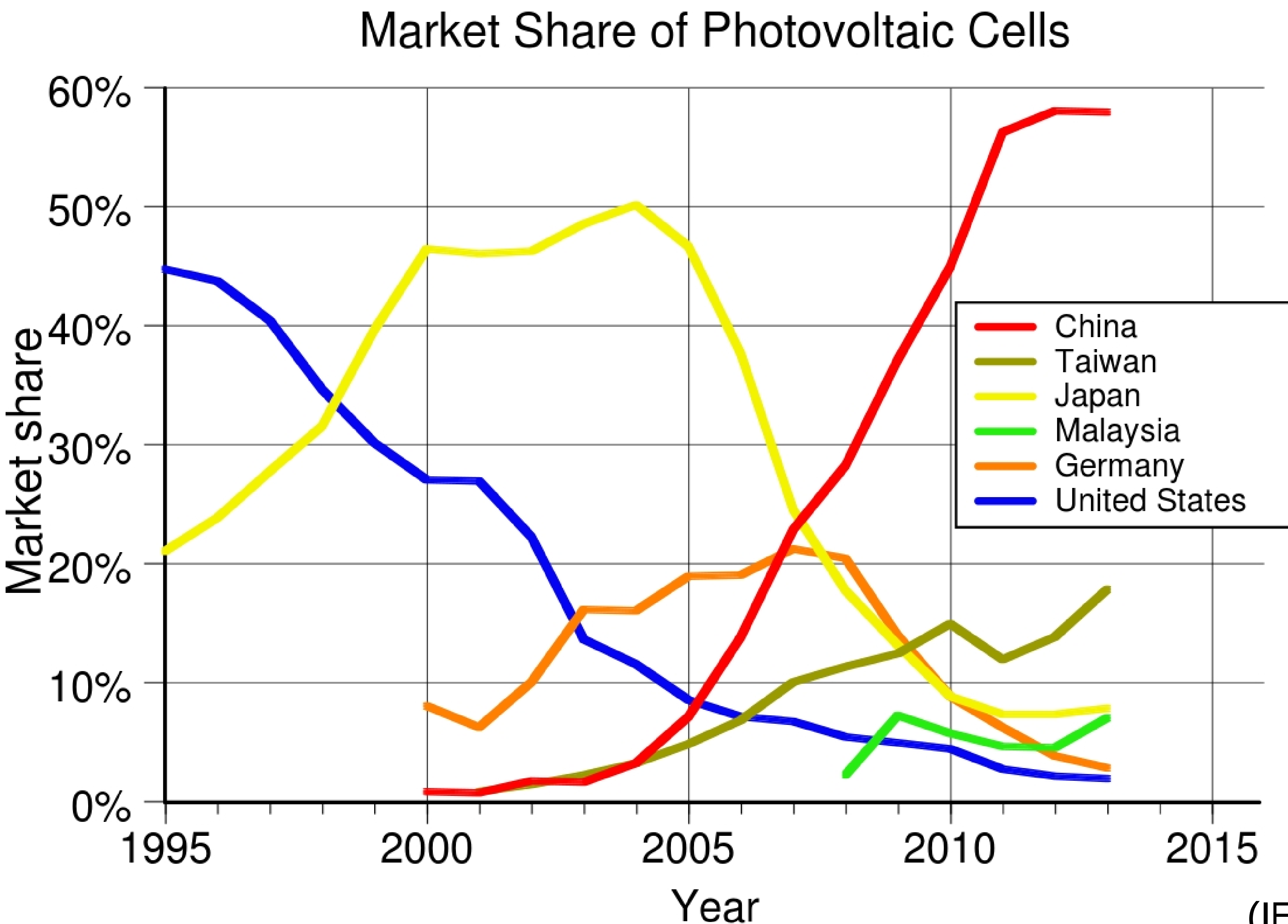


Rapid growth in China.

Substantial in Europe.

US is behind.

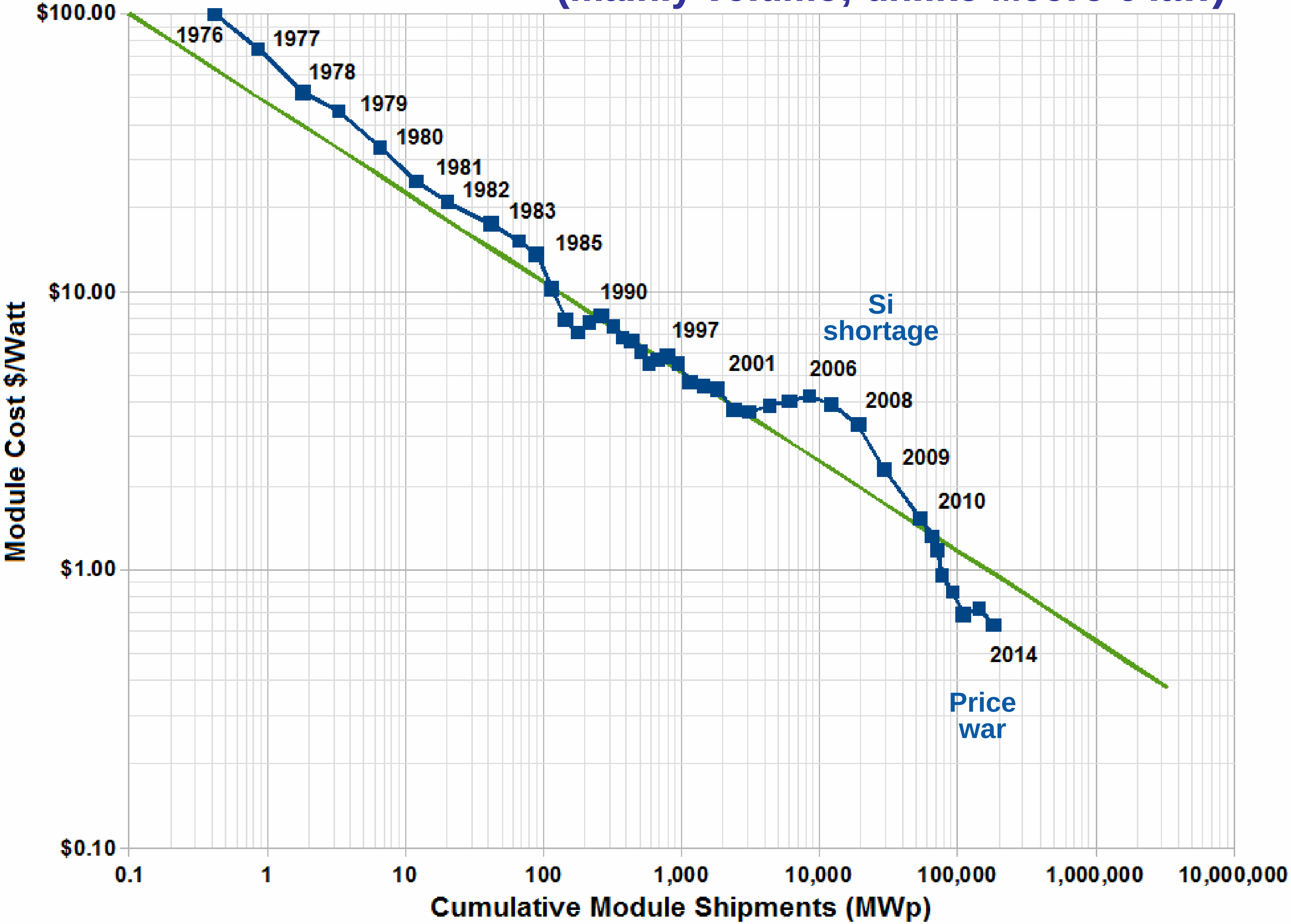
China took over



(IEA-PVPS)

Silicon solar cells dominate, but progress is slow

(mainly volume, unlike Moore's law)



Store solar energy to become self-sufficient

There are many methods, but no obvious winner right now:

Batteries, pump water uphill, store molten salts, …

My favorite for the long term:

Convert solar energy to fuel during the day.

Convert fuel to electricity via fuel cells at night (or during winter).

For the time being:

Store conventional fuel, use it in a backup generator:

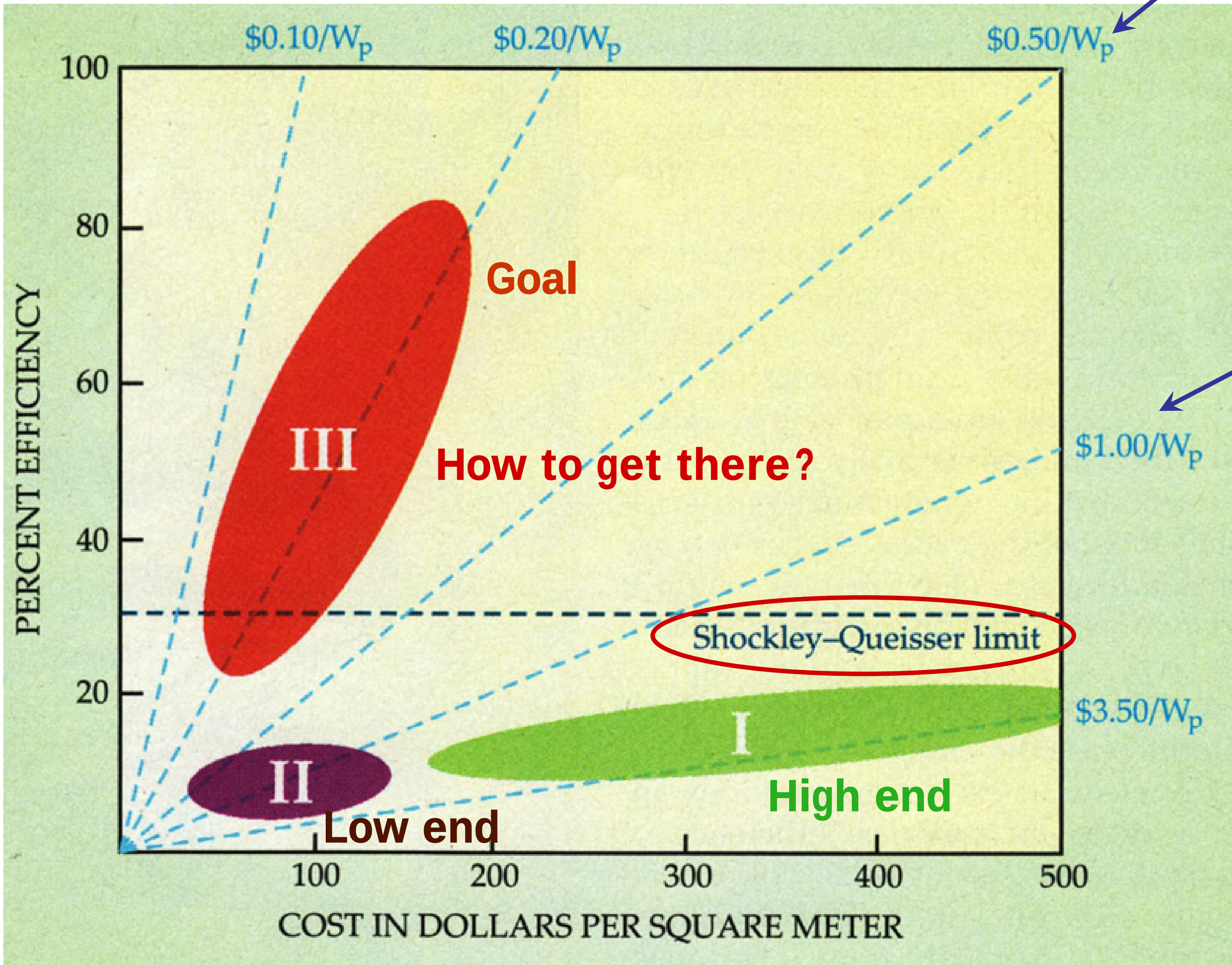
Large scale: Gas-fired power plant (Archimede project in Sicily)

Small scale: Fuel cell (“Bloom box”, Sunnyvale CA)

