

Third Generation Solar Cells

DSSC

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CH5106-AD15

Amorphous silicon (a-Si) generally has higher processability than crystalline silicon (c-Si)

Lower processing temperature: a-Si is typically deposited at relatively low temperatures ($\approx 200\text{--}400\text{ }^{\circ}\text{C}$) using methods like chemical vapour deposition (CVD). c-Si, requires very high temperatures ($\approx 1400\text{ }^{\circ}\text{C}$ for melting and crystal growth). This makes a-Si compatible with flexible substrates, such as glass or plastic.

2. Ease of fabrication

- a-Si can be deposited directly as thin films over large areas — ideal for thin-film transistors (TFTs) and solar cells.
- c-Si requires precise crystal growth and wafer slicing, which are complex and expensive processes.

3. Scalability and cost

- The simpler, low-temperature, and large-area deposition of a-Si translates to lower manufacturing cost and better scalability.
- c-Si offers superior performance but is less cost-effective and less flexible in fabrication.

Trade-off

However, this improved processability comes at a cost:

- Amorphous silicon has a disordered atomic structure, leading to many defects and dangling bonds.
- This results in lower carrier mobility, shorter diffusion lengths, and poorer electrical performance compared to crystalline silicon.

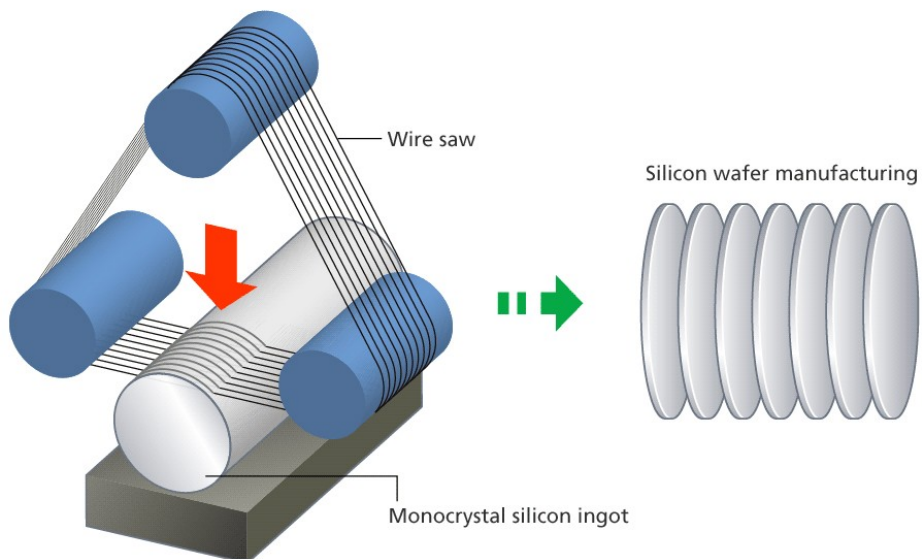
| Property | Amorphous Si (a-Si) | Crystalline Si (c-Si) |
|------------------------|-----------------------------|-----------------------|
| Process temperature | Low (200–400 °C) | High (>1000 °C) |
| Fabrication ease | Easy, large-area deposition | Complex, wafer-based |
| Processibility | High | Low |
| Electrical performance | Low | High |

Schematic of c-Si PV module supply chain



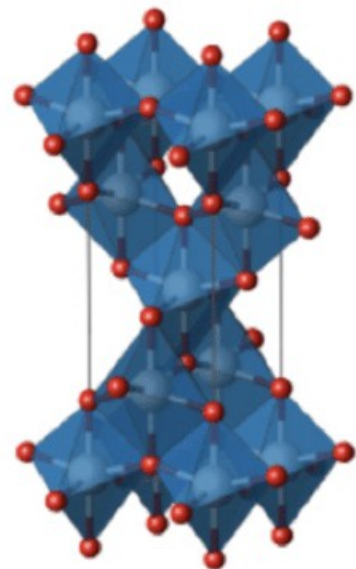
www.cleanenergyreviews.info

Silicon Solar Cell Manufacturing Process



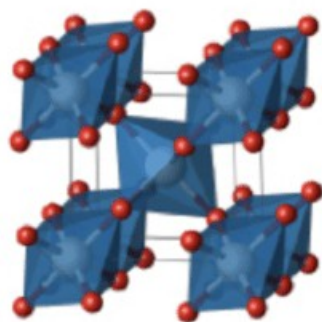
Titanium dioxide, the only naturally occurring oxide of titanium at atmospheric pressure, exhibits three polymorphs: **rutile**, **anatase**, and **brookite**. While rutile is the stable phase, both anatase and brookite are metastable; the latter is difficult to synthesize.

Anatase



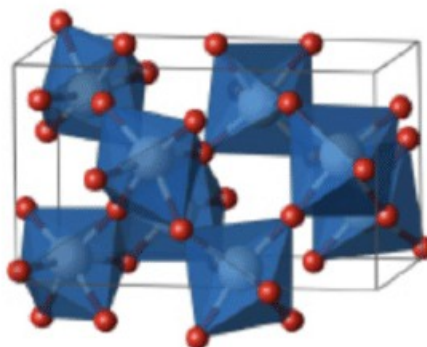
Octahedra form
(001) planes;
Band gap: 3.2 eV

Rutile



Eight share corners and
only two share edges
running along the [110]-
type direction.
Thermodynamically most
stable phase.
Band gap: 3.0 eV

Brookite



Orthorhombic unit
cell, each octahedron
shares three edges.
Band gap: 3.0 – 3.4 eV

The small red spheres represent the oxygen atoms, the big grey ones are the titanium atoms, while the blue polyhedral shapes show the orientation in space of the TiO_6 octahedra.

Degussa P25 nanopowder, a mixture of 75% anatase and 25% rutile, is often employed as a reference photocatalyst in photocatalytic studies and industrial applications. P25 generally displays enhanced photocatalytic performance over pure rutile or anatase nanocrystals

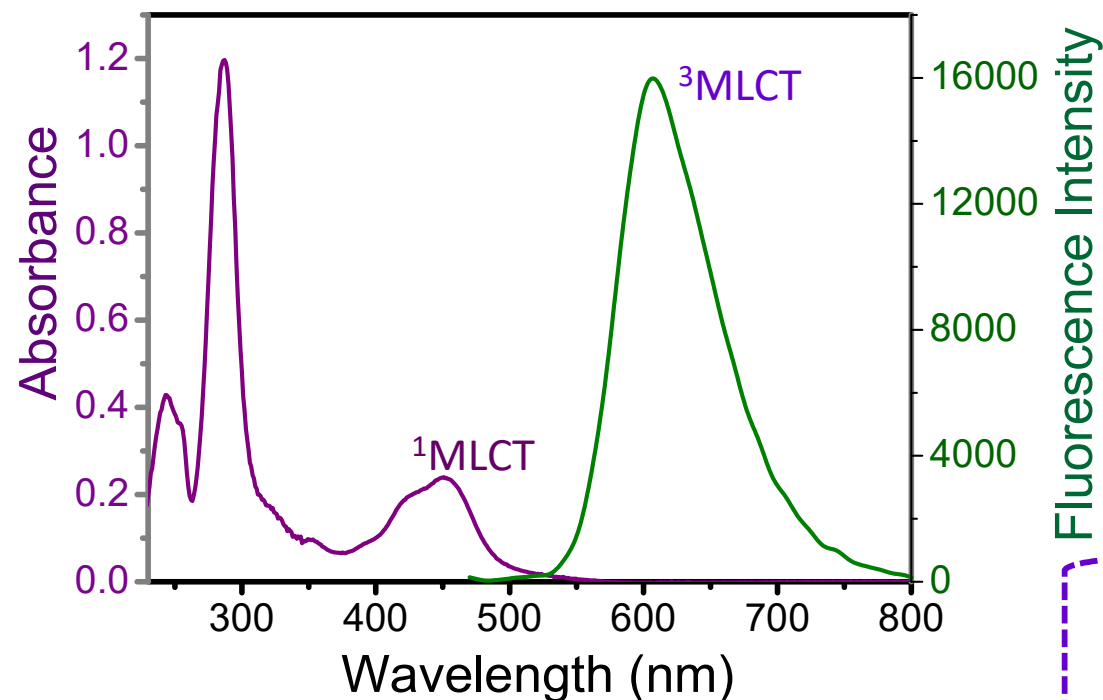
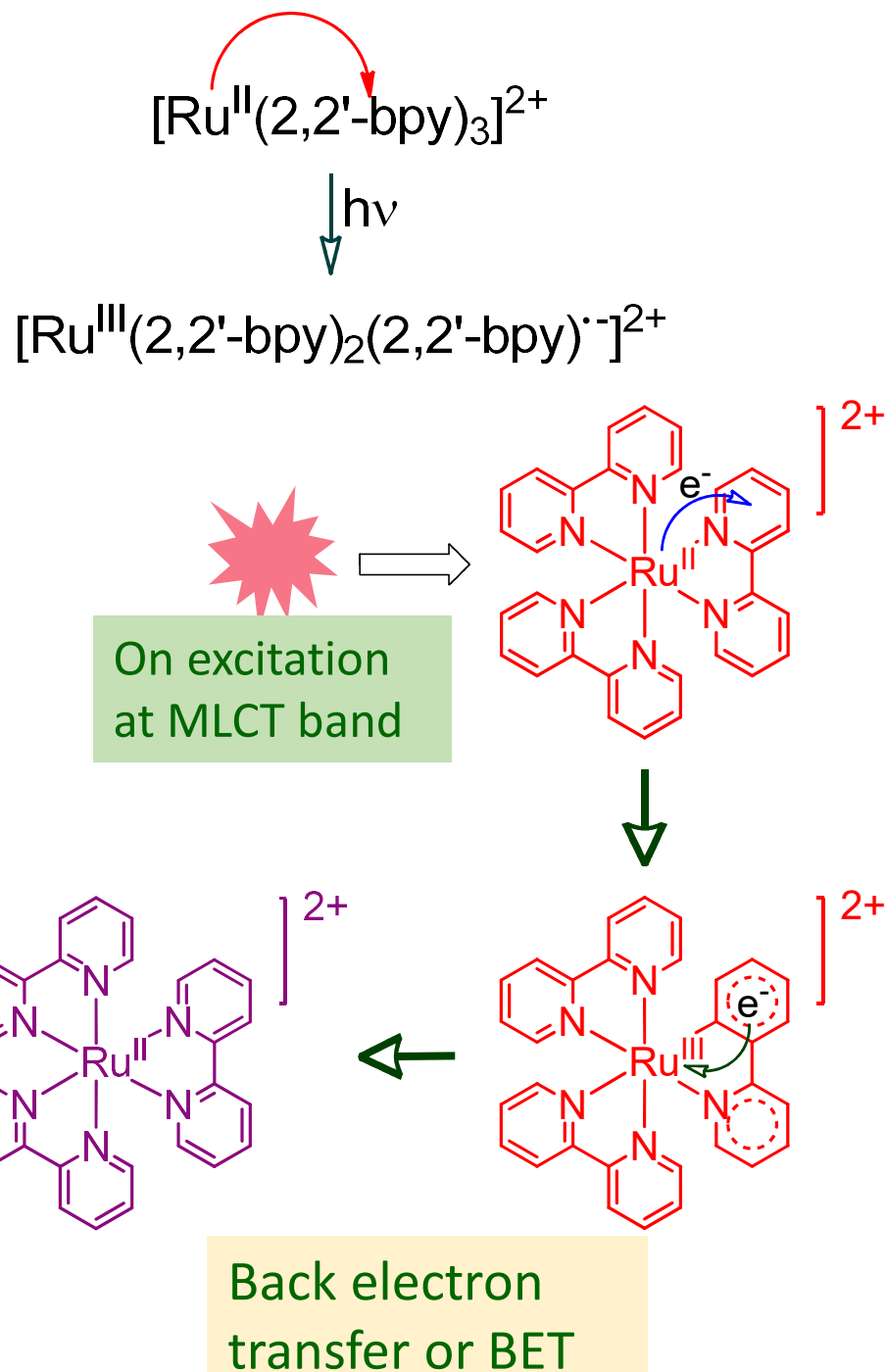
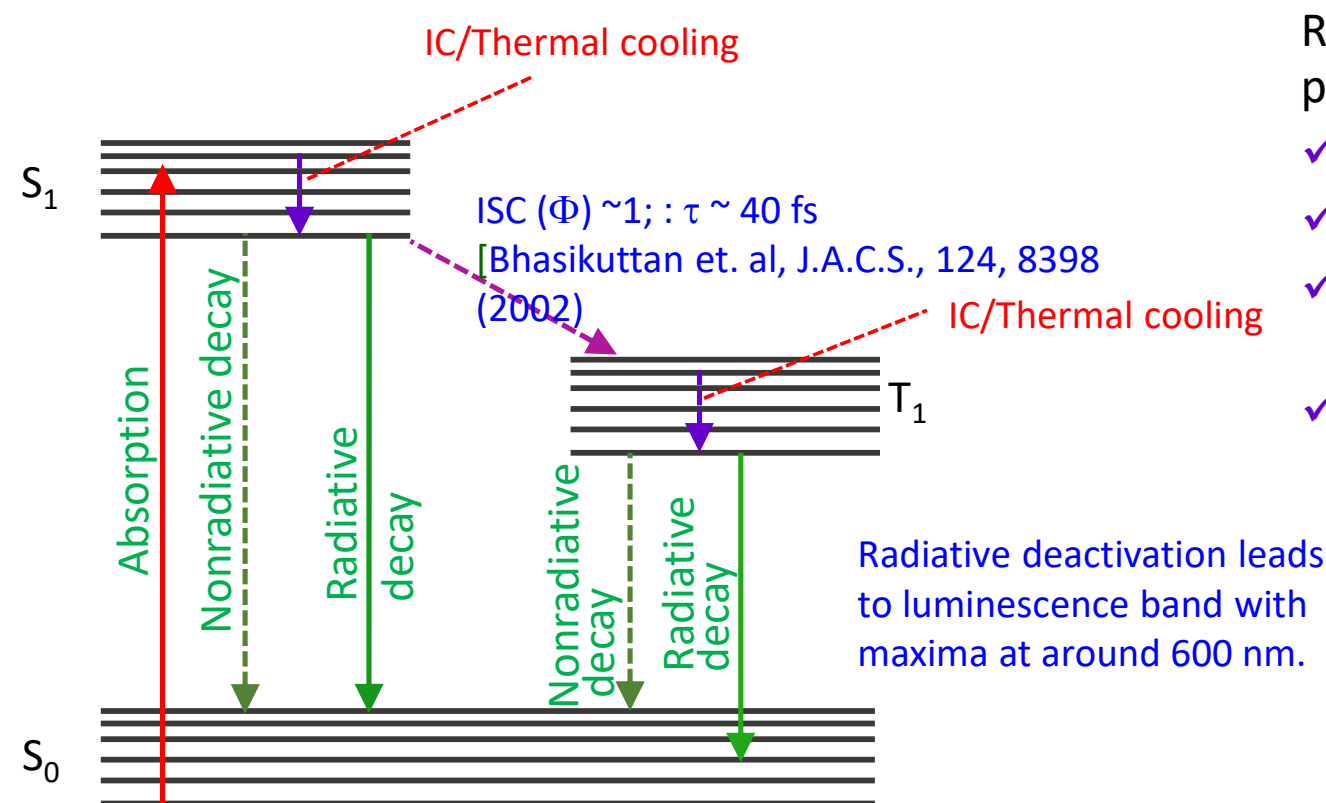


