I) Why and how to harvest energy from sun light

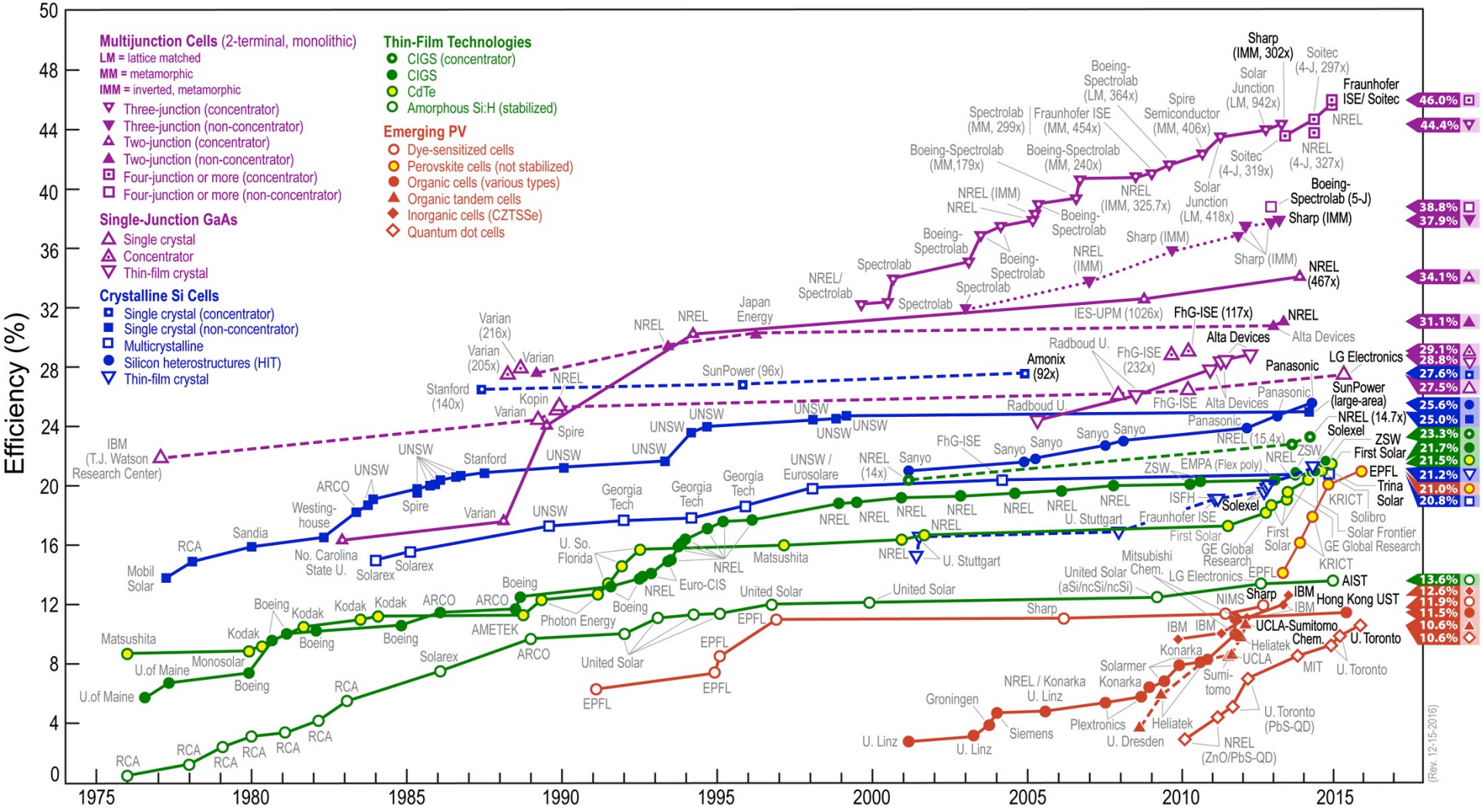
II) Excitonic solar cells

III) Halid Perovskites for solar cells

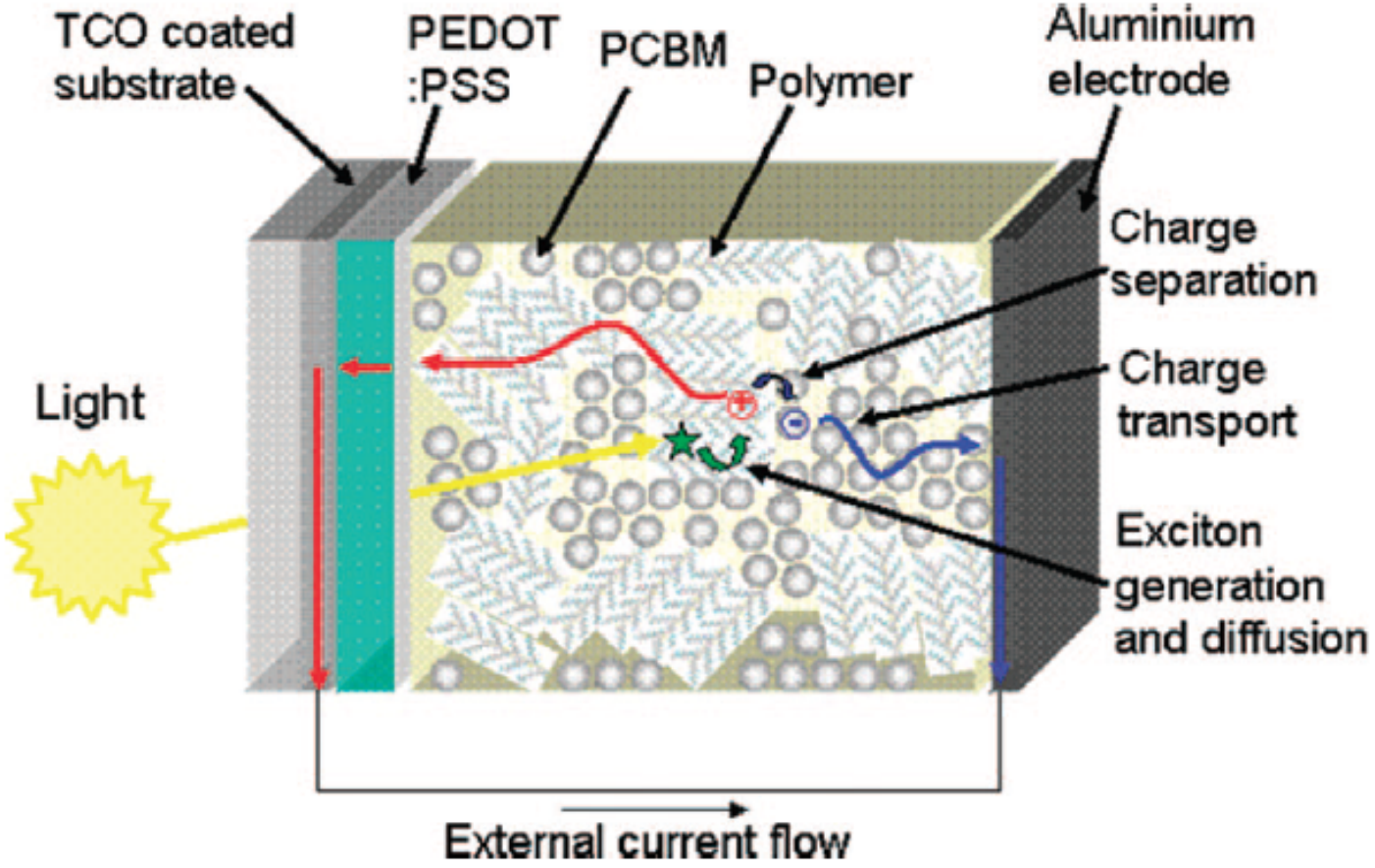
Excitonic solar cells

- Bulk heterojunctions
- Dye solar cells (Graetzel cells)
- Quantum modeling for charge separation

