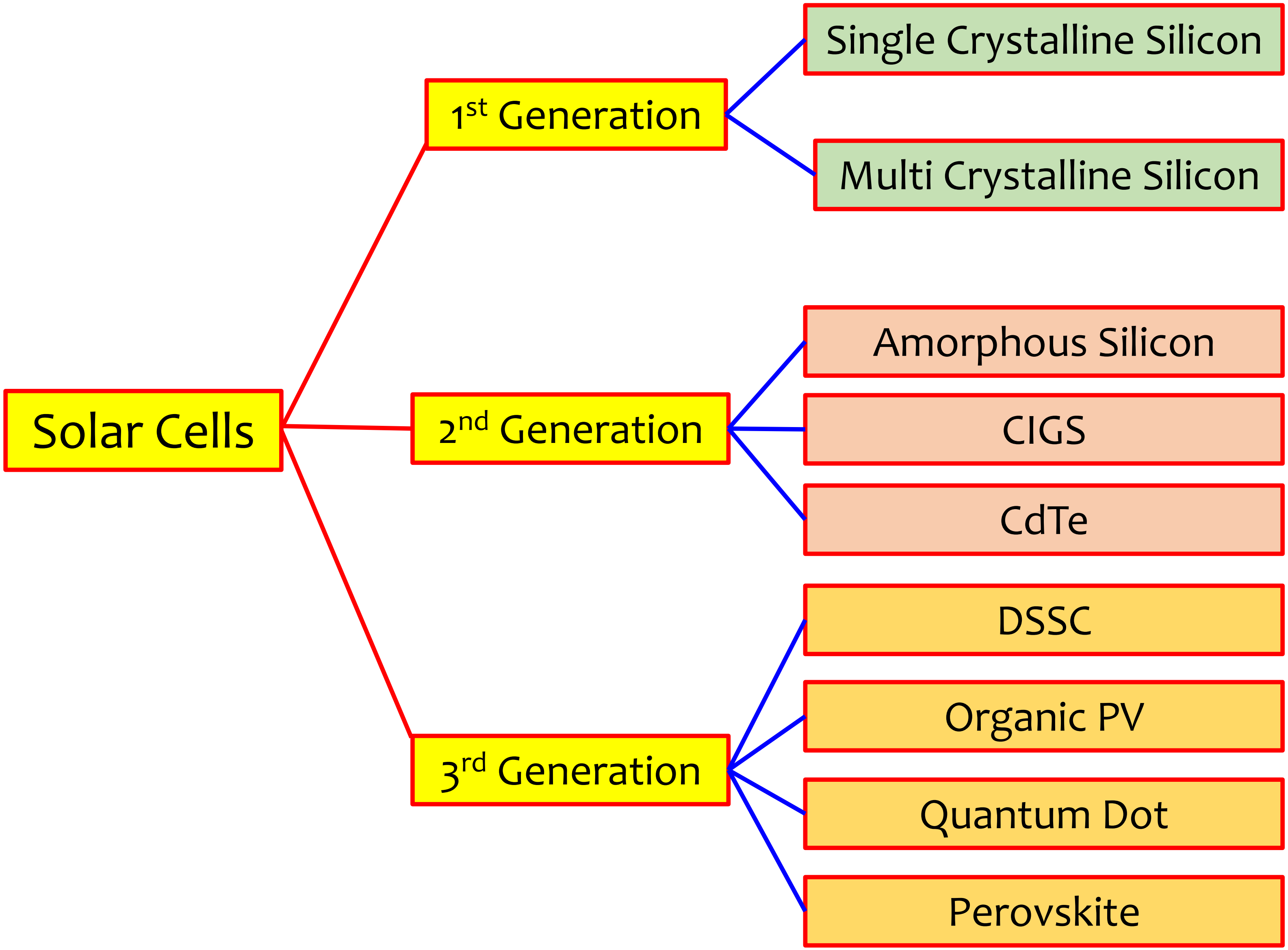
# Third Generation Solar Cells
# DSSC

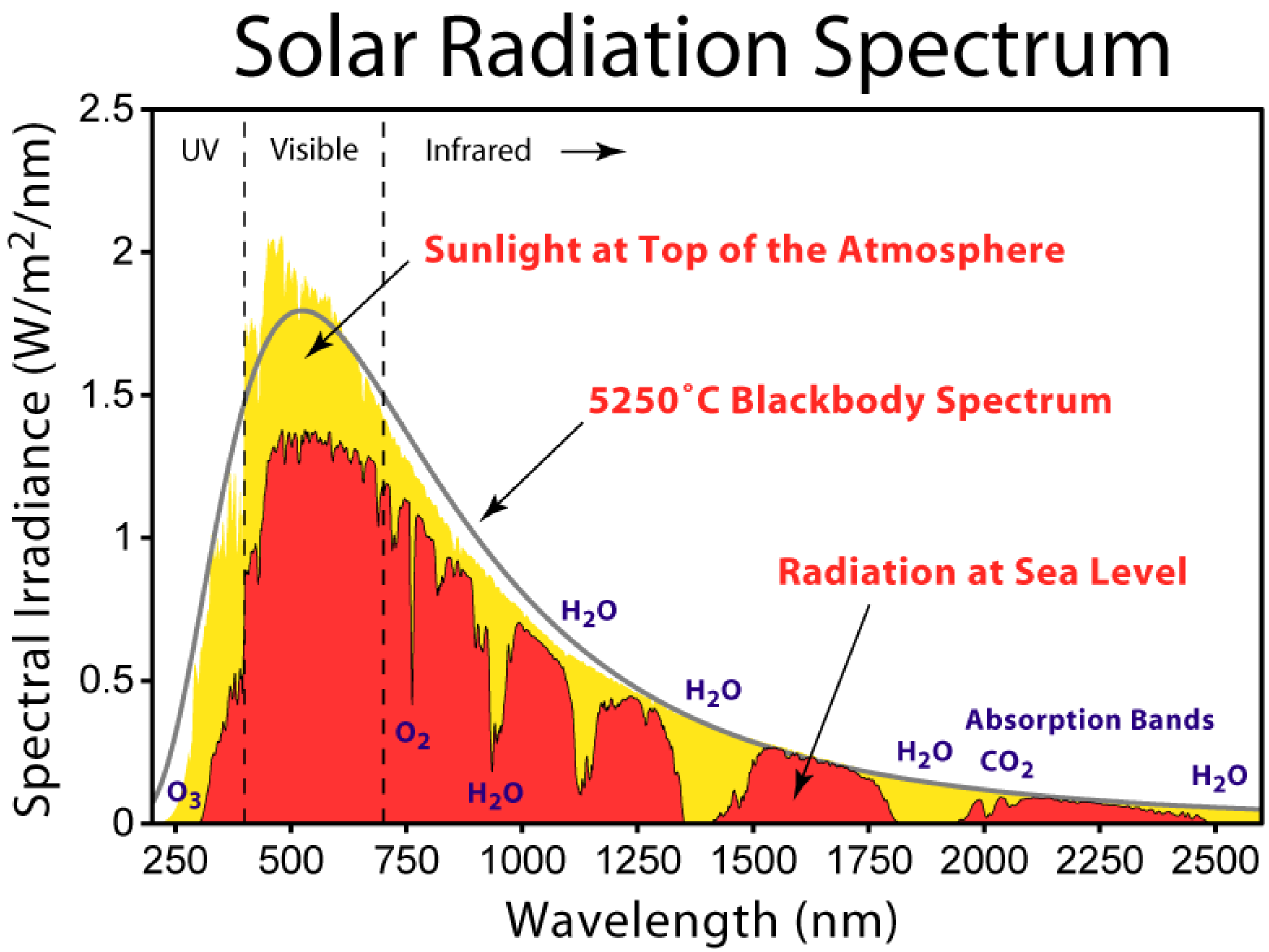
Prof. S. Sivaram
Prof. S. Sengupta
Amitava Das

CH5106-L14 AD

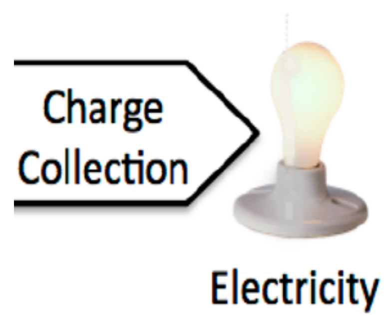
# Solar Cell Developments—Three Generations



O ... it on the Earth's
a ... orbed by the Earth
s ... tmosphere itself.
T ... in a day is sufficient
t ...




S



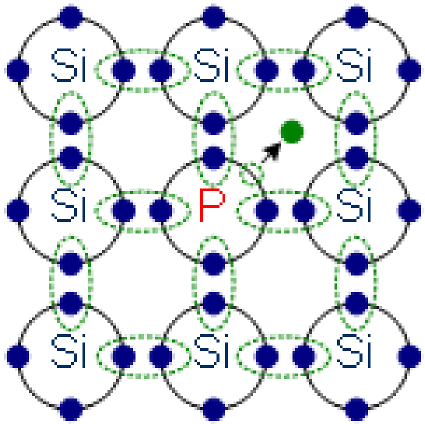

Solar irradiance spectrum above the Earth's atmosphere and at the surface. Data source: www.nrel.gov

Steps involved in conversion of sunlight into electricity in a typical solar cell

Pure silicon (intrinsic silicon) is a poor semiconductor, not an insulator.