Cost versus efficiency

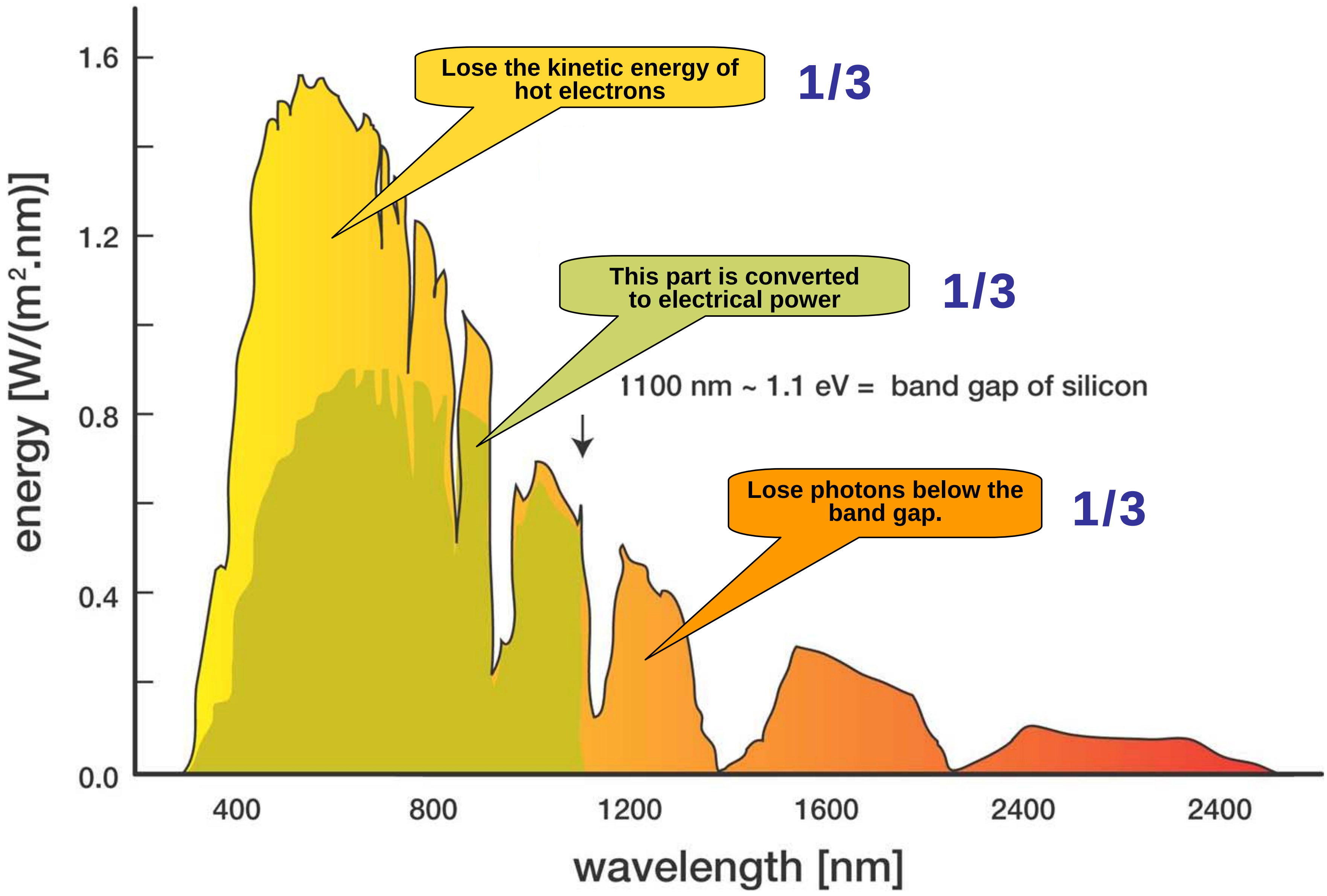
½ $/W now

1 $/W then



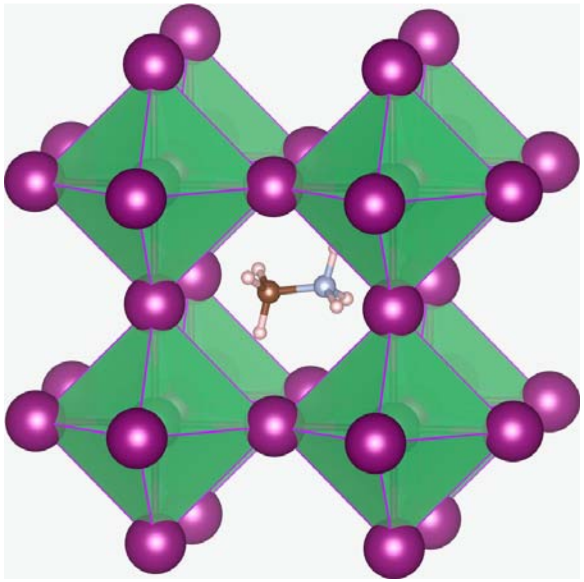
Physics Today
March 2007

33% limit for a single junction ⇒ Multiple junctions in series (Tandem cells)



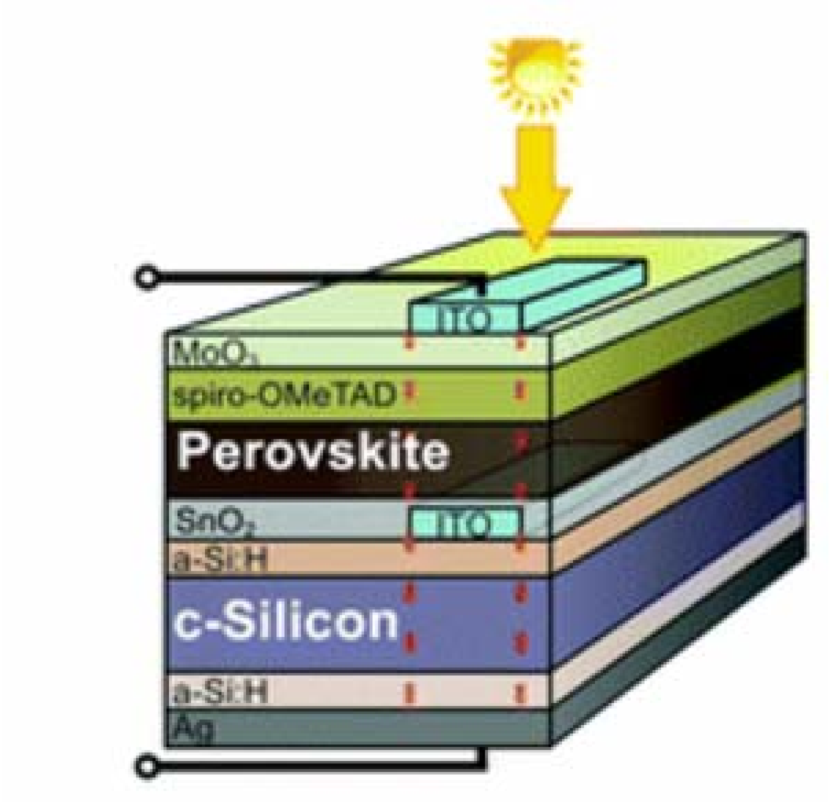
Perovskite on silicon tandem cell

Perovskite



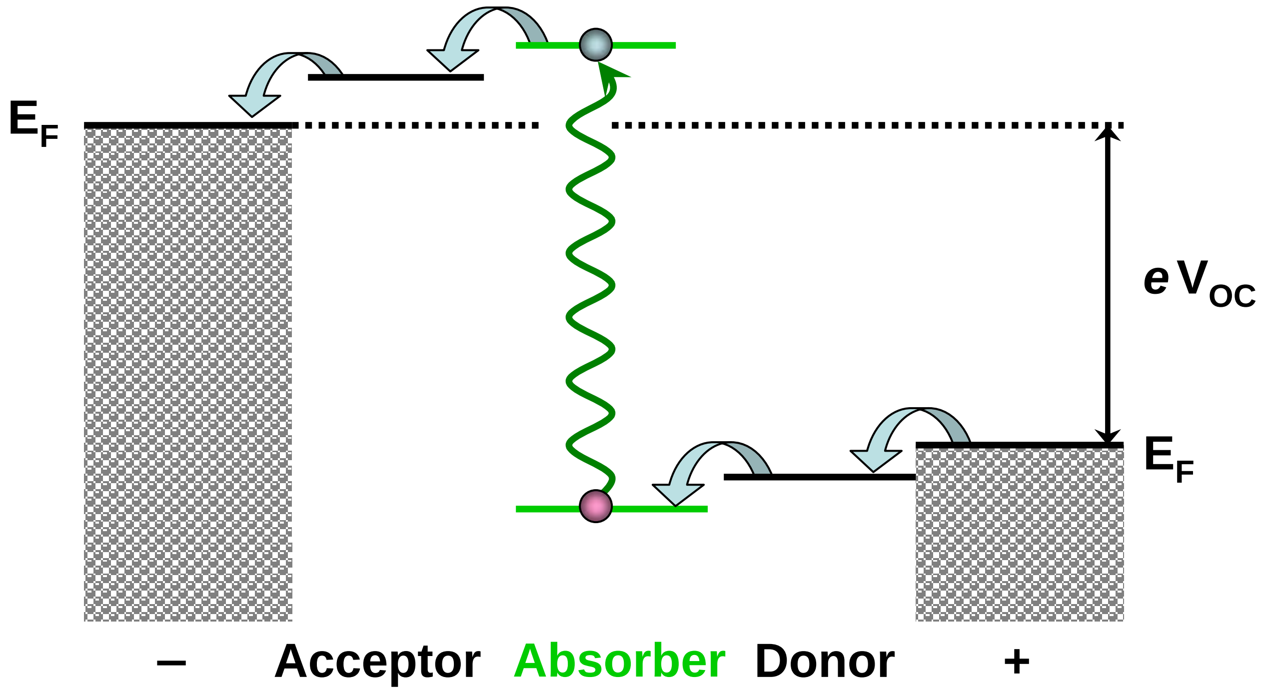
Halogen **(Pb inside)**

Methylammonium molecule



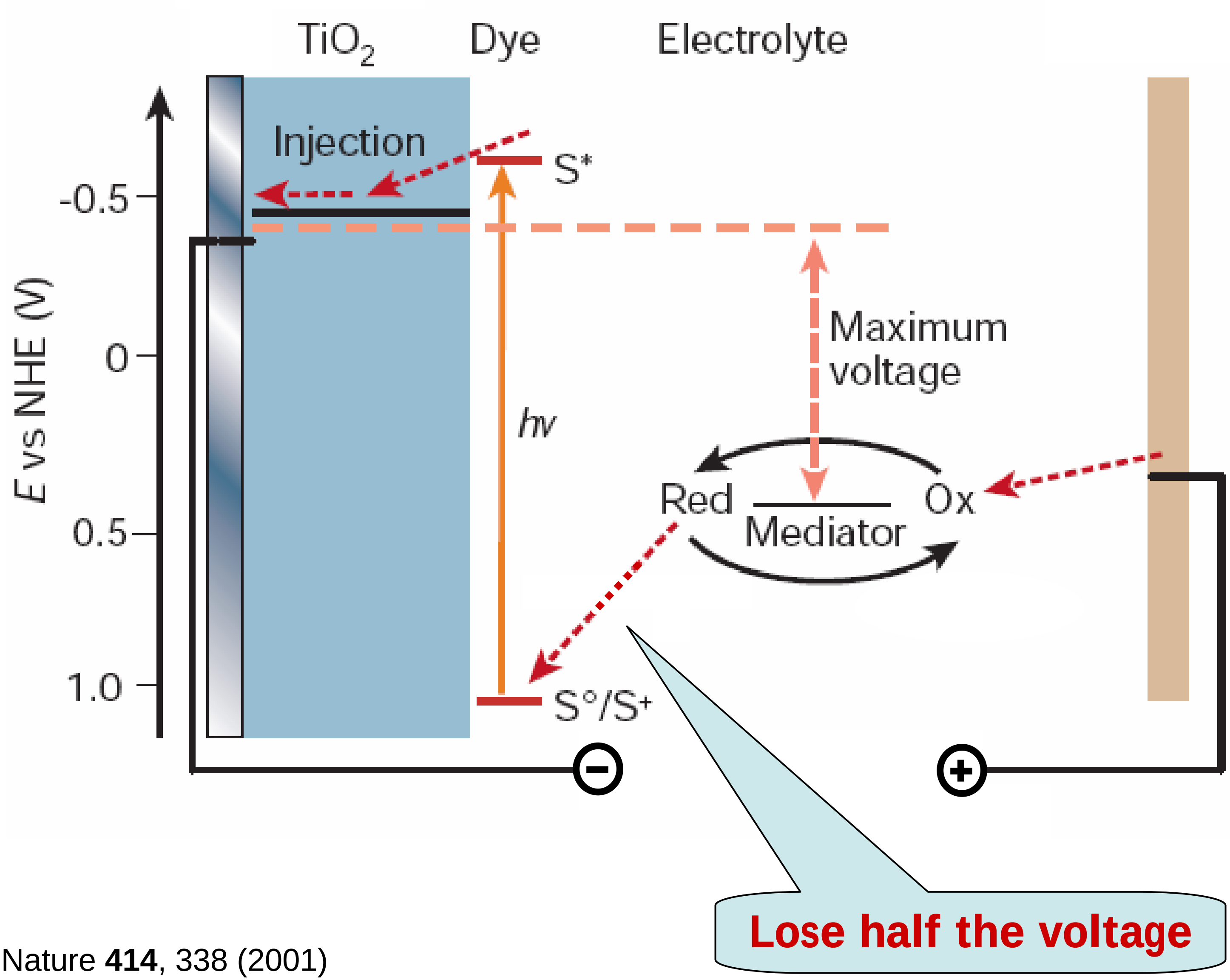
Albrecht et al., Energy Environ. Sci. **9**, 81 (2016).