Photo-induced e^- transfer Processes

Fast BET process is generally not desired for the design of an efficient Dye Sensitized Solar Cell (DSSC).



Back electron transfer or BET



Ru(II)-polypyridyl dyes have been the popular choice because of their

- ✓ strong visible absorption bands,
- ✓ long-lived excited states,
- ✓ excellent photochemical stability, and
- ✓ the ability to fine-tune their electronic properties via ligand modification.

- **Spin-forbidden nature:** In purely organic molecules composed of light elements (C, H, N, O), $S \rightarrow T$ transitions are spin-forbidden because **spin angular momentum must be conserved ($\Delta S = 0$)**. Hence, intersystem crossing (ISC) and phosphorescence are generally weak.
- **Role of spin-orbit coupling:** In heavy atoms (like Ir, Pt, Ru, Os) — the spin-orbit coupling constant (ξ) is large due to relativistic effects. SOC mixes singlet and triplet character in electronic states, effectively relaxing the spin selection rule.
- **Consequence:** Spin-forbidden ($S \leftrightarrow T$) gain partial *allowed*, leading to an efficient intersystem crossing (ISC) from singlet to triplet manifolds.

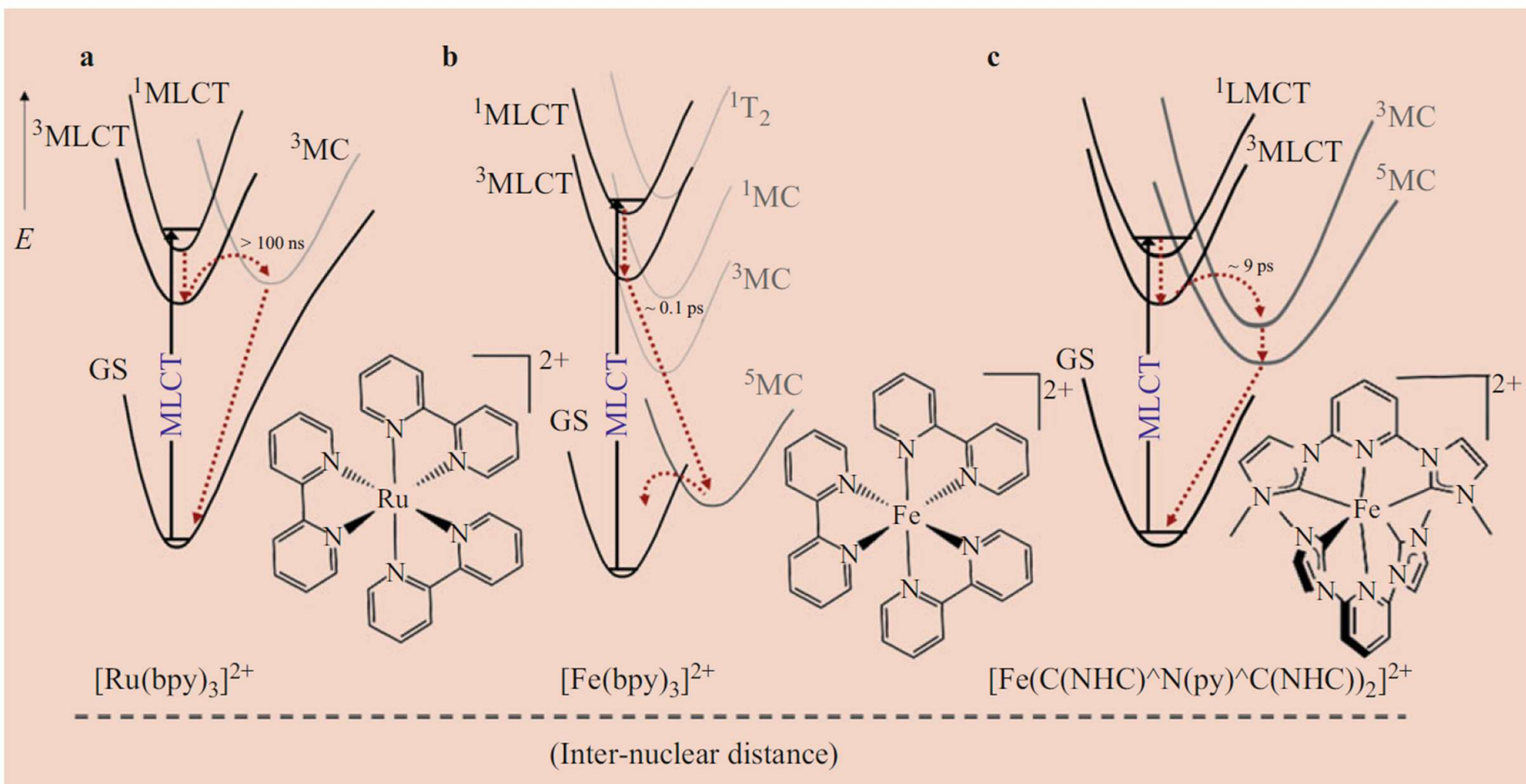
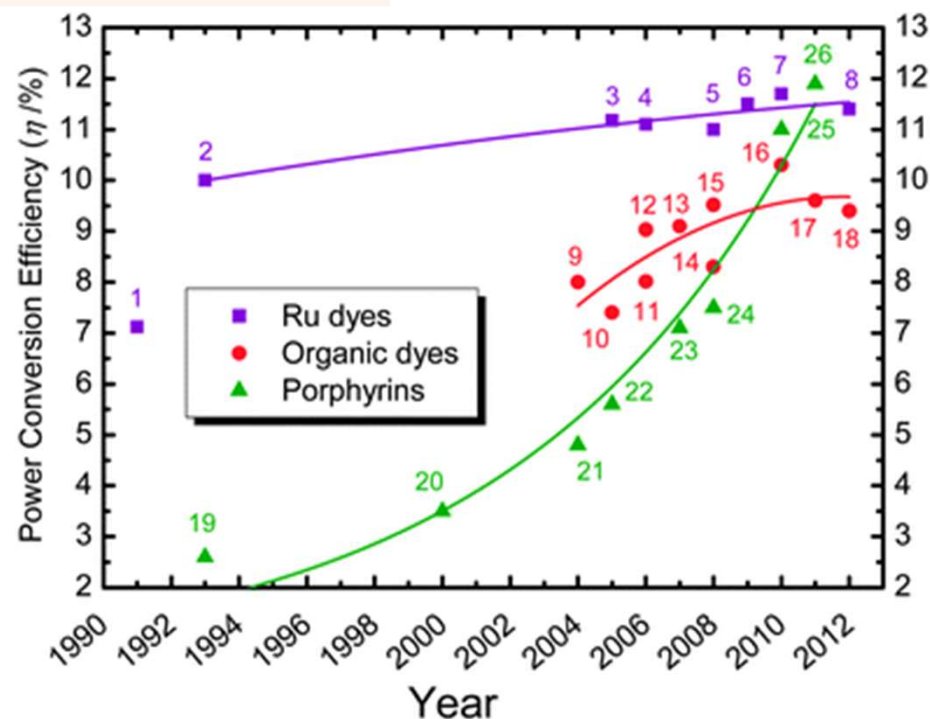
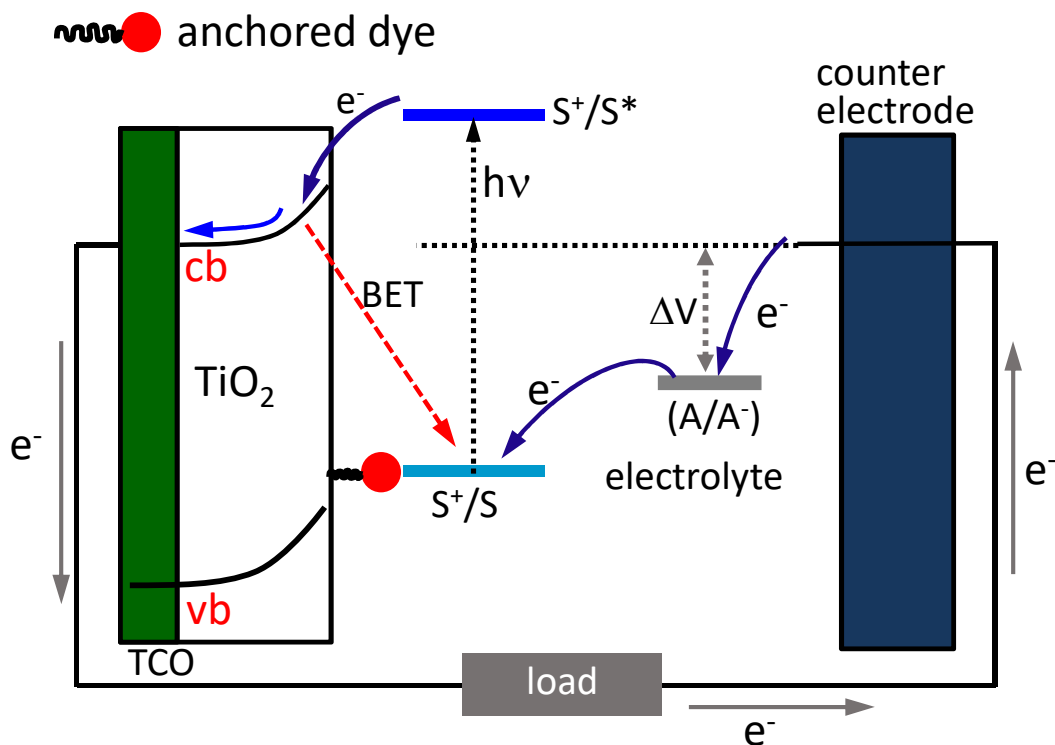