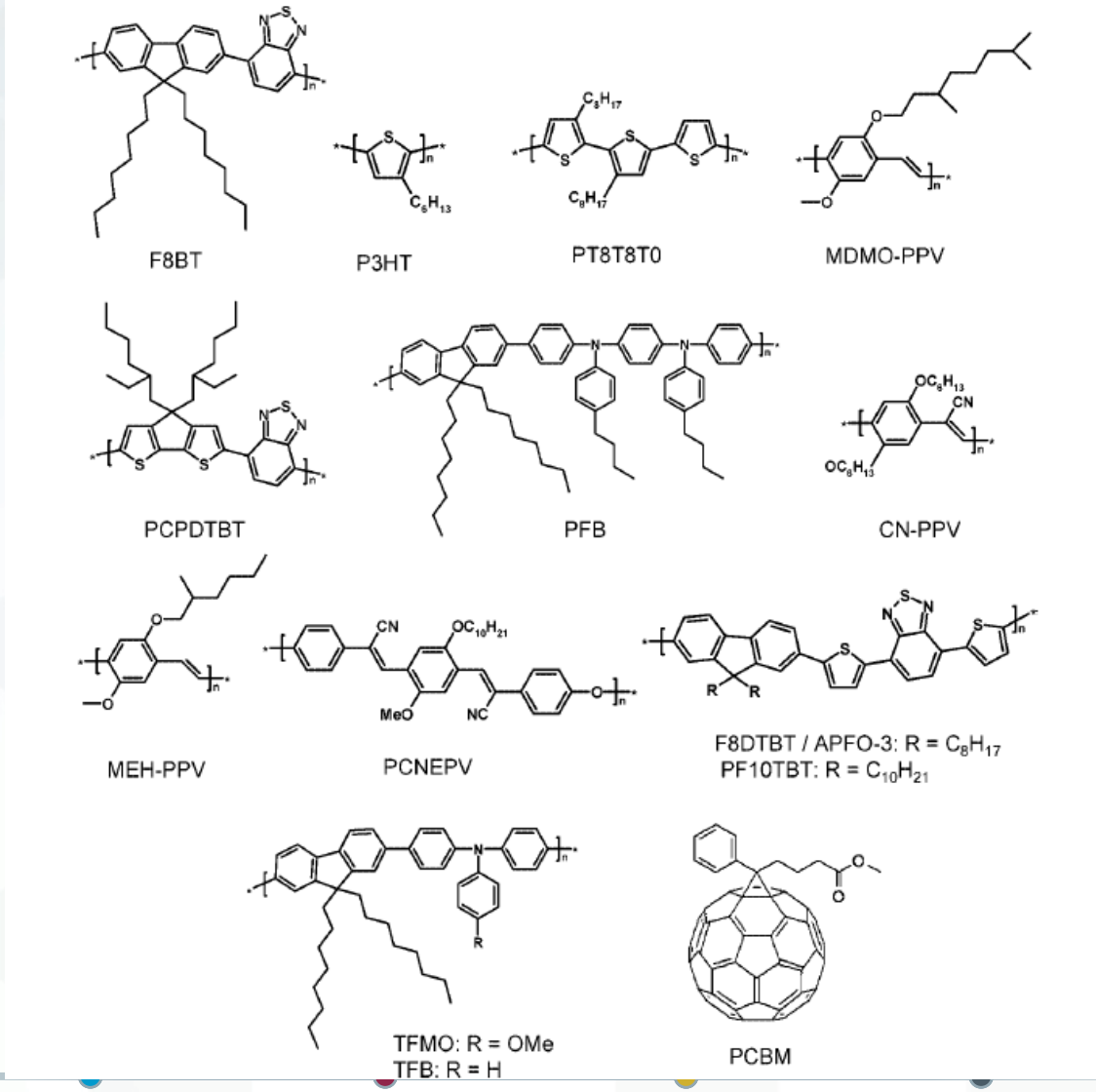
Best Research-Cell Efficiencies



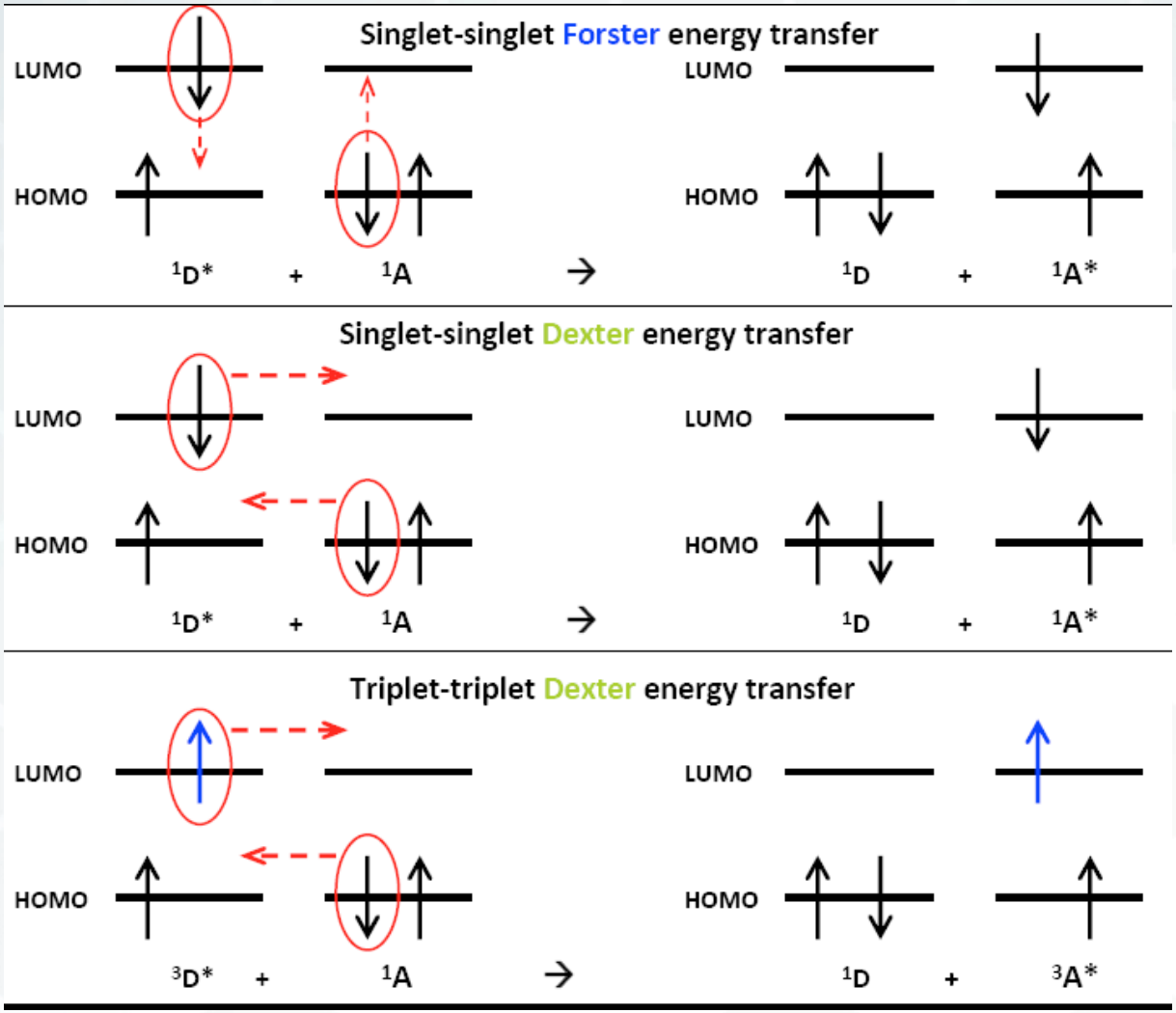
Bulk heterojunction



Donor and acceptor molecules



Mechanisms for energy transfer

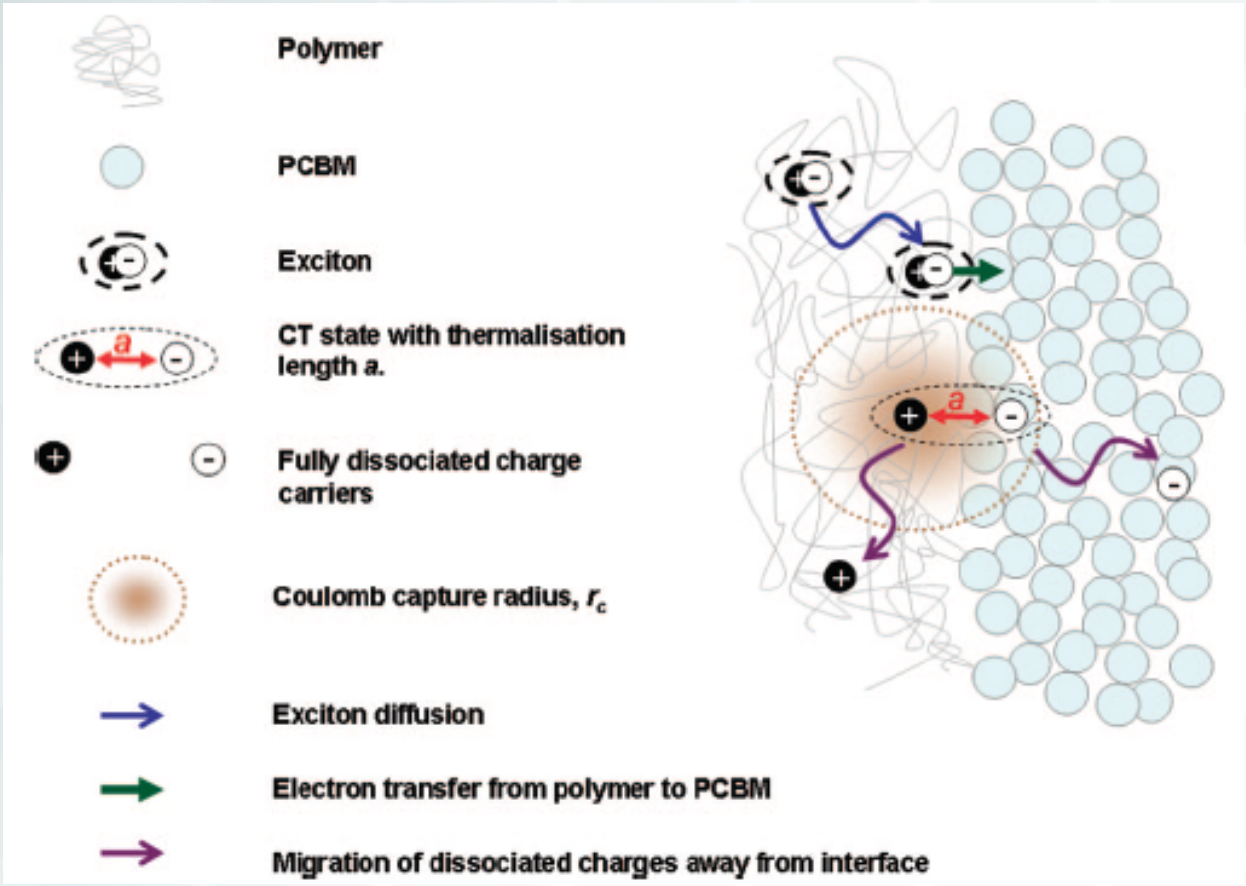


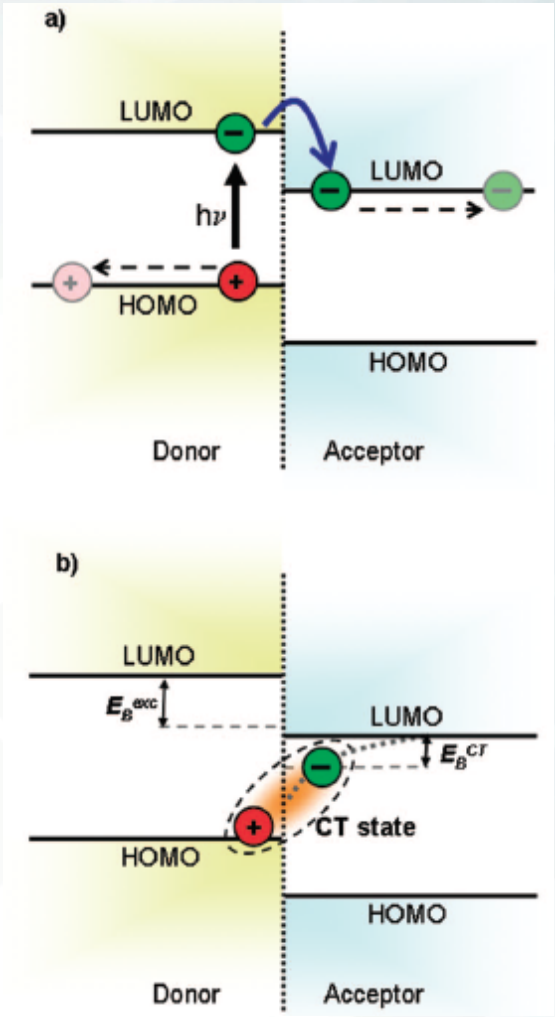
Transfer Efficiency

- Fraction of excitations transferred to acceptor
- Dexter : exponential decrease with distance on a distance of 2-3 Angströms
- R_0 = Förster radius, maximum 10 nm for large overlap