Design a solar cell from scratch:
4 energy levels, 3 materials



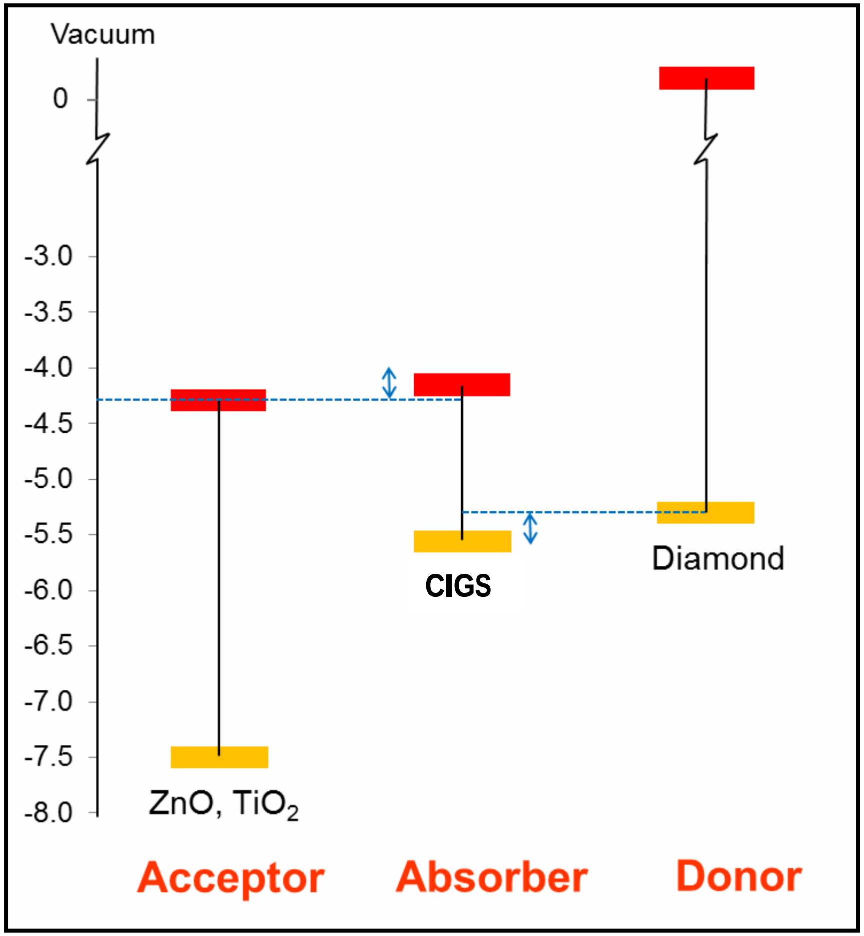
Small energy drop: Large voltage
Large energy drop: Large current
Want both

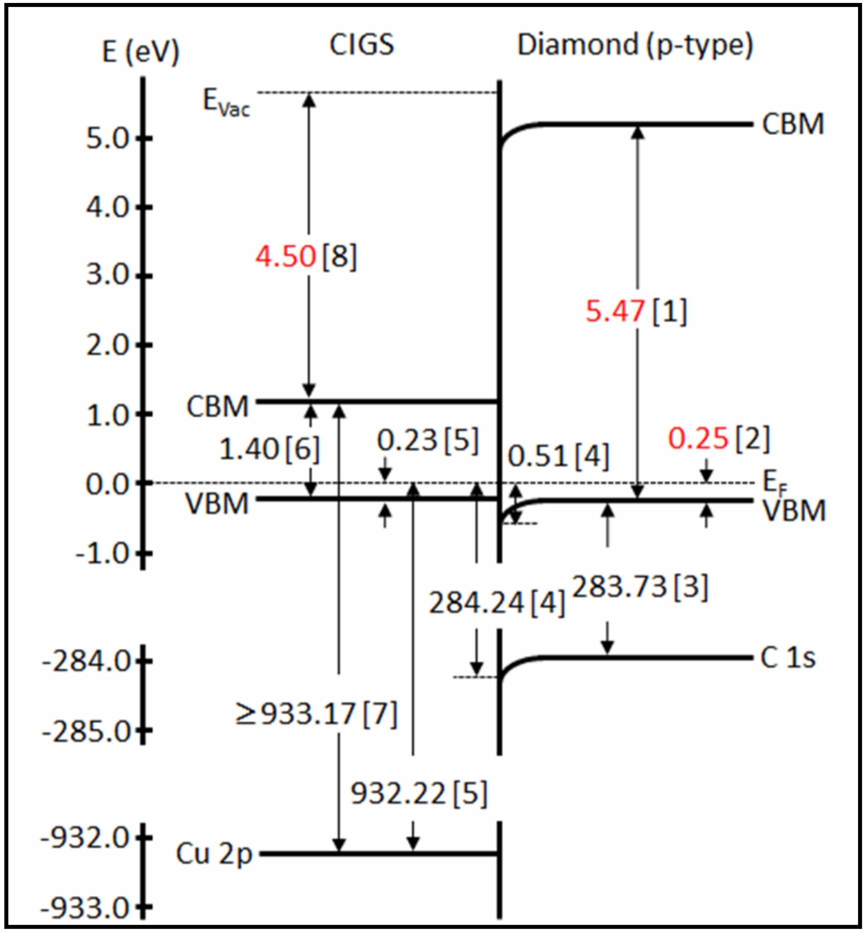
Combine 3 materials in dye-sensitized solar cells



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

Combine 3 semiconductors with tailored energy levels



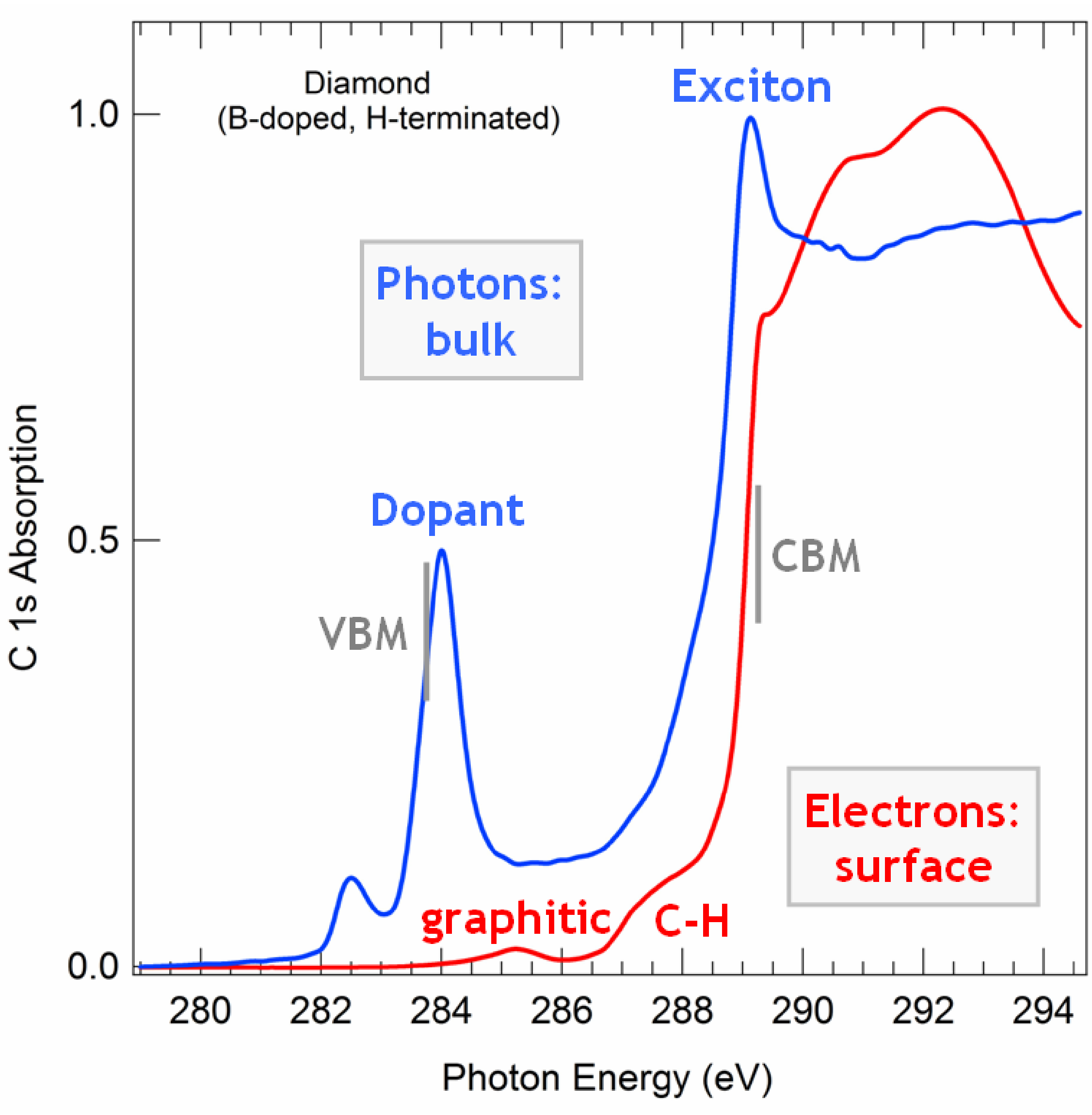


Diamond film as inert, transparent electron donor

Energy levels from various spectroscopies

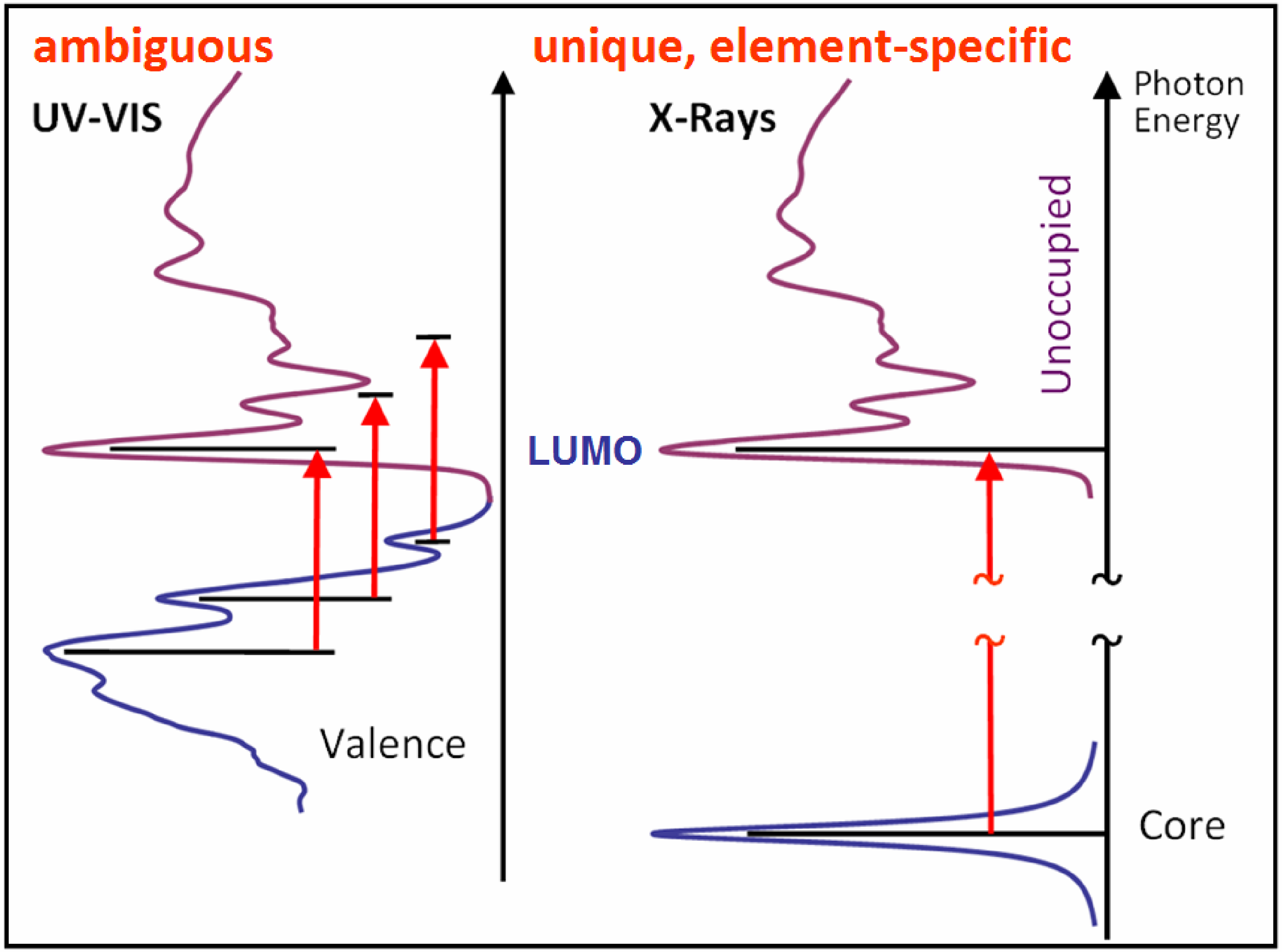
Kapilashrami et al., J. Appl.Phys. **116**, 143702 (2014).