Fig. 20.3 Comparison between the potential energy diagram for the excited states of selected d^6 complexes (a) $[\text{Ru}(\text{bipy})_3]^{2+}$ [30], (b) $[\text{Fe}(\text{bipy})_3]^{2+}$ [31], and (c) $[\text{Fe}(\text{C}(\text{NHC})^{\wedge}\text{N}(\text{py})^{\wedge}\text{C}(\text{NHC}))_2]^{2+}$ [32]

The Dye Sensitized Solar Cell



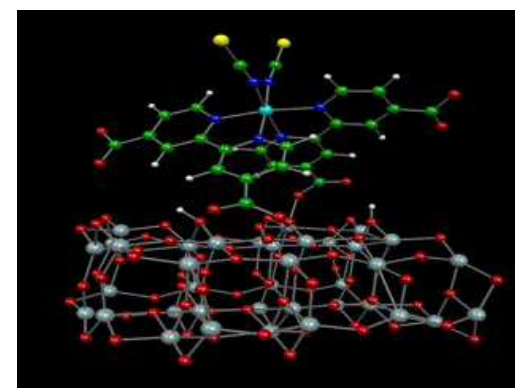
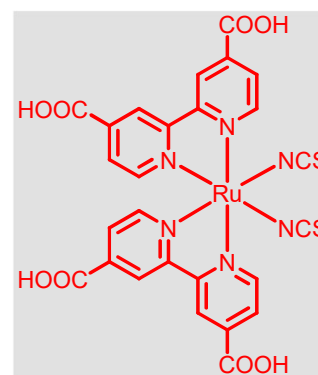
Diau et. al. Chem. Soc. Rev. , 2013, **42**, 291-304

Carboxylate binding has undoubtedly been the most promising so far.....

Limitation:Sensitizers bound to metal oxide surfaces through this linkage exhibit high stability in most anhydrous organic solvents and in acidic aqueous solution only; in neutral and basic aqueous solutions the sensitizers are rapidly desorbed from the surface.

This is due to the related protolytic equilibrium; **the ground state pK_a of carboxylates is too low to ensure strong binding.**

Kalyanasundaram, Coord. Chem. Rev. 1998, **77**, 347

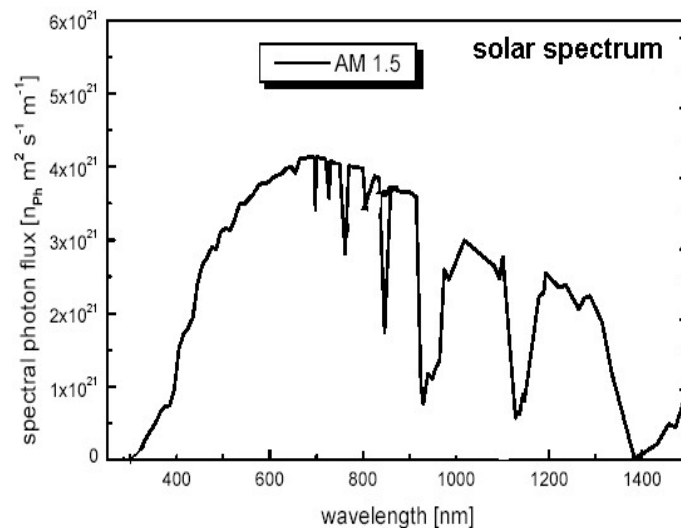
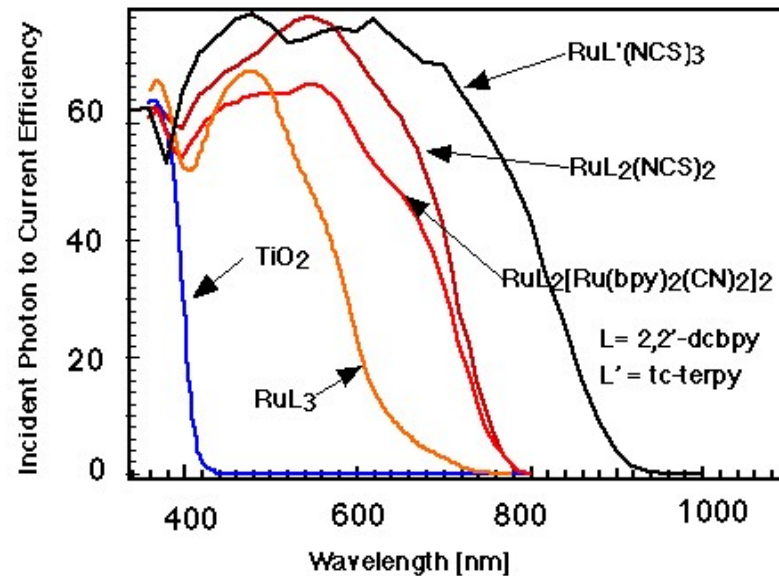
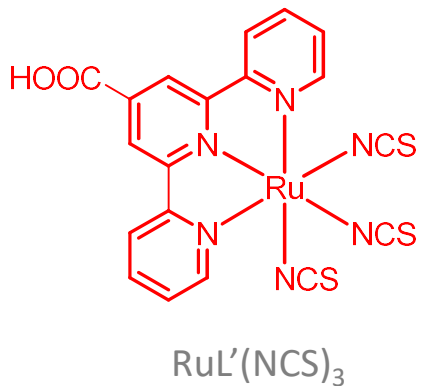
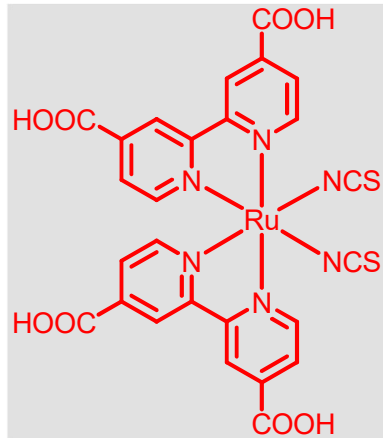


M. Graetzel, *Nature*, **2001**, 414, 338.;
Inorg. Chem. **2005**, 44, 6841

BET happens in μs

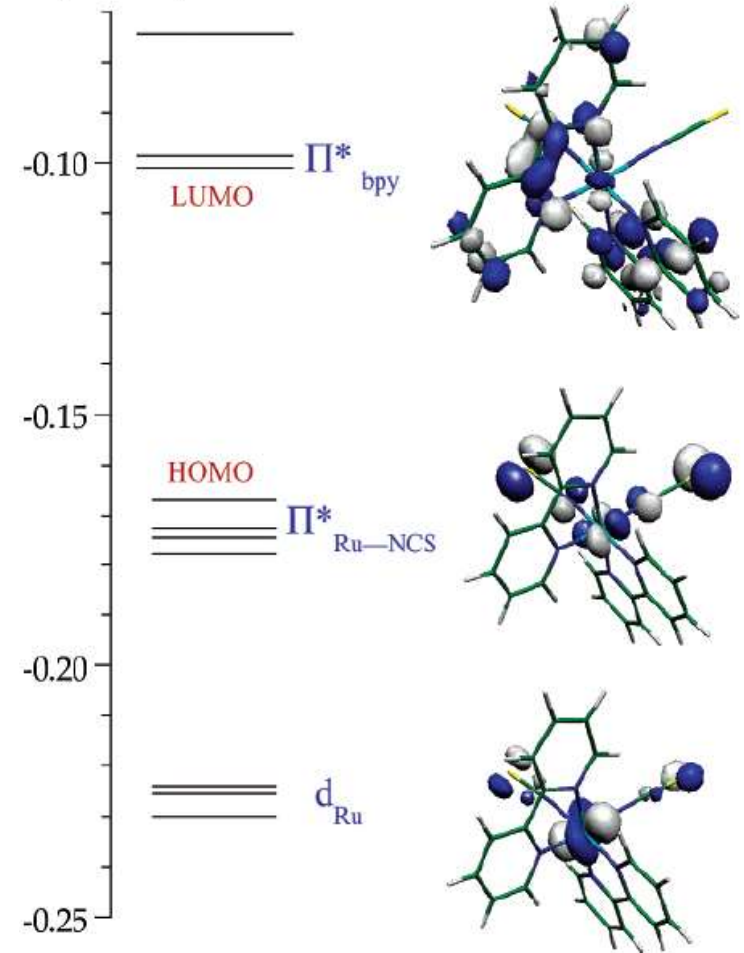
Dyes used in Gratzel Solar Cell

Efficiency of about 12% has been reported

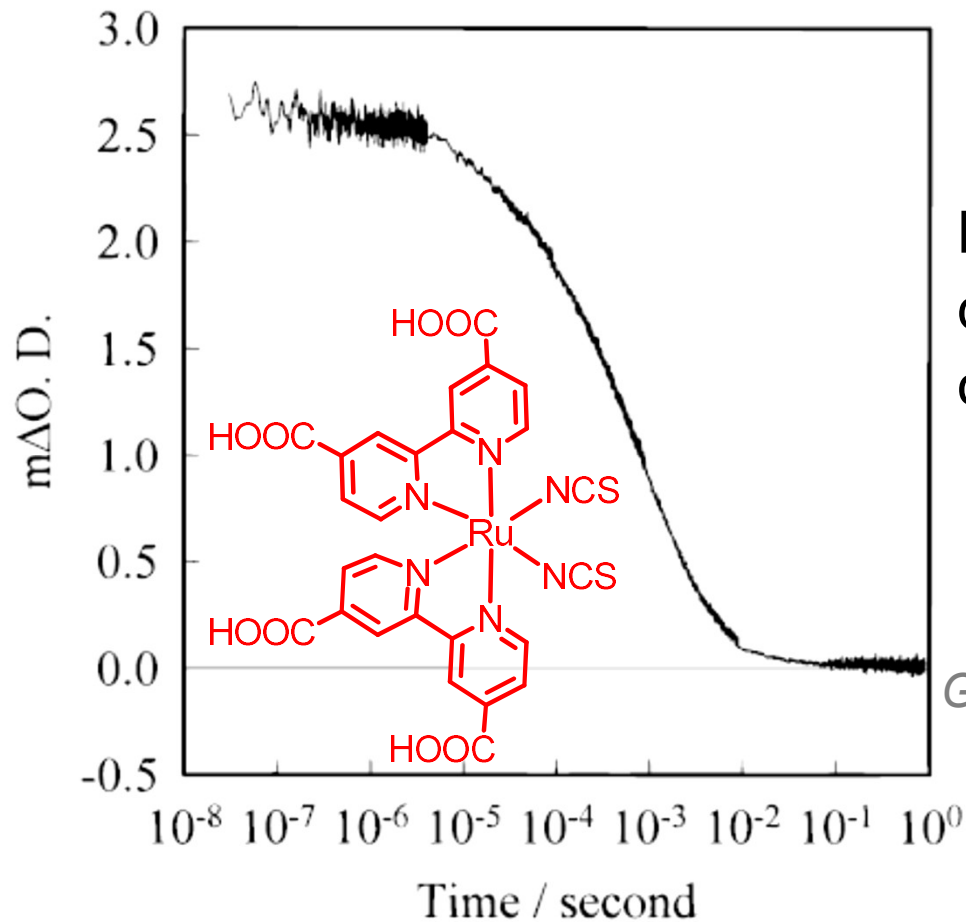


Why -SCN ?