- Band gap: Silicon has a moderate band gap of ~1.12 eV at room temperature — large enough that few electrons are thermally excited to the conduction band, but small enough that some conduction does occur.
- Electrical conductivity: At room temperature, its conductivity is around $10^{-4}$ to $10^{-6}$ S/cm, which is much lower than metals but far higher than true insulators (which have conductivities $<10^{-12}$ S/cm).
- Temperature dependence: As temperature increases, more electrons are thermally excited across the band gap, and conductivity rises sharply — a hallmark of semiconductors.

- At 0°K : Behaves like an insulator (no free charge carriers).
- 300°K : Behaves as a poor (intrinsic) semiconductor.
- Doped with P/B: A good semiconductor (n-type or p-type).

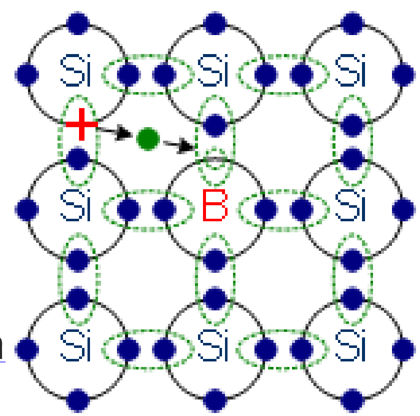



## N-Type (Negative)

Silicon is doped with phosphorus gas to make it conductive. A silicon atom has four electrons in its outer shell and bonds tightly with four surrounding silicon. However, phosphorus has five electrons, and when combined, the fifth electron becomes a "free" electron that moves easily within the crystal when a voltage is applied. Because the charge carriers are electrons, n-type refers to a negative charge.

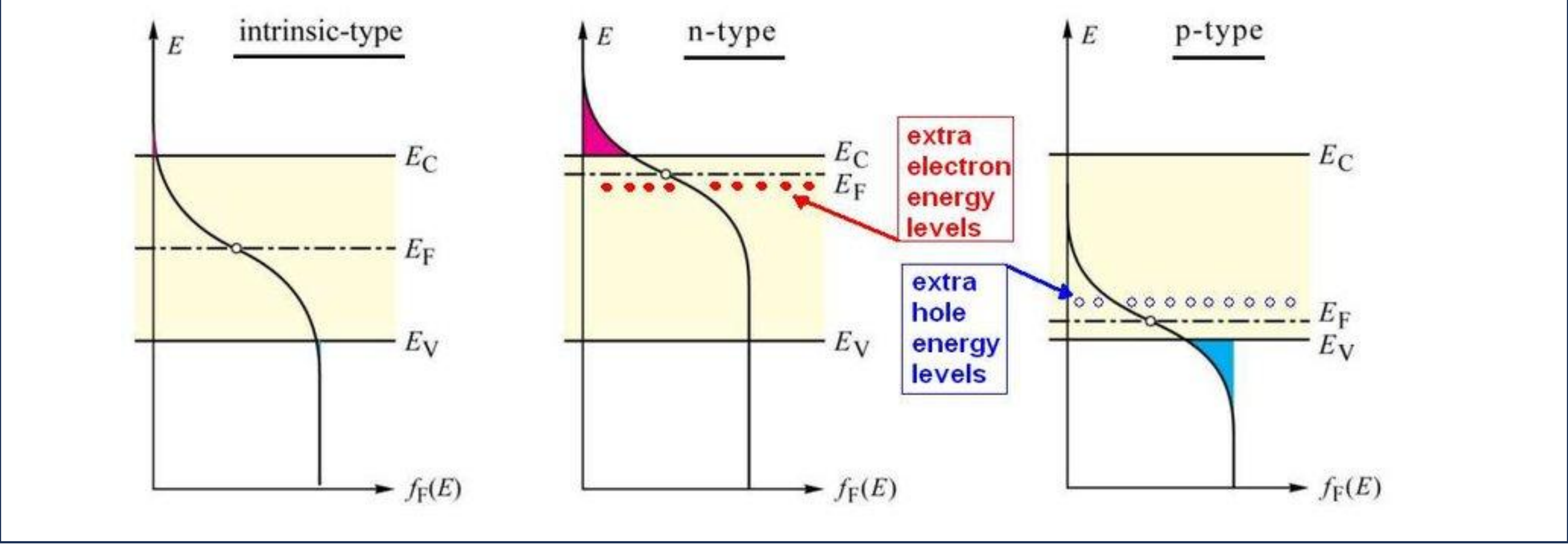
## P-Type (Positive)

Silicon doped with boron gas that turns it into a conductive material that readily accepts electrons when voltage is applied. Boron has only three electrons in its outer shell and can bond with only three of the four surrounding silicon atoms. This leaves one silicon atom with a vacant location in its outer shell, called a "hole," that readily accepts an electron. Because the charge carriers are holes, p-type silicon is said to have a positive charge.




Pure silicon is a poor conductor. When doped (e.g., with phosphorus for n-type or boron for p-type), the number of charge carriers increases dramatically, and it becomes a good semiconductor.

Chapter 1: Silicon Solar Cells, by P. M. Ushasree* and B. Borab; Inorganic Materials Series No. 3
Solar Energy Capture Materials; Edited by Elizabeth A. Gibson © The RSC 2019




The Fermi level determines the probability of electron occupancy at different energy levels. The closer the Fermi level is to the conduction band energy, the easier it will be for electrons in the valence band to transition into the conduction band. Electrons settle into the lowest available energy states at absolute zero temperature.

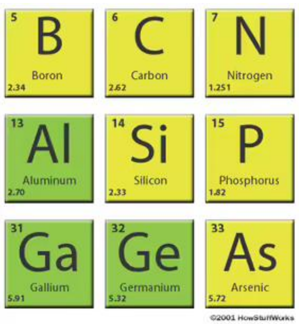
The gap between the valence and conduction bands is called the energy gap. At the Fermi level (when $E=E_f$), the probability simplifies to ½ and thus $E_f$ lies halfway between the valence and conduction band, or in the middle of the energy gap ($E_{gap}/2$).

Impurities and temperature can affect the Fermi level. Semiconductor atoms are closely grouped together in a crystal lattice and so they have very few free electrons to be good conductors. The ability of semiconductors to conduct electricity can be greatly improved by introducing donor or acceptor atoms to the crystalline structure, either producing more free electrons or more holes. This process is called "doping" and as the semiconductor material is no longer pure, these donor and acceptor atoms are collectively referred to as "impurities". For both N-type or P-type semiconductors, the position of the Fermi level relative to the band structure can be controlled to a significant degree by doping.

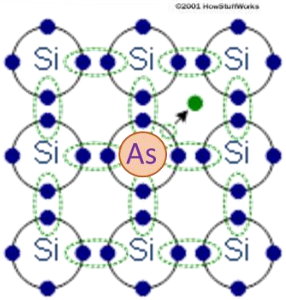
Gallium Arsenide (**GaAs**): External quantum efficiency (EQE) and reflectance curves of the fabricated GaAs thin-film solar cell. The sudden increase in the spectral response of the EQE around 880 nm corresponds to the band gap energy of GaAs. The high EQE of >80% occurs in the 500–800nm wavelength range.

The GaAs thin-film solar cell is a top contender in the thin-film solar cell market in that it has a high power conversion efficiency (PCE) compared to that of other thin-film solar cells. The efficiency of ~ 28.9%, while this is the most expensive.

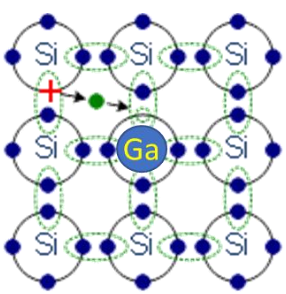
Scientific Reports | 6:30107 | DOI: 10.1038/srep30107




N-Type




P-Type




The following graph is the famous limit efficiency (%) of Shockley-Queisser for p-n junctions in function of the energy band gap (eV):

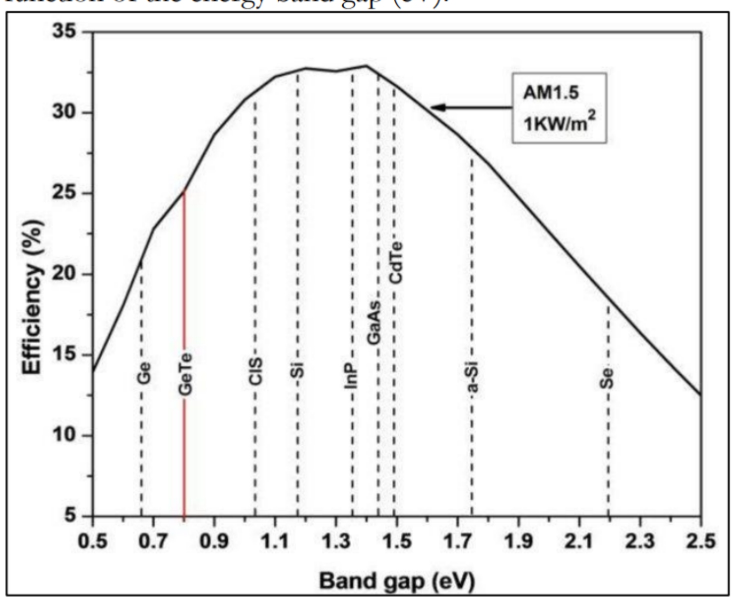



*Illustration 6 - S.Q. efficiency limit in function of the energy band gap and the correspondence for different solar cells materials.*

The maximum efficiency is reached around 33,7% for a single pn-junction PV cell, assuming AM 1.5 solar spectrum and a temperature of the cell of 300 K and it occurs at a band gap of 1.34eV, which is very close for silicon solar cells, which have a band gap of 1.12eV.

