Computational chemistry and the design of dye sensitized solar cells

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Chimie-ParisTech

A chemical engineering College founded in 1896 by Charles Friedel

located in the heart of the Latin Quarter
on the “Montagne” Sainte Geneviève

Chemists who intend to industry will have a scientific education as strong as those who wanted to devote himself to purely scientific careers

Charles Friedel

8 laboratories
106 researchers
100 technical and administrative staff
90 PhD students
200 papers/year

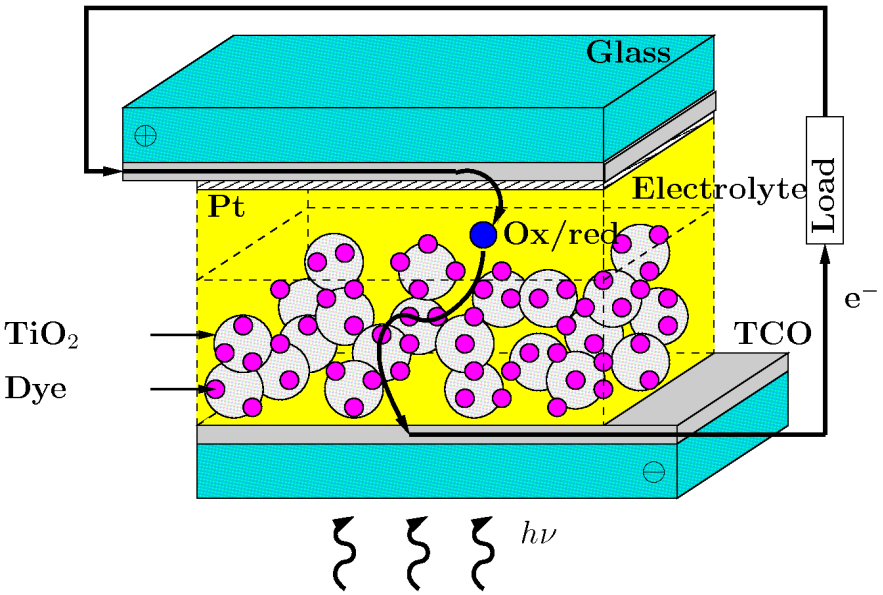
MSC group created in Sept. 2000

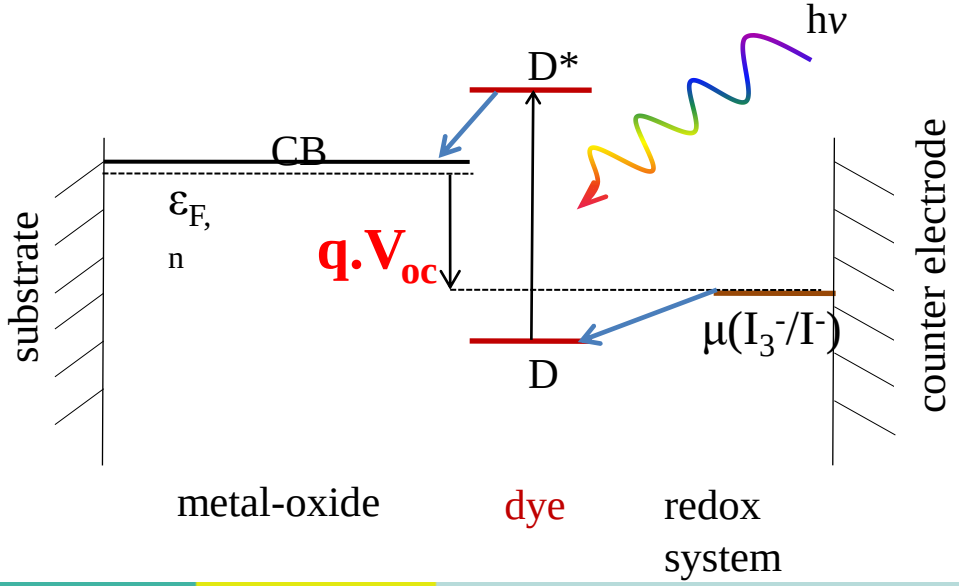
Outline

1. Basic working principles of DSSC
2. The computational protocol
3. Classical DSSCs: N3/TiO2 & EY/ZnO
4. Computational protocol
5. New (isolated) dyes
6. Dye/ZnO
7. Additives and Solvent co-adsorption
8. Conclusions

For a recent review: ACR 2012

DSSC: basic working principles





Up to now η<12%

DSSC: Real Devices

Self-Energy Generating Glasses

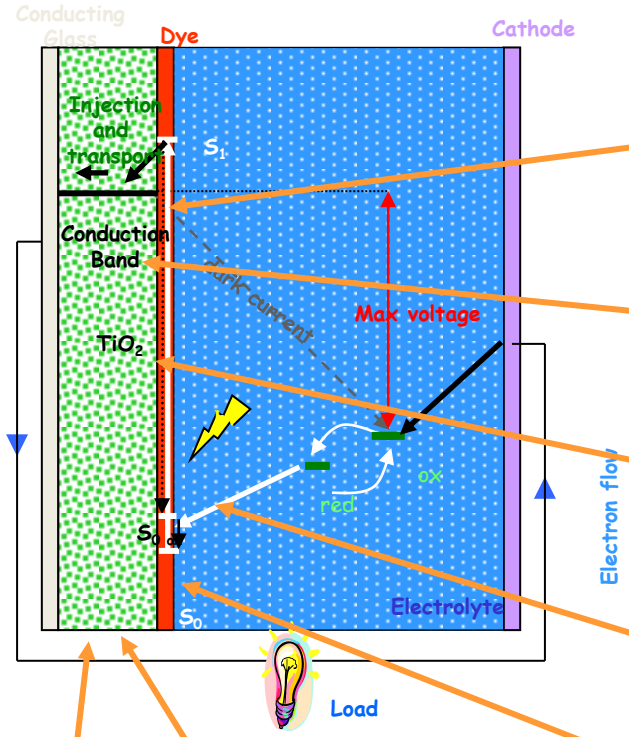
Sony Lamp « Hana Akari »

« Solar » Windows

Mascotte Solar Backpack powered by G24i

DSSC as a complex system

Decompose the problem in the elementary steps



Mechanism of the Electron Transfer

Dye-surface interaction

Dye-solvent interaction

Dye-redox pair interaction

Properties of the dye

TiO_2 bulk effects

Diffusion in TiO_2

A great variety of :
- Phases
- Properties
- Interactions

Density Functional Theory

within the KS formalism

$$E[\rho]=T_{kin}+ E_{N\text{-}e}[\rho] + E_J[\rho] + E_{XC}[\rho]$$ **approximate**

PBE0
global hybrid

$$E_{xc}^{PBE\,0} = \frac{1}{4} E_x^{HF} + \frac{3}{4} E_x^{PBE} + E_c^{PBE}$$

No fitted parameters

The same DFT approach for :

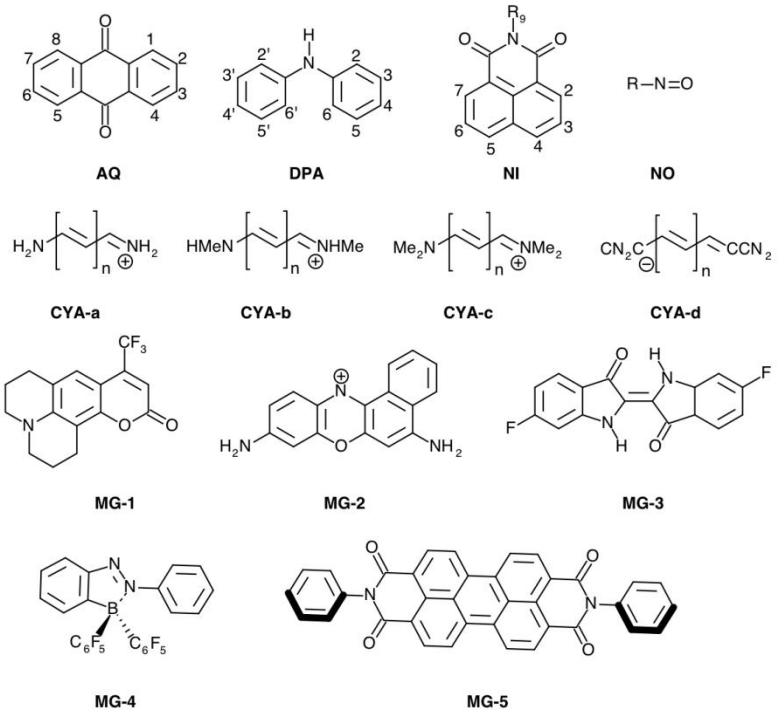
- molecules, surface and bulk (using PBC)
- gas-phase and solution (through PCM approach)
- ground and excited states

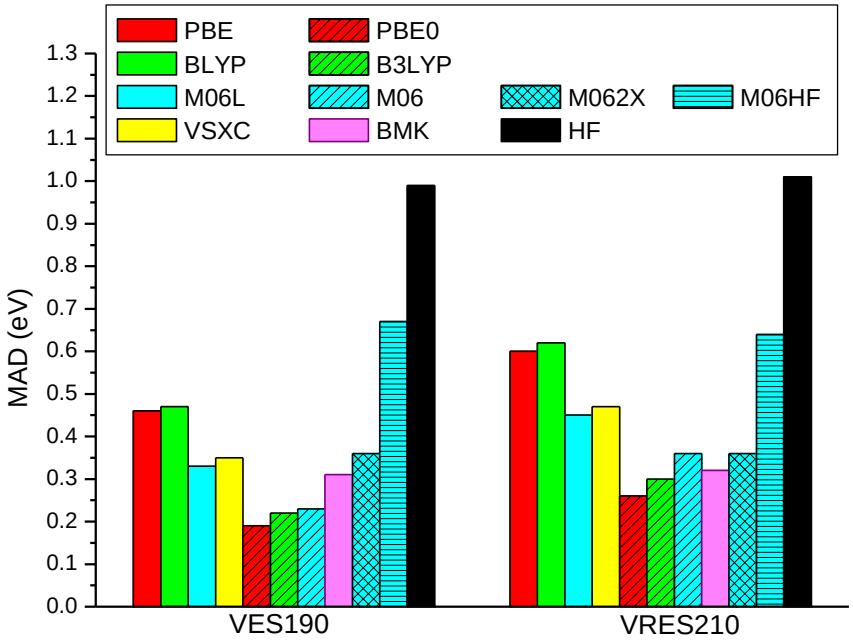
→ **Validation**

JCP 99

Computational Method: Validation

Versus Experiments (VE) set





VRES= 190 valence (VE & VT sets)
+ 20 Rydberg excitations

basis set: 6-311+G(2d,p)

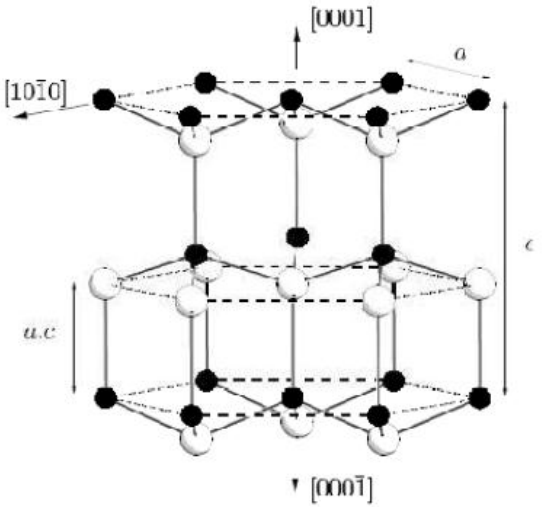
JCTC 09
ACR 09
JCTC 10

Computational Method: Validation

The bulk ZnO

TABLE II. Main properties of the density of states of ZnO wurtzite bulk structure obtained with different Hamiltonians and the Zn^*-O^* basis sets. W refers to the width of a band, $S(O_{2p}-Zn_{3d})$ is the separation between the O_{2p} and Zn_{3d} bands, and D refers to a direct gap. All data are in eV.