Vary the probing depth by detecting photons vs. electrons



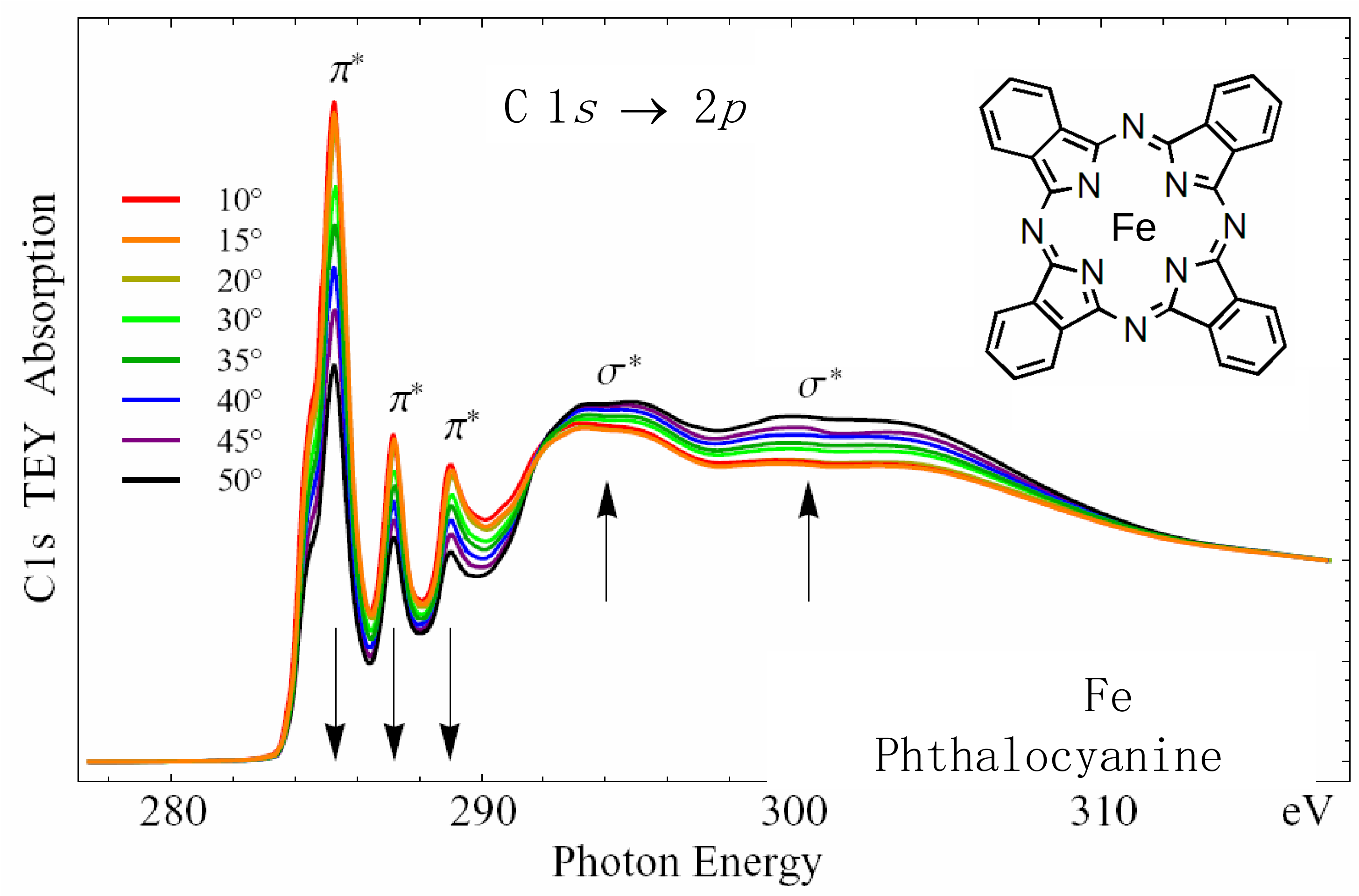
Zegkinoglou et al.
J. Phys. Chem C
116, 13877 (2012).

Energy levels from absorption spectroscopy



X-ray absorption spectra vs. polarization

Distinguish π orbitals (perpendicular to the molecule) from σ orbitals (in-plane)



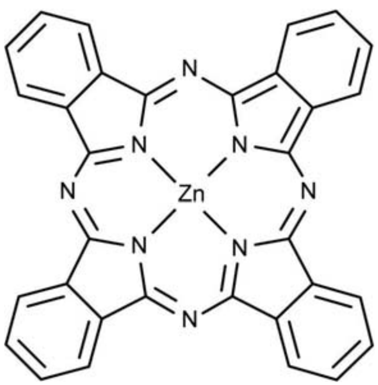
Cook et al., J. Chem. Phys. **131**, 194701 (2009).

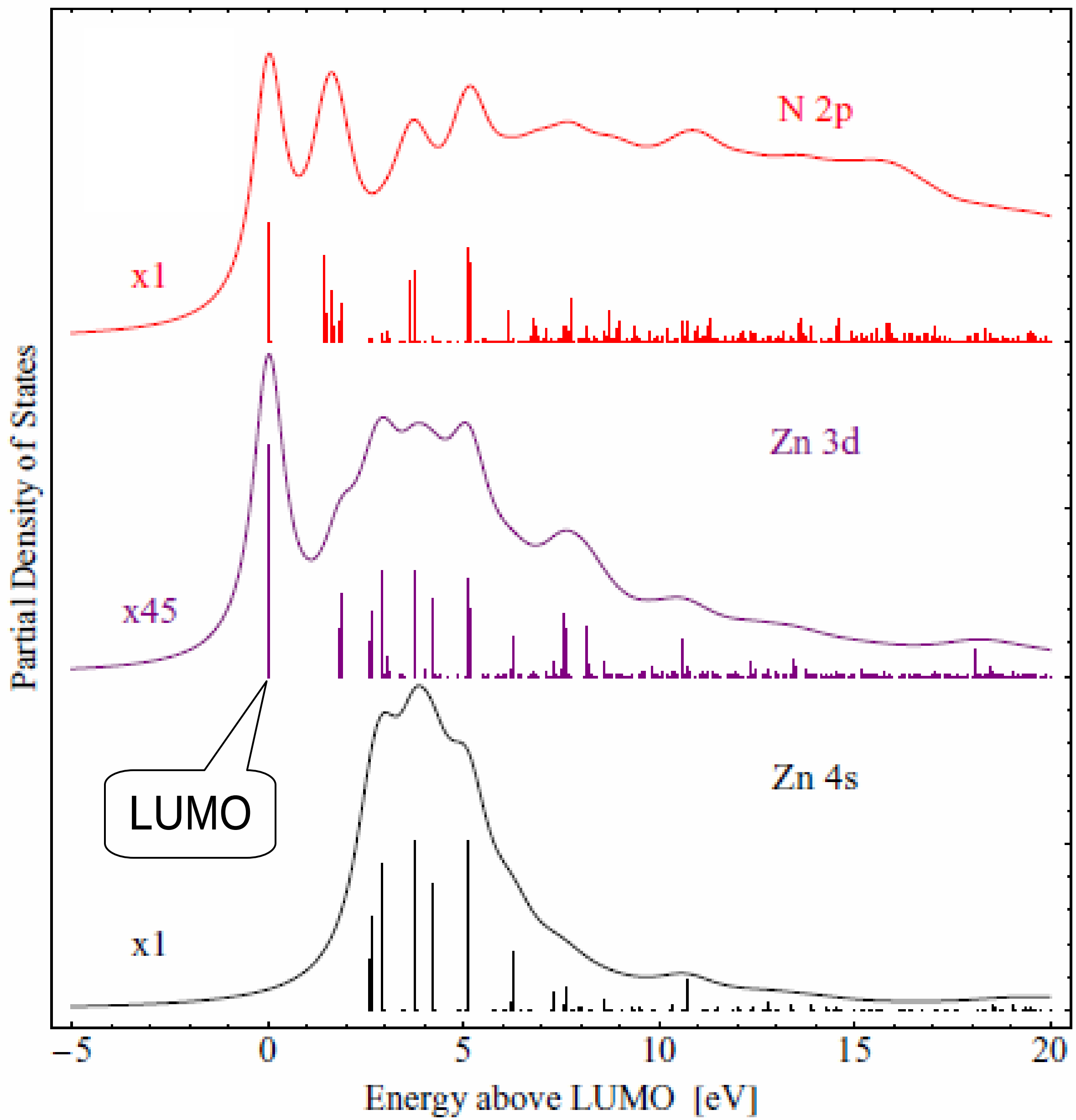
Calculate where these electrons reside, which orbital

Levels get very dense at higher energies.

Electrons quickly trickle down to the LUMO.

Focus on the LUMO.