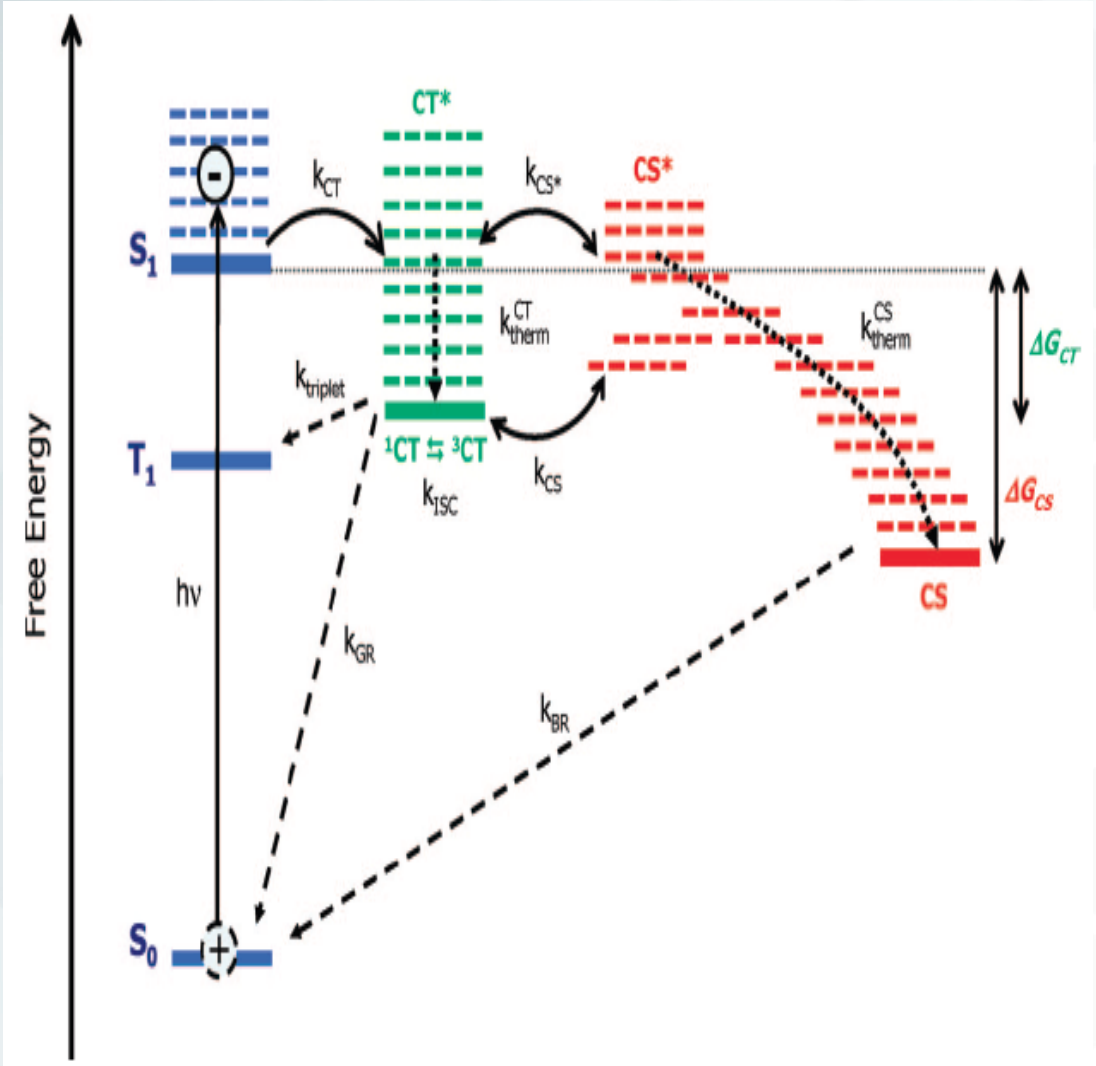
$$E = \frac{k_{DA}}{k_{DA} + k_{fD}} = \frac{1}{1 + \left(\frac{R}{R_0}\right)^6}$$