	$W(Zn_{3d})$	Zn_{3d} center	$W(O_{2p})$	$S(O_{2p}-Zn_{3d})$	Gap (D)
HF	1.20	−9.87	5.22	3.80	6.45
LDA	1.52	−5.73	4.20	0.10	1.46
PBE	1.86	−4.98	3.90	0.18	1.46
B3LYP	1.47	−5.93	4.51	0.38	3.46
PBE0	1.59	−6.13	4.35	0.37	3.93
HSE[a]	1.7	−6.2	⋯	⋯	2.90
Exp.		−8.6;[b] −7.5[c]	5.2[d]–5.4[e]		3.44[f]



JCP 09

Computational Method: Validation

Non polar wurzite (10-10) surface

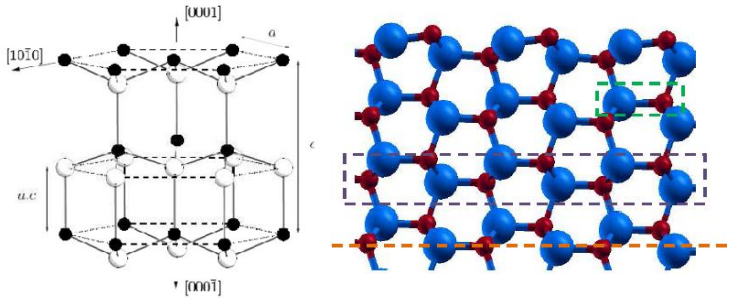


TABLE IV. Computed PBE0 atomic displacements (in angstrom) of the ZnO (10$\bar{1}$0) surface upon relaxation with both all-electron (Zn^*–O^*) and large core pseudopotentials basis sets. n refers to the number of atomic planes in the slab. $\Delta d_\perp$ and $\Delta d_\parallel$ denote displacements along [10$\bar{1}$0] and [000$\bar{1}$], respectively.

		$\Delta d_\perp$		$\Delta d_\parallel$	
Basis	n	Zn	O	Zn	O
Zn^*–O^*	8	−0.34	−0.02	+0.17	−0.00
Zn^*–O^*	4	−0.45	+0.01	+0.14	−0.05
Pseudopotentials	4	−0.29	−0.09	+0.10	−0.04
Exp.[a]		−0.45 ± 0.10	−0.05 ± 0.01	+0.10 ± 0.2	

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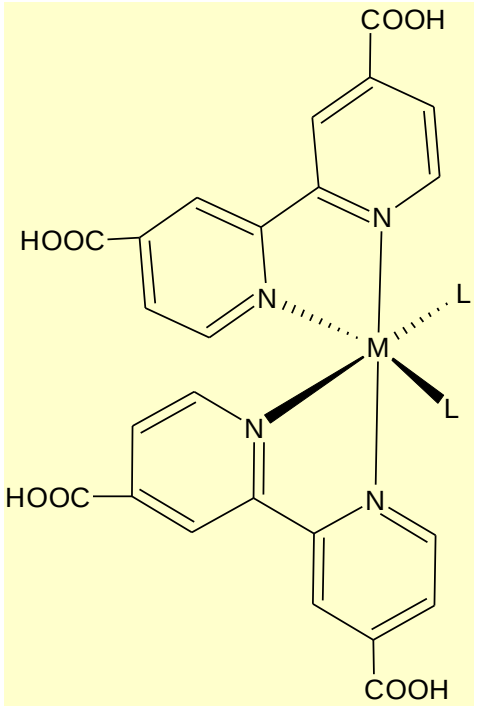
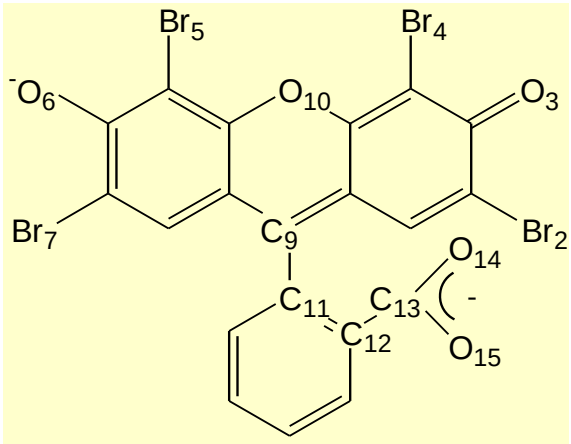
Classical DSSC

N3/TiO2 : the standard



[M(II)-(4,4'-(CO_2H)2-2,2'bipyridine)$_2L_2$]
M=Ru, Os and L=CN, NCS, Cl, SO

EY/ZnO: cheap self-assembly

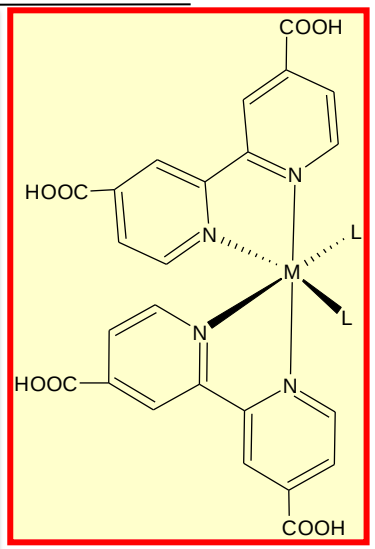


Eosine Y

11% vs. 2% efficiency

The *isolated* Dye

	Transition	isolated	solution	exp **(solution)**
$Ru(bpy)_2(CN)_2$	S0→S1	357	367	376
	S0→S2	532	478	496
	S0→T1	849	614	not observed
$Os(bpy)_2(CN)_2$	S0→S1	364	397	382
	S0→S2	538	482	508
	S0→T1	892	689	≈ 680
$Ru(bpy)_2(NCS)_2$	S0→S1	412	370	398
	S0→S2	554	487	538
	S0→T1	1025	623	not observed
$Os(bpy)_2(NCS)_2$	S0→S1	427	415	412
	S0→S2	546	498	530
	S0→T1	1060	756	≈ 780