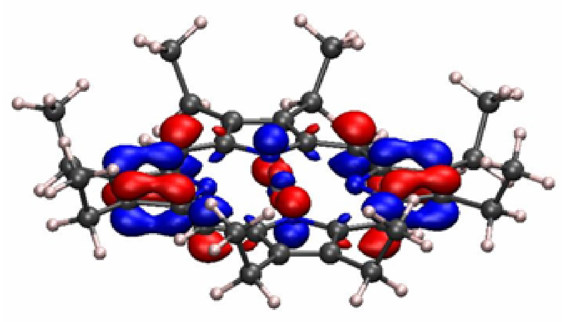


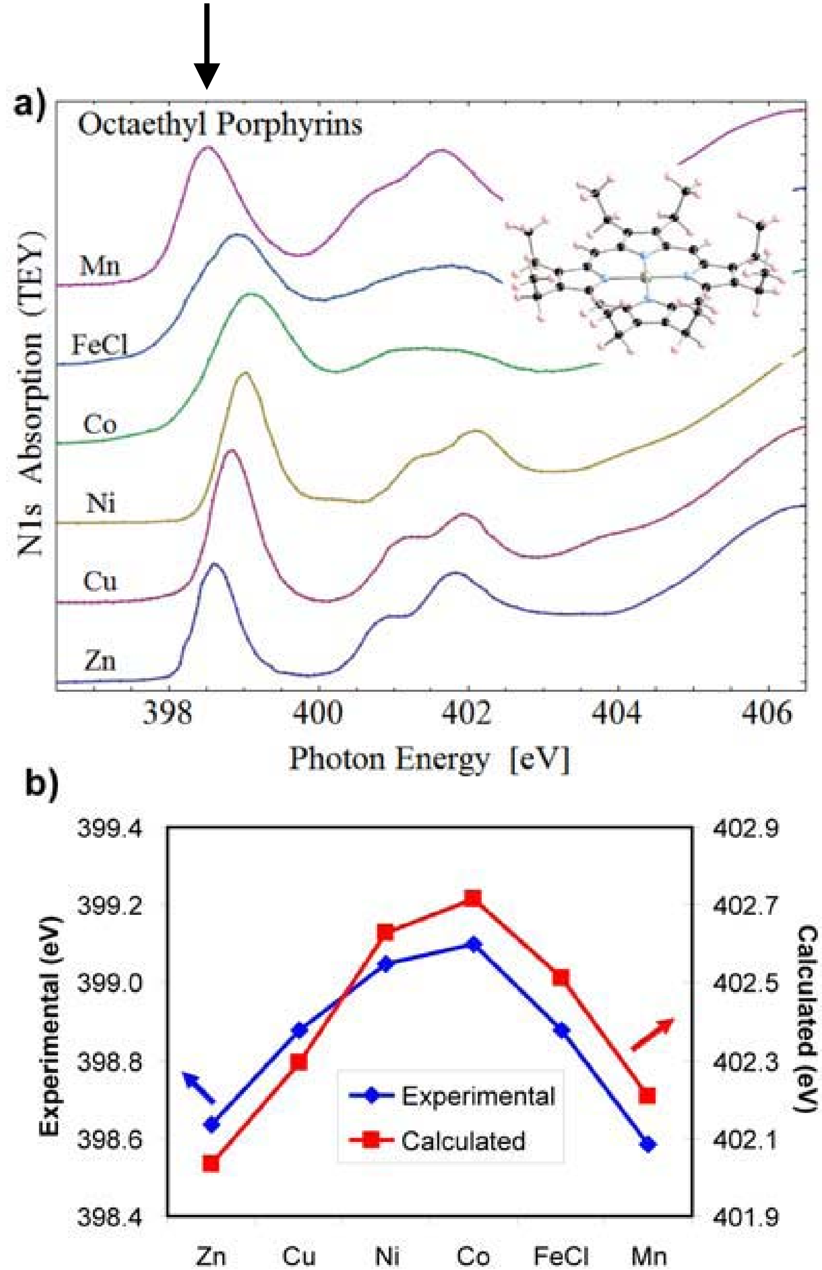


P. L. Cook et al., J. Chem. Phys. **134**, 204707 (2011).

Systematics: N1s → LUMO transition in various porphyrins

LUMO mostly N →





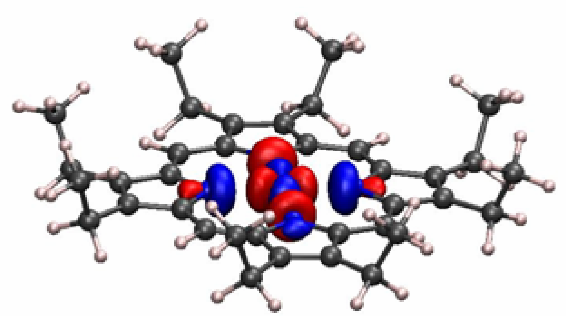
N 1s core level shift dominates.

Due to variable electron transfer from metal to nitrogen. Depends on the metal electronegativity.

Garcia-Lastra et al., J. Chem Phys. **133**, 151103 (2010)

Systematics: Metal 2p → 3d transitions at the metal atom

HOMO

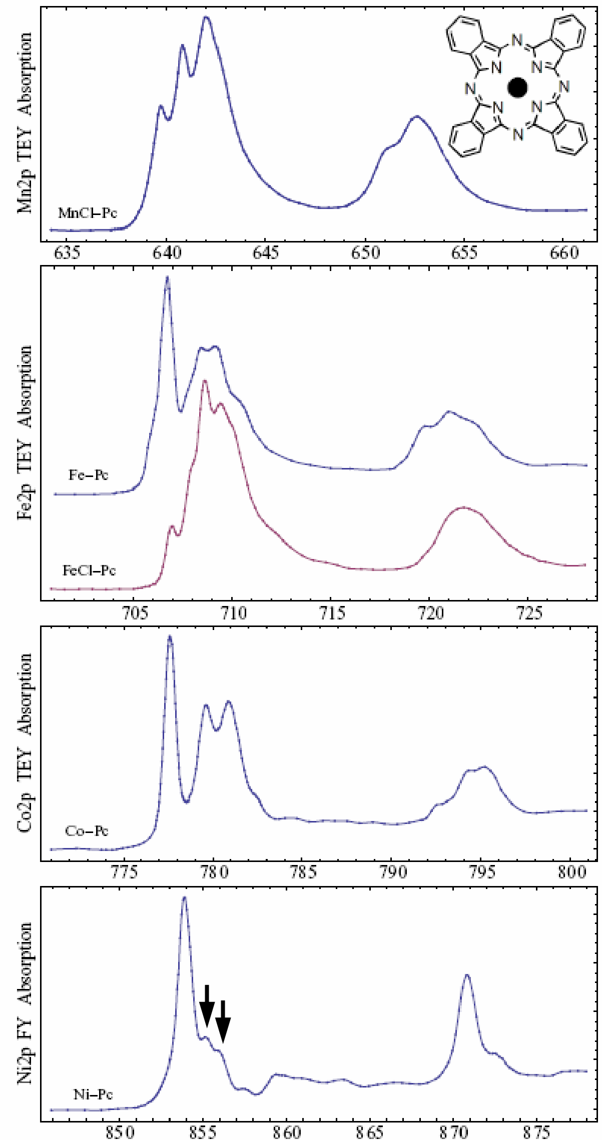


The multiplet structure reveals oxidation state and ligand field strength.

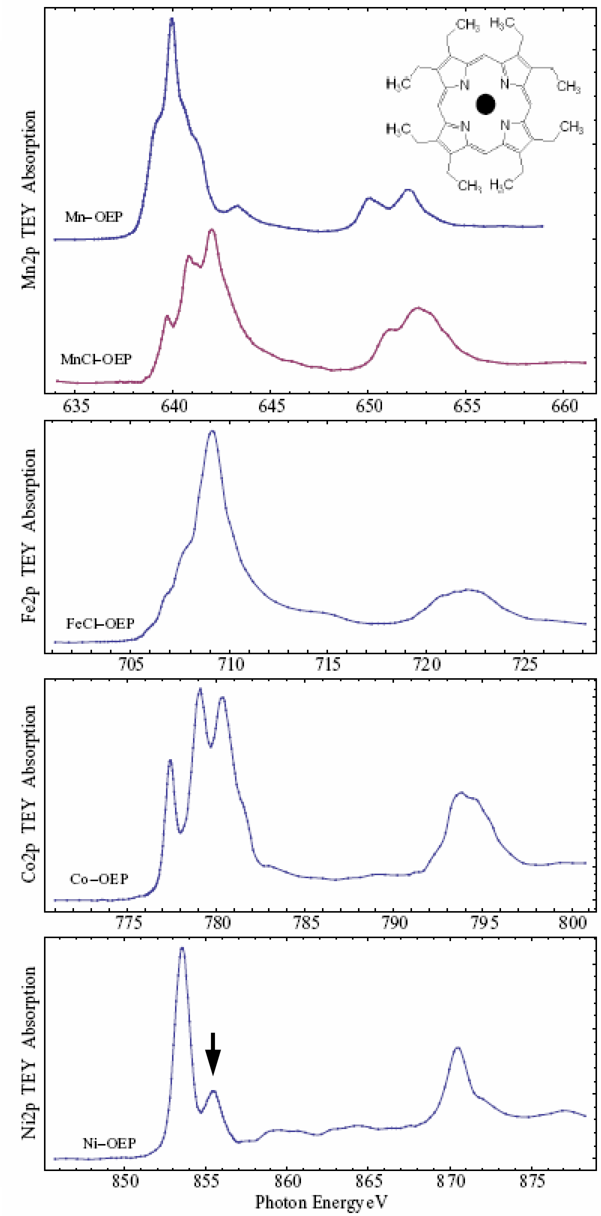
Fe, Mn are stable in both the 2+ and 3+ oxidation states. These elements catalyze charge transfer reactions in biochemistry.

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

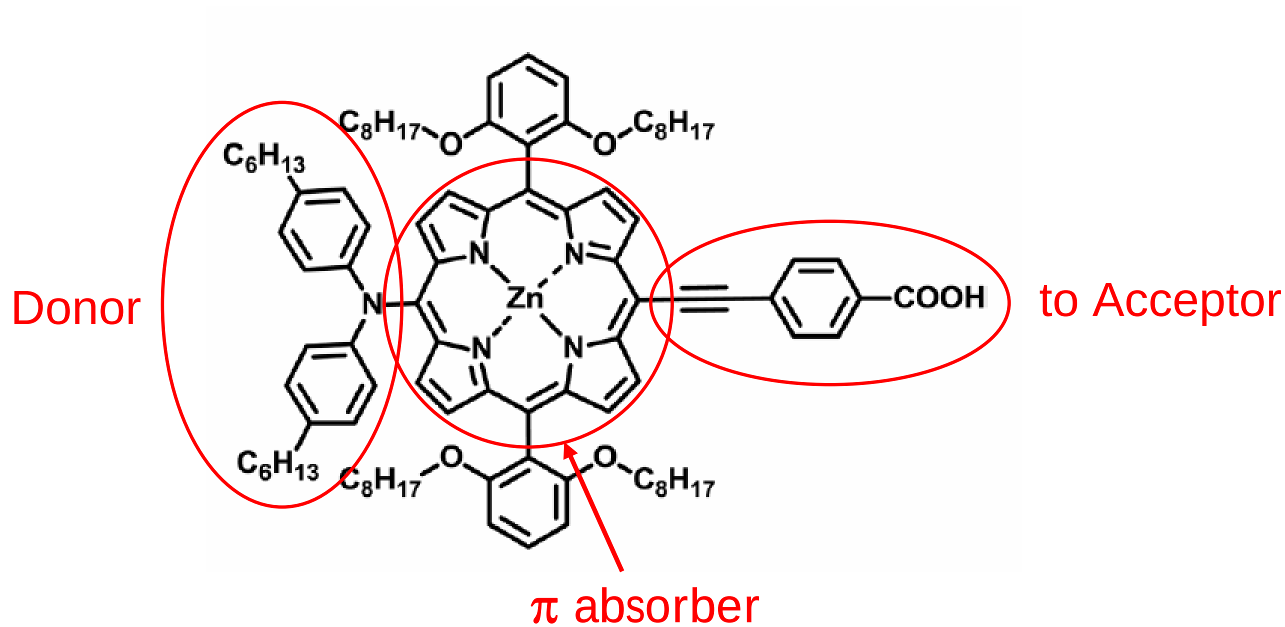
Phthalocyanines



Porphyrins



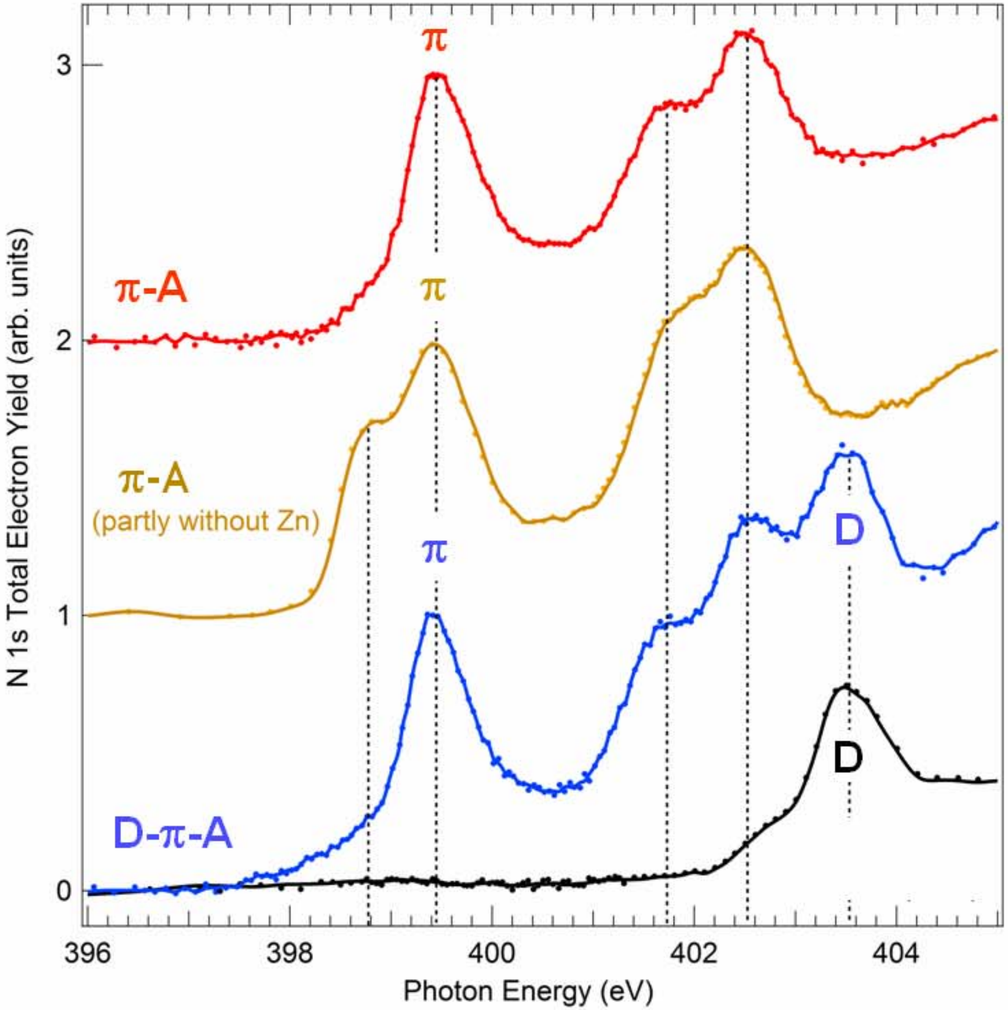
Combine the 3 components of a solar cell in one molecule with atomic perfection