E (hartrees)



Gratzel dye
Photophysics



Kinetics of charge recombination of the dye-coated TiO₂ film, monitored by decay of the **radical absorption band at 820 nm**.

Grätzel et. al; Nature 1991, 353, 737

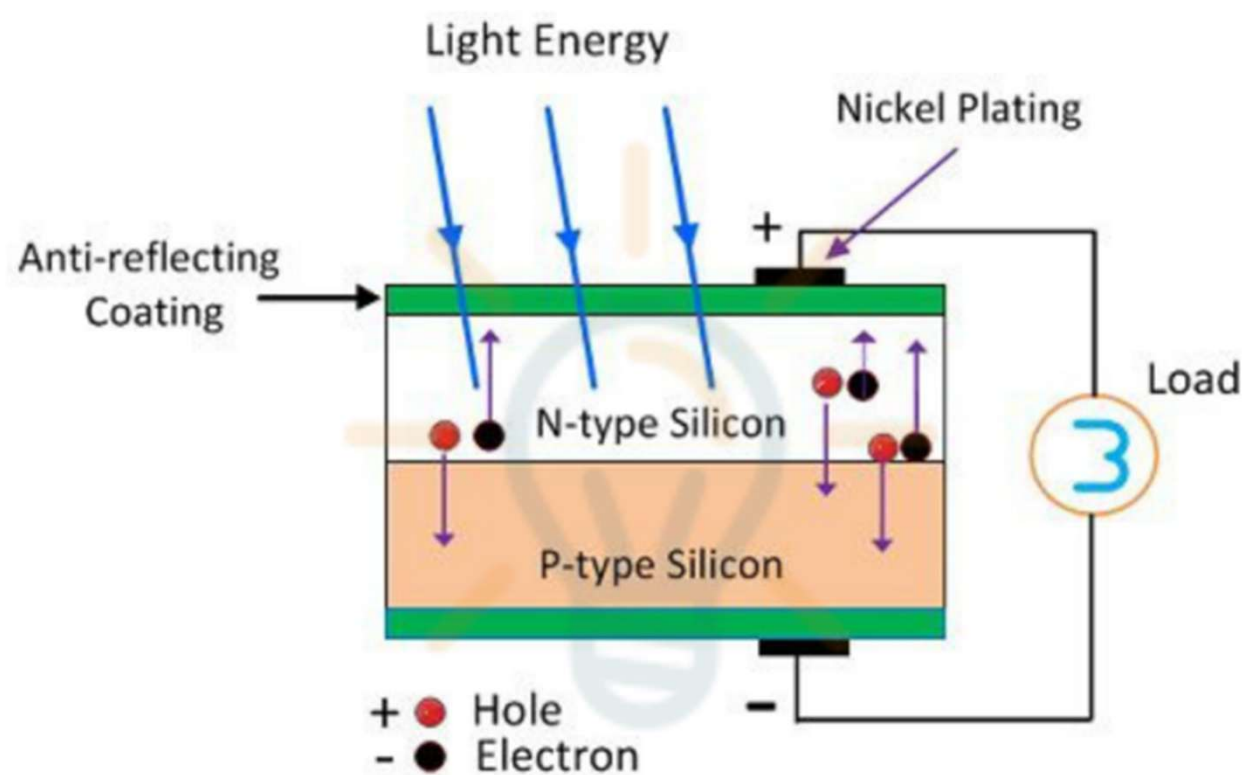
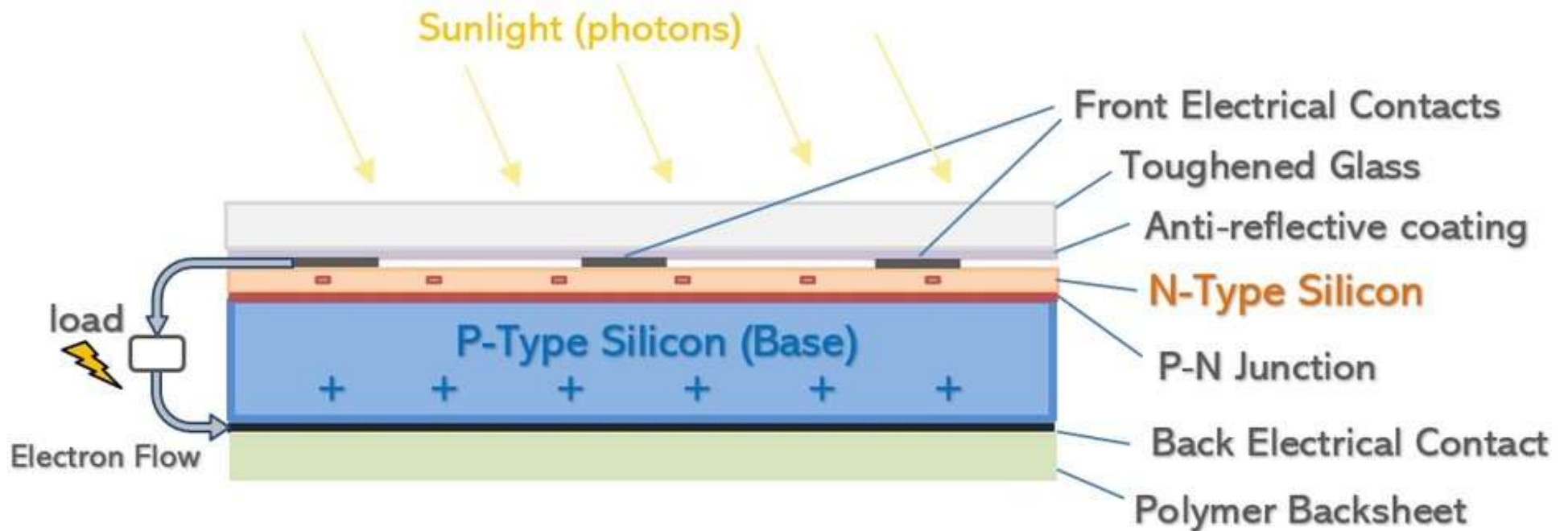
J. Phys. Chem. 1996, 100, 20056

Account of Chem. Res. 2009, 42, 1788.

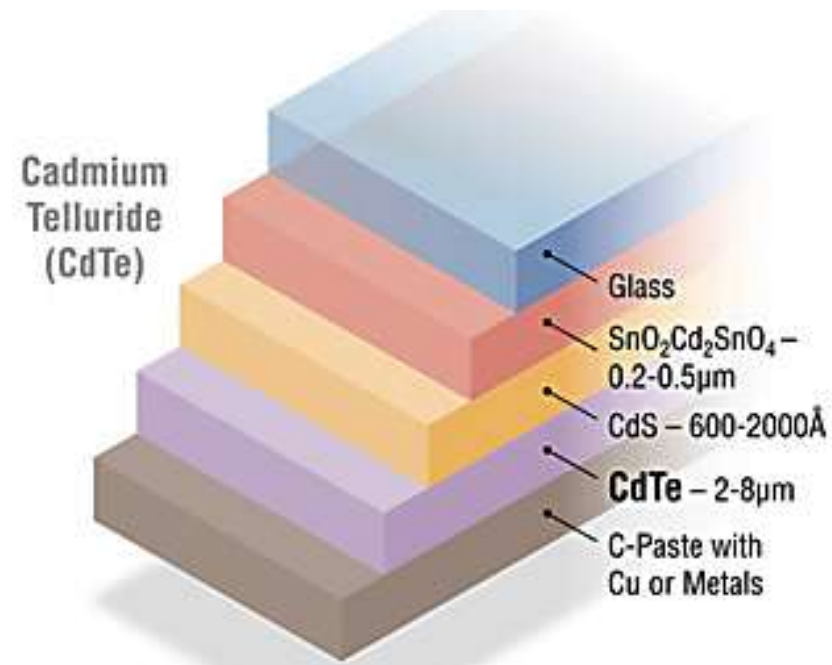
Disadvantages with carboxylate as anchoring group:

The ground state pK_a of the carboxylates is too low to ensure strong and in presence of water, slow desorption of the photosensitizers can occur which can limit the long-term stability of the cell.

Phosphonate has also been investigated as anchoring groups; phosphonates (pK_a ~ 6.5) provide stronger binding than **carboxylates** (pK_a ~ 4). However, these anchoring functionalities have intrinsic problems with slow dissociation of the dye.