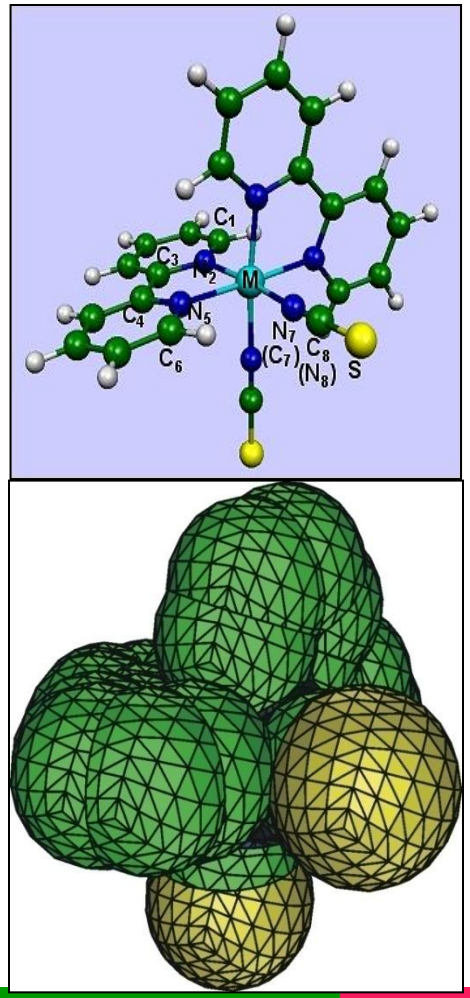
Quantitative agreement

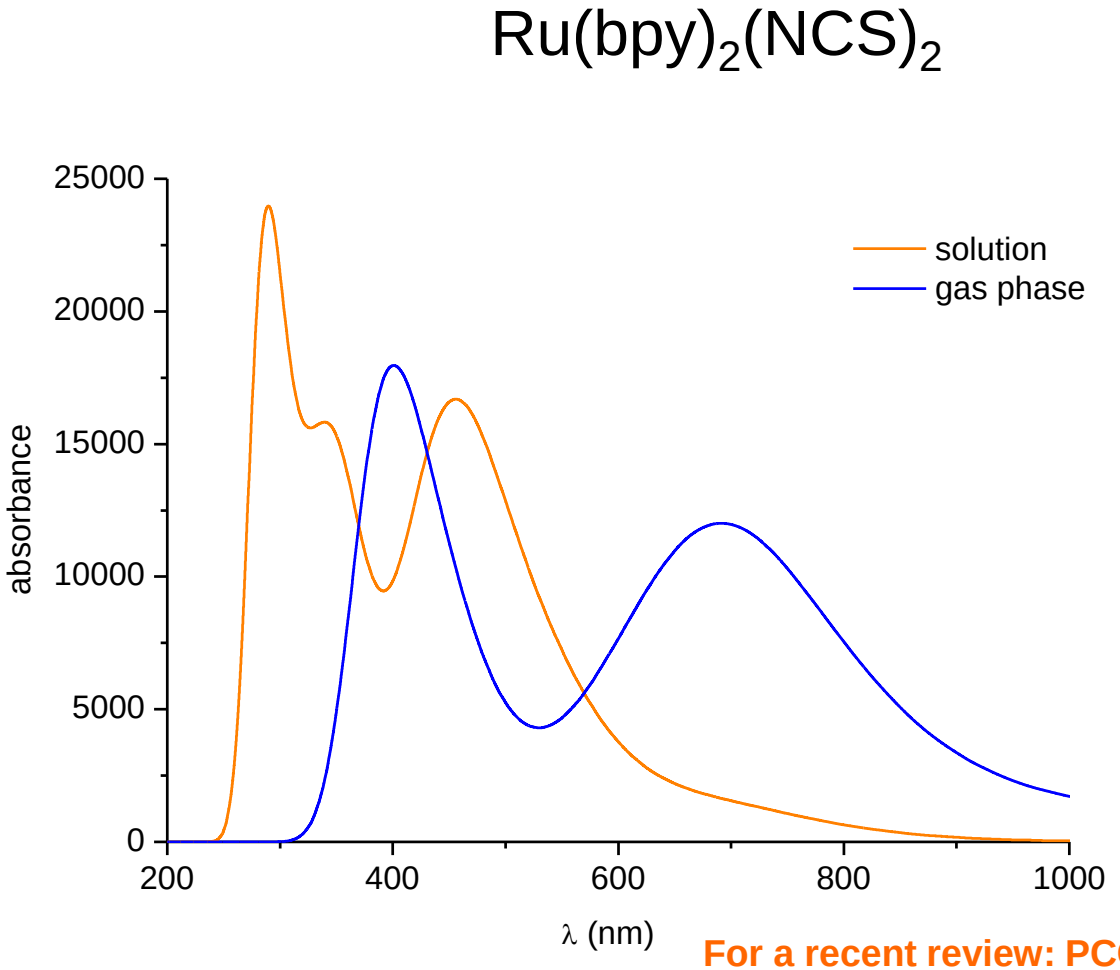
All MLCT bands

$d \rightarrow \pi^*$

Red shift from Ru to Os

Solvent effects on UV-vis spectra

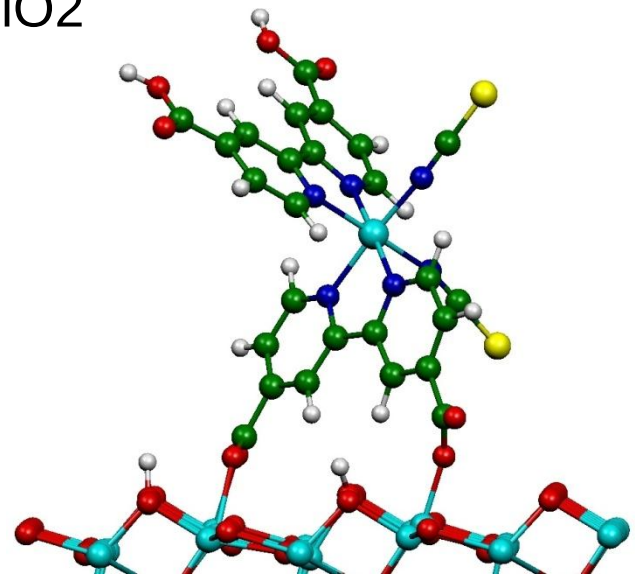




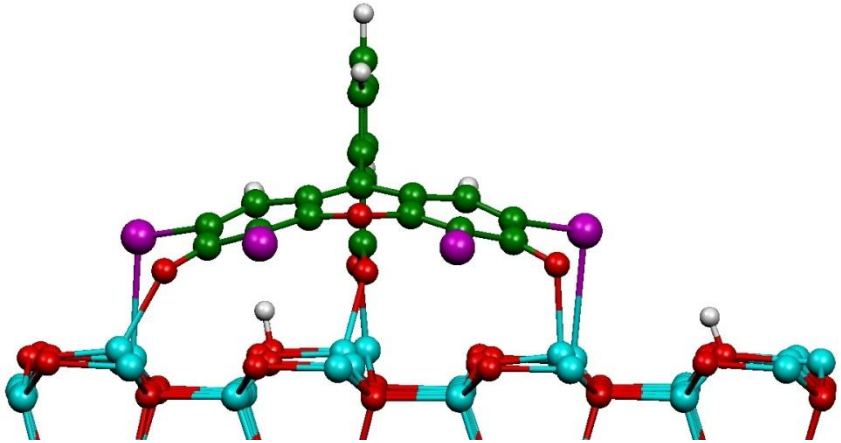
For a recent review: PCCP 2011

Dye/substrate assemblies

N3/TiO2



EY/ZnO

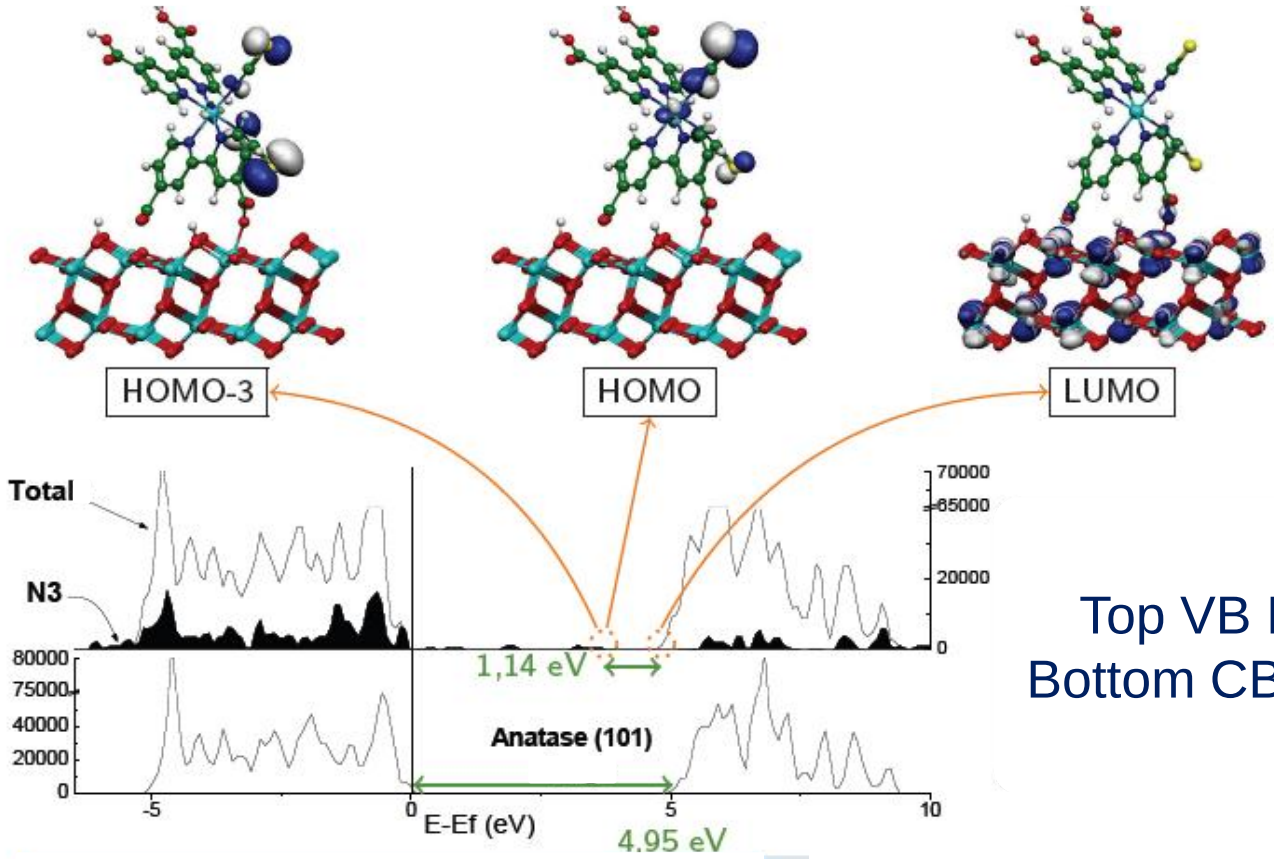


11% vs. 2% efficiency

PBE0/GTO 2D periodic systems

(LANL2DZ + Opt PBC basis for C,O, N)