Record efficiency for dye-sensitized solar cells (12.3%)

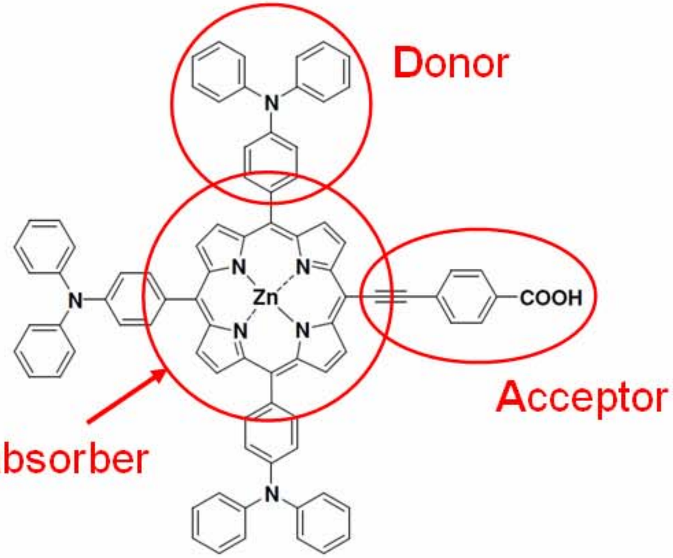
Grätzel group: Yella et al. Science **334**, 629 (2011).

D–π–A complexes



This led to improved synthesis.

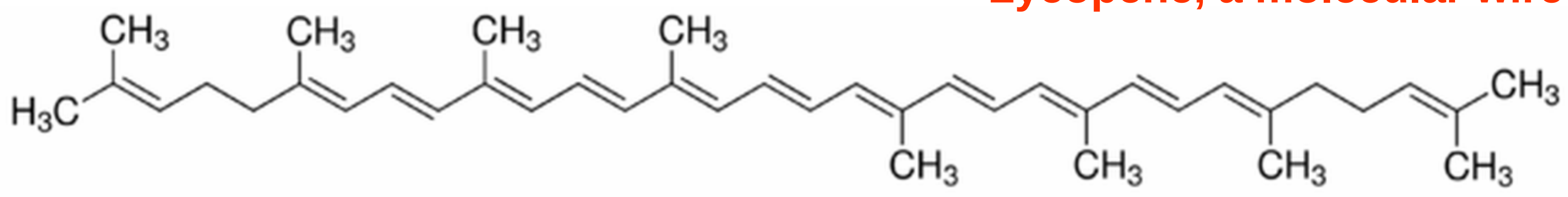
Weak point in the synthesis identified by theory (missing Zn atom).



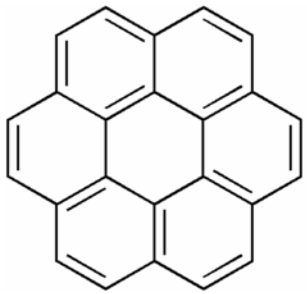
Zegkinoglou, Pemmaraju, Prendergast, et al., J. Phys. Chem. C **117**, 13357 (2013).

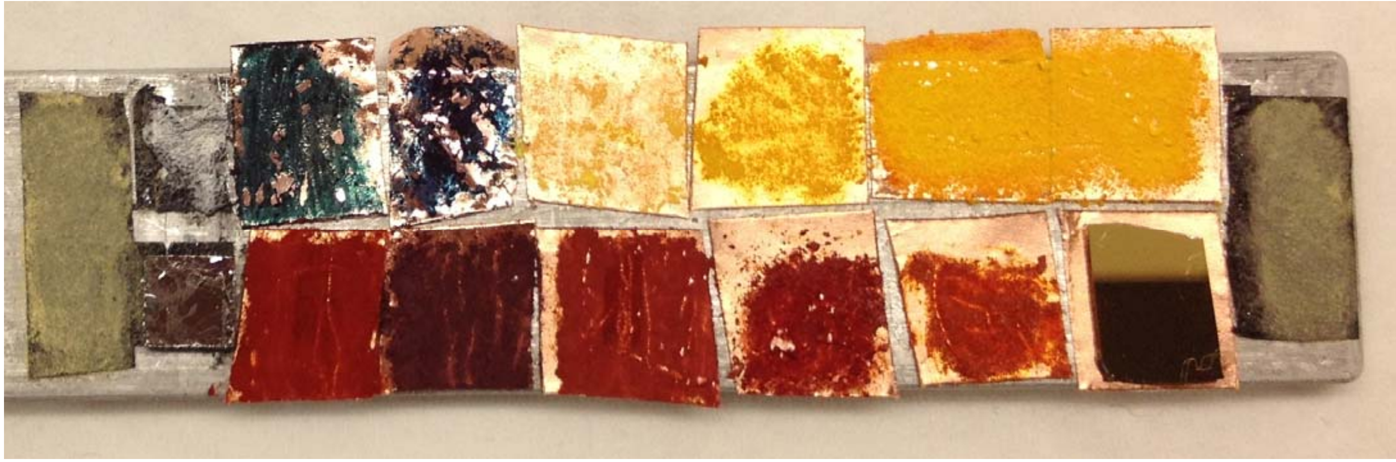
Molecular wires as connectors

Lycopene, a molecular wire



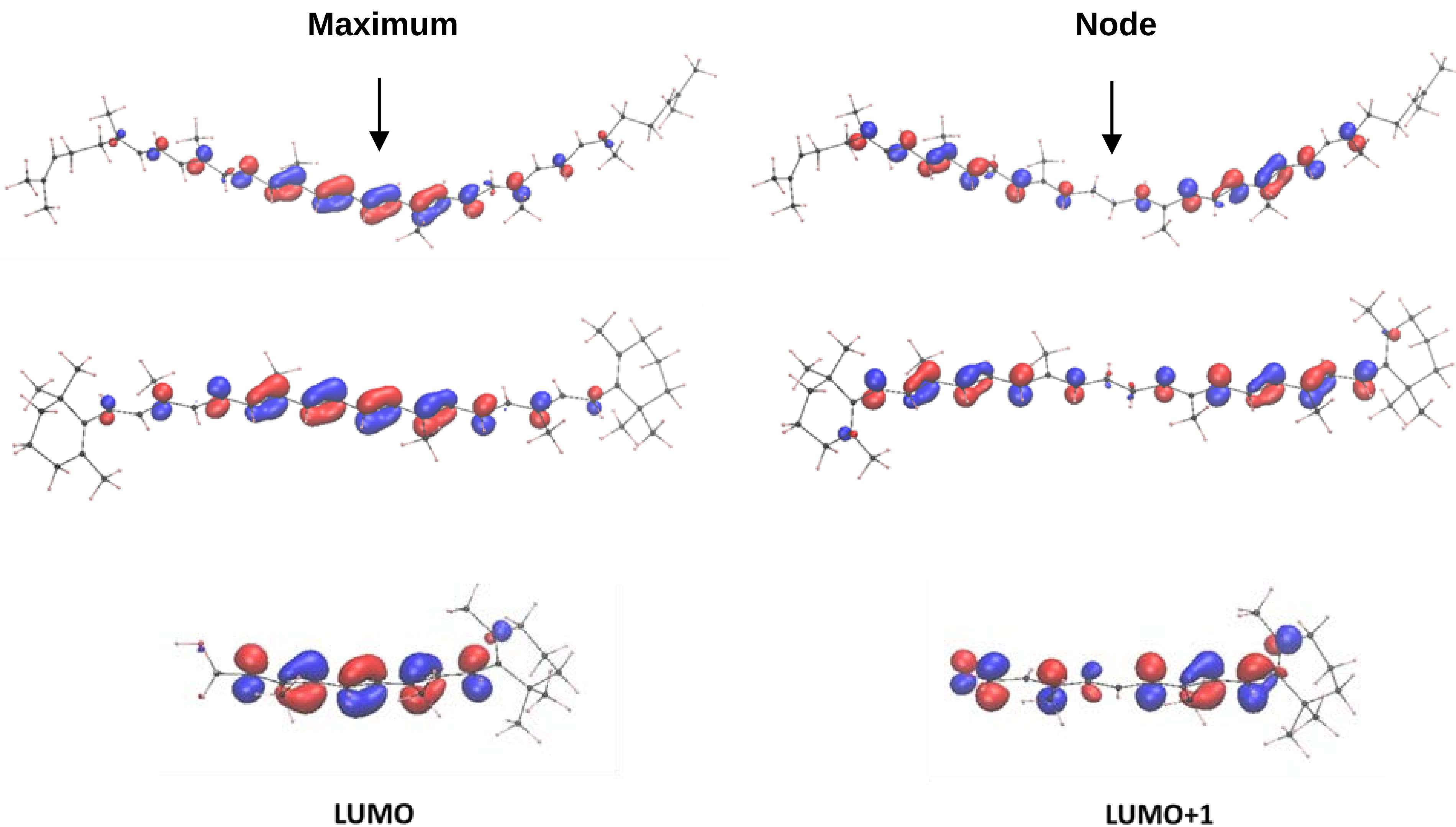
Coronene, a molecular dot





Garcia-Lastra et al., J. Phys. Chem. C, in press (2016).

Wave functions of molecular wires: vibrating strings



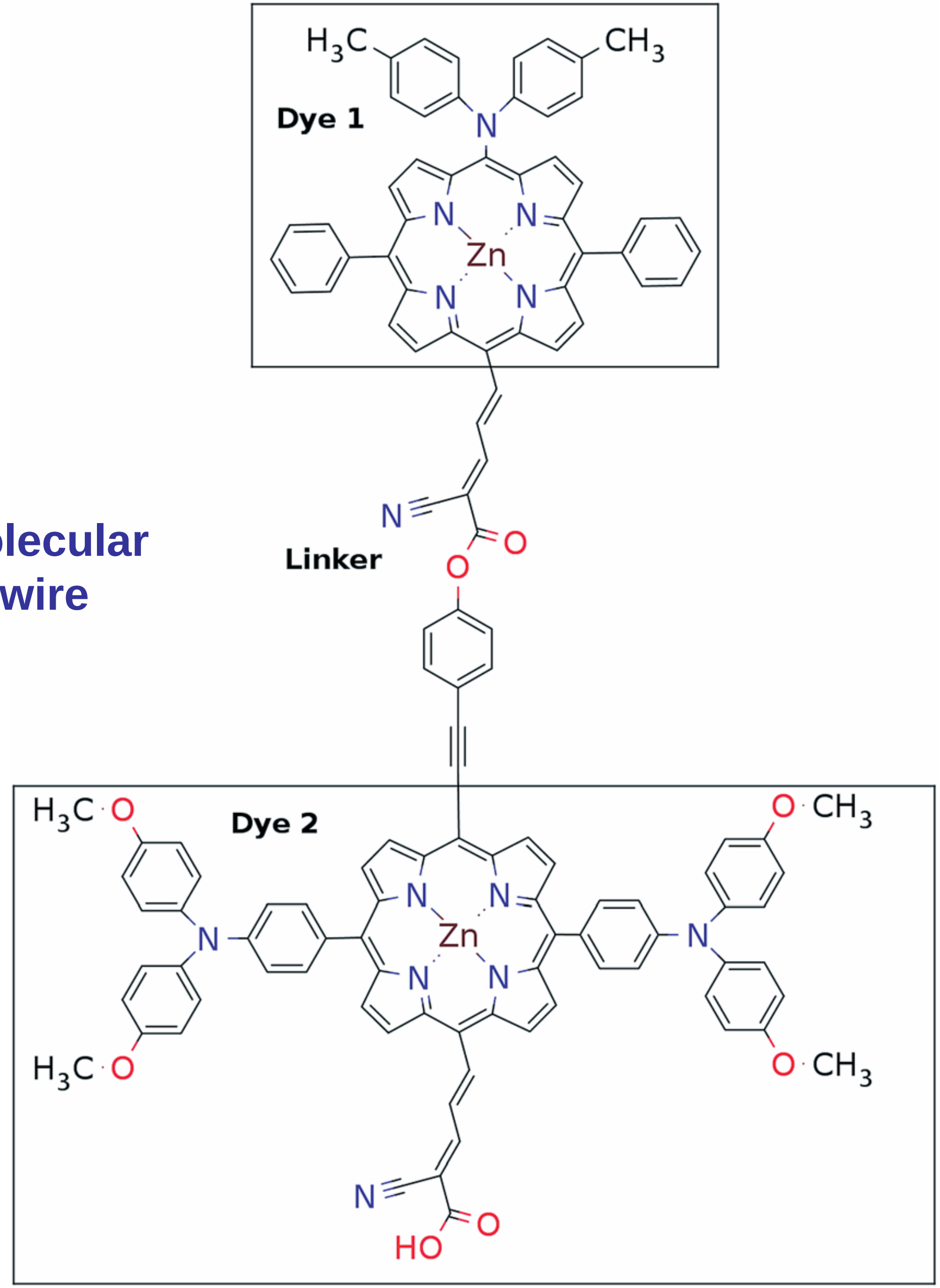
Design tandem cells with atomic precision