Need to redo

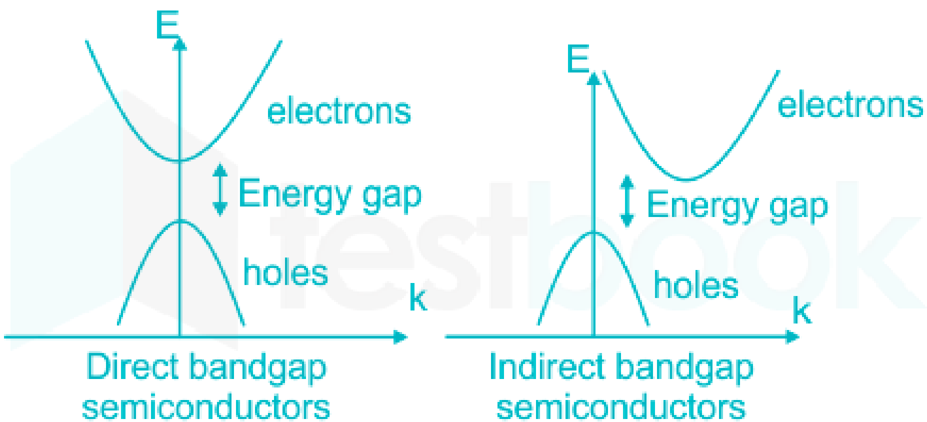
Gallium arsenide offers significant advantages over silicon, such as higher electron mobility and better performance in optoelectronic applications due to its direct bandgap. Silicon is an indirect band gap semiconductor with a band gap of 12 eV .

Drawbacks for GaAs: Higher manufacturing costs, more brittle compared to silicon.

Toxicity studies in experimental animal systems have shown gallium nitrate and gallium arsenide to produce toxicity to the lungs, immune system, kidneys, and hematopoietic systems. The International Agency for Research on Cancer (IARC) has classified gallium arsenide as a human carcinogen.

**Direct Band Gap (DBG) Semiconductors:**

**The semiconductor in which the top of the valence band and the bottom of the conduction band occur at the same value of momentum.**




https://testbook.com/objective-questions/mcq-on-direct-and-indirect-band-gap-semiconductors--5eea6a0c39140f30f369dfa4

**Since Silicon is an Indirect Band Gap semiconductor** so electron cannot fall directly to the valence band but must undergo a momentum change as well as a change in energy. So, energy is released as heat along with light.

| Type of Solar Panel | Pros | Cons |
|---|---|---|
| Monocrystalline | • Highest efficiency, which means more kilowatt-hours per square foot covered.<br>• Longer lifespan (25+ years) | – Most expensive type of solar panel |
| Polycrystalline | • Balanced cost and efficiency: intermediate between monocrystalline and thin-film solar panels (best suited for installations where space is not a constraint).<br>• Long lifespan (25+ years) | – Lower efficiency than mono panels<br>– Higher temperatures affect productivity and durability |
| Amorphous | • High temperatures only have a small impact on their productivity.<br>• Lightweight<br>• Low cost<br>• Flexible and adhesive panels are available | – Low efficiency, which means unfit for the average home<br>– Shorter lifespan than mono and poly panels |

https://www.ecowatch.com/amorphous-solar-panels.html

Amorphous silicon (a-Si) is the non-crystalline form of silicon used for solar cells. Used as semiconductor material for a-Si solar cells, or thin-film silicon solar cells, it is deposited in thin films onto  a variety of flexible substrates, such as glass, metal and plastic. Amorphous silicon cells generally feature low efficiency, but are one of the most environmentally friendly photovoltaic technologies, since they do not use any toxic heavy metals such as cadmium or lead.

**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 (≈200–400 °C) using methods like chemical vapour deposition (CVD). c-Si, requires very high temperatures (≈1400 °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**

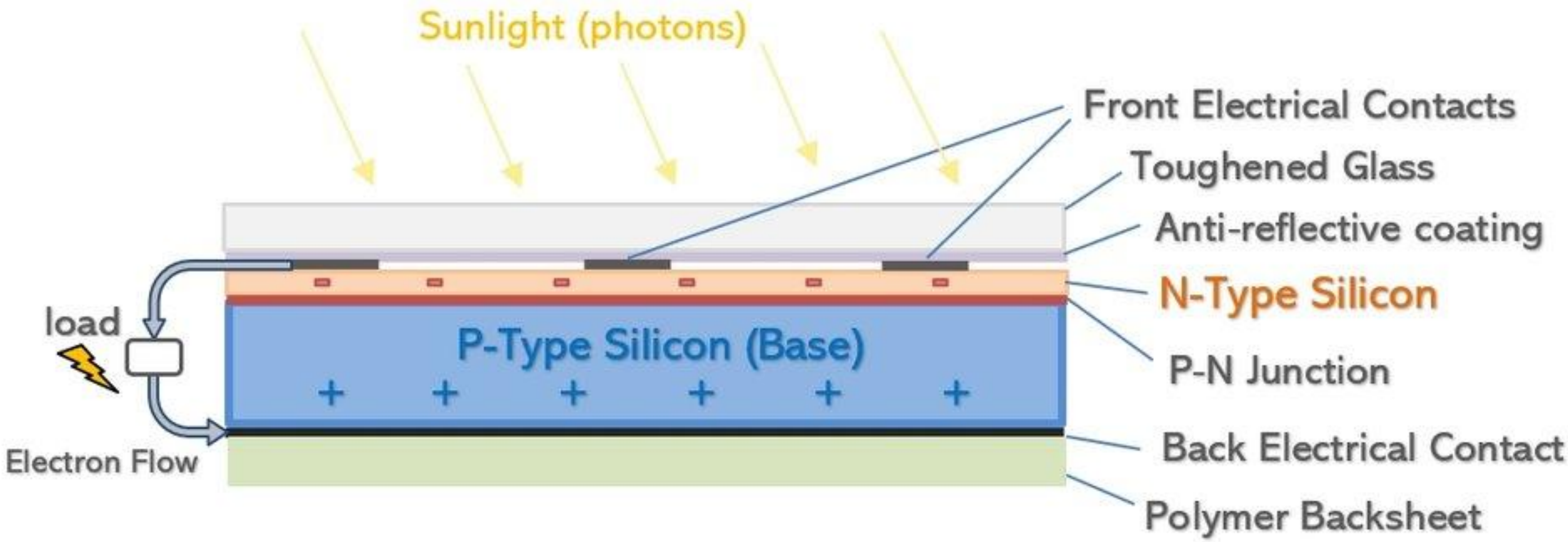
- The simpler, low-temperature, and large-area deposition of a-Si translates to lower manufacturing cost and better scalability.
- c-Si offers superior performance but is less cost-effective and less flexible in fabrication.

**Trade-off**

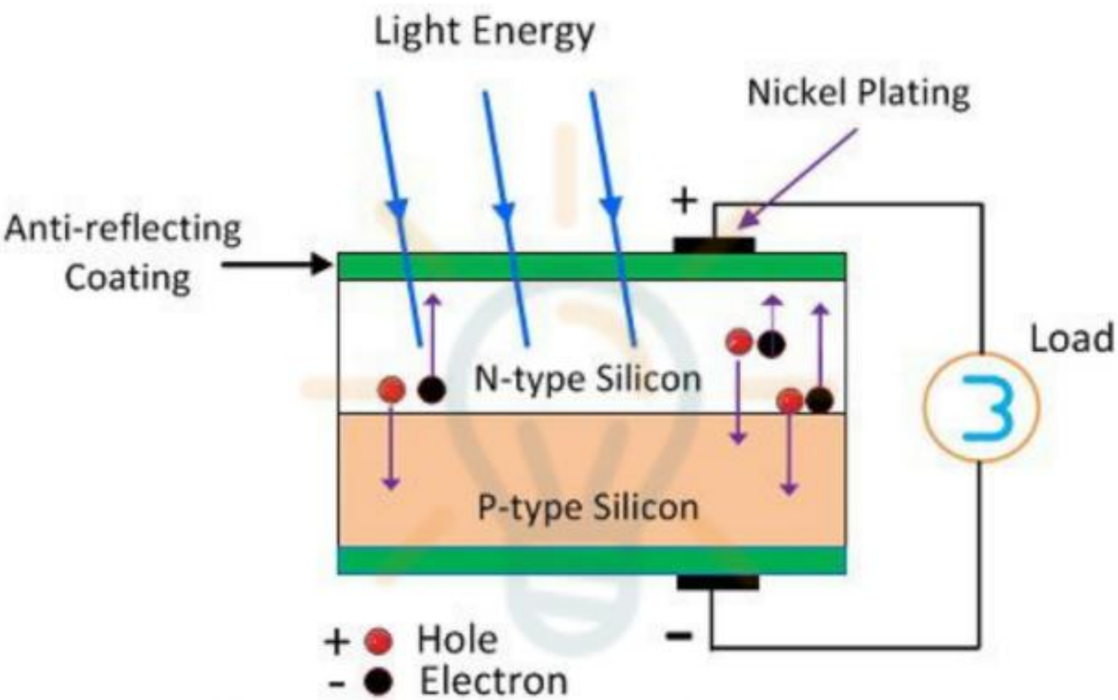
However, this improved processability comes at a cost:

- 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 |

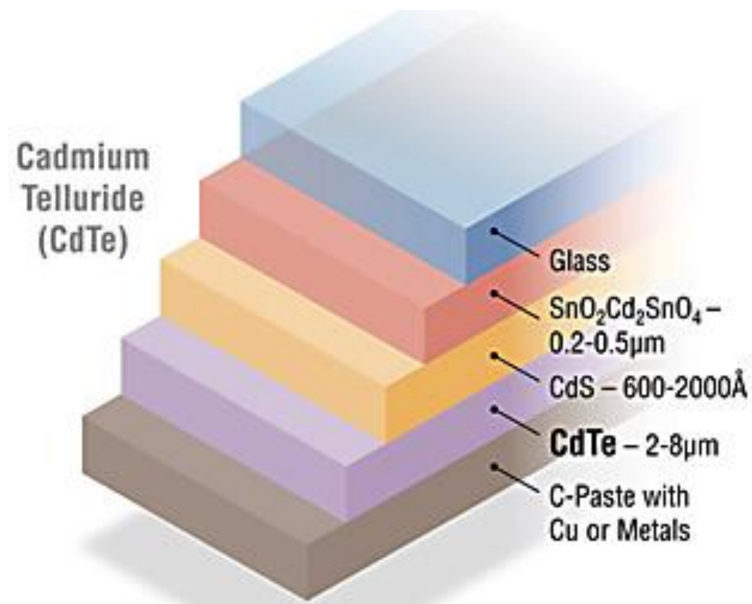


Sunlight (photons)
Front Electrical Contacts
Toughened Glass
Anti-reflective coating
N-Type Silicon
P-Type Silicon (Base)
P-N Junction
load
Back Electrical Contact
Electron Flow
Polymer Backsheet

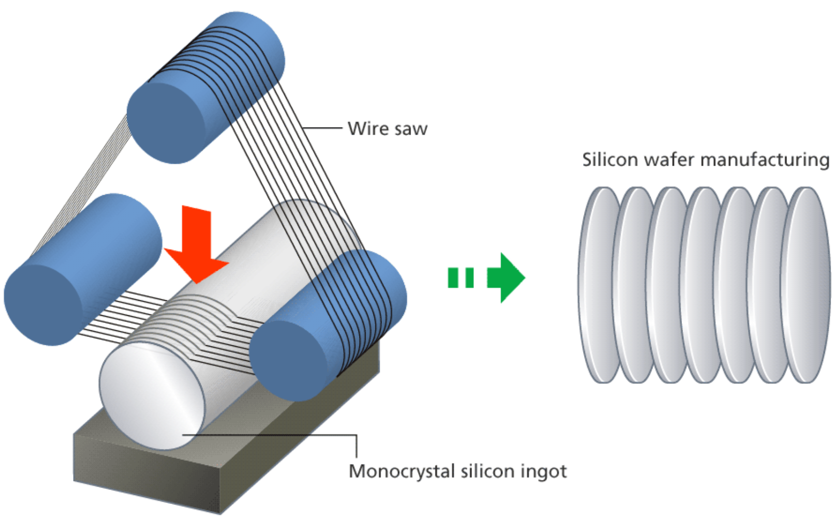
Light Energy
Nickel Plating
Anti-reflecting Coating
N-type Silicon
Load
P-type Silicon
+ Hole
- Electron


Need to redo



Cadmium Telluride (CdTe)
Glass
$SnO_2Cd_2SnO_4$ – 0.2-0.5μm
CdS – 600-2000Å
CdTe – 2-8μm
C-Paste with Cu or Metals

# Schematic of c-Si PV module supply chain

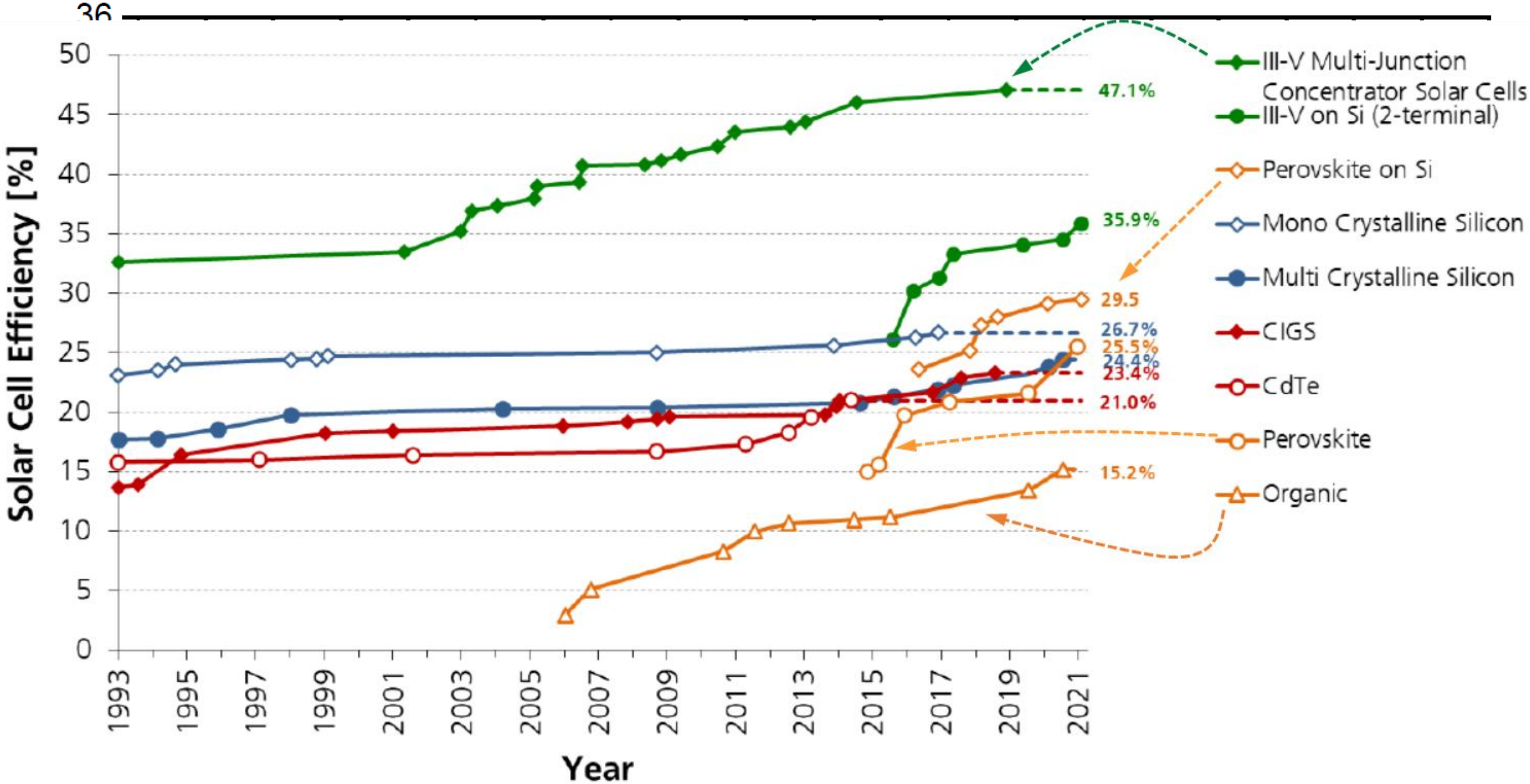




Technical Report; NREL/TP-6A20-72134; Revised February 2020

# 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.

| Feature | $[Fe(bpy)_3]^{2+}$ | $[Ru(bpy)_3]^{2+}$ |
|---|---|---|
| Metal | Fe(II), $3d^6$ | Ru(II), $4d^6$ |
| Ligand field strength | Moderate | Strong |
| MC state energy | **Low-lying** | High-lying |
| MLCT lifetime | <100 fs | ~1 μs |
| Emission | **Quenched (none)** | Strong MLCT phosphorescence |