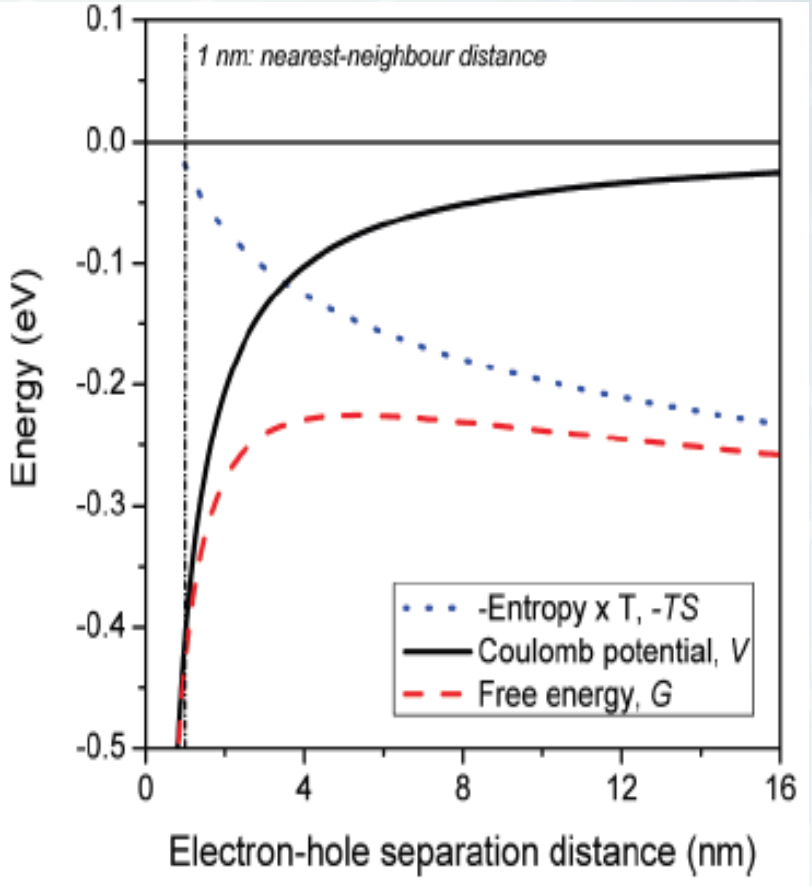
Charge separation



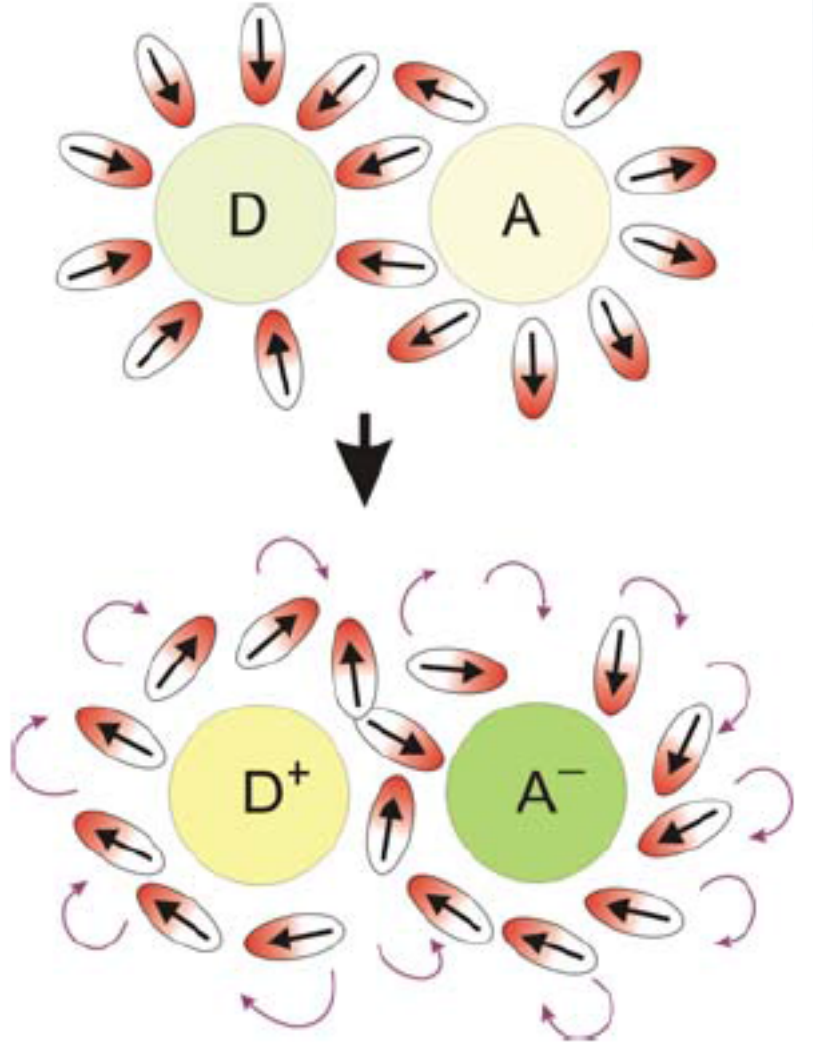


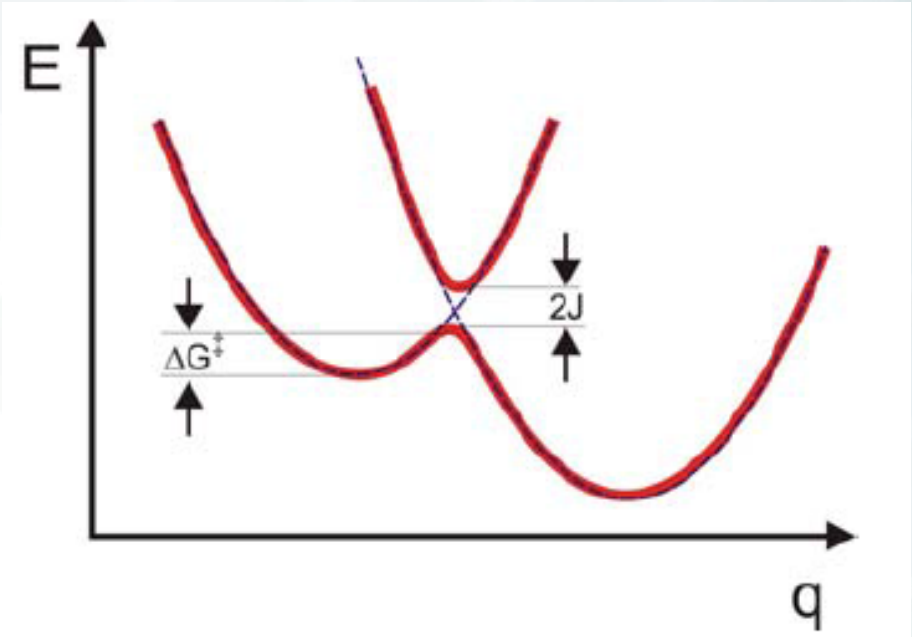
Charge separation





Charge transport



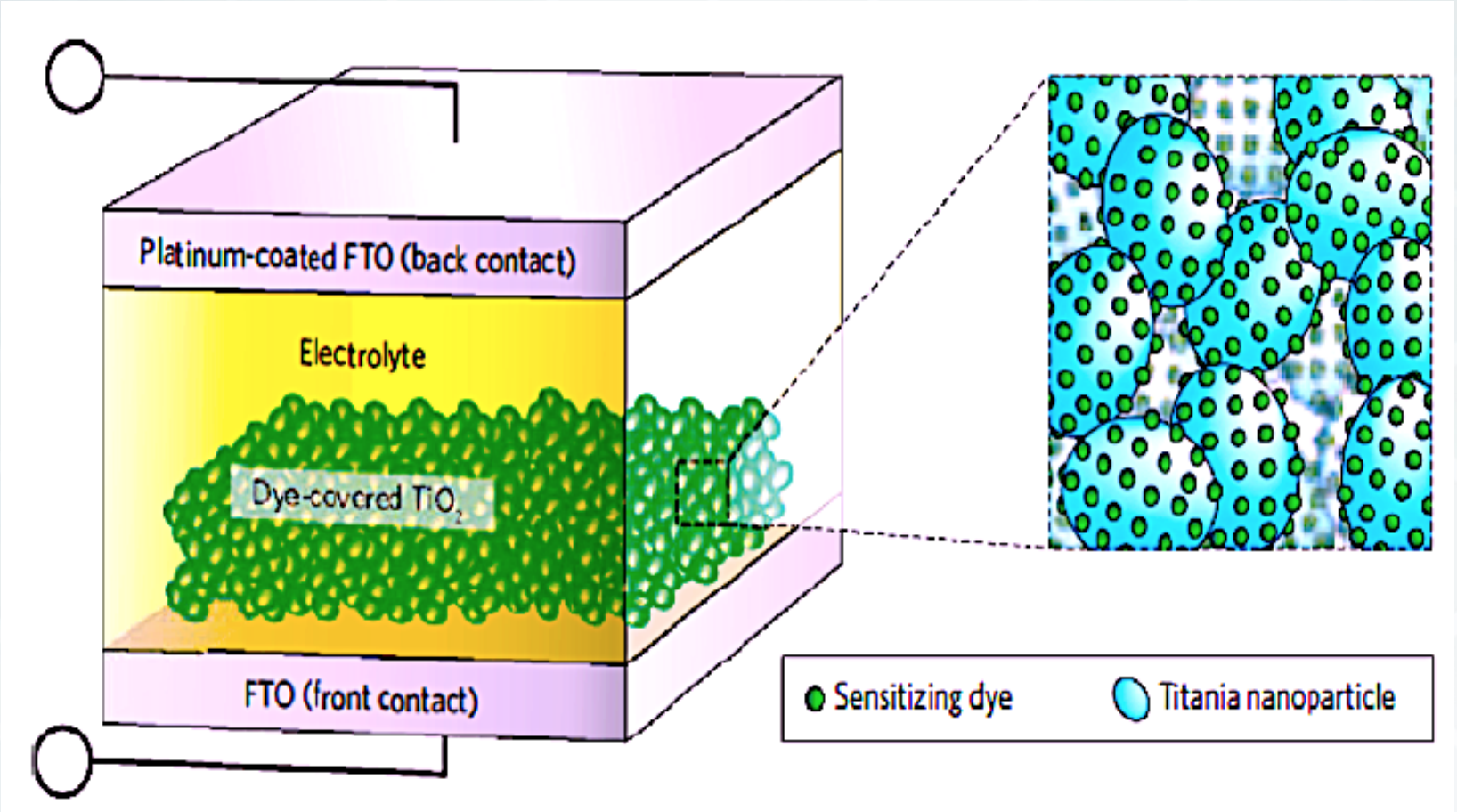


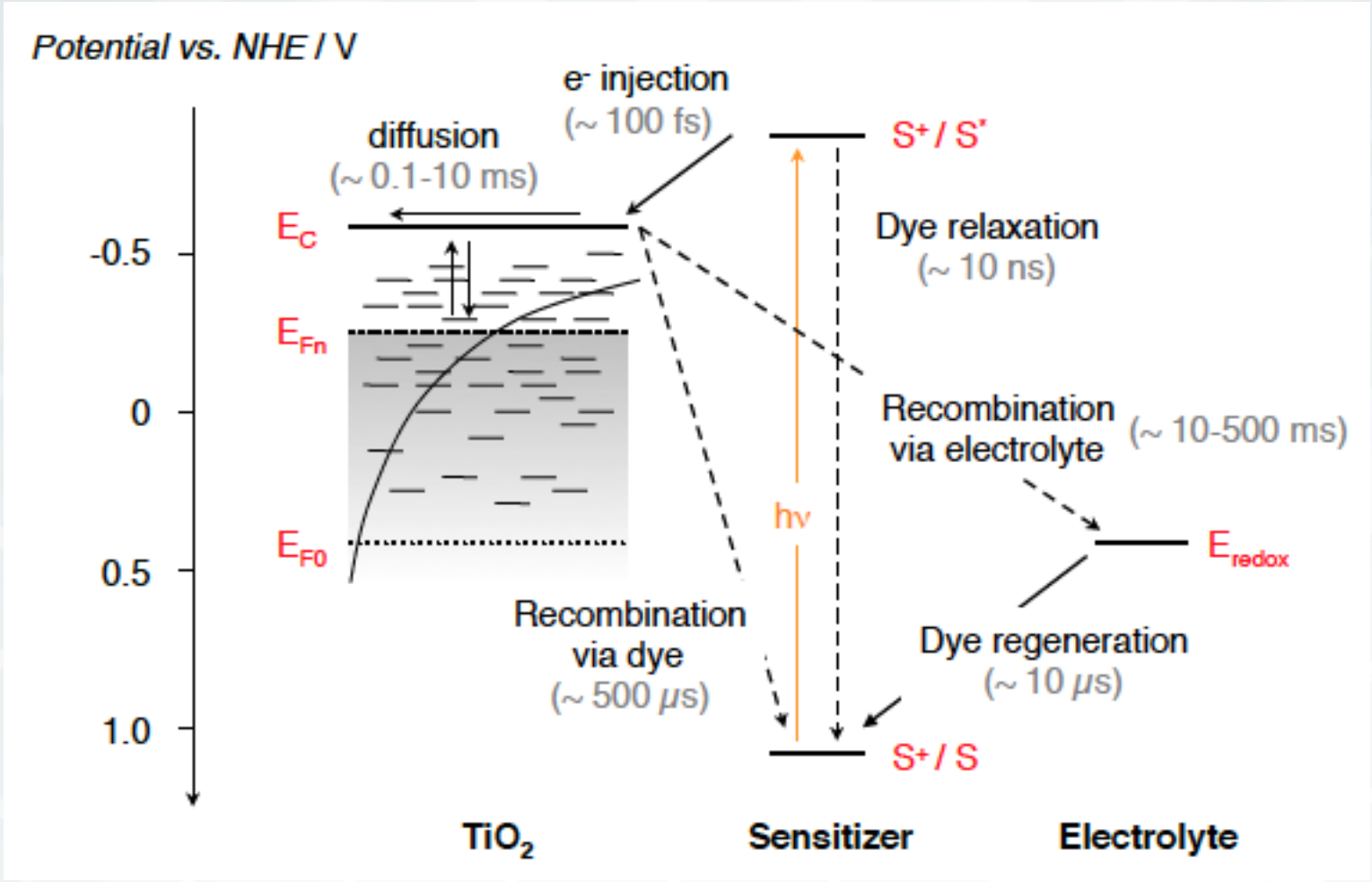
$$w_{ET} = \frac{|J|^2}{\hbar}\sqrt{\frac{\pi}{\lambda kT}}\exp\left[\frac{-(E_A - E_D + \lambda)^2}{4\lambda kT}\right]$$

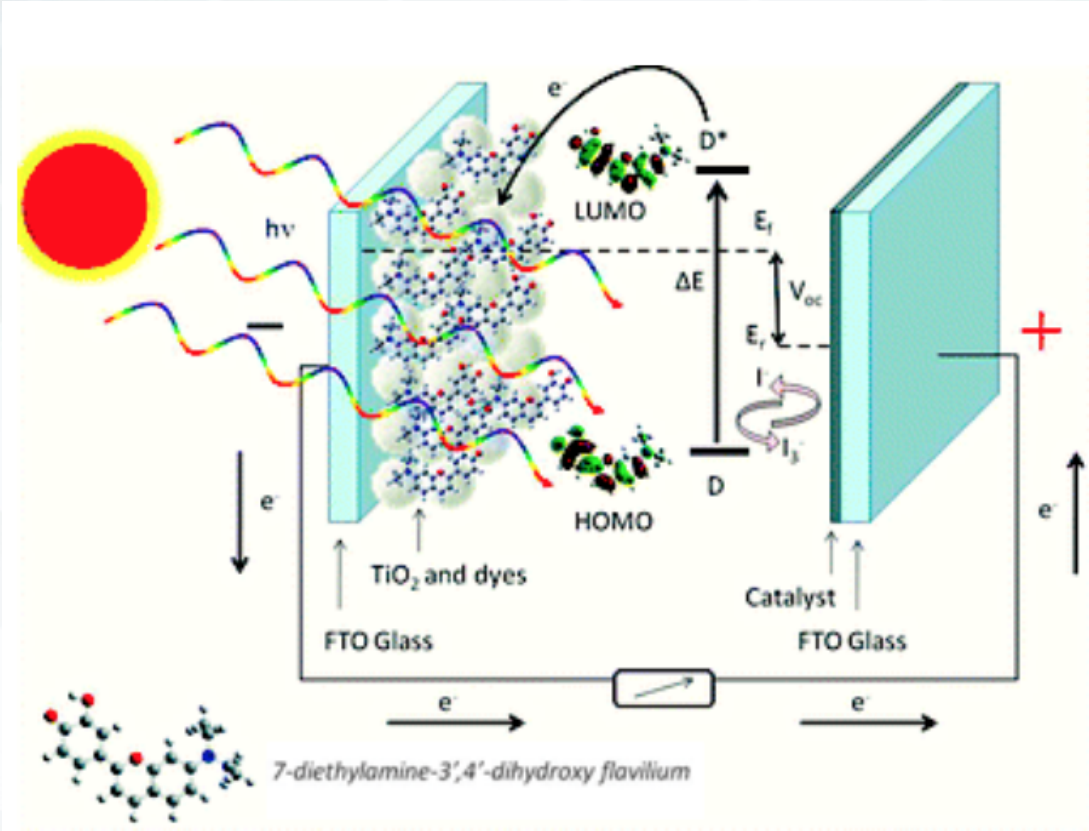
Marcus theory

Polaron physics

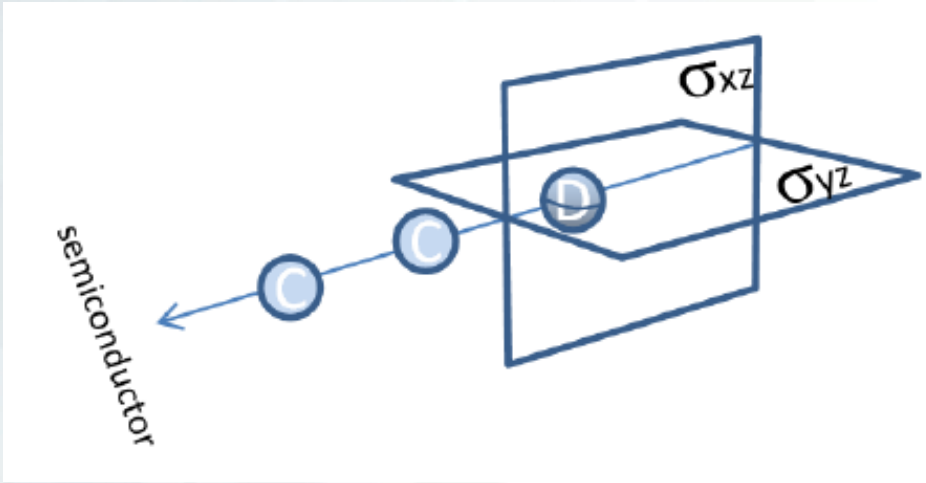
Dye Solar cell (Graetzel cell)