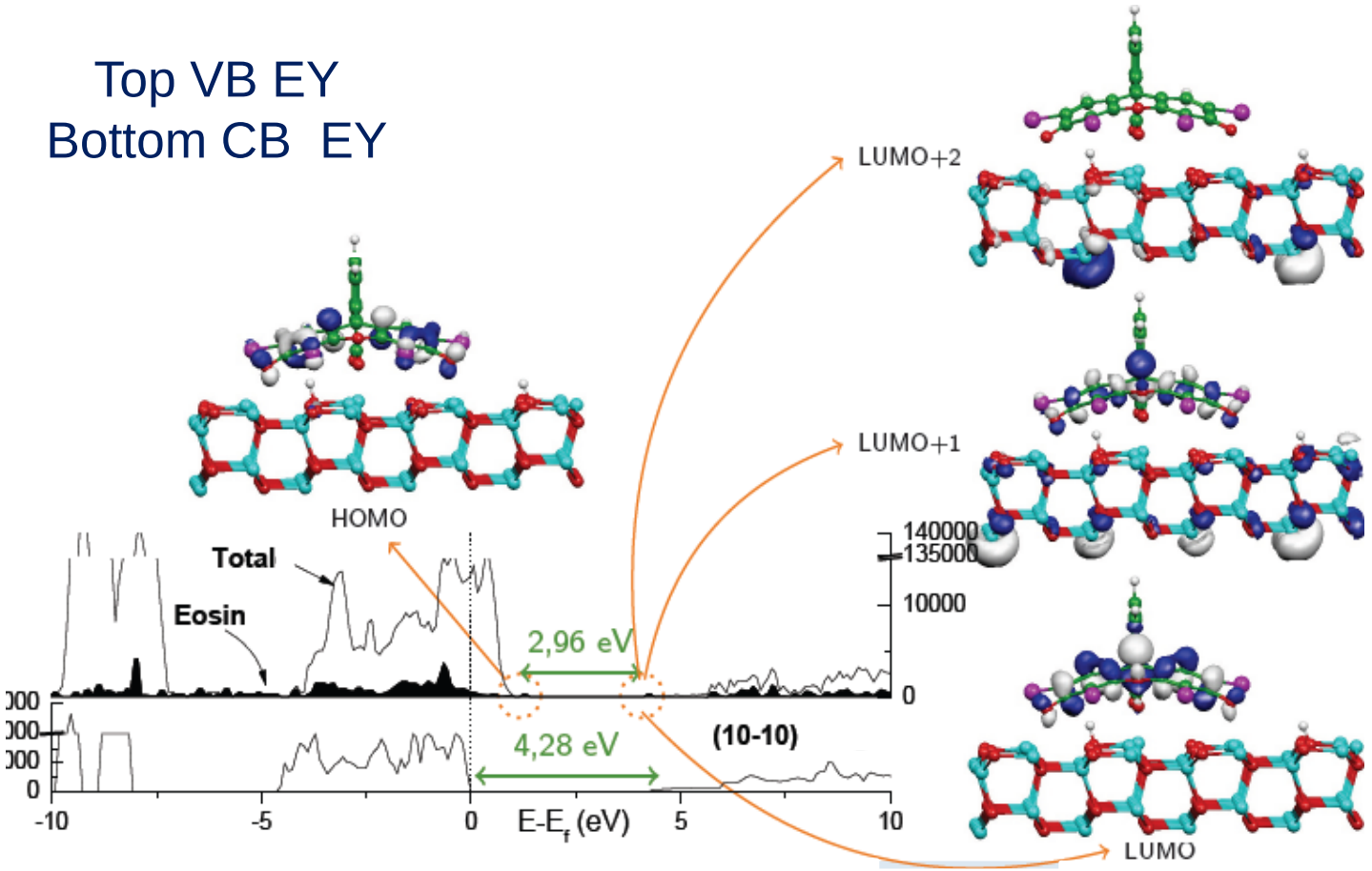
N3/TiO_2



Top VB N3;
Bottom CB TiO_2

EY/ZnO

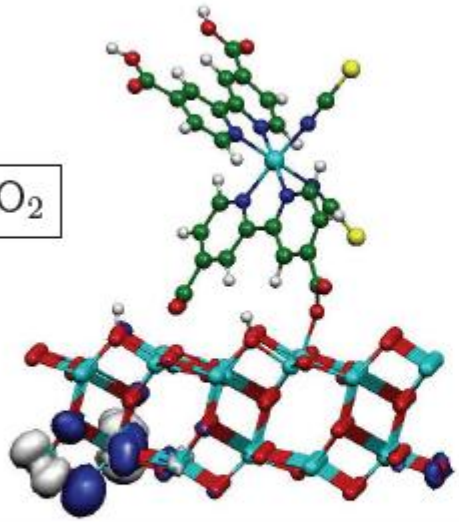
Top VB EY
Bottom CB EY



Simulating Electron Injection

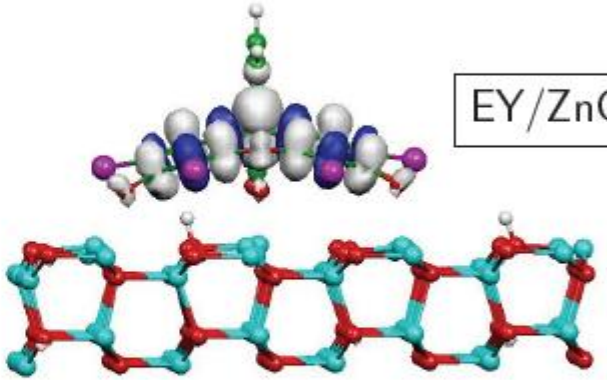
Reduced Species

N3/TiO_2



+1e$^-$: 100% on TiO2

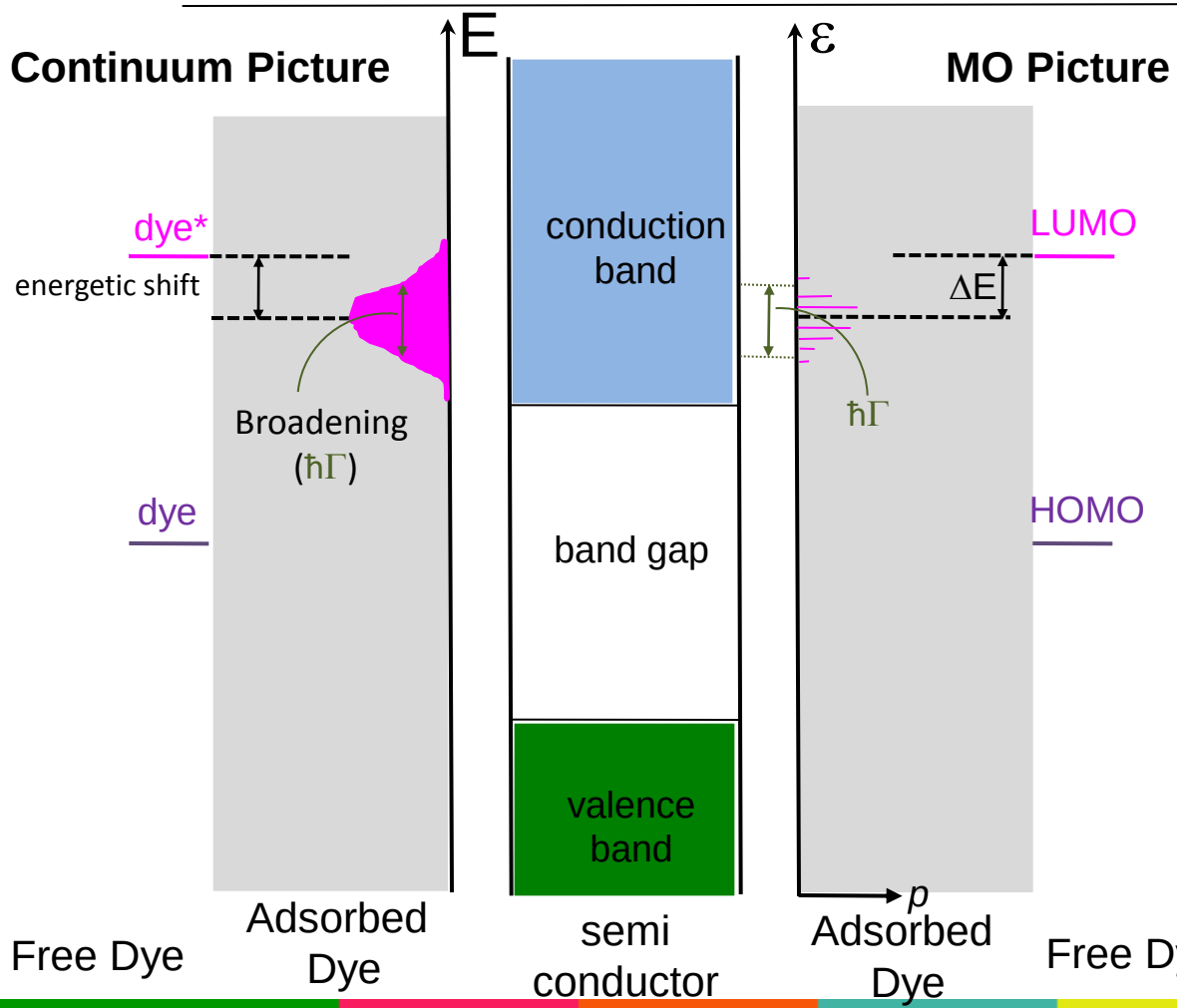
EY/ZnO



+1e- : 30% on ZnO
+2e- : 50% on ZnO

Spin Density Map

Simulating Electron Injection



Newns-Anderson model

$$\hbar\Gamma = \sum_i p_i \left| \varepsilon_i - E_{LUMO}(ads) \right|$$

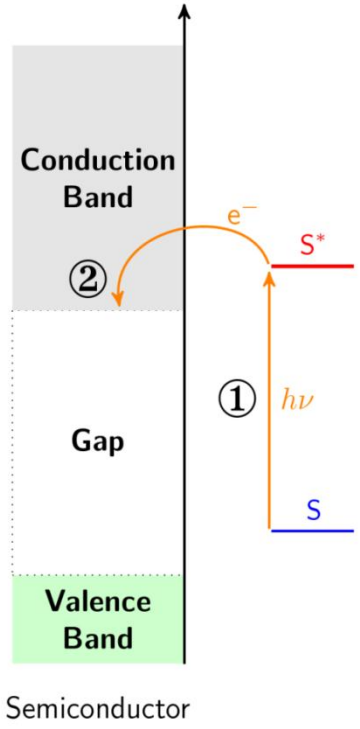
$$\tau(fs) = 658 / \hbar\Gamma(meV)$$

N3/TiO2	**EY/ZnO**
Exp.: 28-50 fs	
Calc.: 22 fs	No injection
dcbpy/TiO2	**$(EY/ZnO)^-$**
Exp.: < 3 fs	
Calc.: 2 fs	Calc: 8fs

JACS 2009

How to increase yields

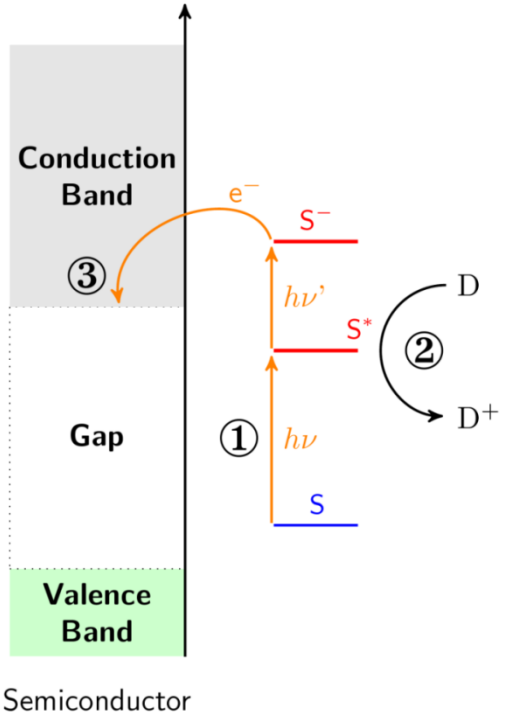
N3/TIO2



Semiconductor

injection from
the dye excited state

EY/ZnO



Semiconductor

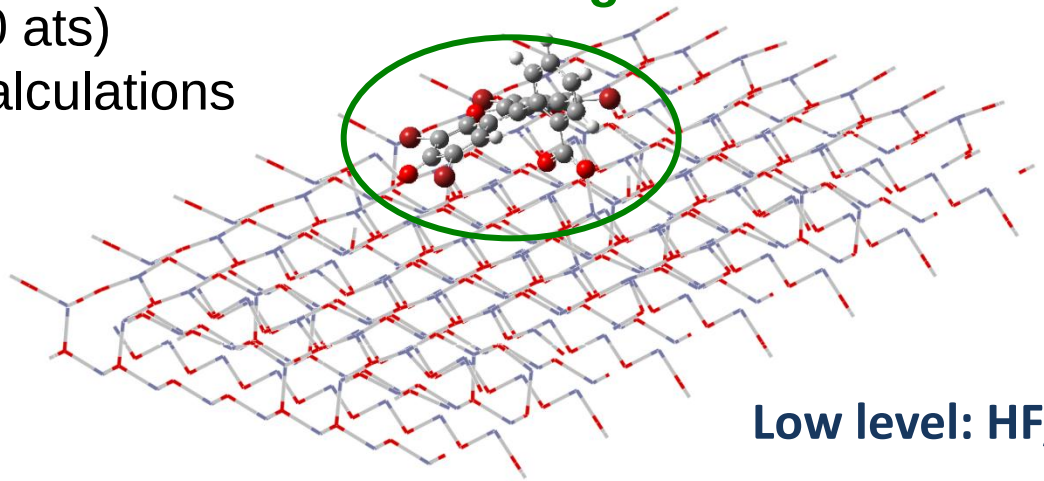
injection from
the dye reduced state

In situ dye spectrum

An ONIOMQM:QM-EE Approach

Cluster (530 ats)
from PBC opt calculations

High level: TD-PBE0/6-31+G(d) + EE



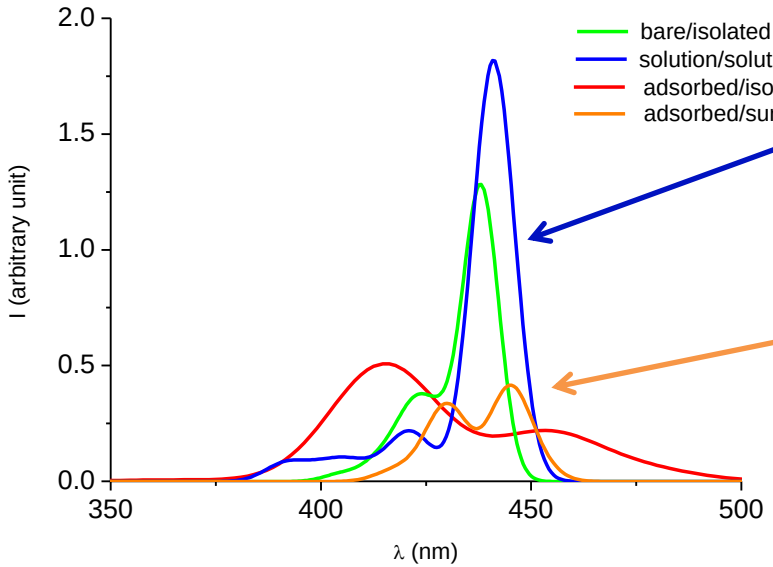
Low level: HF/LANL2DZ

EE: $V^{\mathrm{emb}}_{\mathrm{MH};\mu_H\nu_H} = -\sum_A \langle \mu_H | r^{-1}_{IA} | \nu_H \rangle q_A,$

Mulliken charges $q_A = z_A - \sum_{\alpha} \sum_{\beta \in A} P_{\alpha\beta} S_{\alpha\beta},$

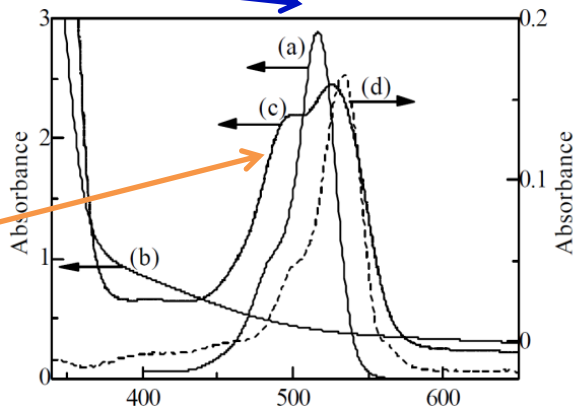
JACS 2009

In situ dye spectrum



EY

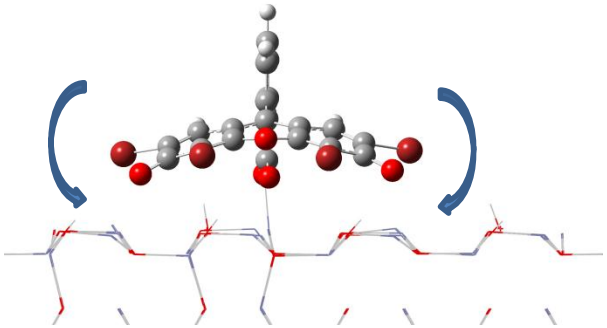
EY/ZnO



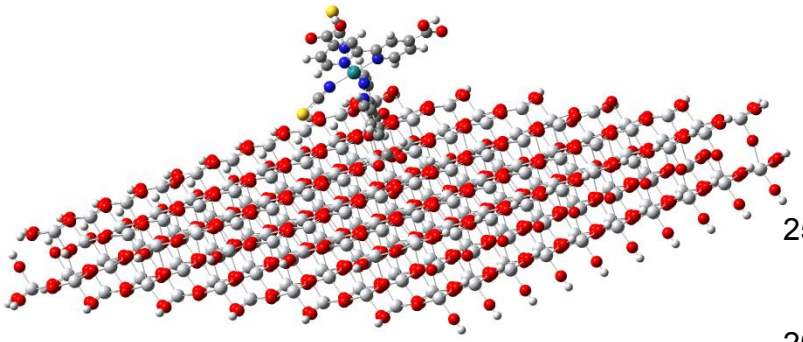
o-o-p motion

red shift (≈15 nm)

Two peaks

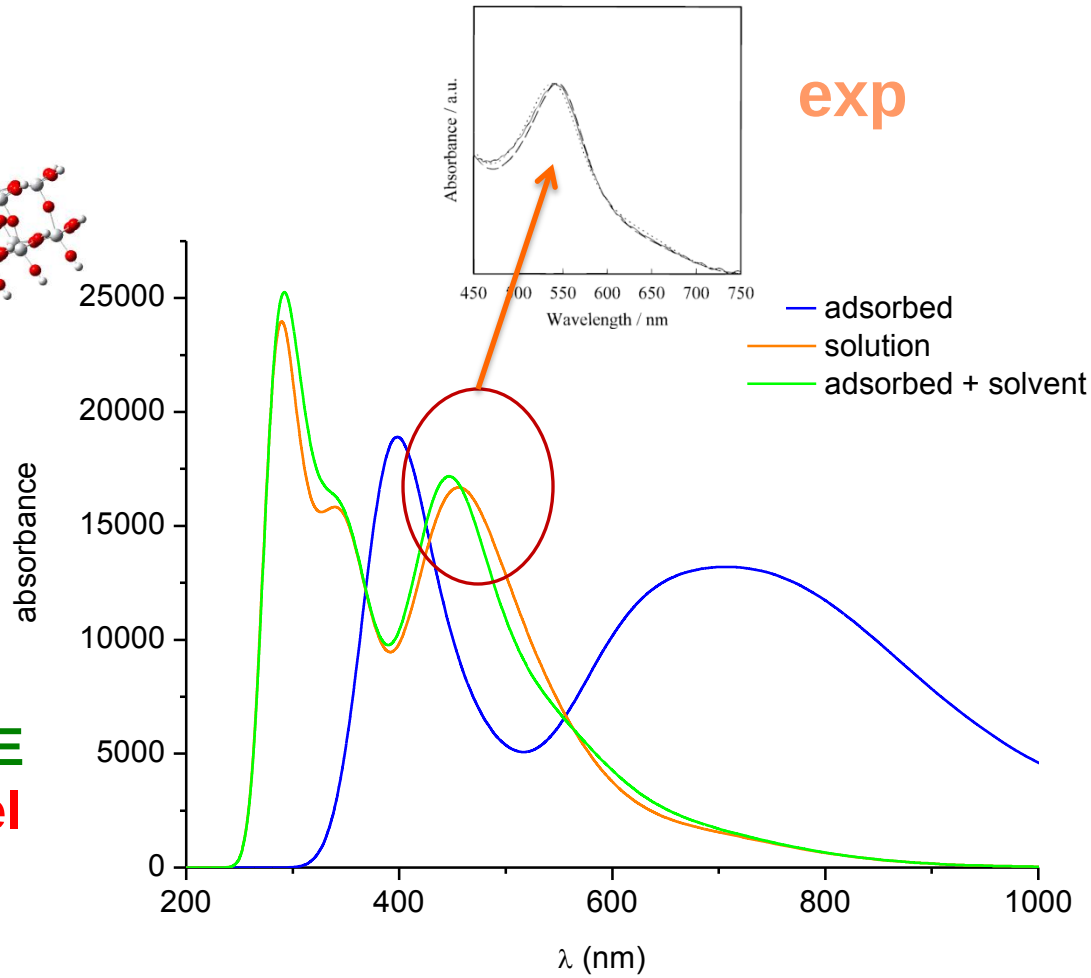


In situ dye spectrum



Cluster (896 ats) from PBC opt calculations

ONIOM: (HF:TD-PBE0) + EE + continuum solvent model



JPC C 2011

Learning from modeling of DSSCs

Development of a computational protocol

1. Prescreening of a family of dyes based on the calculations of the isolated dye PBE0 / PCM level (molecular level)

- *Energy criteria :* LUMO higher than CB
- *Dipole criteria:* increasing upon excitation
- *CT criteria :* CT toward surface