Ornso et al,

Chemical Science

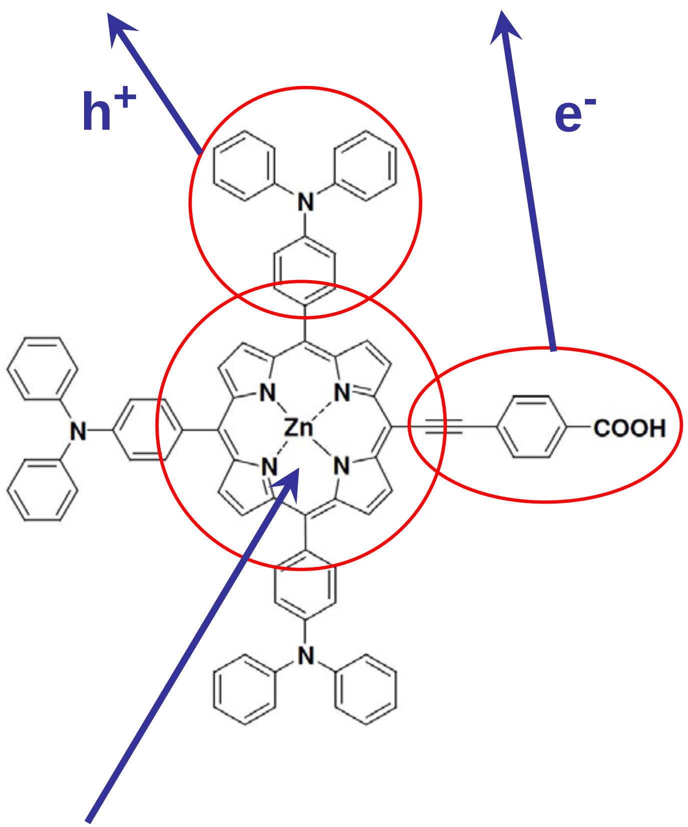
6, 3018 (2015).

Molecular wire



Beyond energy levels: Lifetimes vs. charge transfer rates

Probe the carriers along their way out with X-rays.



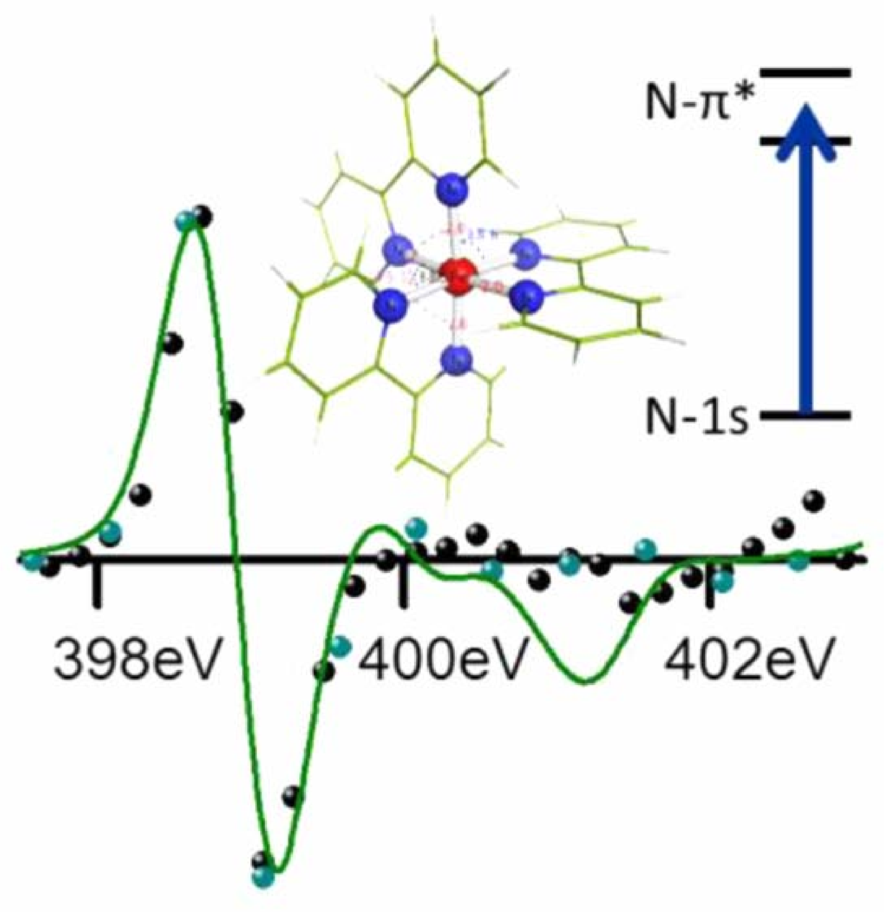
Pump the center with visible.

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

Add time as variable (fs-ns). Already used in the UV/vis (nonlinear optics, transient absorption , two - photon photoemission).

Need element-specific X-ray probes. “Heroic” experiments demonstrate proof of principle. X-ray lasers will make it mainstream.

"Heroic" demonstration experiments (1 spectrum / day)



Pump the central Fe atom with visible light. That flips its spin.

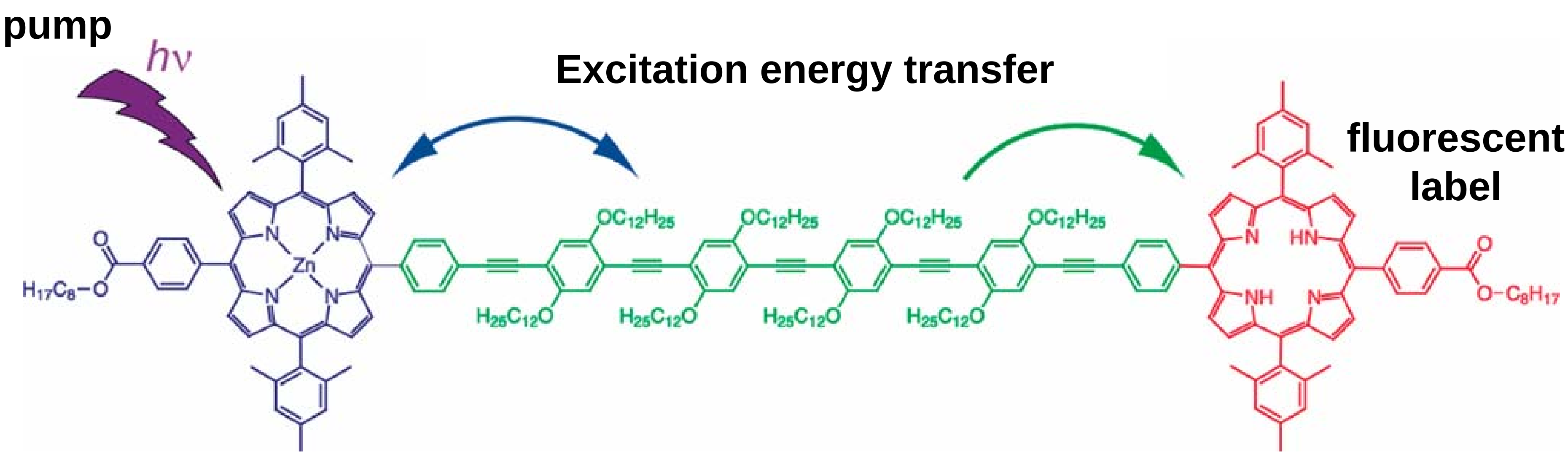
Probe the resulting changes in the absorption spectrum.

The N 1s → π* transition energy changes when Fe flips its spin.

Use this to find out when the hot electrons arrive at the N atoms.

Van Kuiken,…, Huse, J. Phys. Chem. Lett. **7**, 465 (2016).

Propagation of carriers along a molecular wire (UV/Visible)



Vary the length of the connecting molecular wire to find the individual transfer rates.

Make models of rate constants.

Duvanel, Grilj, Vauthey, J. Phys. Chem. A **117**, 918 (2013).

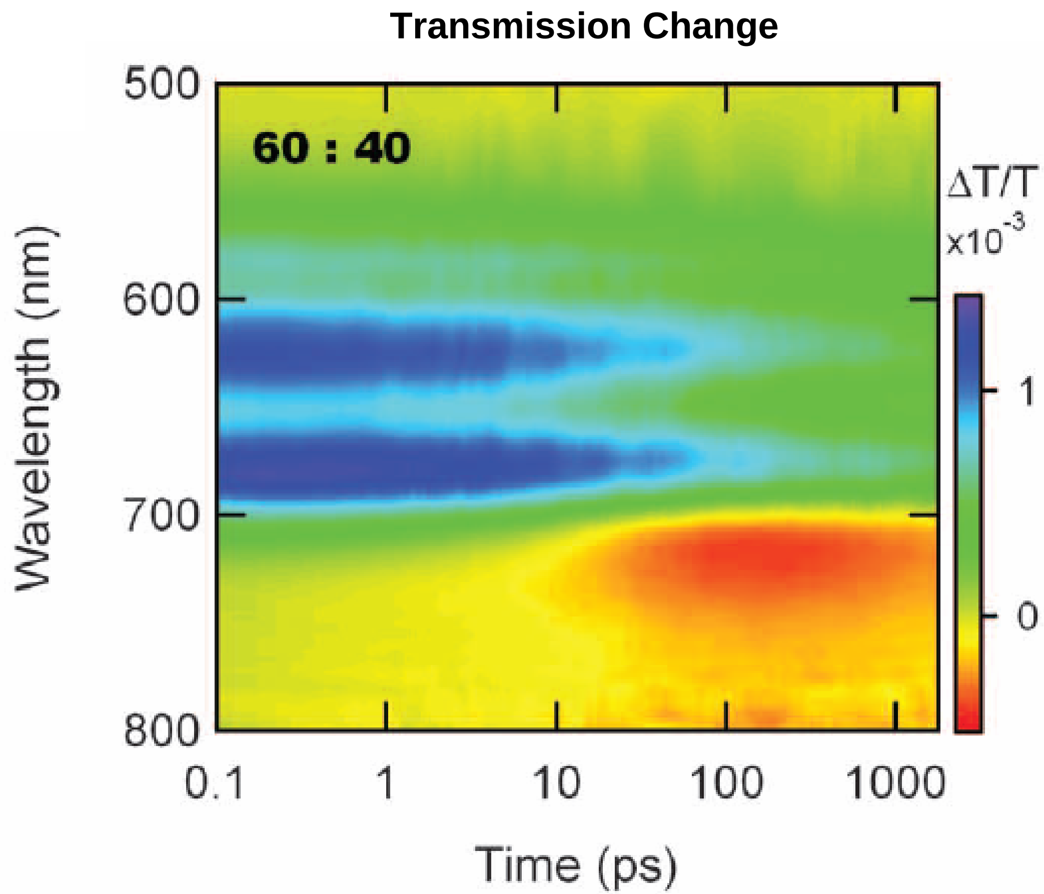
Transient absorption in the UV/Visible (standard tool)

Bleaching by depopulation of the ground state.

Extra transitions starting from excited states.

Time constants: ps … μs
The longer the better.

Gelinas et al., Science **343**, 512 (2015)



But where are the carriers lost ? At impurities, interfaces, … ???

Need element-specific data from soft X-rays (sharpest core levels).