Potential vs. NHE / V
e⁻ injection
(~ 100 fs)
diffusion
(~ 0.1-10 ms)
S⁺ / S*
Dye relaxation
(~ 10 ns)
E_C
E_Fn
E_F0
-0.5
0
0.5
1.0
Recombination
via electrolyte
(~ 10-500 ms)
hν
E_redox
Recombination
via dye
(~ 500 μs)
Dye regeneration
(~ 10 μs)
S⁺ / S
TiO2
Sensitizer
Electrolyte


e⁻
D*
LUMO
hν
E_f
ΔE
V_oc
E_r
I⁻
I₃⁻
D
HOMO
e⁻
e⁻
TiO₂ and dyes
Catalyst
FTO Glass
FTO Glass
e⁻
e⁻
7-diethylamine-3',4'-dihydroxy flavilium

Avoiding recombination by decoupling the HOMO orbital



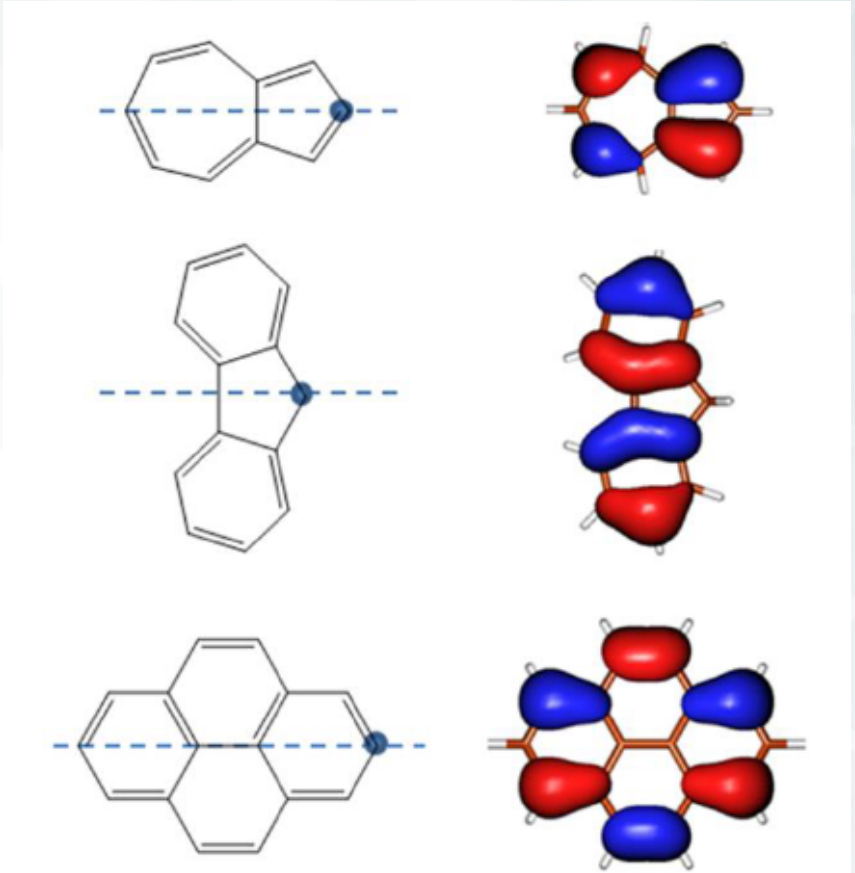


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Figure 28. The azulene, fluorene, pyrene molecules with an illustration of their symmetry plane which crosses a carbon atom that can be connected to a bridge. The HOMO of these molecules is antisymmetric with respect to this plane.

Avoiding recombination by decoupling the HOMO orbital

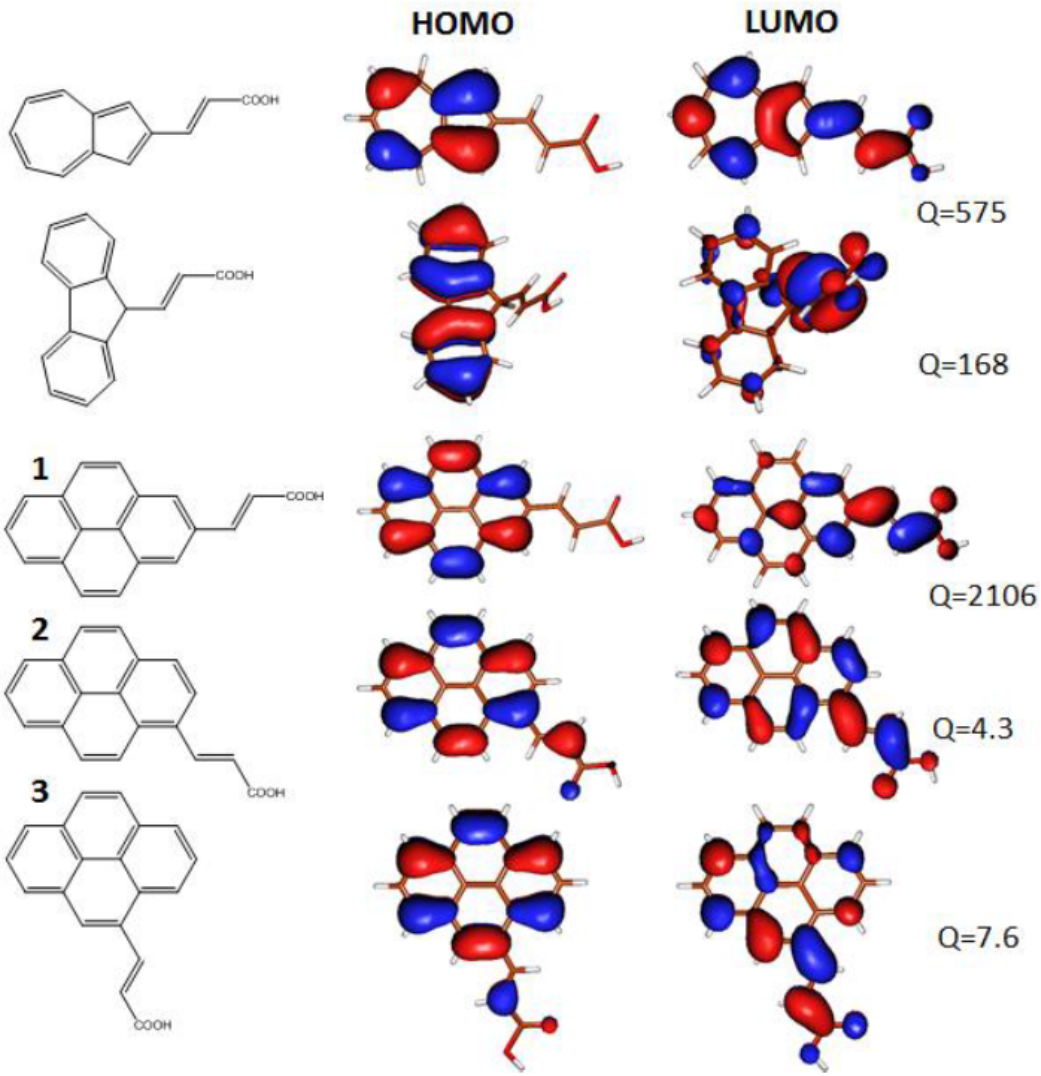

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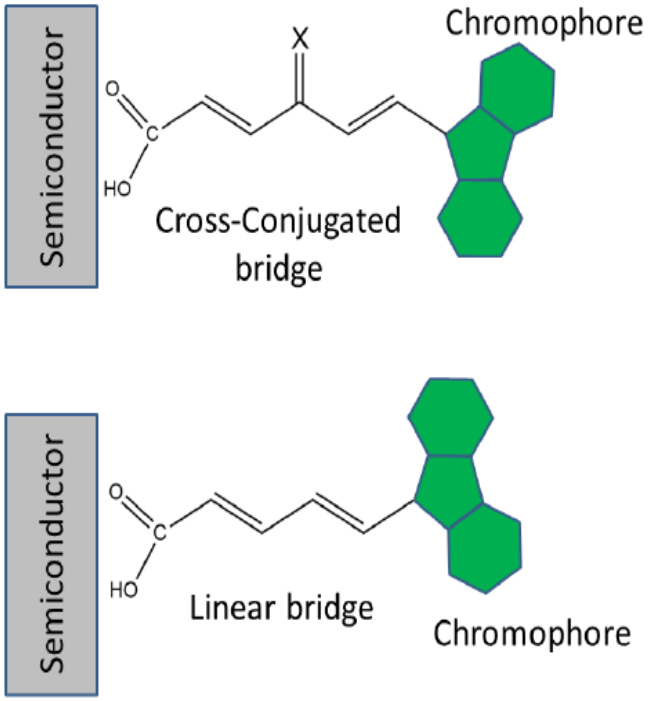
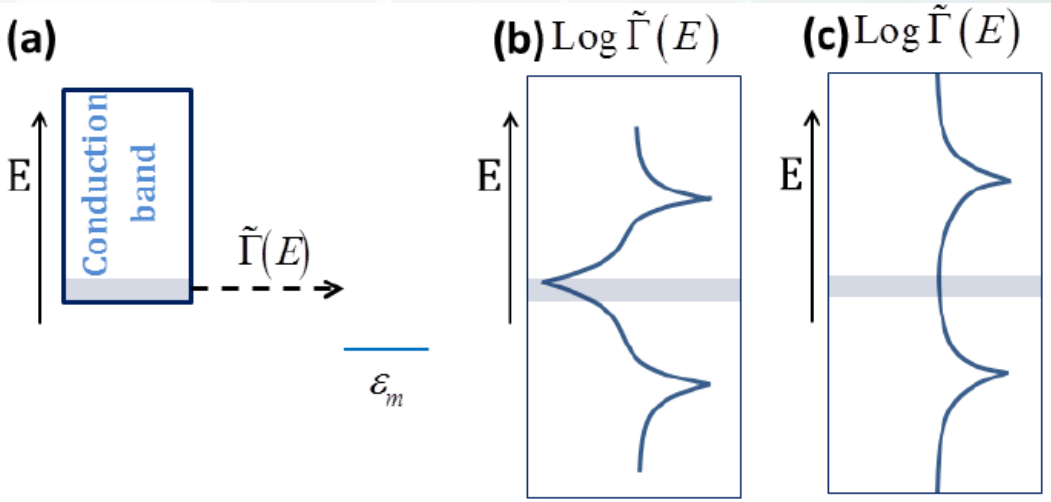
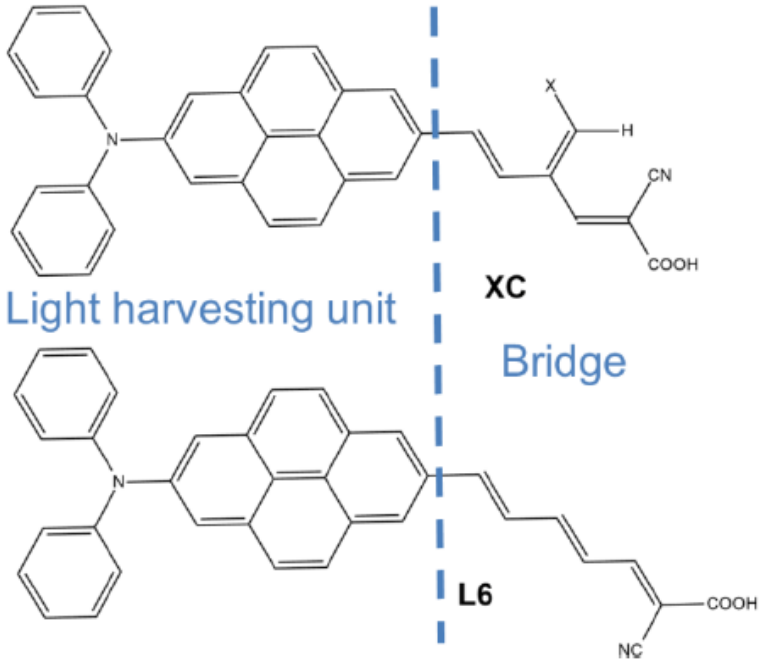
Figure 29. Chemical diagrams and HOMO and LUMO plots of three molecules substituted with a bridge in the symmetry position that isolates the HOMO from the bridge (top three rows). Alternative, non-symmetric substitutions of pyrene that do not isolate the HOMO