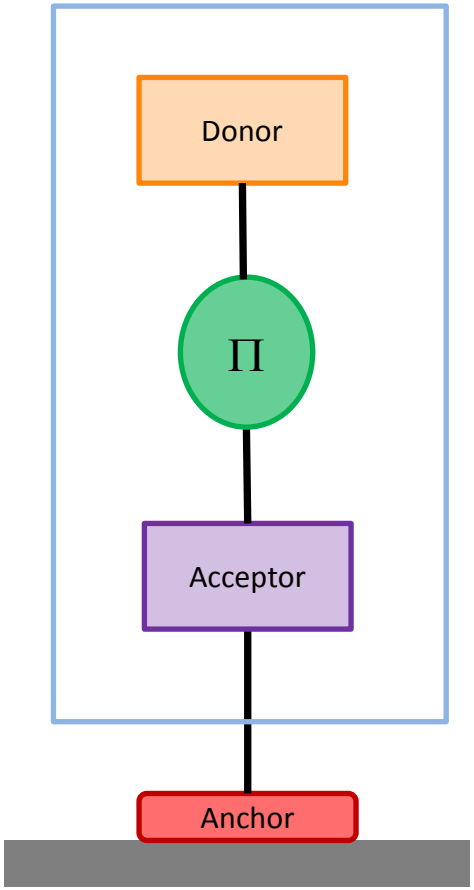
2. Selection of a limited number of dyes

3. Study the dye/ZnO system
   PBE0/ PBC level

4. Other effects (solvent, additives, etc..)

Granting for a transferability of results (same method for molecular and PBC calculations)

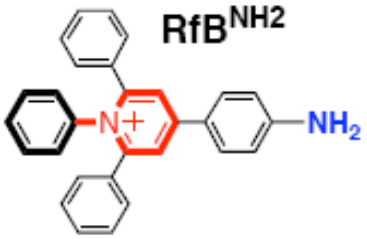
Design of new dyes

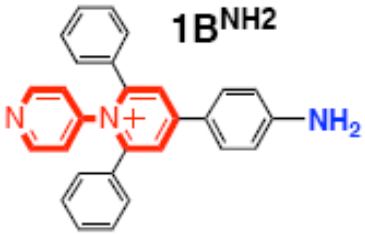


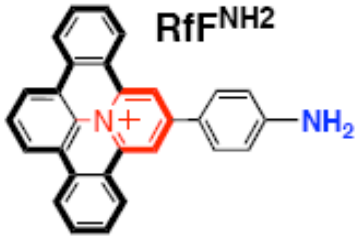
$D^+ - A^-$

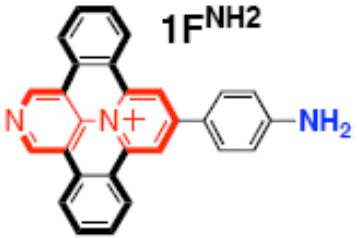
CT excited state

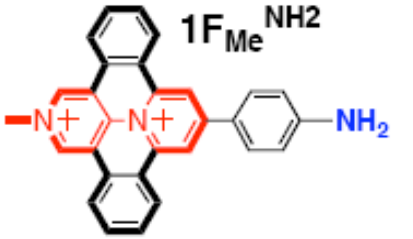
D = $-NH_2$ A = $-N^+$











Acceptor unit: JACS *132* (2010), 16700–16713
J. PHYS CHEM A 114 (2010) 8434-8443.
CHEM. EUR. J 16 (2010) 11047–11063

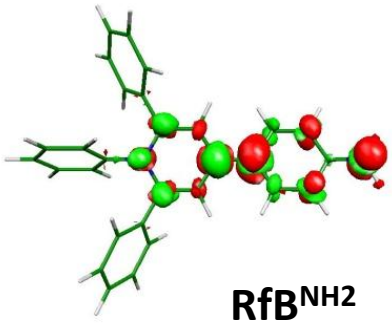
Spectral Properties

	λ (f)										
RfB^{NH2}	397 (0.70)	306 (0.21)	232 (0.12)	226 (0.21)							
RfF^{NH2}	424 (0.86)	329 (0.15)	291 (0.43)	279 (0.60)	267 (0.18)	236 (0.48)	230 (0.33)	220 (0.25)	219 (0.27)		
$1B^{NH2}$	403 (0.97)	309 (0.20)	249 (0.11)	234 (0.15)	233 (0.14)						
$1F^{NH2}$	436 (0.87)	378 (0.11)	292 (0.31)	279 (0.45)	269 (0.18)	249 (0.13)	222 (0.34)	221 (0.15)	218 (0.11)	215 (0.11)	
$1B_{Me}^{NH2}$	475 (0.46)	388 (0.65)	342 (0.10)	294 (0.12)	235 (0.18)	226 (0.13)	207 (0.16)				
$1F_{Me}^{NH2}$	496 (0.91)	384 (0.25)	378 (0.14)	316 (0.24)	297 (0.21)	290 (0.36)	276 (0.29)	257 (0.23)	244 (0.11)	233 (0.39)	209 (0.32)	208 (0.12)

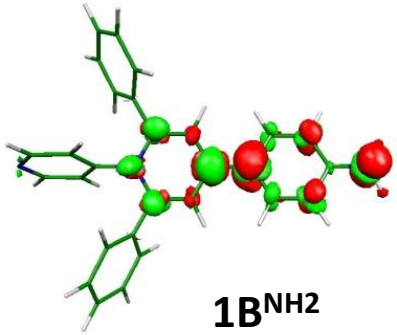
λ In n nm, f in a.u.

Spectral Properties

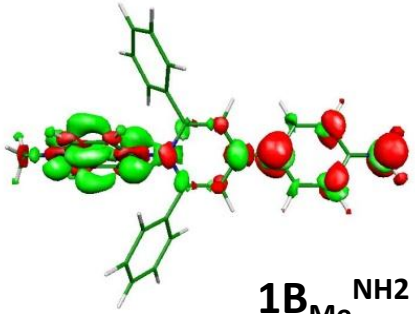
Difference density maps: CT character of the first transition



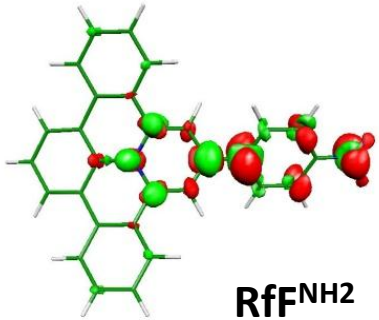
RfB^{NH2}



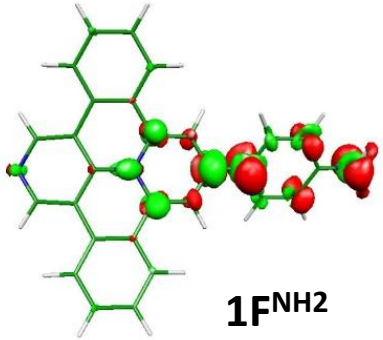
$1B^{NH2}$



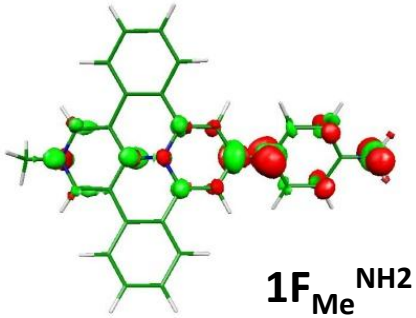
$1B_{Me}^{NH2}$



RfF^{NH2}



$1F^{NH2}$



$1F_{Me}^{NH2}$

(TDDFT PBE0 6-31+G(d)/ PCM)

Spectral Properties

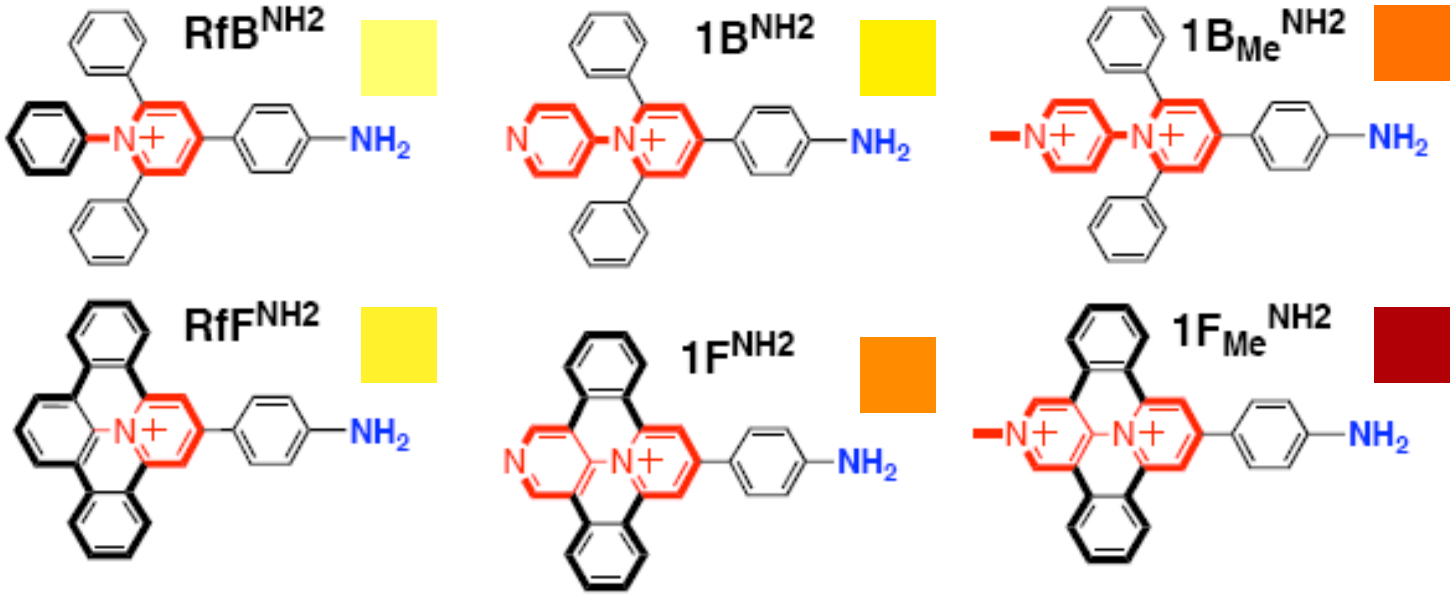
$$X = K \int S(\lambda)\, \bar{x}(\lambda)\, T(\lambda)\, d\lambda$$