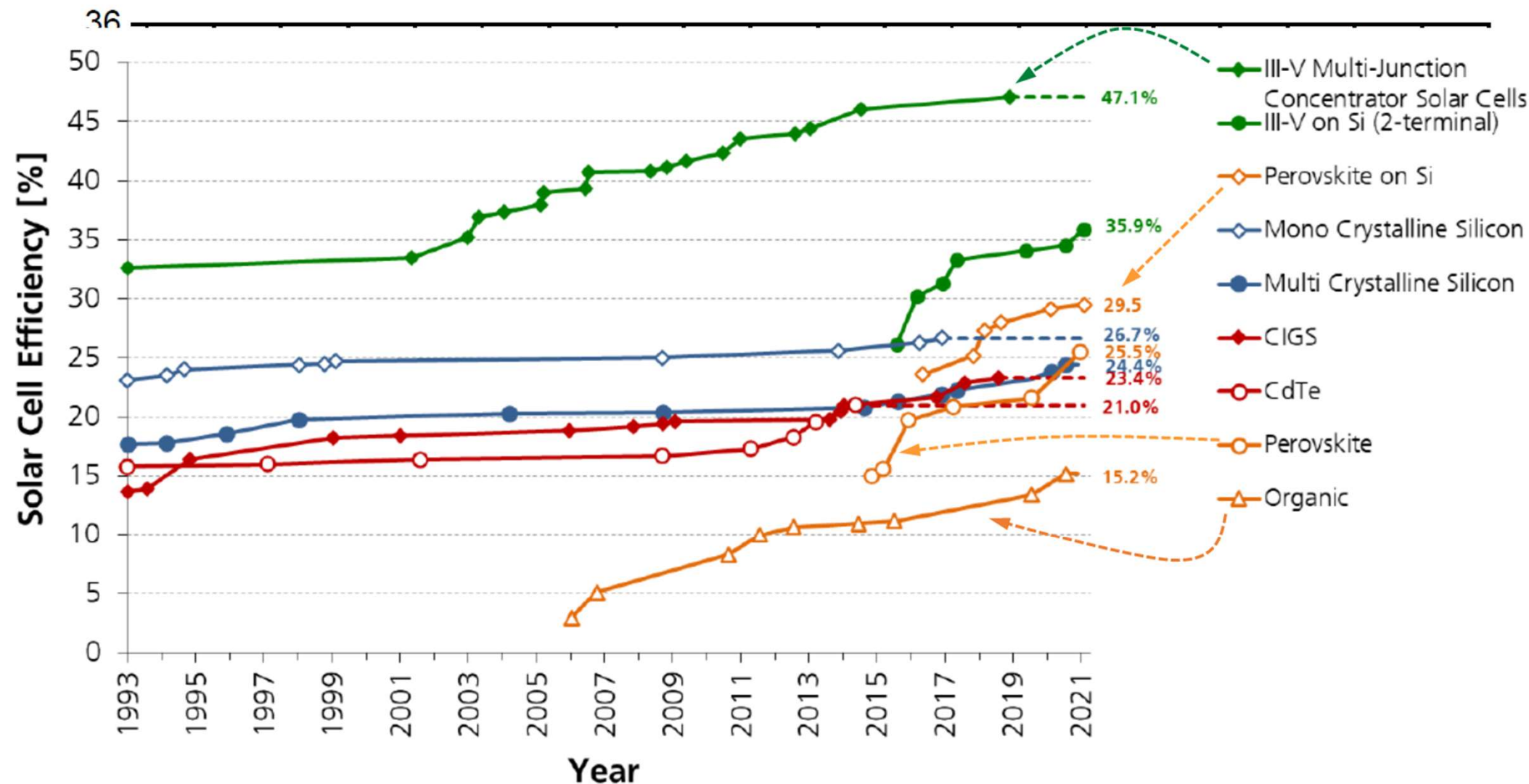
Need to redo



Development of Laboratory and Commercial Solar Cell Efficiencies

What's Next?

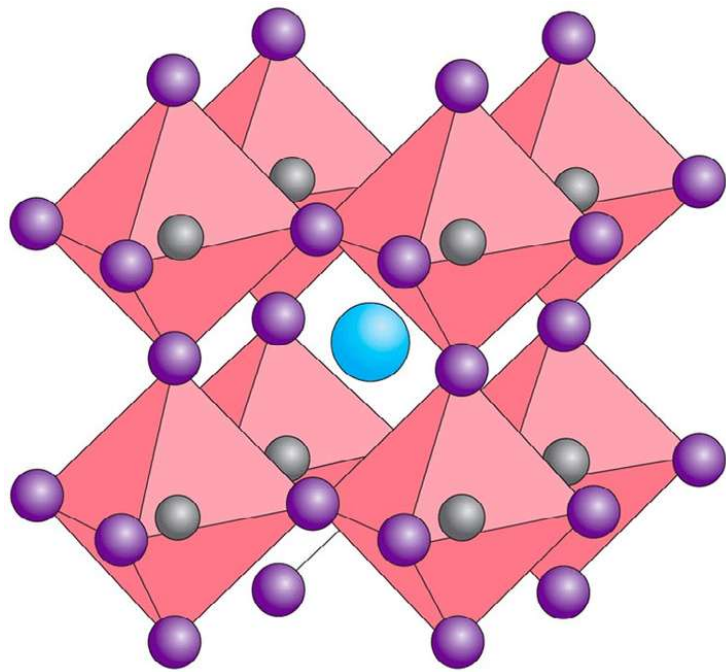
Development of Laboratory Solar Cell Efficiencies



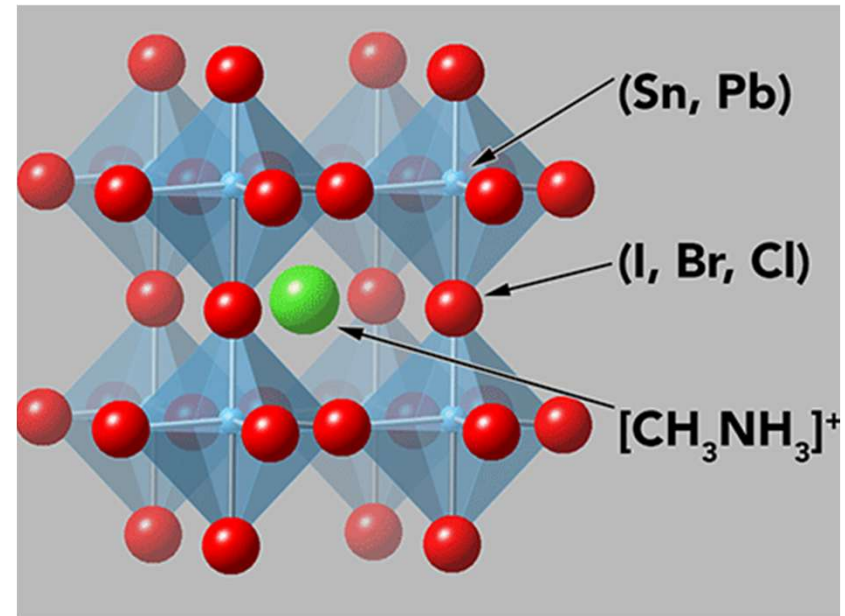
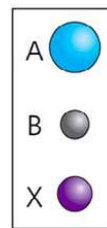
Data: Solar Cell Efficiency Tables (Versions 1 to 58), Progress in Photovoltaics: Research and Applications, 1993-2021.
Graph: Fraunhofer ISE 2021

The current efficiency record of c-Si solar cells is 26.7%, against an intrinsic limit of ~29%. Current research and production trends aim at increasing the efficiency, and reducing the cost, of industrial modules.

The terms "perovskite" and "perovskite structure" is a type of mineral that was first found in the Ural Mountains and named after Lev Perovski (the founder of the Russian Geographical Society). True perovskite (the mineral) is composed of calcium, titanium and oxygen in the form CaTiO_3 . Meanwhile, a perovskite structure is anything that has the generic form ABX_3 and the same crystallographic structure as CaTiO_3 .