Avoiding recombination by decoupling the HOMO orbital





Avoiding recombination by decoupling the HOMO orbitalÒ



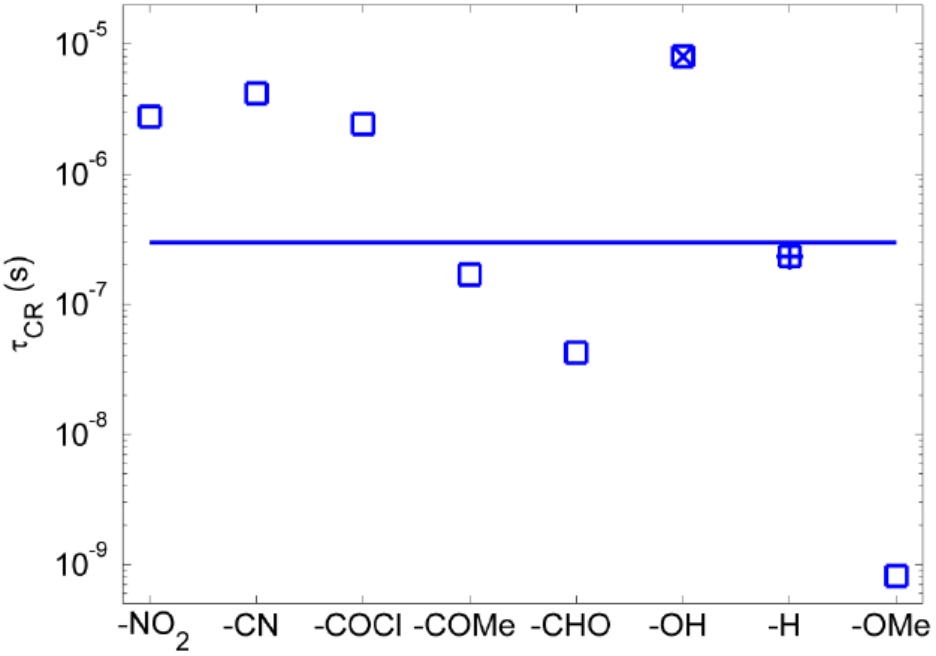


Figure 42. Charge recombination lifetimes for cross-conjugated molecules (with the lifetime for the linearly conjugated bridge L6 shown by a solid line), as a function of the chemical substituent.

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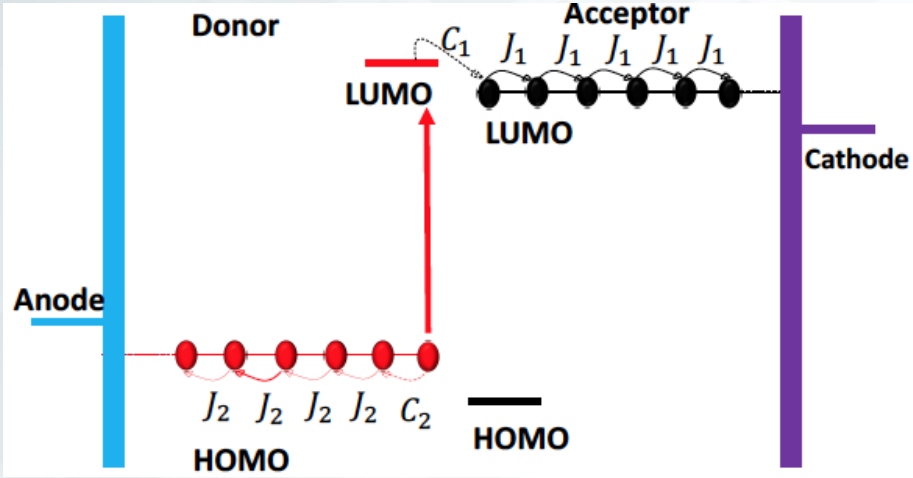
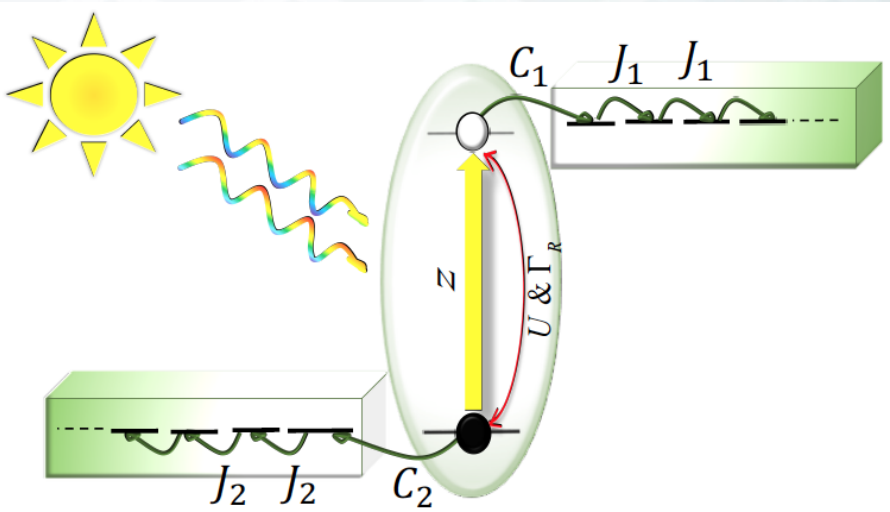
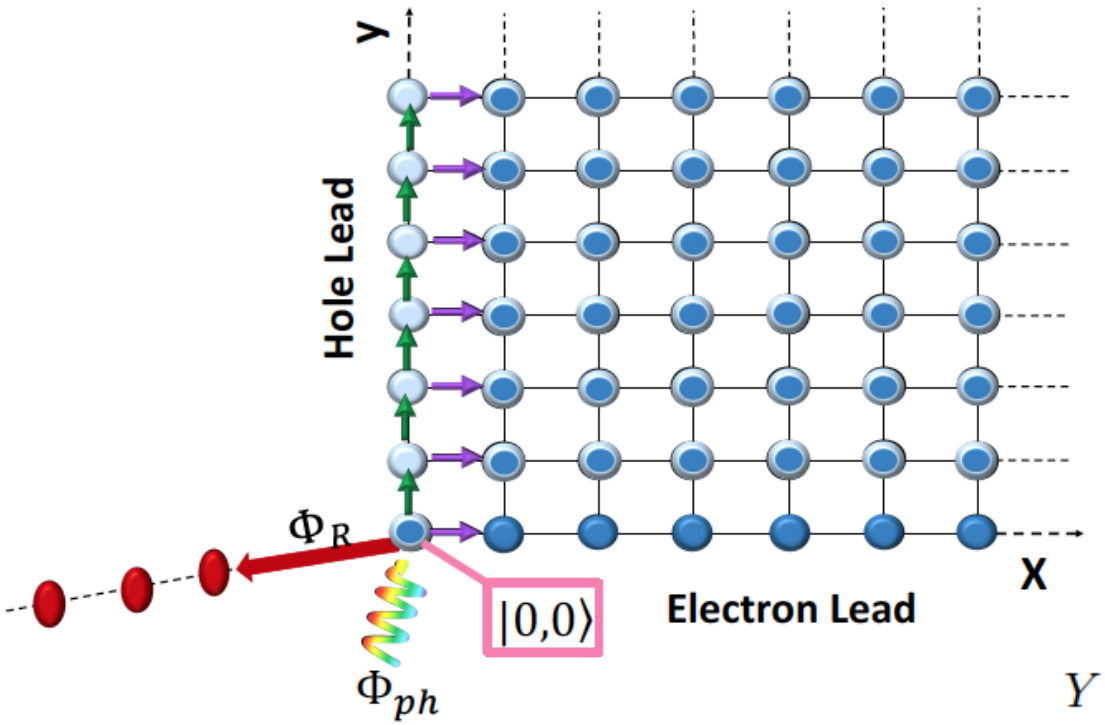
The two-level model



Exciton at the BHJ interface



Dye sensitized cell



$$Y = \int_{Continuum} \frac{-\operatorname{Im}\Sigma_0(E)}{\frac{\Gamma_R}{2} - \operatorname{Im}\Sigma_0(E)} n(E)dE$$

Figure 2-7: Flux conservation. Flux of current, recombination and photons are represented on the square lattice. The sum of the two fluxes starting from site (0,0) (violet and green) is equal to the flux of electron–hole pairs injected in the material. The sum of all the violet contributions is equal to the flux of electron injected in its lead. If there are no localized states these two fluxes are equal. The recombination flux is denoted by red arrow. $|0,0\rangle$ determines either the first excited state or the D–A interface.