T= Transmission spectra $T(\lambda) = 10^{-A(\lambda)}$

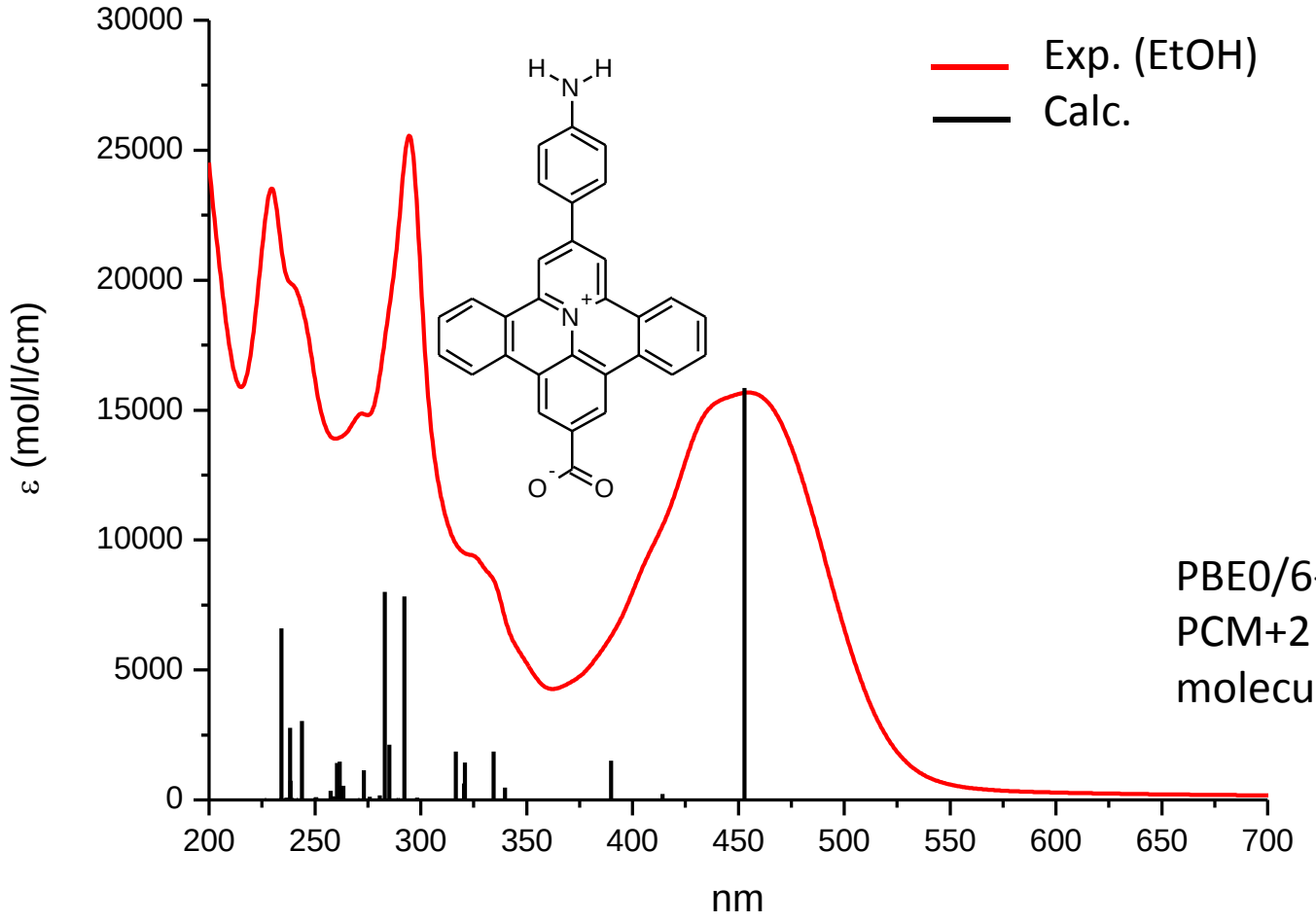
$$K = \frac{100}{\int S(\lambda)\, \bar{y}(\lambda)\, d\lambda}$$

S =Source spectral density (D65)

X,y,z =Observer colorimetric function



How does it compares to exp.?



PBE0/6-31++G(d,p)
PCM+2 explicit solvent molecules (EtOH)

DSSC suitability criteria

Energy: $LUMO_{dye}$ higher in energy than CB ZnO

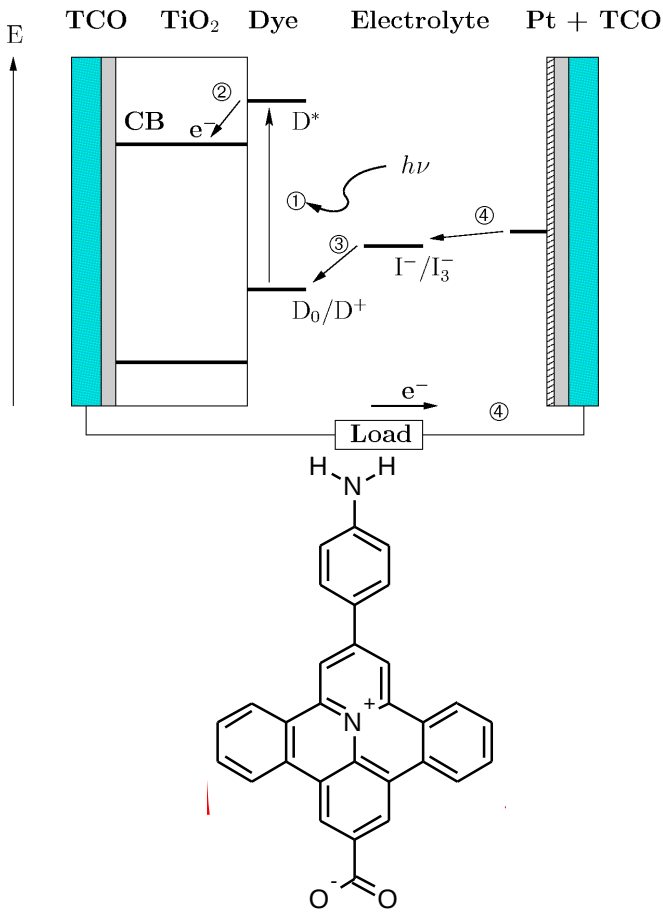
0.2 eV — satisfied

Dipole: Increase in dipole moment going from GS to ES

13.6 Debye — satisfied

CT: Presence of a CT band towards the surface

Analyzed by a CT index
JCTC *7* (2011) 2498–2506 — satisfied



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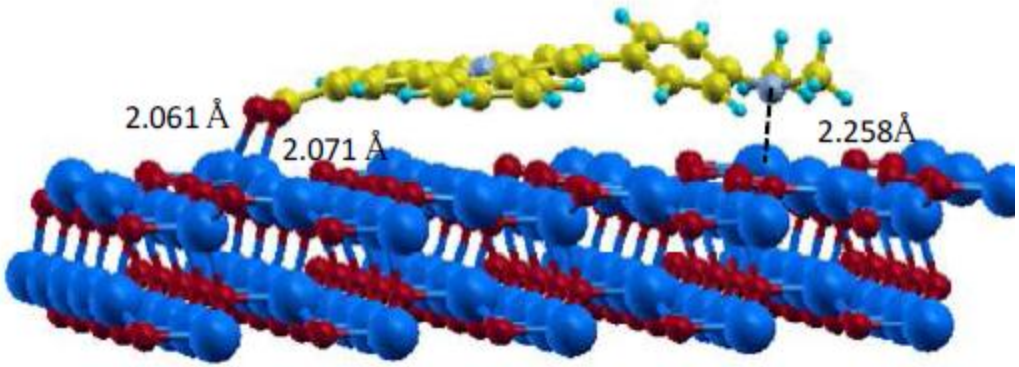
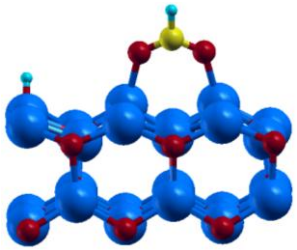
Adsorption on ZnO

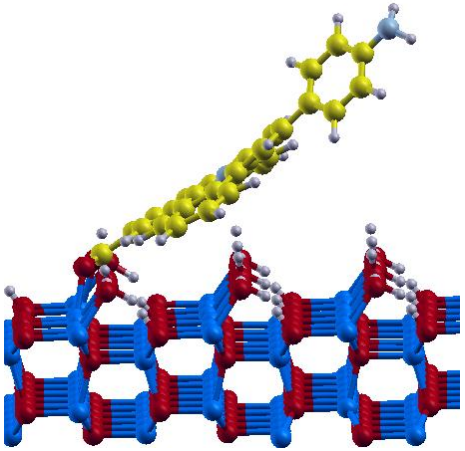


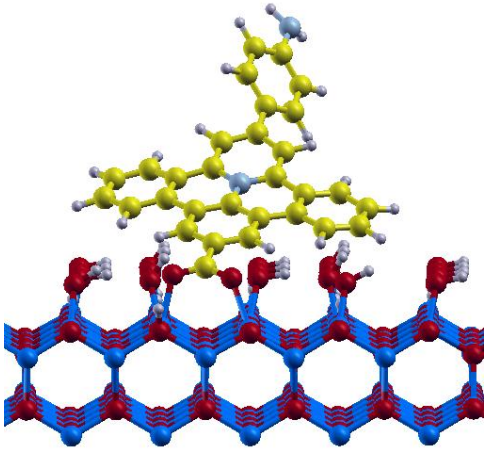
Non physical

More realistic model for surface: Solvation

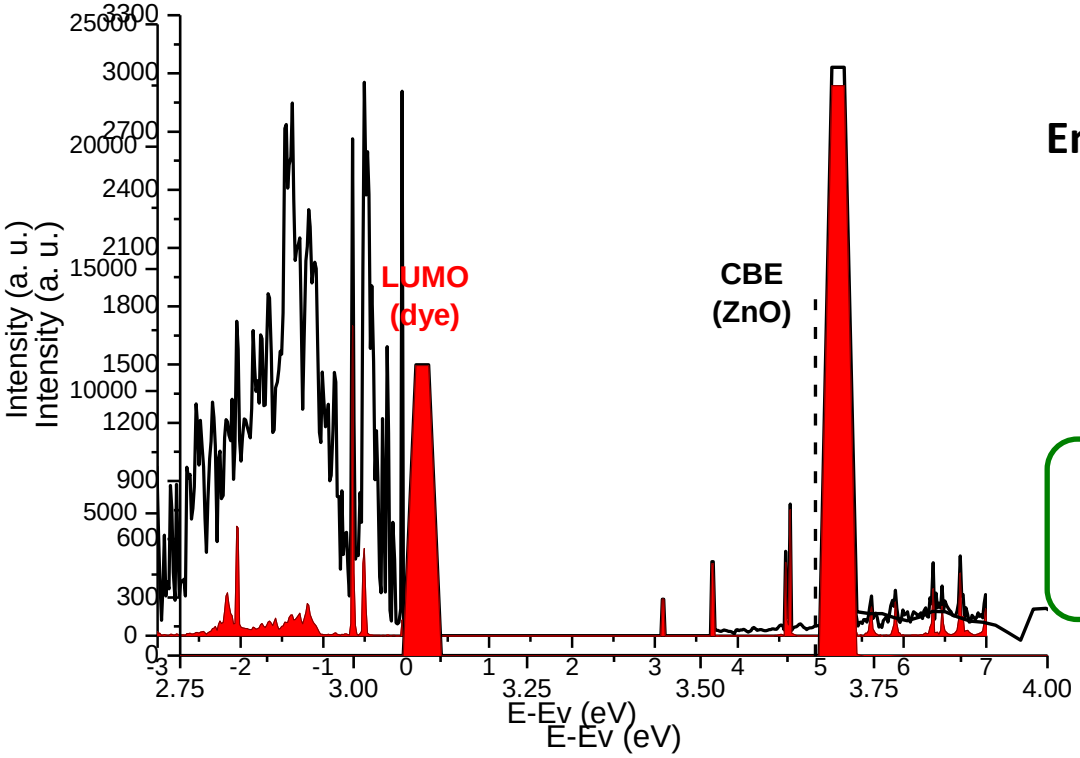


Binding mode: bidentate
Eads =352 kJ/mol





DOS dye/ZnO_{H_2O}



Injection is not favored
Energy criterium not satisfied

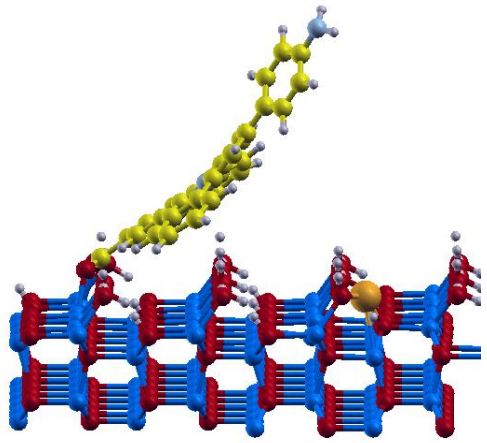
Change the LUMO energy
⇒functionalise dye