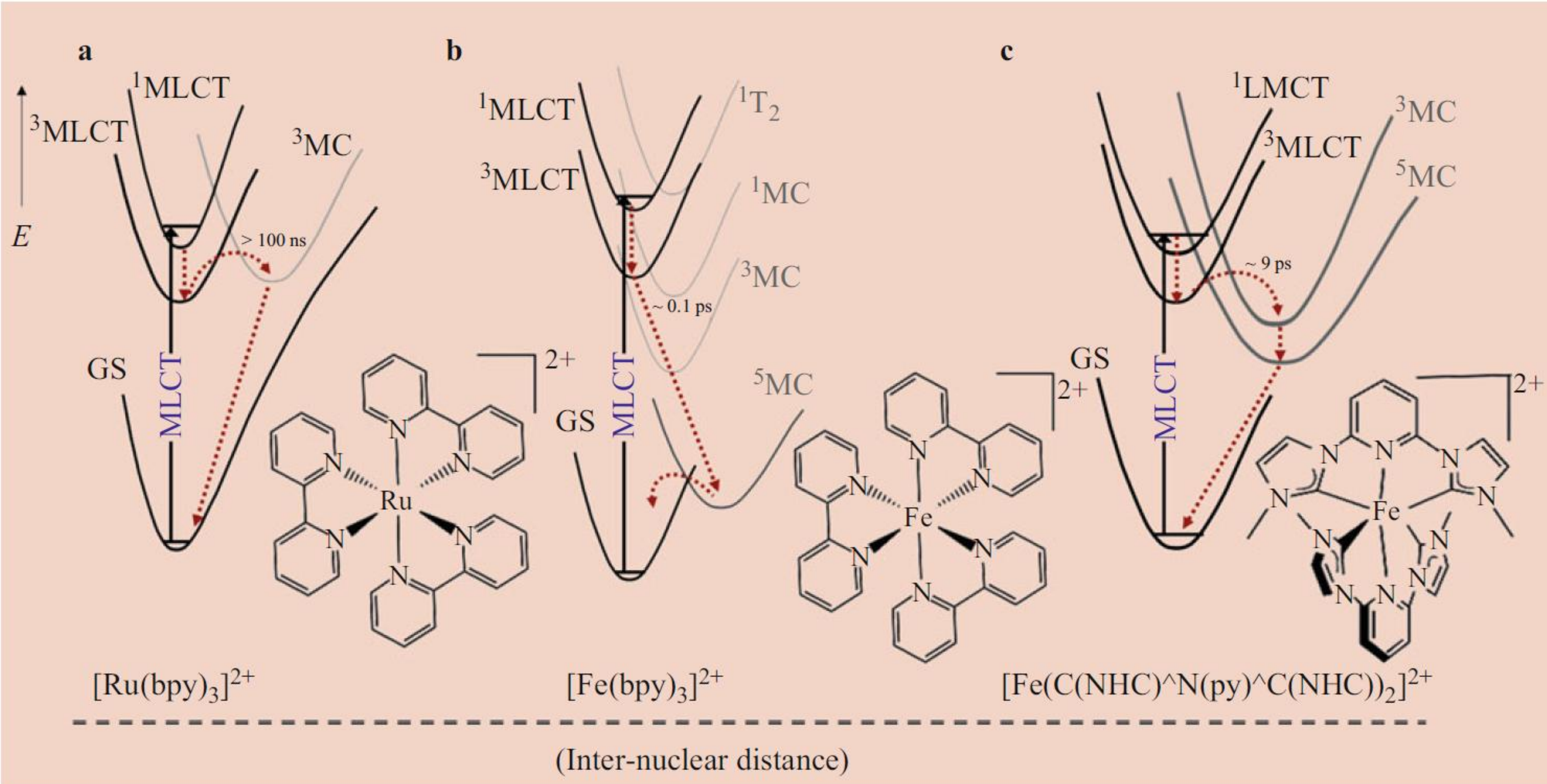
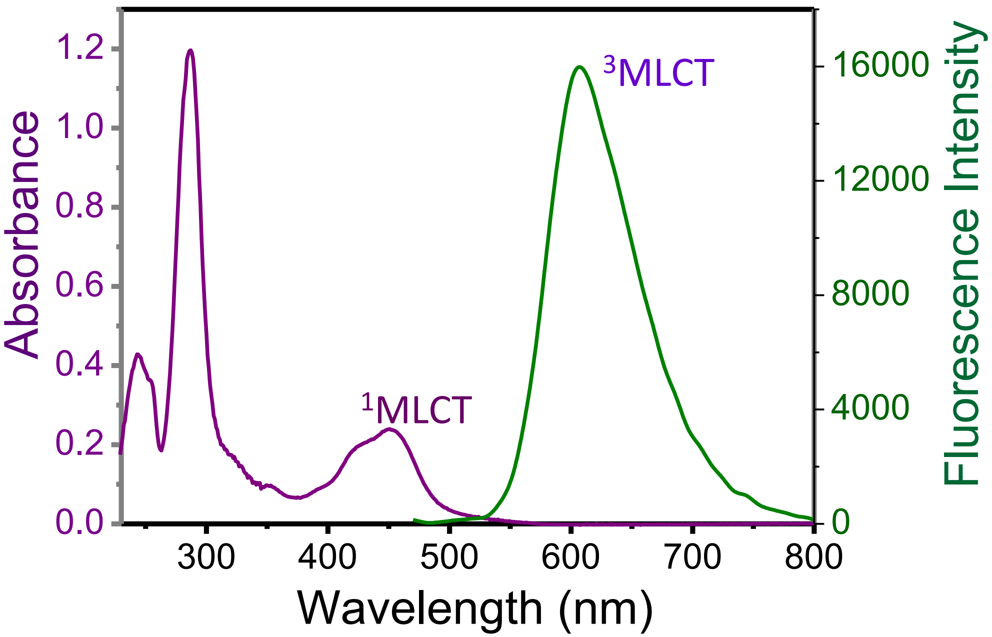



**Fig. 20.3** Comparison between the potential energy diagram for the excited states of selected d$^6$ complexes (**a**) [Ru(bipy)$_3$]$^{2+}$ [30], (**b**) [Fe(bipy)$_3$]$^{2+}$ [31], and (**c**) [Fe(C(NHC)^N(py)^C(NHC))$_2$]$^{2+}$ [32]

Handbook of Inorganic Photochemistry. Springer Handbooks. Springer, Cham.
https://doi.org/10.1007/978-3-030-63713-2_20

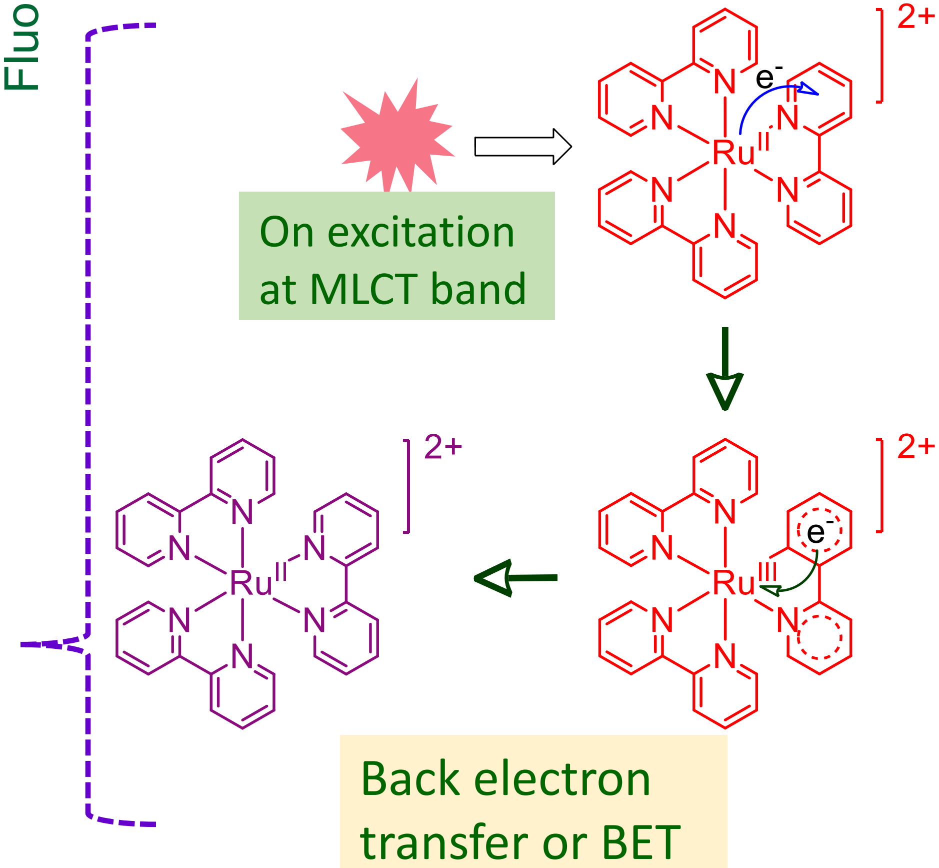
# Third Generation Solar Cells DSSC

Need to redo




$$[Ru^{II}(2,2'\text{-bpy})_3]^{2+} \xrightarrow{h\nu} [Ru^{III}(2,2'\text{-bpy})_2(2,2'\text{-bpy})^{\cdot -}]^{2+}$$