Symmetric case

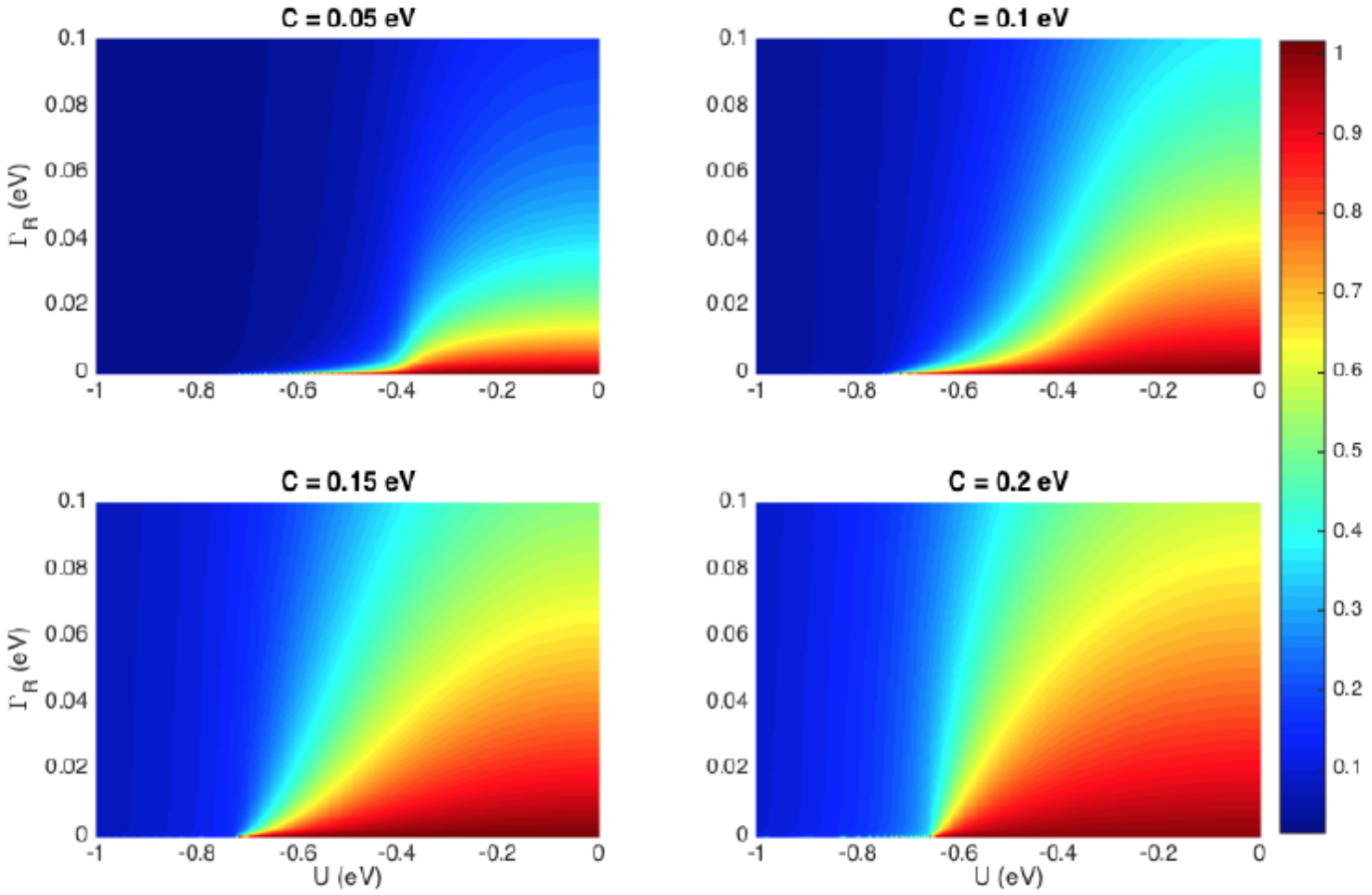


Figure 3-9: Photovoltaic yield as a function of interaction energy (U) and recombination rate (Γ_R) in a mono–channel system for different values of coupling parameters (C_1 and C_2).

Non symmetric case

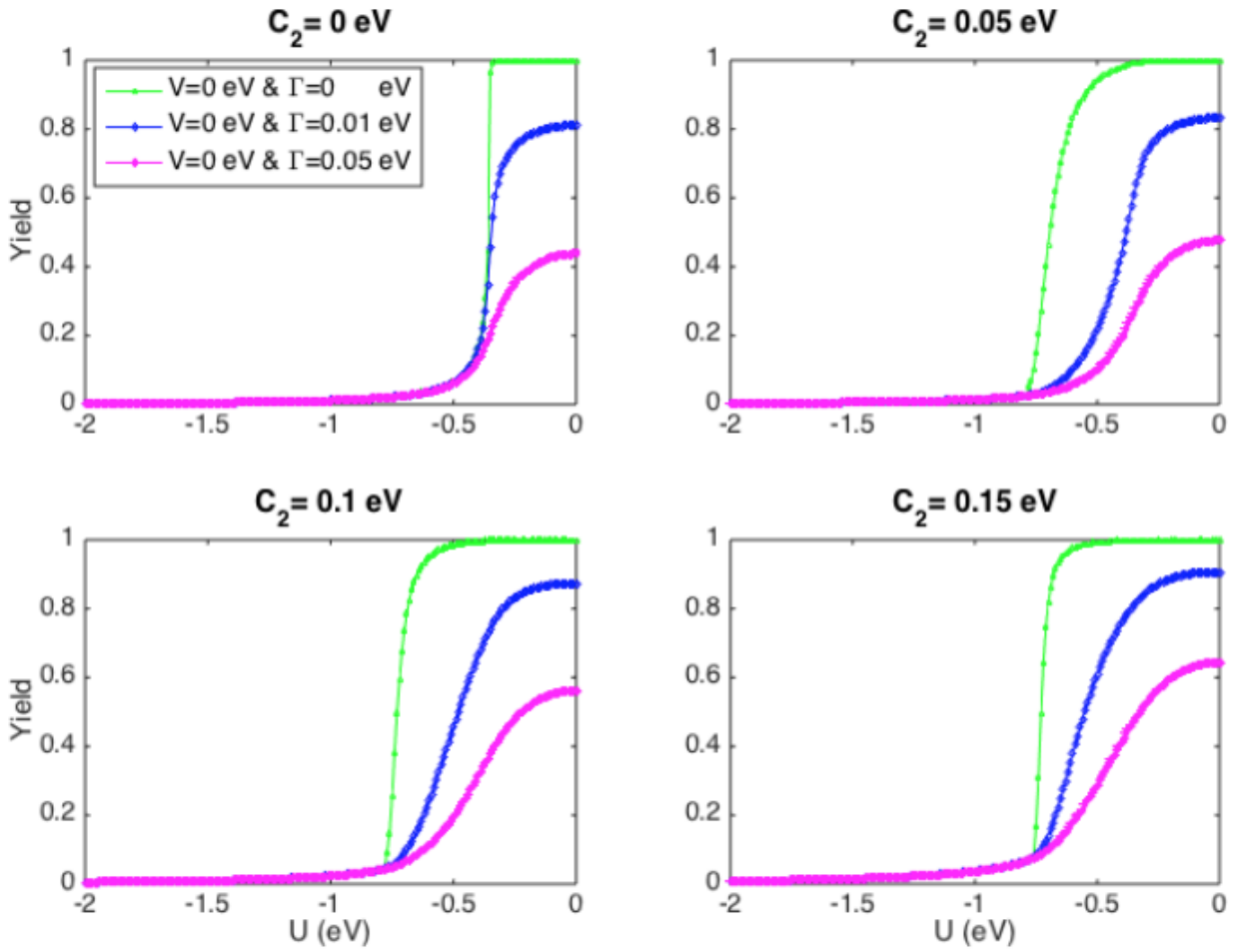
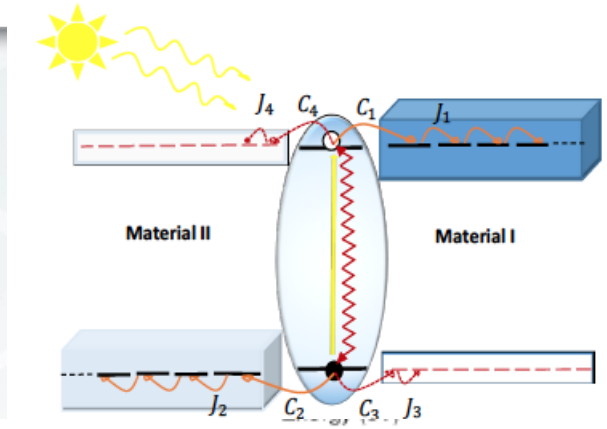
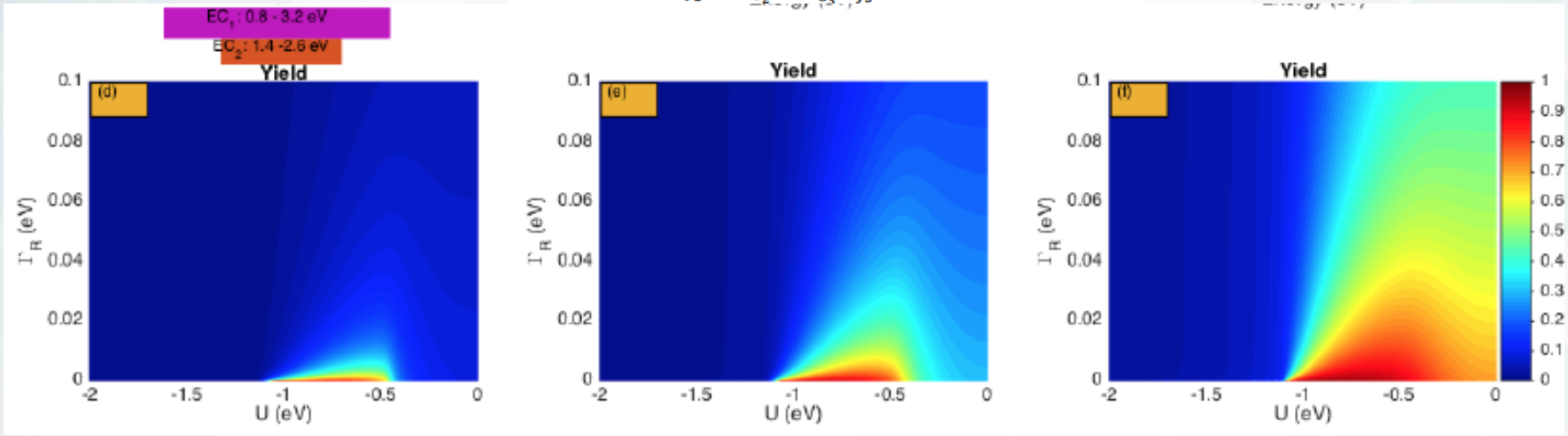