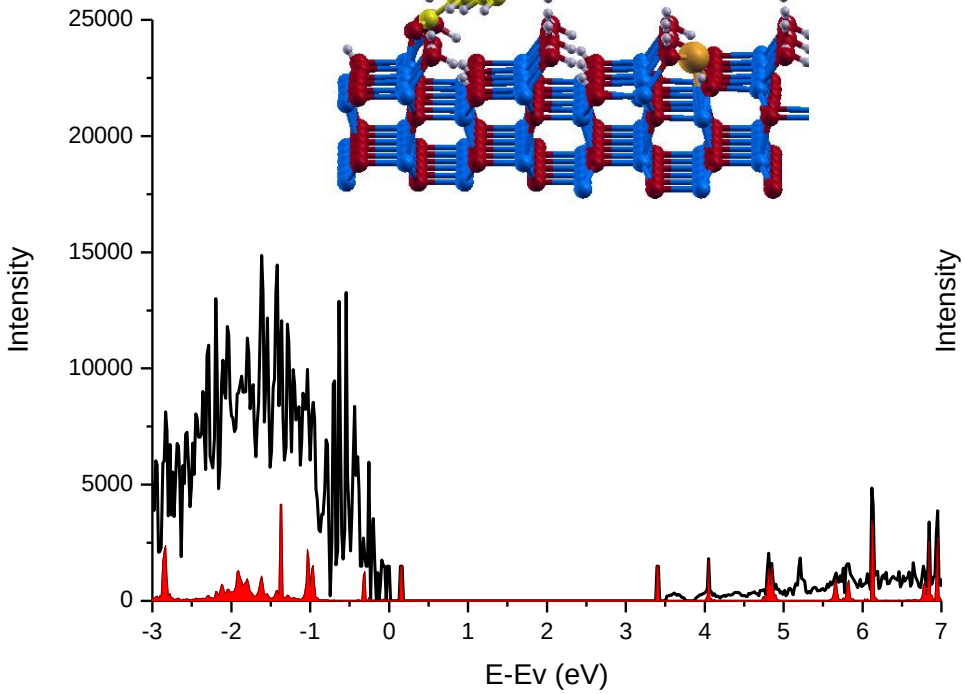
Modify the CB level
=> Additives

JACS *133* (2011) 8005–8013

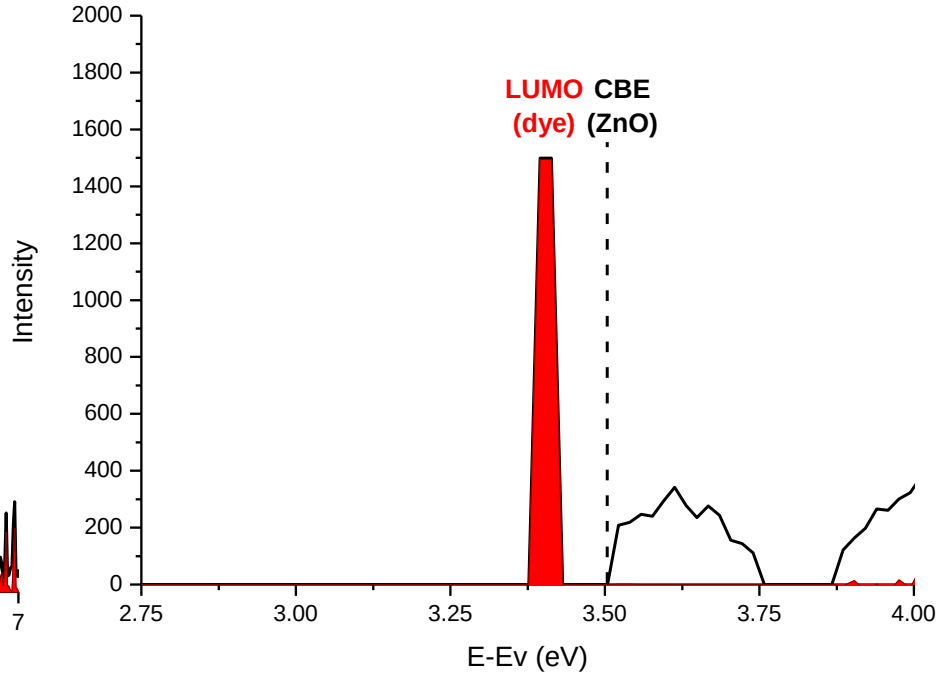
Additive effects: Li^+

dye+Li^+/ZnO_{H_2O}



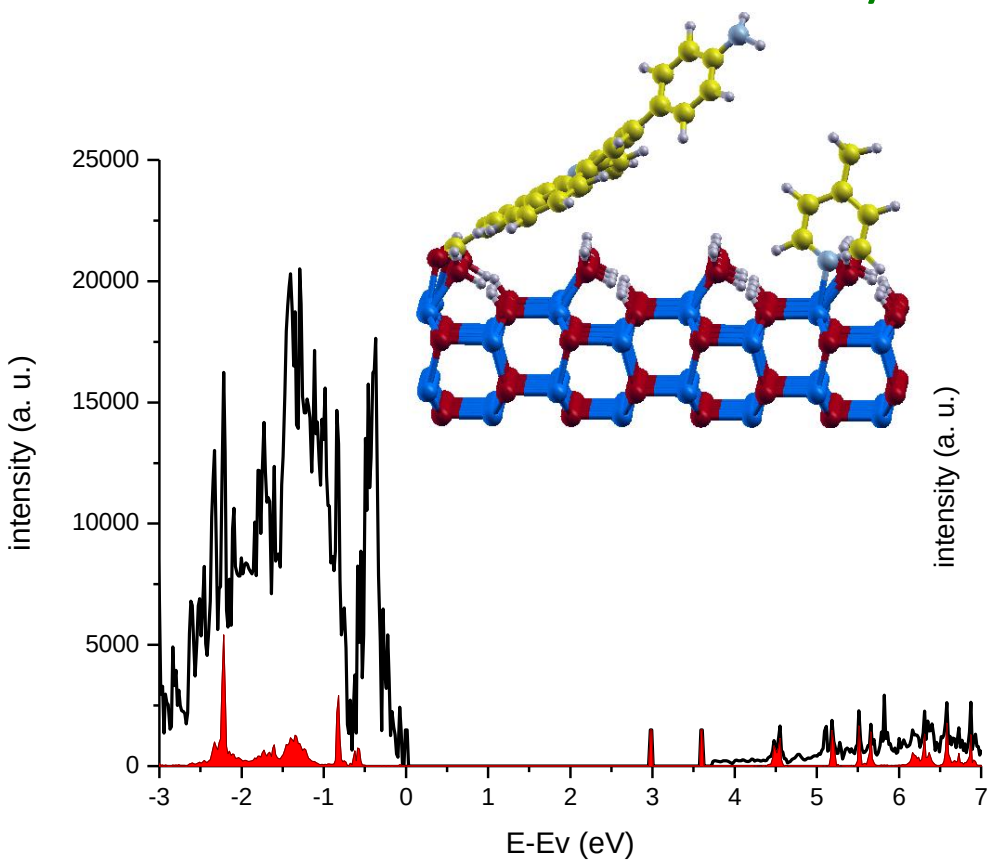


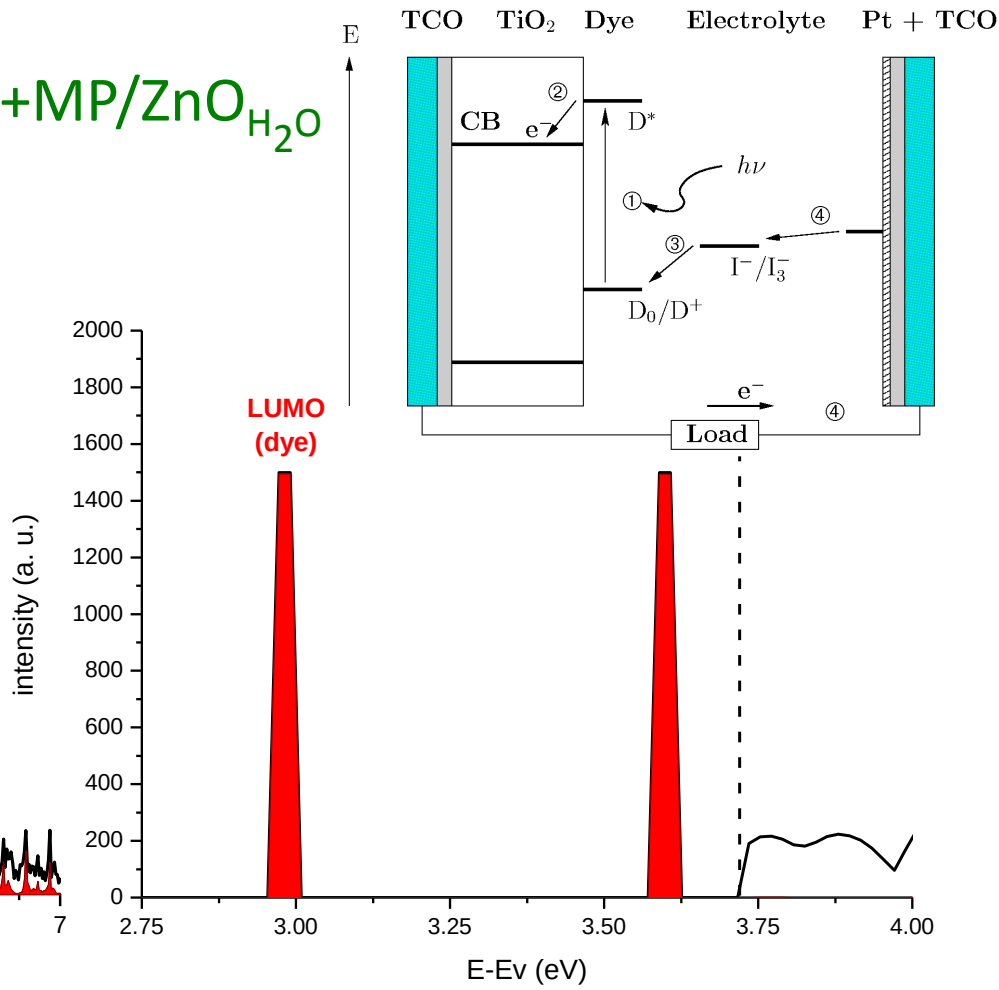
Injection should be possible



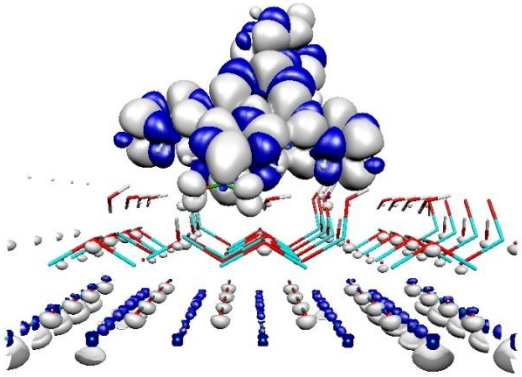
Additive effects: TBP

dye+MP/ZnO$_{H_2O}$

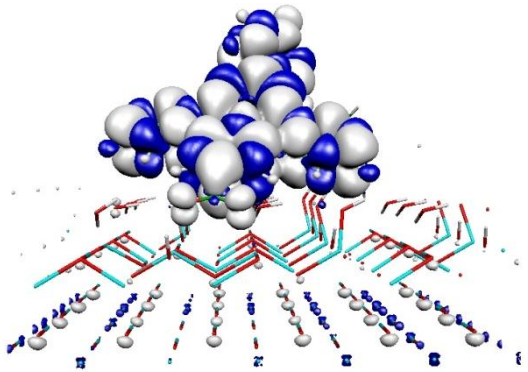




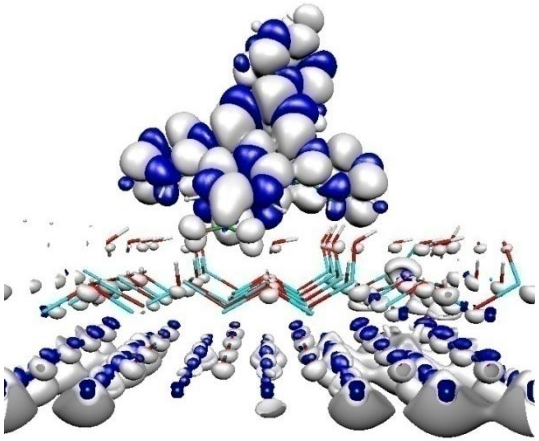
Reduced systems : spin density



Dye/ZnO_{H2O} 18%



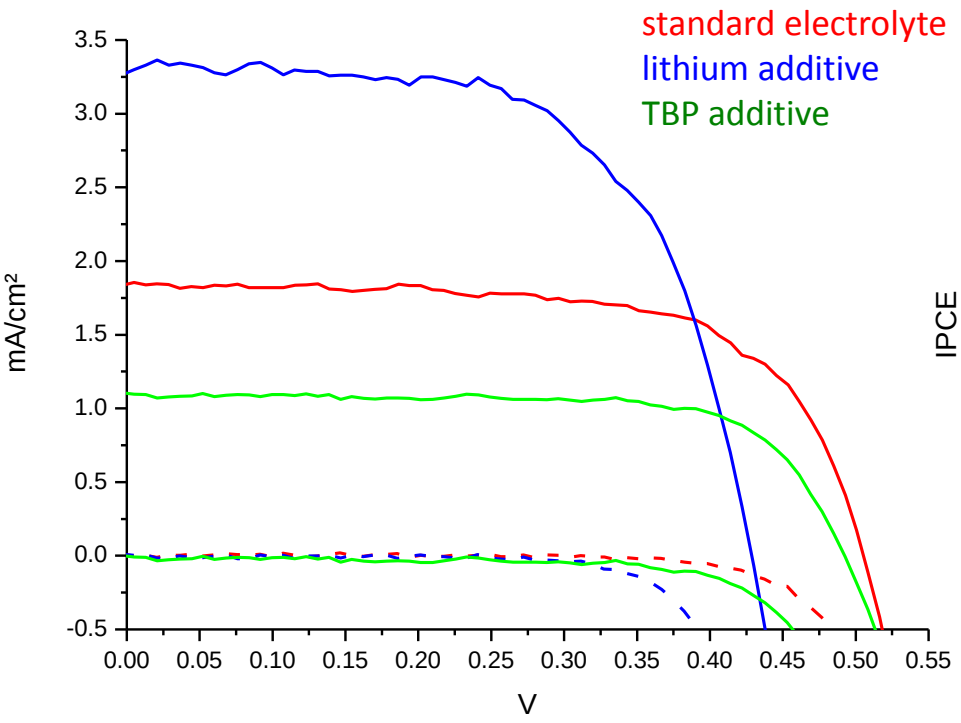
Dye+MP/ZnO_{H2O} 9%

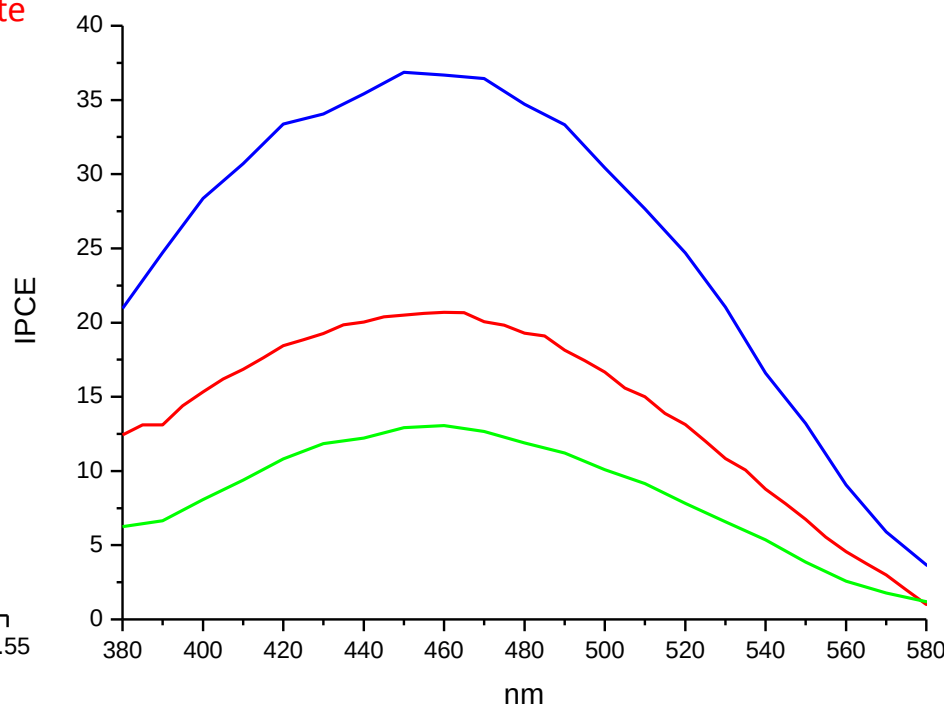


Dye+Li^{+}/ZnO_{H2O} 43%

JACS *133* (2011) 8005–8013

The proof of the pudding is in the eating





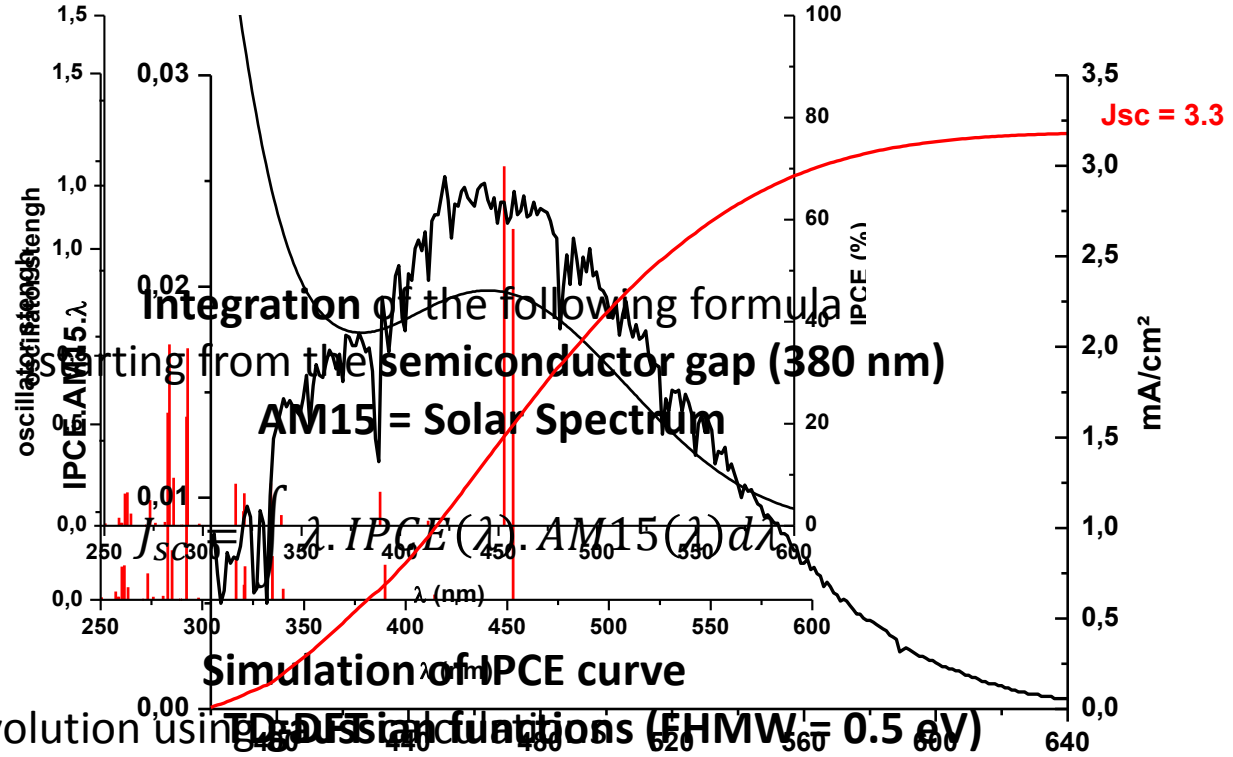
Voc = open circuit voltage

Jsc= short circuit current density

FF = Fill Factor ($V_{max}J_{max}/V_{oc}J_{sc}$)

IPCE = Incident photon to electron conversion efficiency

'Ab-initio' evaluation of IPCE and J_{SC}