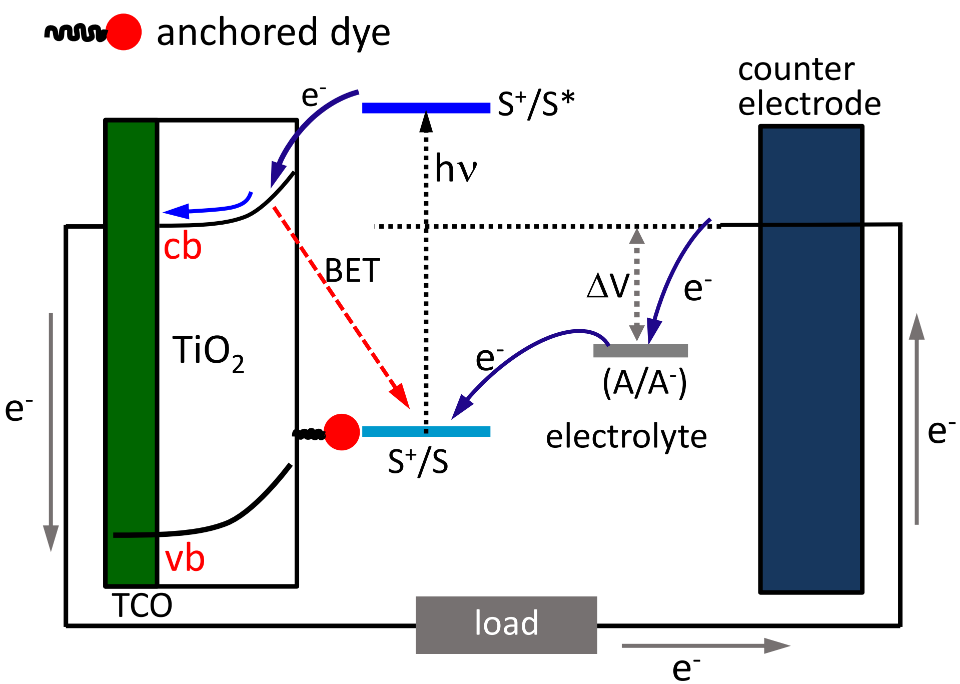
Photo-induced $e^-$ transfer Processes

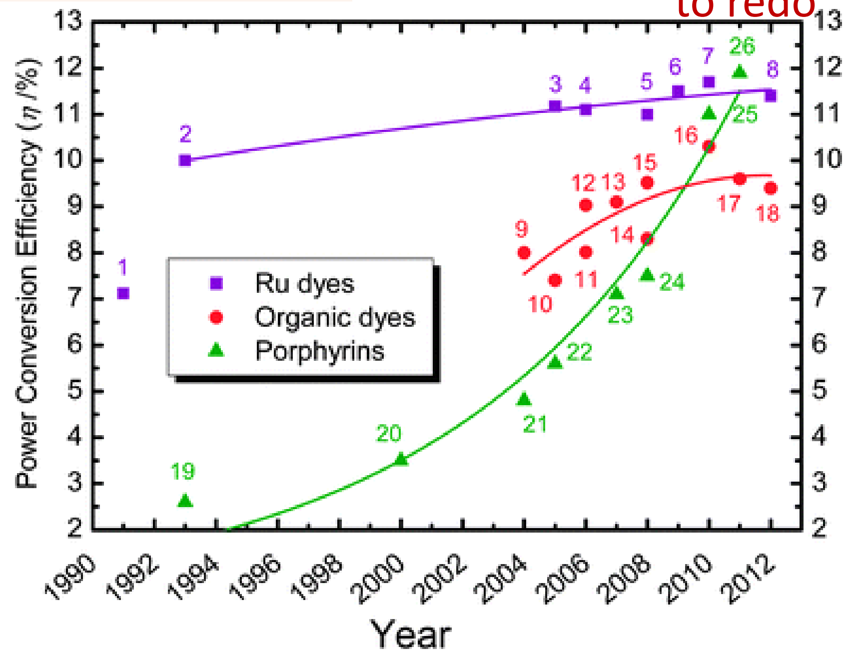



Fast BET process is generally not desired for the design of an efficient Dye Sensitized Solar Cell (DSSC).

# The Dye Sensitized Solar Cell

Need to redo



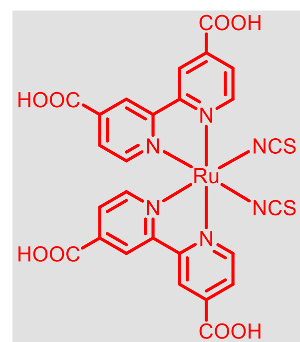

Diau et. al. Chem. Soc. Rev. , 2013, **42**, 291-304

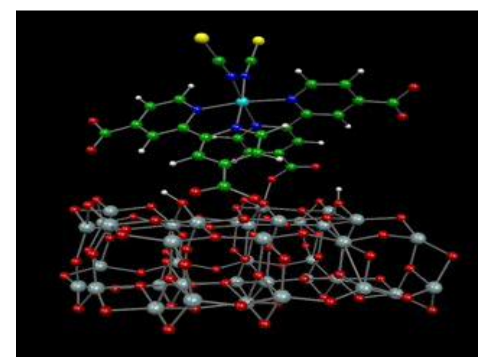
Carboxylate binding has undoubtedly been the most promising so far.....

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



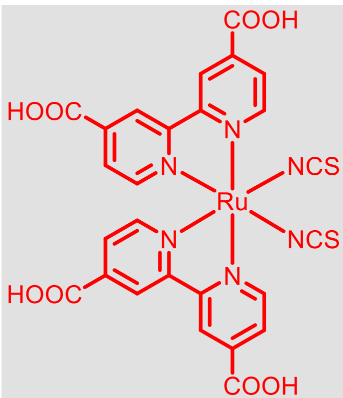
M. Graetzel, *Nature*, **2001**, 414, 338.;
Inorg. Chem. **2005**, 44, 6841

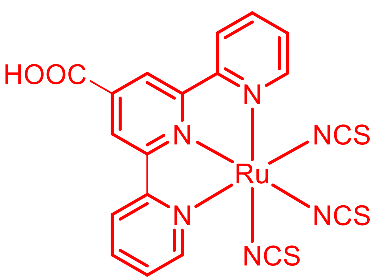
BET happens in μs

# Dyes used in Gratzel Solar Cell

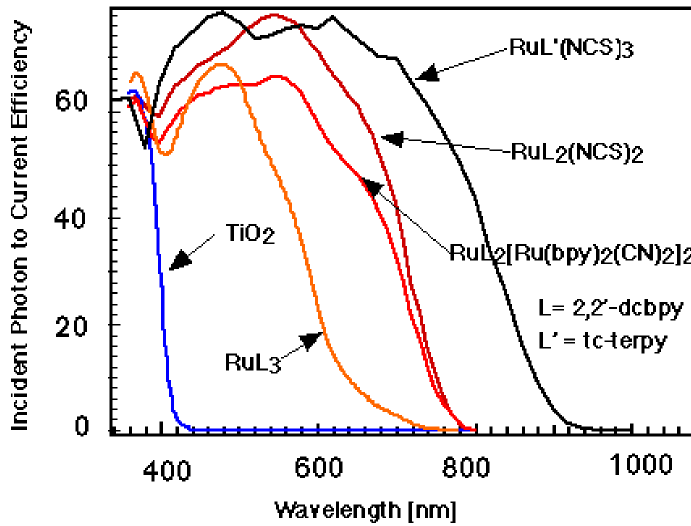
## Efficiency of about 12% has been reported