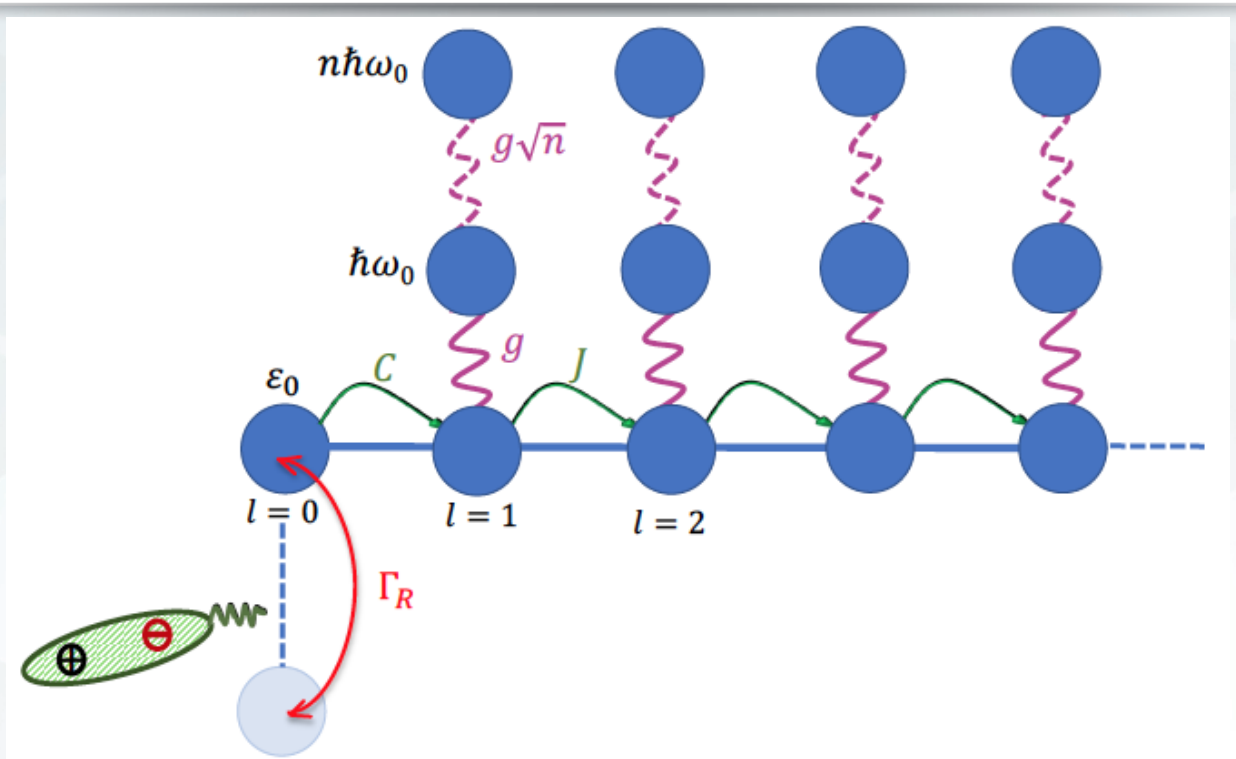
Figure 3-6: Yield (Y) of charge separation as a function of short–range interaction energy U obtained with different first coupling energies to the hole lead. The legend presented in the first panel, is valid for all the other panels. Γ_R is the recombination rate. The strength of long–range interaction V is assumed to be zero.





The energy continuums EC_1 (electron in material I and hole in material II) and EC_2 (electron and hole in material I) ranges are shown by colored bands below the plot.

of C_3. (d, e, f) Photovoltaic yield in a multi–channel system with different energy continuums as a function of interaction energy (U) and recombination rate (Γ_R) for different values of coupling parameters of the hole to material II and material I (C_2 and C_3).



$$H = \varepsilon_0\, c_0^\dagger c_0 + \sum_{l=1}^{N} \frac{V}{l}\, c_l^\dagger c_l + C\,(c_0^\dagger c_1 + c_1^\dagger c_0) + J \sum_{l=1}^{N-1} (c_l^\dagger c_{l+1} + c_{l+1}^\dagger c_l)$$

$$+\hbar\omega_0 \sum_{l=1}^{N} a_l^\dagger a_l + g \sum_{l=1}^{N} c_l^\dagger c_l (a_l^\dagger + a_l)$$

Polaronic bands

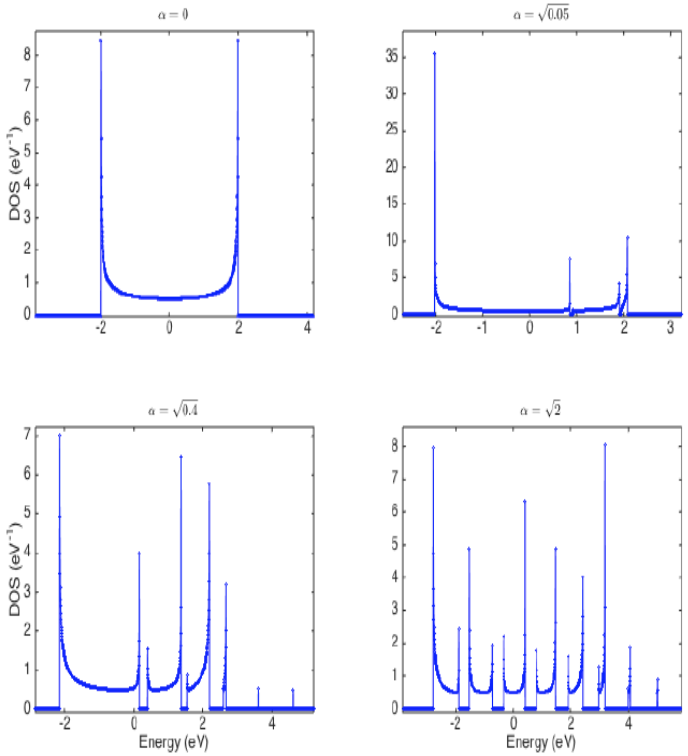


Figure 4-12: The local density of states in the bulk part for different electron–phonon coupling constant α. The figures are obtained for $\hbar\omega_0 = J = 1\ eV$.

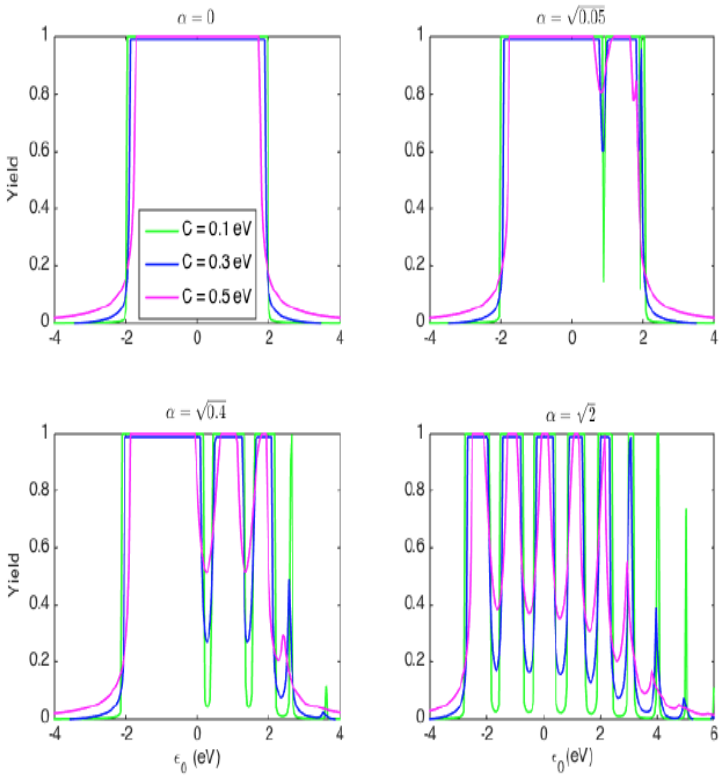


Figure 4-17: Yield as a function of incoming electron energy ε_0, for various values of the electron–phonon coupling constant α and coupling parameter C.

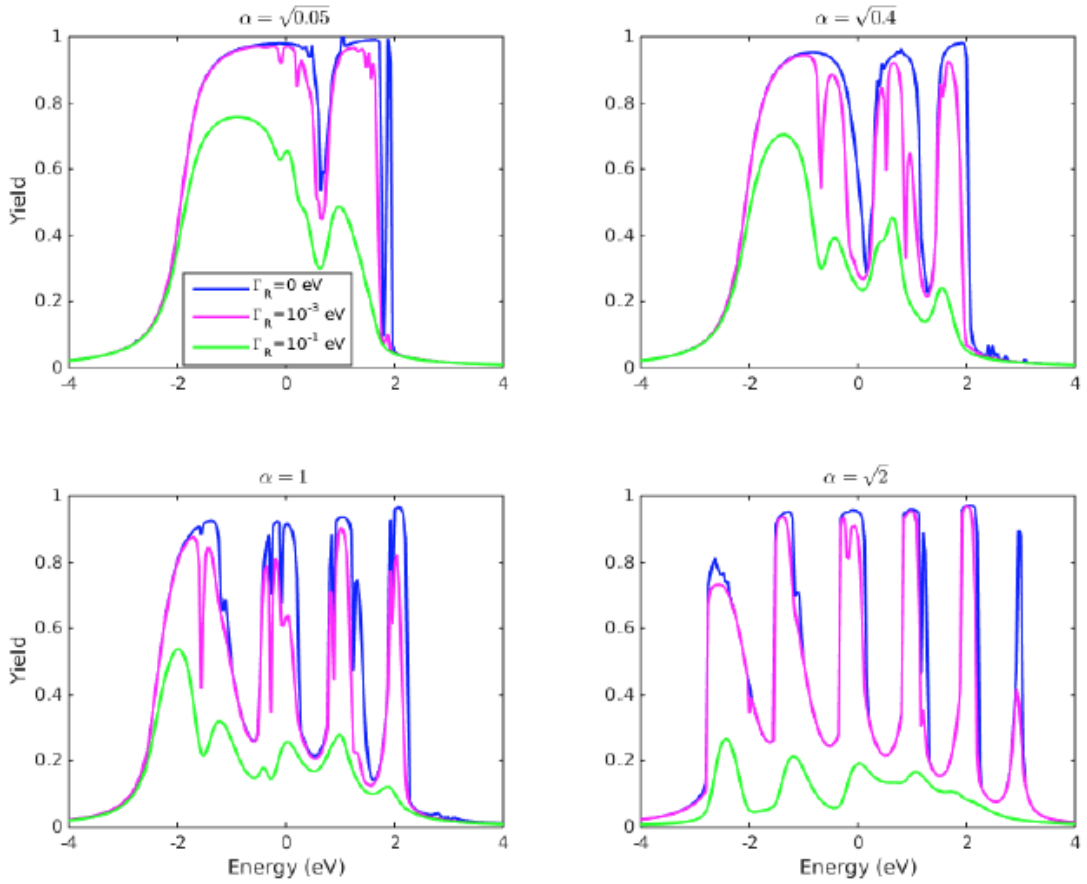


Figure 4-20: Yield as a function of incoming electron energy ε_0, in the presence of long–range electron–hole interaction $V = -1\ eV$, for various values of the electron–phonon coupling constant α and electron–hole recombination rate Γ_R. The legend presented in the first panel is valid for all the other panels.

Message to take home

- Bulk Heterojunction: strong analogy with first step of photosynthesis (exciton formation and propagation)
- Dye solar cells : charge separation is analogous to that of BHJ
- Quantum modeling so far is mainly based on ab-initio studies of energy levels, shape of the wavefunctions…
- New approaches to flux of charges and energy