Messages

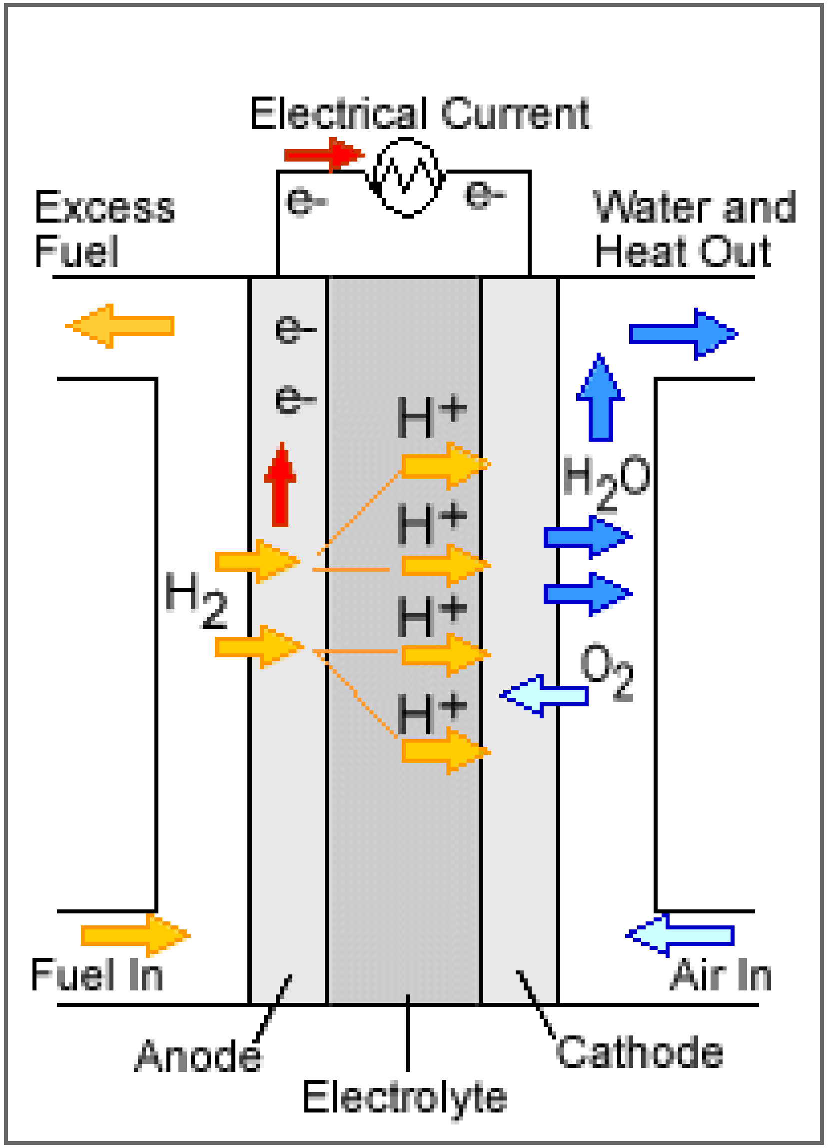
- Need to improve the efficiency. (Cost is less important.)
  Use tandem cells.

- Measure and tune the energy levels.

- A dream experiment:
  Follow the electrons in real time through a solar cell.
  Pump with visible light, probe with soft X-rays.
  Need to be non-destructive (small pulses + high rep rate).

Backup Slides

Fuel cell

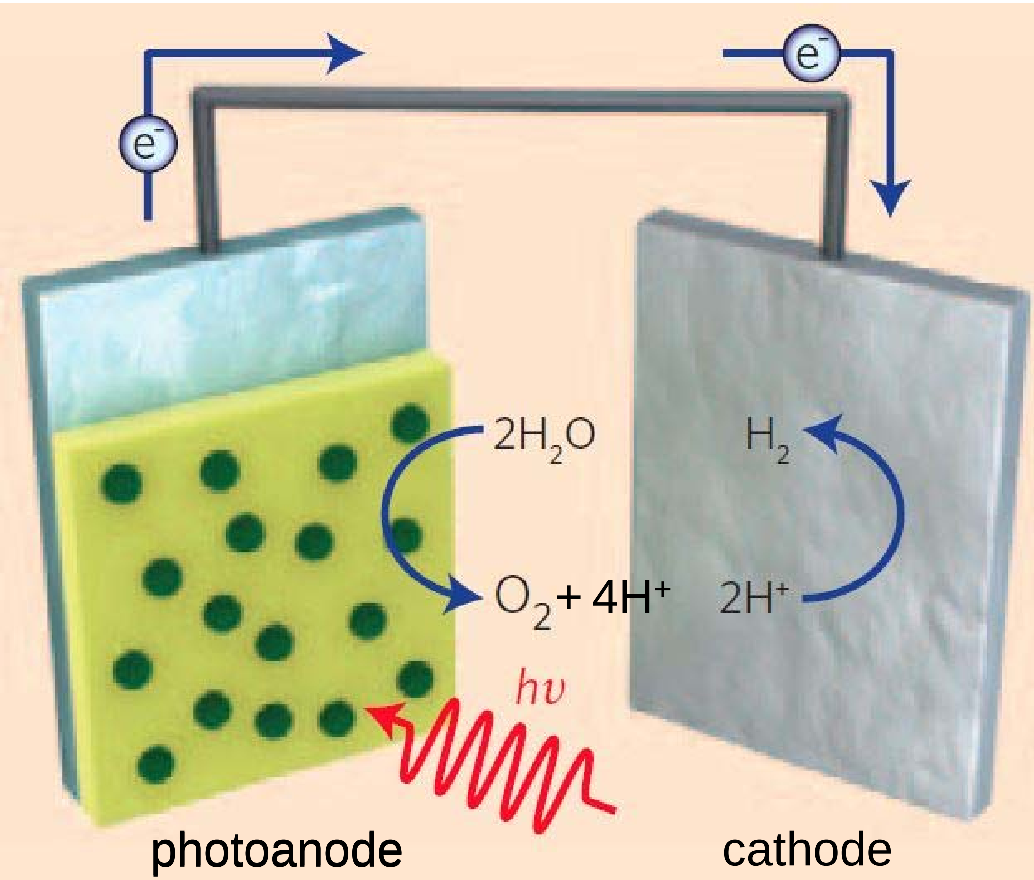


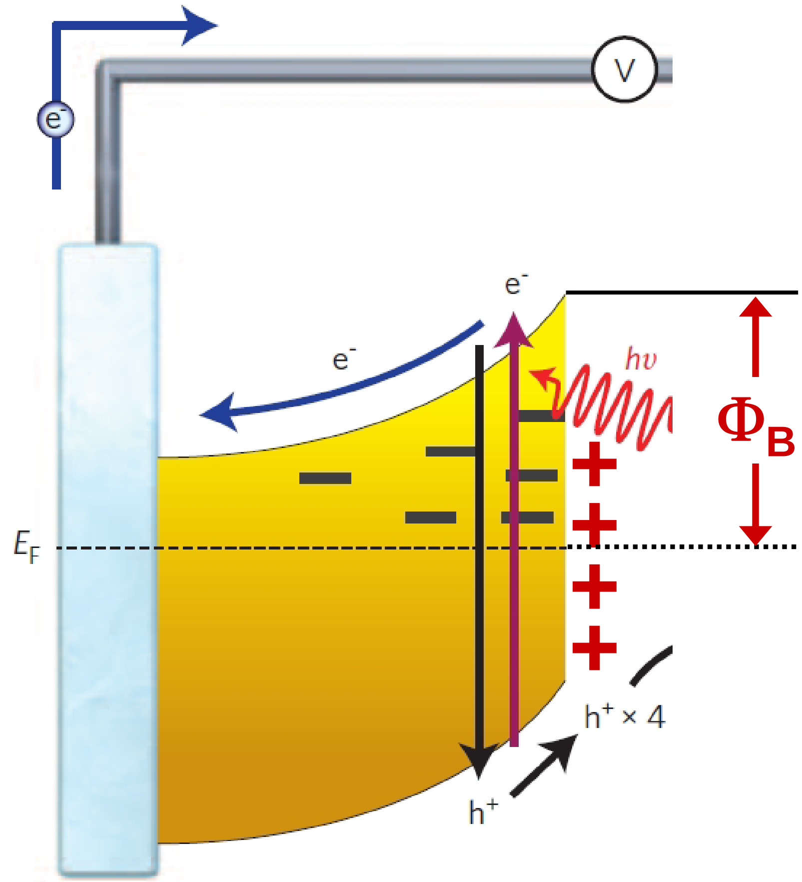
A fuel cell converts fuel directly into electricity without generating heat. That why its efficiency reaches 60% (versus 25% for a diesel generator).

The Apollo program used fuel cells for electric power. When the oxygen tank of Appollo 13 exploded, the crew sent the famous message: "Houston we've had a problem."

Fuel cells are commercially available as backup generators ("Bloom Box").

Artificial photosynthesis: water splitting



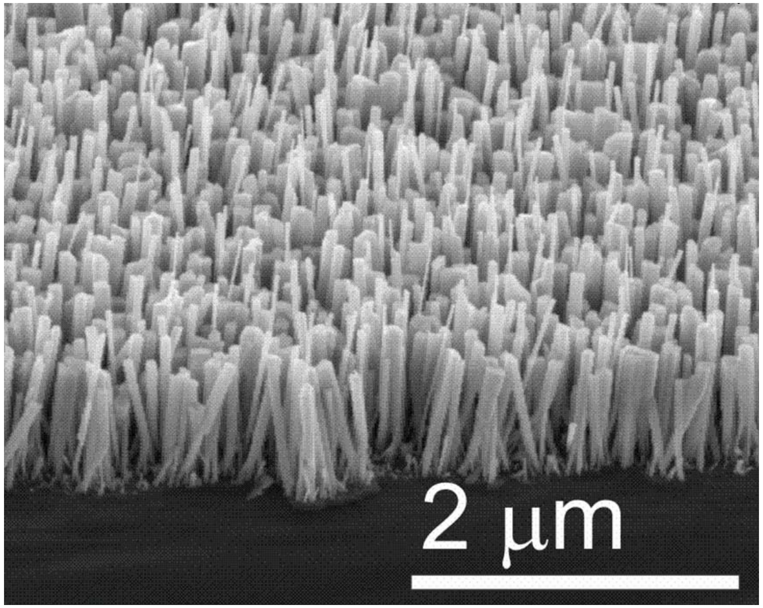


Surface charge creates Schottky barrier Φ_B

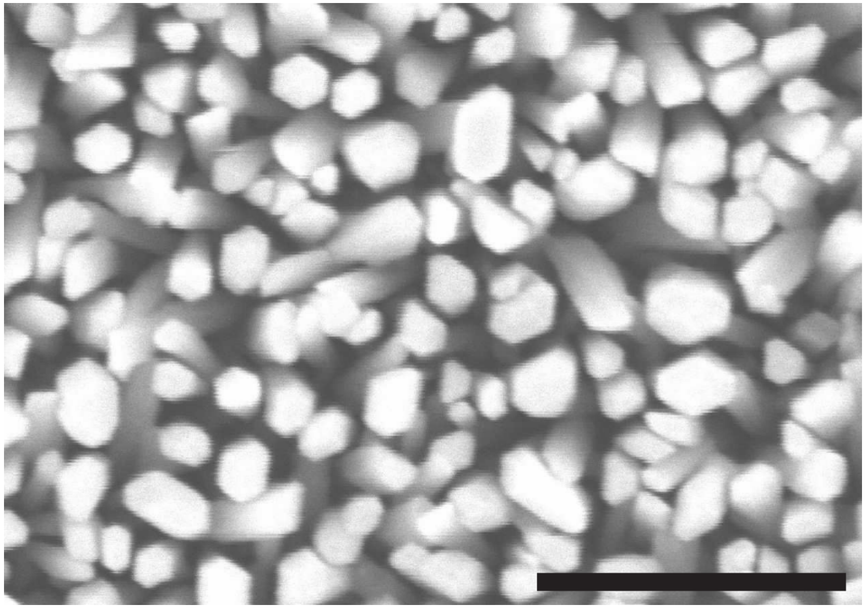
Tachibana, Vayssieres, Durrant, Nature Photonics **6**, 511 (2012)

GaN nanorods for water splitting

Achieved 100× increase in quantum efficiency by engineering the surface charge.



Efficient carrier transport by single-crystal nanorods



50-75 nm diameter

500 nm

Zetian Mi's group: Kibria et al., Nat. Commun. **5**:3825 (2014).

Best Research-Cell Efficiencies