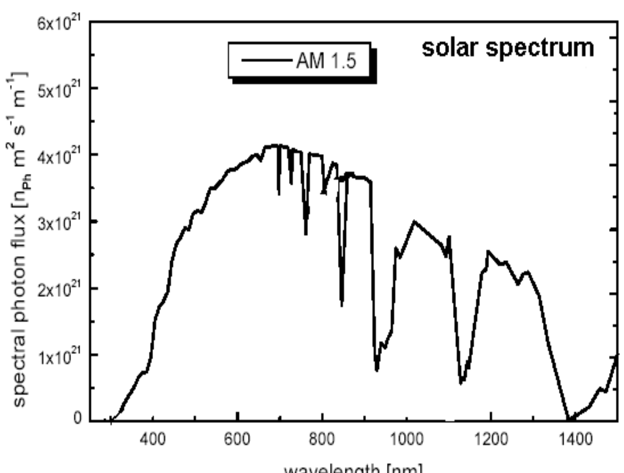
**Why –SCN ?**

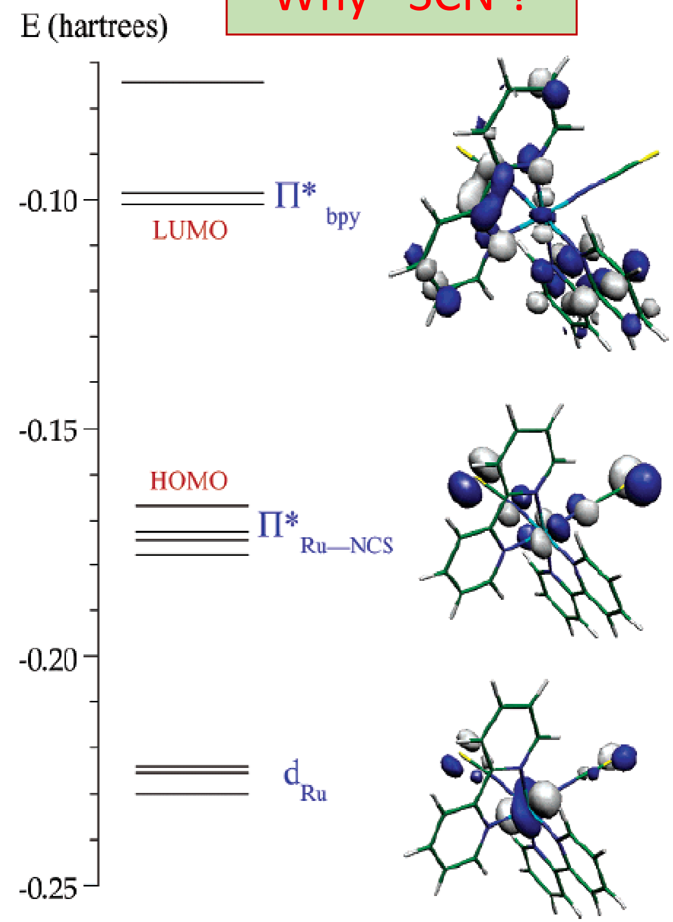



RuL'$(NCS)_3$




M. Grätzel *Nature* 1991, *353*, 737

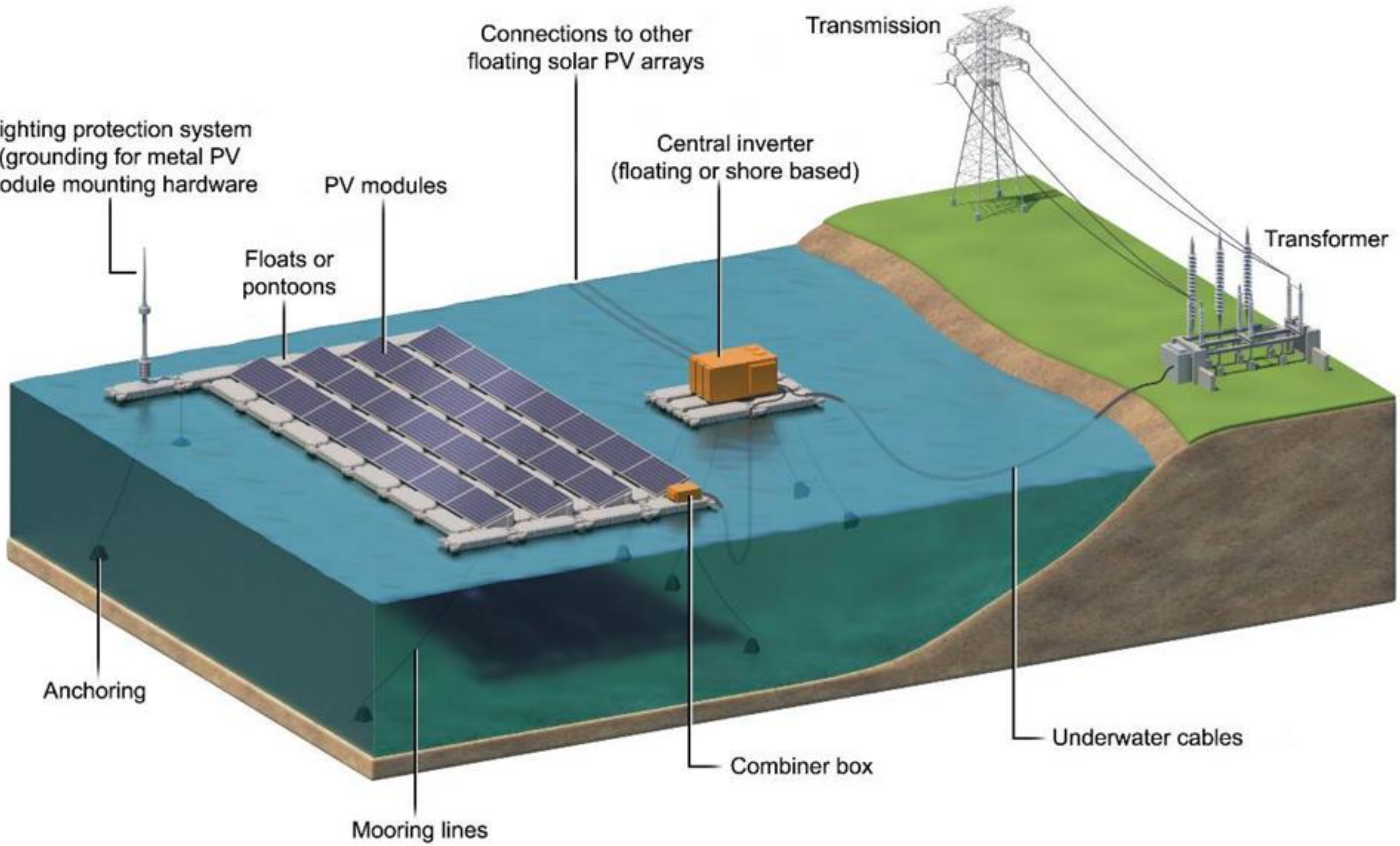



**Figure 2.** Schematic of a typical large-scale floating photovoltaic (FPV) system. Reprinted with permission from ref. [49]. Copyright 2021 Elsevier.

Sustainability 2021, 13, 4317 & Renew. Energy 2020, 162, 1415–1427

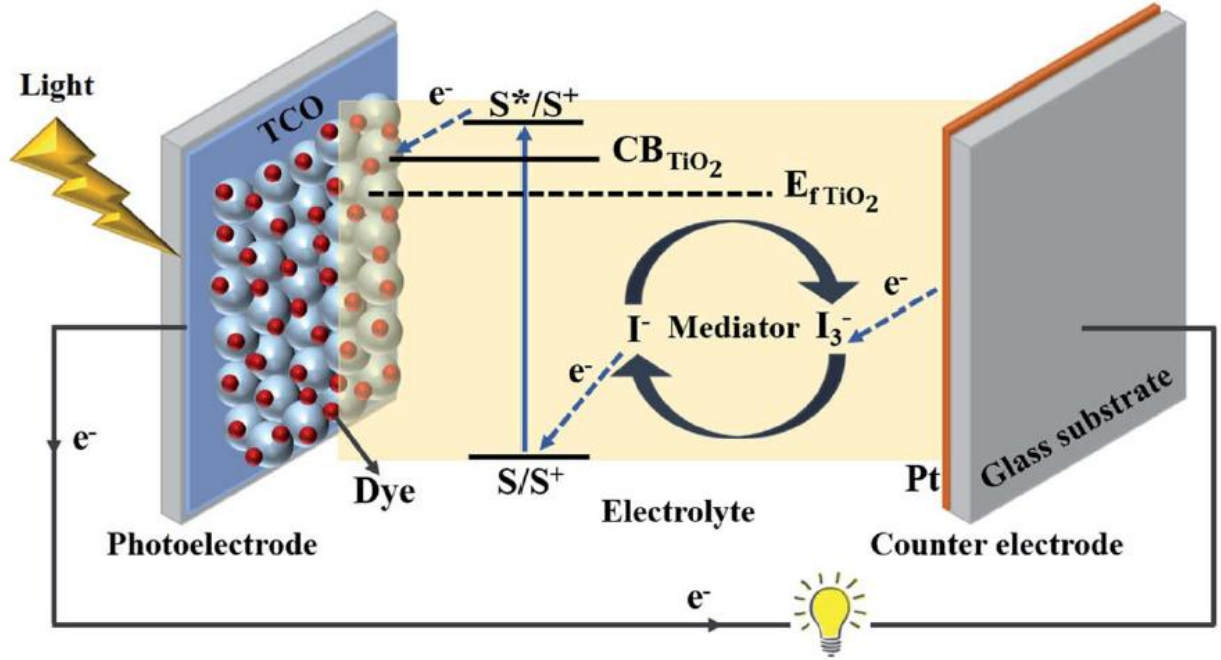



Fig. 2 Schematic illustration representing device structure and working principle of a dye-sensitized solar cell. CB = conduction band, $E_{f\ TiO2}$ = fermi level of $TiO_2$, S = ground state of dye sensitizer molecule, S* = excited state of dye sensitizer molecule, $S^0$ = oxidized dye, $S^+$ = charge separation, $I^-$ = iodide ion and $I_3^-$ = triiodide ion.