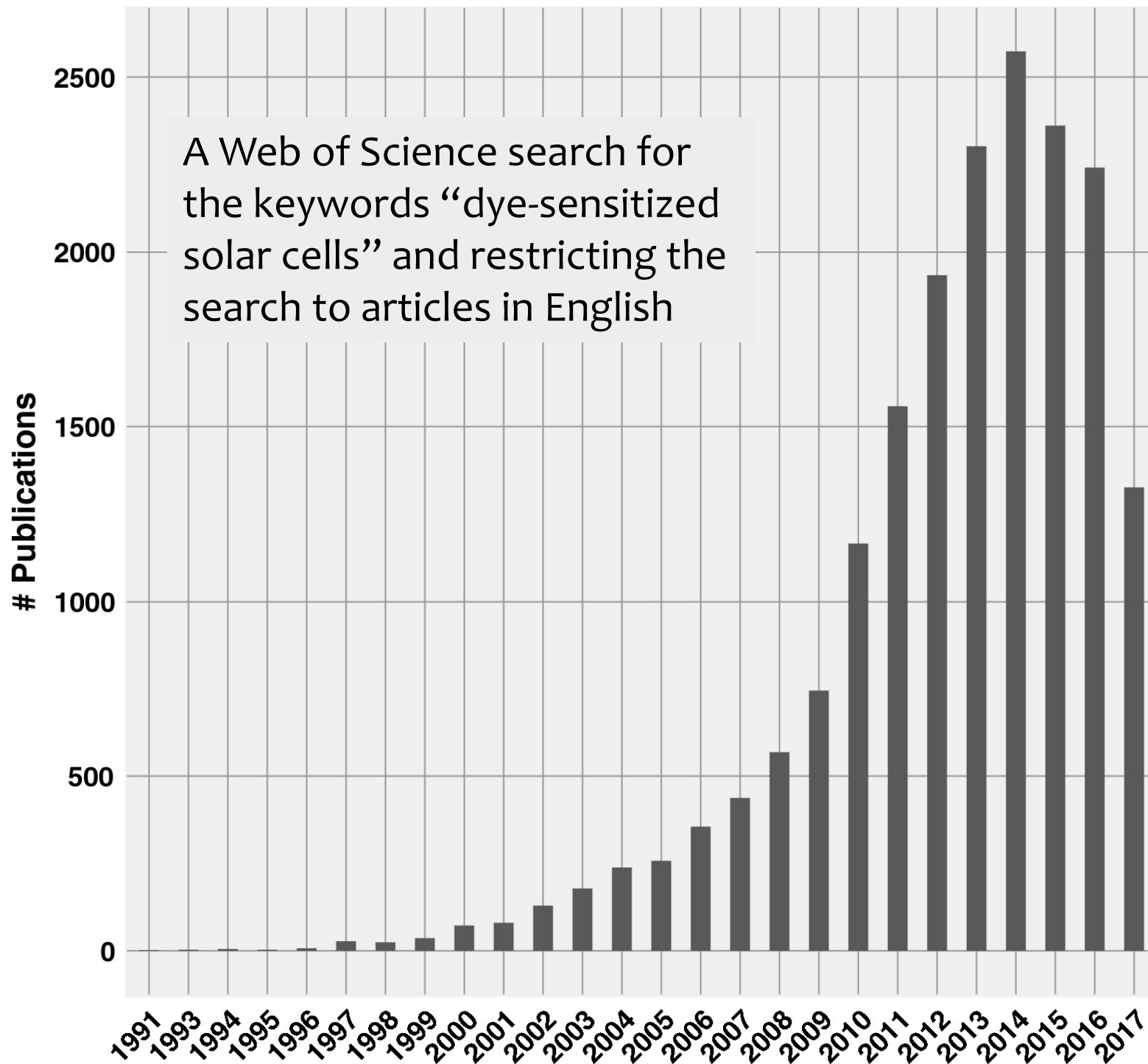
Nat. Photonics.
2014;8:506–514



Science, Vol. 2012, 338, 643–647

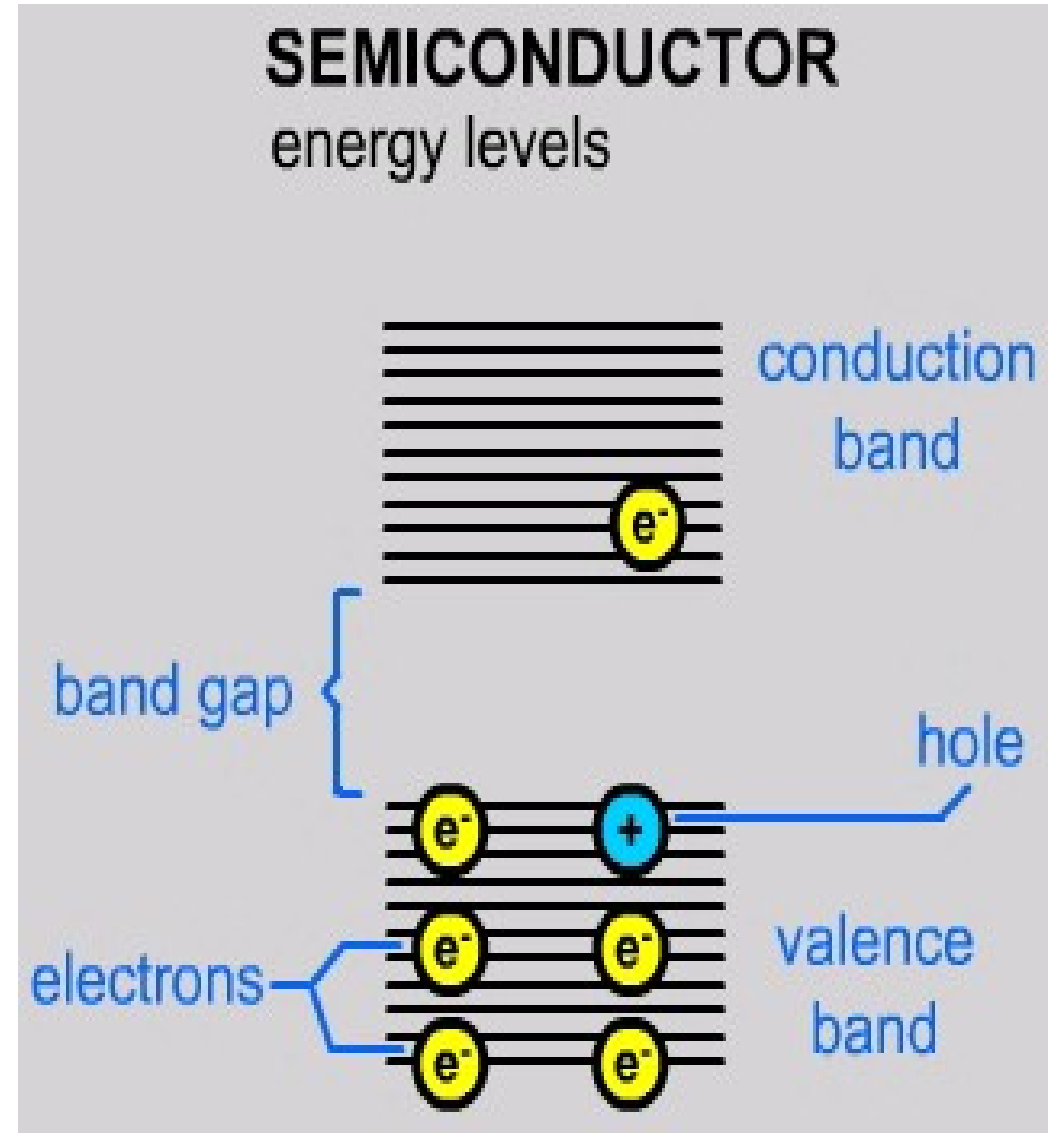
Perovskites were first successfully used in solid-state solar cells in 2012, and since then most cells have used the following combination of materials in the usual perovskite form ABX_3 :

A = An organic cation - CH_3NH_3^+ or $\text{NH}_2\text{CHNH}_2^+$; **B** = A big inorganic cation - usually Pb^{2+} & **X₃** = A halogen anion – usually Cl^- or I^-

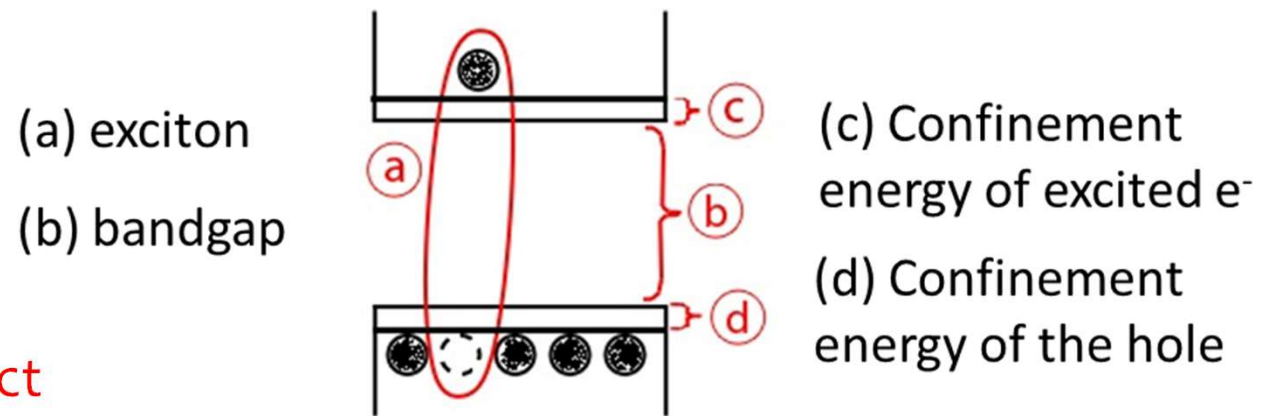


The dye-sensitized solar cell database
J Cheminform, 2018, 10:18; doi: 10.1186/s13321-018-0272-0

- The average distance between an electron and a hole in an exciton is called the **Excited Bohr Radius**.
- When the size of the semiconductor falls below the Bohr Radius, the semiconductor is called a quantum dot.



Quantum dot solar cells have the potential to produce high efficiencies with a relatively cheap cost to construct them. Furthermore, quantum dots have the capability of multiple electrons being excited from one photon of light (in comparison to organic dyes which generally only have one electron excited per single photon)

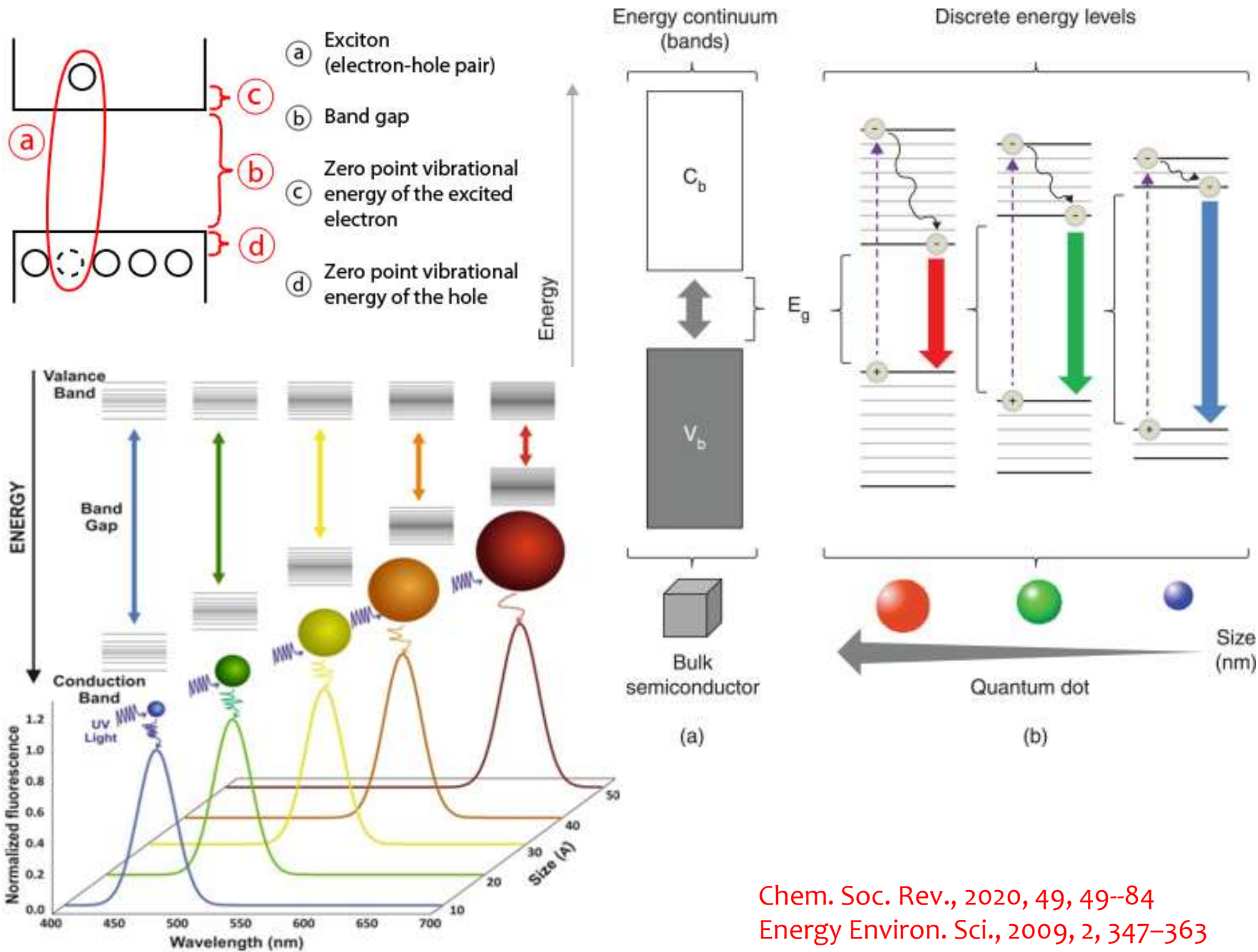


Quantum confinement effect

Generally, when the size of the quantum dot is equal to or smaller than the exciton Bohr radius of the corresponding bulk material, the movement of the carrier electron-hole pair is in a strongly restricted state. As the particle size becomes smaller, the energy gap increases and the energy in the semiconductor material is quantified. The energy after quantification of the semiconductor material is:

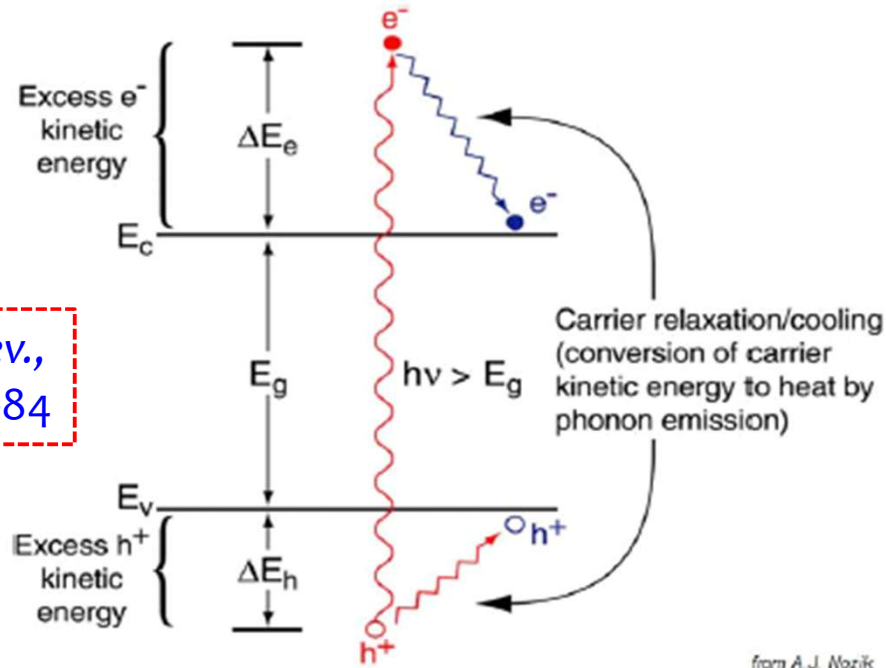
$$\Delta E_g = E(R) + \left[\frac{h^2}{8R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) \right] \quad [E(R) \text{ is the lowest excitation energy}]$$

In the formula, ΔE_g is the bulk band gap, m_e and m_h are the mass of electrons and holes, respectively, R is the radius of the particle, and $E(R)$ is the lowest excitation energy.