Integration of the following formula starting from the **semiconductor gap (380 nm)**

AM15 = Solar Spectrum

$$J_{SC} = \int \lambda . IPCE(\lambda) . AM15(\lambda) d\lambda$$

Simulation of IPCE curve

TD-DFT calculations (FHMW = 0.5 eV)

IPCE values between 0% and 100% from TD

Convolution using Gaussian functions

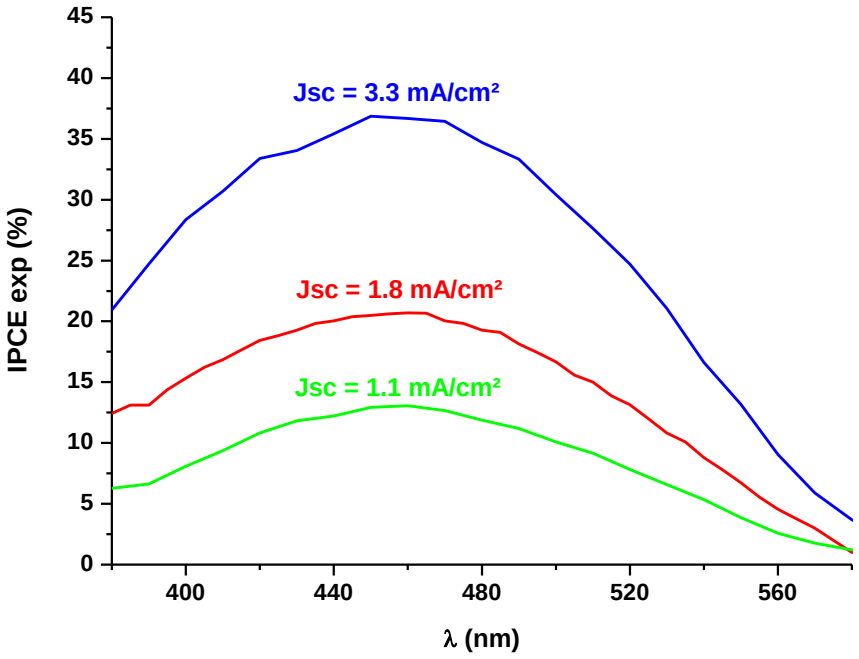
Max = Weighted absorbances maxima and relative intensities of reduced system)

Jsc= short circuit current density

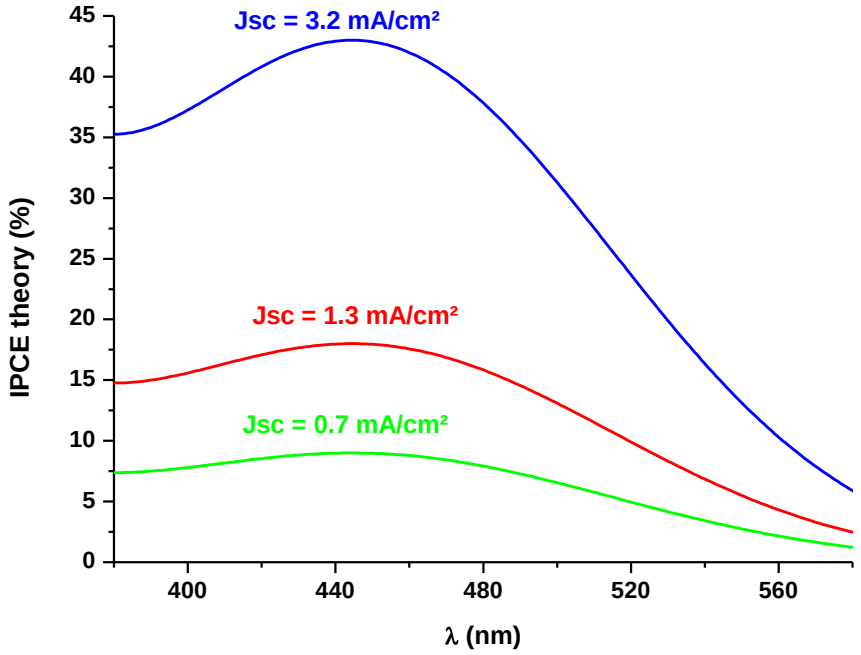
IPCE = Incident photon to electron conversion efficiency

IPCE and J_{SC} : theory vs exp.

Exp.



Theo.



ACR, in press

Conclusions

Promising ab-initio Approach for DSSCs' optimization

- Isolated Molecule approach
  - Light-molecule interactions (λ_{abs}, λ_{em}, f…)
  - Excited state properties($\Delta\mu$, $\Delta\rho$)
- PBC approach
  - Dye/semiconductor structural and electronic properties
  - Injection
  - Effect of co-adsorbed molecules

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