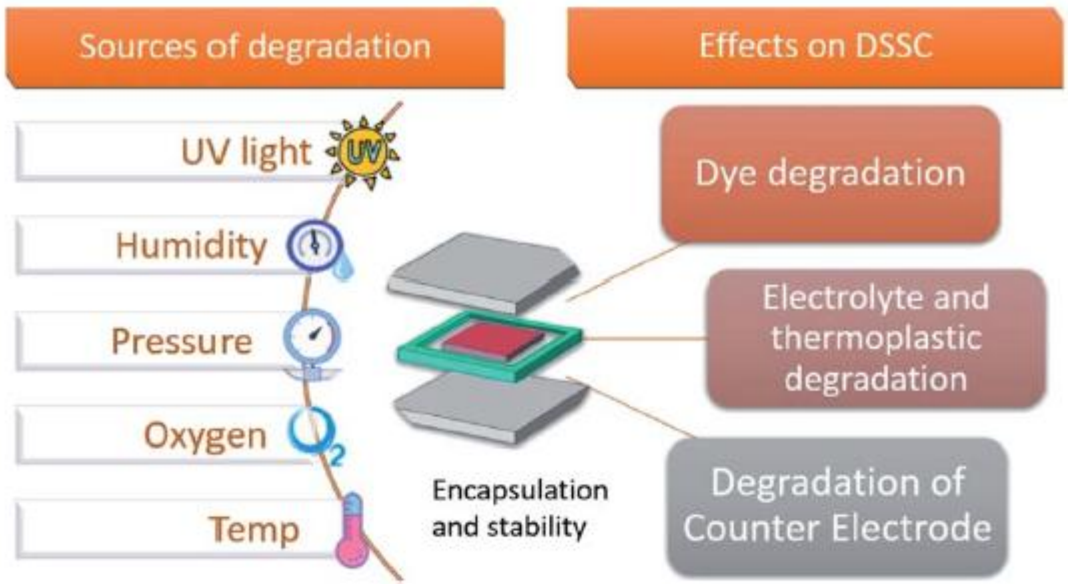
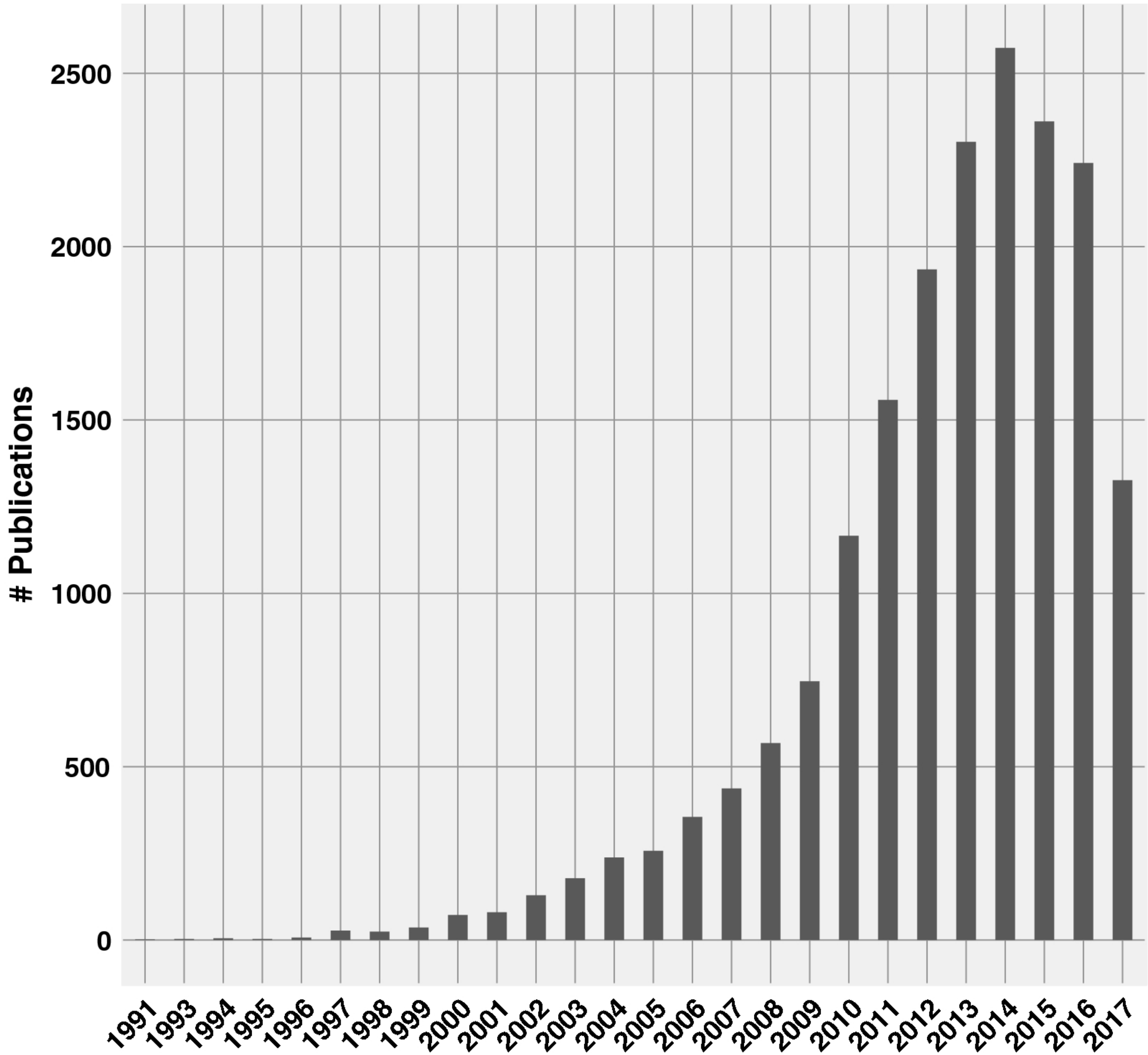
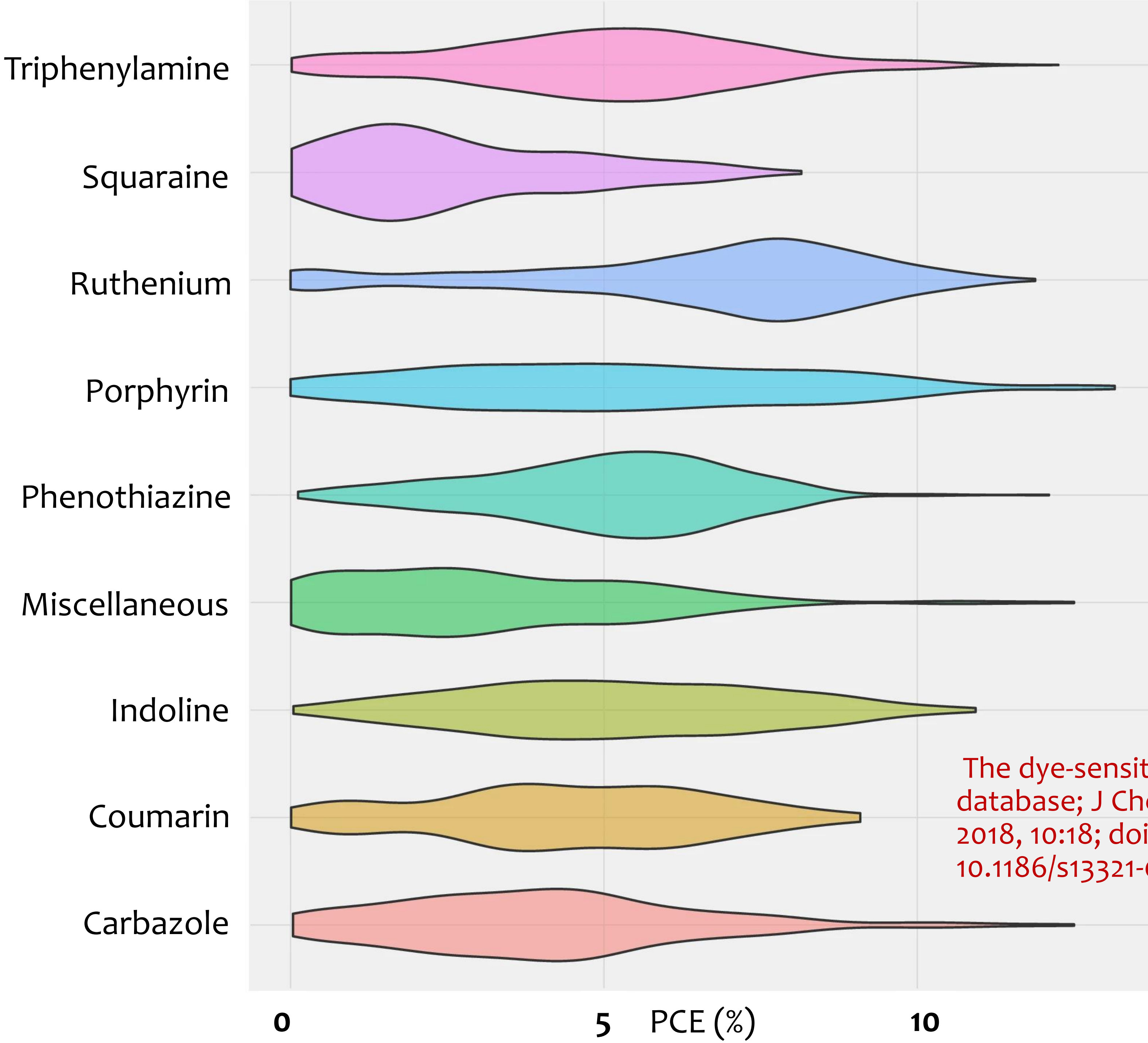



Illustration of the factors that affect DSSC devices and their possible consequences which hinder the photovoltaic performance

J. Mater. Chem. A, 2021, 9, 10527–10545



# Publications
2500
2000
1500
1000
500
0
1991
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017




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