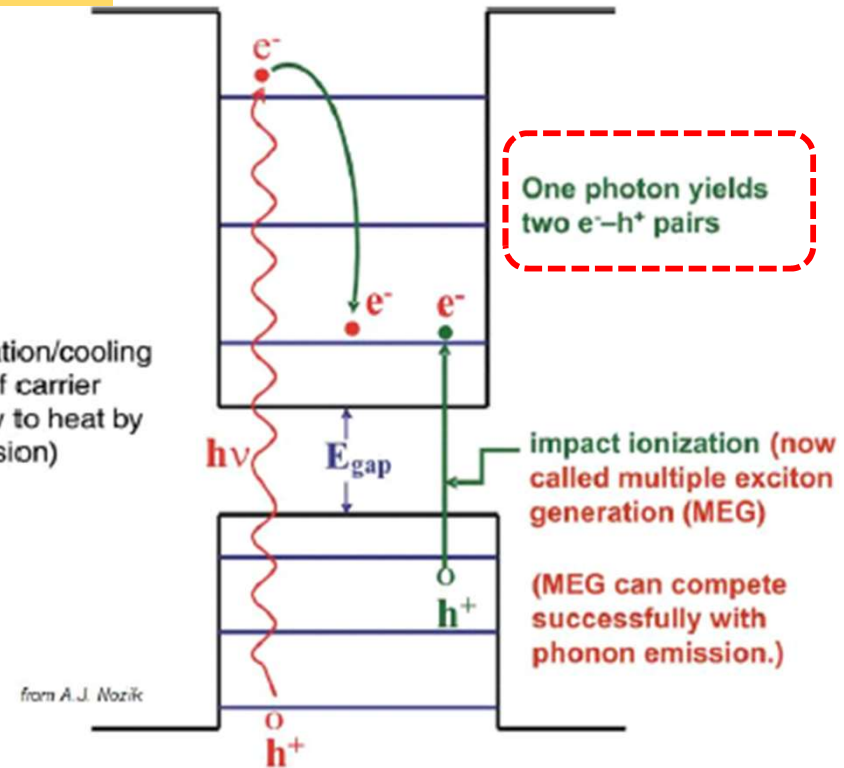


Chem. Soc. Rev., 2020, 49, 49–84
 Energy Environ. Sci., 2009, 2, 347–363

Chem. Soc. Rev.,
2020, 49, 49--84



(a) Bulk Semiconductor



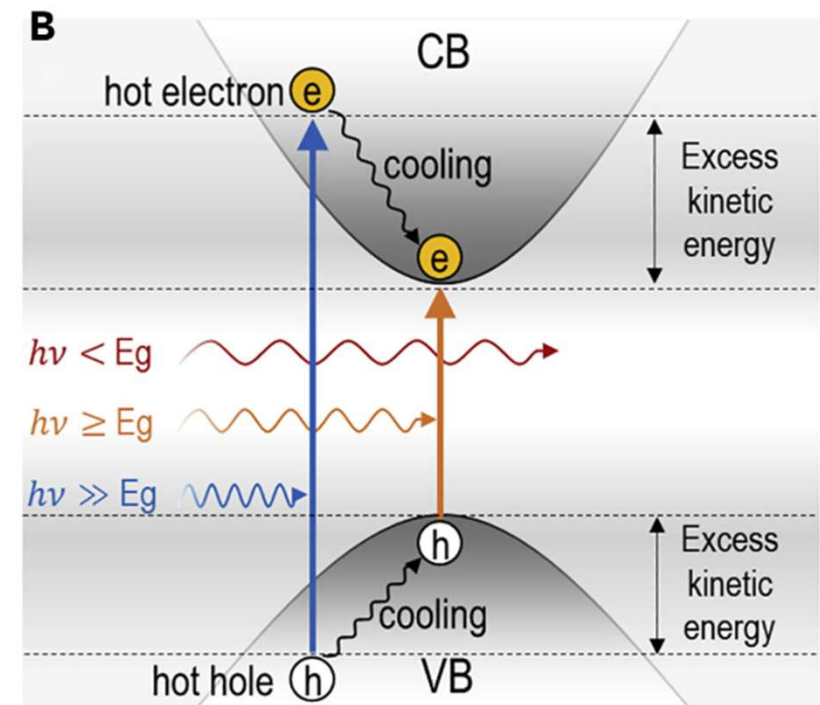
(b) Quantum Dot

From A.J. Nozik

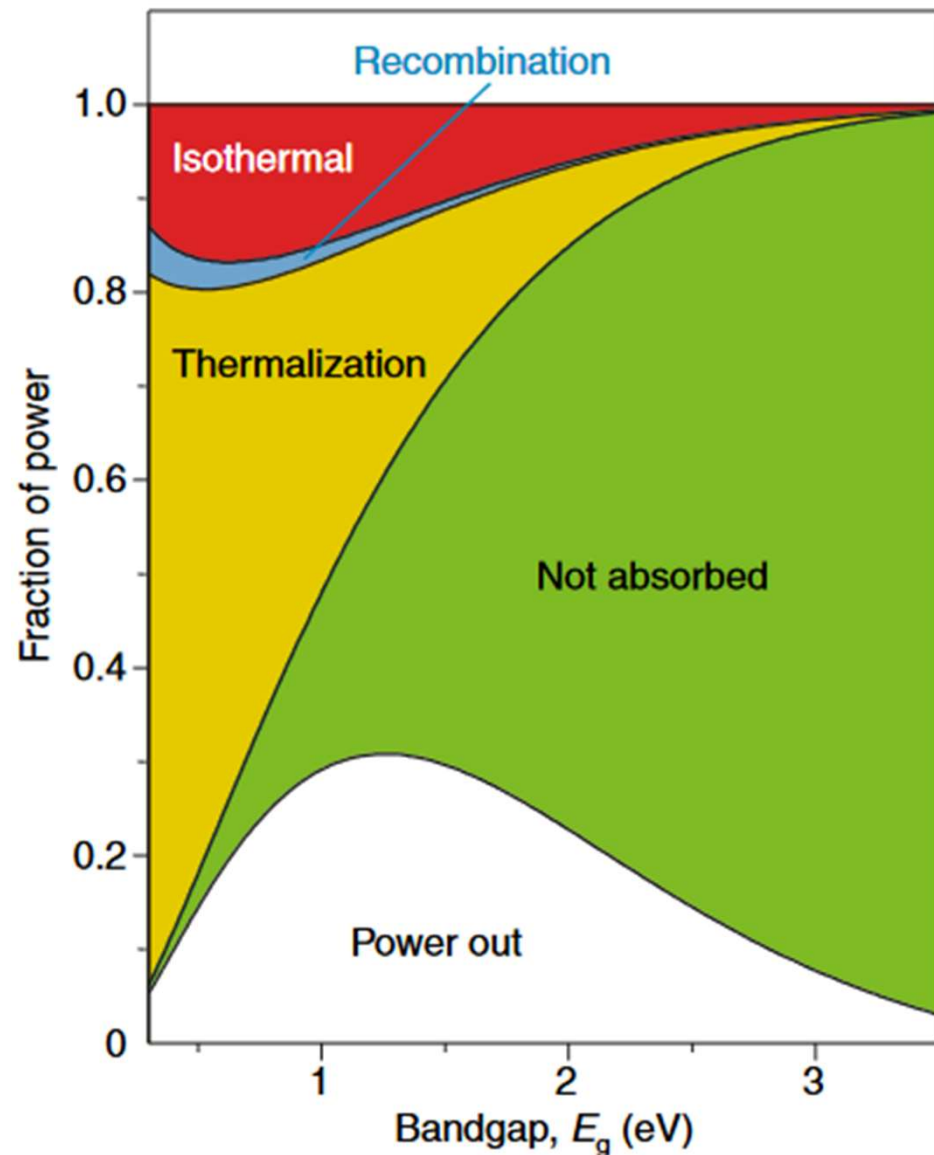
In **Bulk Semiconductor** hot electrons and holes release the excess energy to the band gap energy via successive emission of phonons and cool to the band edge quickly within femtosecond and the excess energy is lost in the form of heat energy. It is difficult to extract the electrons from their higher energy state.

For **QDs** the cooling process becomes slower and electrons with excess energy more than the band gap energy can create another electron-hole pair known as multiple exciton generation, which could enable QDSCs to break the Shockley–Queisser efficiency limit of 32.9 % for a single junction (single absorber) solar cells.

The Shockley–Queisser (SQ) limit describes the theoretical sunlight-to-electricity conversion efficiency of a single-junction solar cell. The SQ limit (33.7% under AM1.5g illumination (109,870 lux)). SQ limit refers to the maximum theoretical efficiency of a single-junction solar cell and is calculated by examining the amount of electrical energy extracted per incident photon. Using an AM 1.5 solar spectrum, a solar cell with an ideal band gap light absorber (band gap, $E_g = 1.4$ eV) could have an upper limit on PCE of 33.7%,⁶ i.e., a maximum electrical power generation of 337 Wm^{-2} . A major loss factor is related to the energy mismatch between the broad wavelength distribution of sunlight and the mono-band gap of the light absorber in the cell.



The Limitations of Silicon Solar Cells



- Optical:** Photons with energy lower than the bandgap are not absorbed. The higher the bandgap, the higher the amount of non-absorbed photons (~ 19% of the total losses).
- Thermal:** Photons with an energy that exceeds the Bandgap ($E > E_g$) are absorbed. The generated carriers are thermalizing down to the band edge. The excess energy is released as heat to the solar cell (~ 33% of the total losses).
- Electronic:** Loss due to radiative charge recombination, i.e. the pair recombines and, eventually, a photon is emitted. (~ 15% of the total losses).
- Isothermal losses:** An additional electronic contribution due to the power dissipation along the band-edge (constant temperature of the carrier).

These losses result in about 68% of the total sunlight not being converted into electricity

<https://www.fluxim.com/perovskite-silicon-tandem-pv-record-updates>

| Type of Perovskite | Example | Band Gap Type | Notes |
|--------------------------|--------------------------------------|------------------------------|-------------------------------------|
| Organic–inorganic halide | $\text{CH}_3\text{NH}_3\text{PbI}_3$ | Direct | Strong absorption, photoluminescent |
| All-inorganic halide | CsPbBr_3 | Direct / quasi-direct | Phase-dependent |
| Oxide perovskite | SrTiO_3 | Indirect | Weak emission |

Excellent Optoelectronic Properties

- **Direct band gap:** Enables strong light absorption and efficient photoluminescence.
- **High absorption coefficient:** $>10^5 \text{ cm}^{-1}$ — allows complete light absorption in thin films.
- **Long carrier diffusion lengths:** Often $>1 \mu\text{m}$, enabling efficient charge collection.
- **Balanced electron and hole mobilities:** Facilitates low recombination losses.

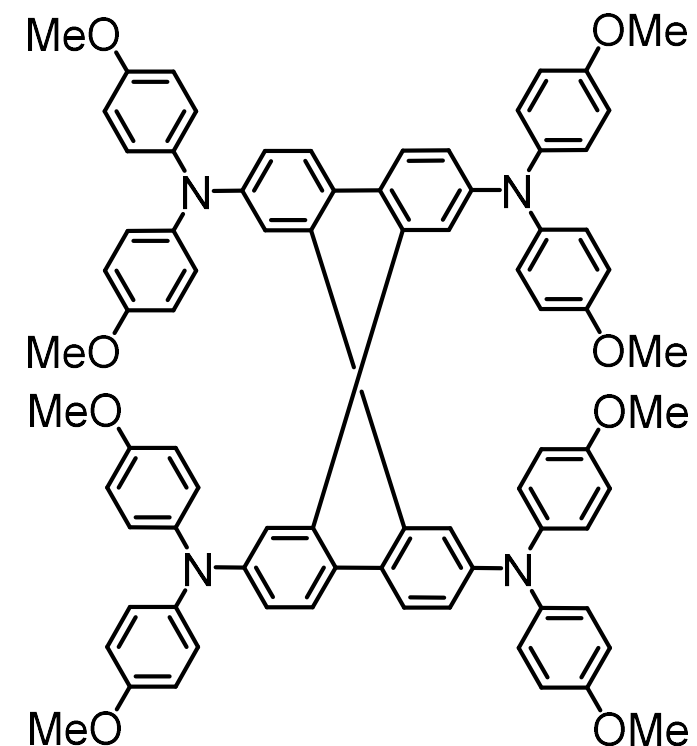
Tunable Band Gap

- The band gap can be precisely tuned (1.2–2.3 eV) by varying:
- Halide composition (I^- , Br^- , Cl^-)
- A-site cation (MA^+ , FA^+ , Cs^+)
- Dimensionality (3D, 2D, quasi-2D)
- This allows optimisation for **solar cells, LEDs, photodetectors, and lasers.**

| Advantage | Origin | Application Impact |
|--|-------------------------|---------------------------------|
| Direct, tunable band gap | Hybrid lattice design | High efficiency, broad spectrum |
| High absorption, long diffusion length | 3D crystal structure | Thin-film photovoltaics |
| Solution processability | Soft hybrid lattice | Low-cost, scalable fabrication |
| Defect tolerance | Ionic bonding nature | Stable performance |
| High PLQY | Radiative recombination | LEDs, lasers |
| Flexibility | Organic component | Flexible devices |

ORGANIC–INORGANIC HYBRID PEROVSKITES

- Hybrid Organic Inorganic Semiconductor
- Inorganic - Lead (Strong light absorption, Provide high efficiencies, even above 20 % as per NREL)
- Organic- Methyl Ammonium (Soluble in Polar Solvents, Provides low temperature processing - low cost and energy saving)
- First three-dimensional organic–inorganic hybrid perovskite:
Replacing Cs^+ in CsPbX_3 ($\text{X} = \text{Cl}, \text{Br}$ or I) with $\text{MA} (\text{CH}_3\text{NH}_3)^+$ in 1978.
- $\text{CH}_3\text{NH}_3\text{PbI}_3$ is most common used materials for making high efficiency perovskite solar cells.



Due to the lack of planarity, organic modifications not to affect the ionization potential appreciably.

Typical properties:

HOMO = -5.15 eV

LUMO = -2.10 eV

$E_{\text{ox}}(\text{DCM}) = 0.65 \text{ V vs. NHE}$

Hole mobility = $1.9 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

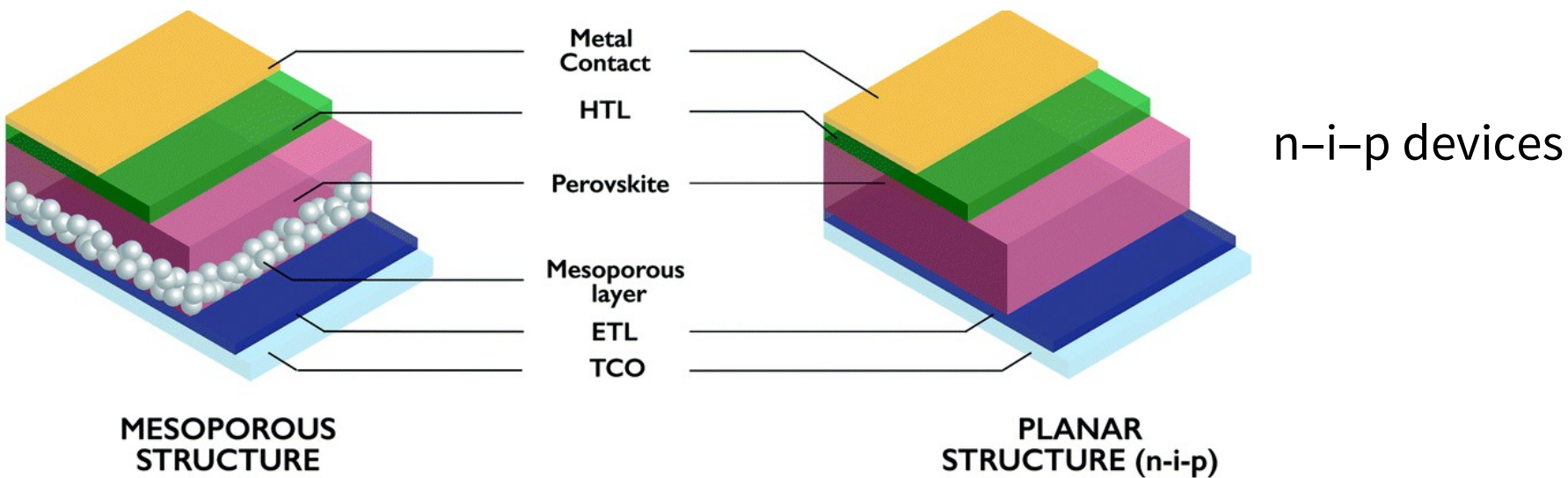
$\lambda_{\text{abs}} = 387 \text{ nm}$

$E(\text{eV}) = 1240 / \lambda$
(expressed in nm)

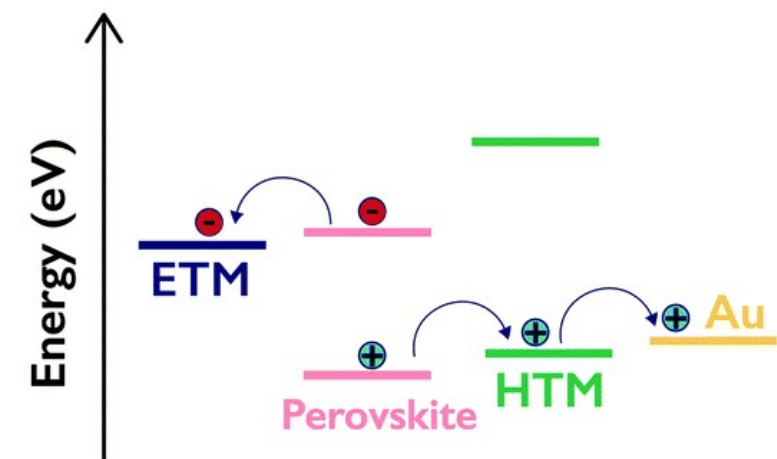
Energy & Environmental Science,
2016, DOI: [10.1039/C6EE00056H](https://doi.org/10.1039/C6EE00056H)

A prominent solid-state HTM is **2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)9,9'-spirobifluorene** (**spiro-OMeTAD**) used for solid-state dye-sensitized solar cells as well as an efficient HTM in the rapidly developing area of perovskite solar cells. In particular, the ionization potential of **spiro-OMeTAD** matches well with that of the light absorbers (perovskites or dye-sensitizers), and good contact at their interfaces is promoted by the remarkable glass forming properties of spiro-OMeTAD. These advantages make spiro-OMeTAD the most extensively studied organic HTM for hybrid organic-inorganic solar cells

[Flexible Electronics (2017) 1:2 ; doi:10.1038/s41528-017-0002-0]



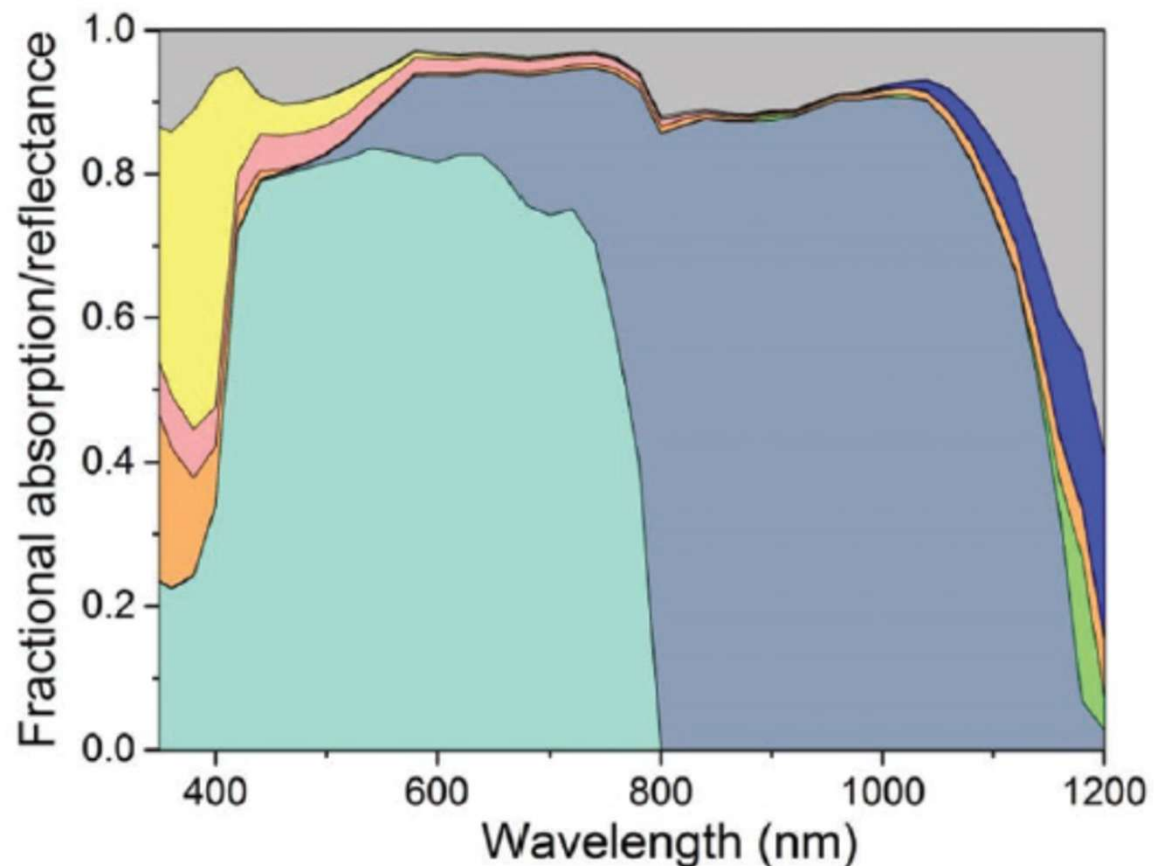
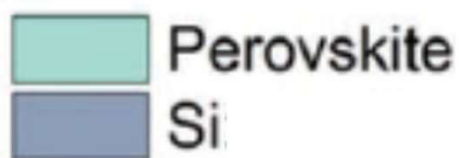
Chem. Soc. Rev., 2018, **47**, 8541-8571



Conventional n-i-p perovskite solar cells:
The general device configuration is:
TCO / c-TiO₂ / m-TiO₂ / perovskite / HTM / metal,
where TCO denotes a transparent conducting
oxide (e.g., FTO or ITO).

The typical stack is: TCO / ETM / perovskite / HTM / metal, where ETM is an electron-transporting material (e.g., SnO₂, TiO₂, or PCBM). The absence of a mesoporous scaffold simplifies fabrication and is compatible with low-temperature processing.

The development of high-efficient silicon solar cells is, however, approaching its theoretical efficiency limit of 29.4%.



As a next step, the concept of silicon-based tandem solar cells is promising to break this limit. Stacking two solar cells on top of each other, the top cell — with a high band gap (metal halide perovskite having ABX_3 crystal structure) material — utilizes high energy photons while the silicon bottom cell utilizes low energy photons. Perovskite have a tunable band gap — the parameter that determines which part of the solar spectrum is utilized.