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# Zooming in an excitonic solar cell: An ab initio investigation of the optically active site

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# ZOOMING IN AN EXCITONIC SOLAR CELL: AN AB INITIO INVESTIGATION OF THE OPTICALLY ACTIVE SITE

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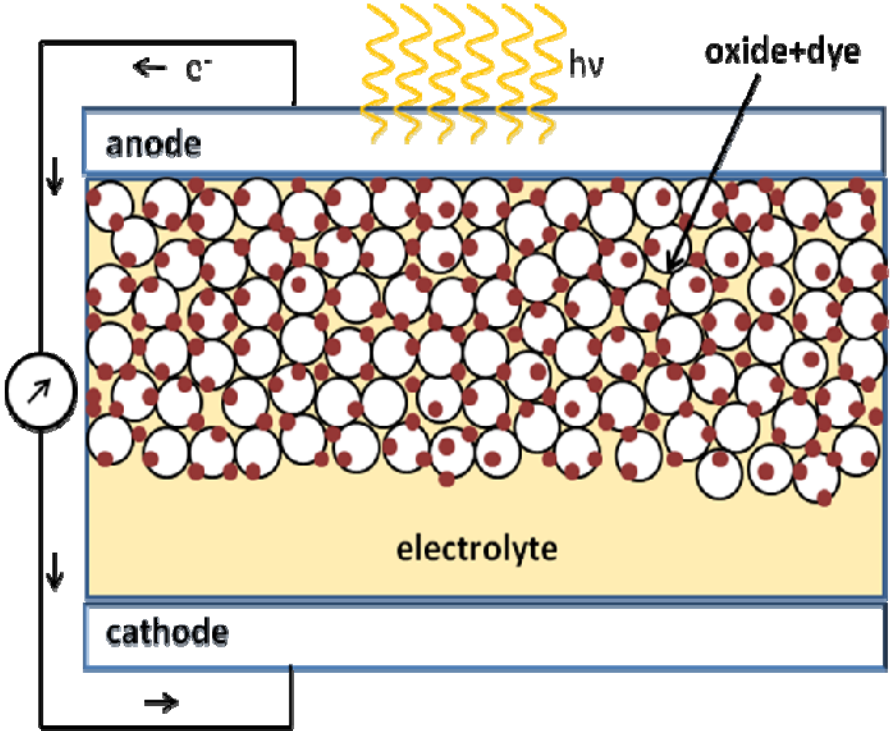
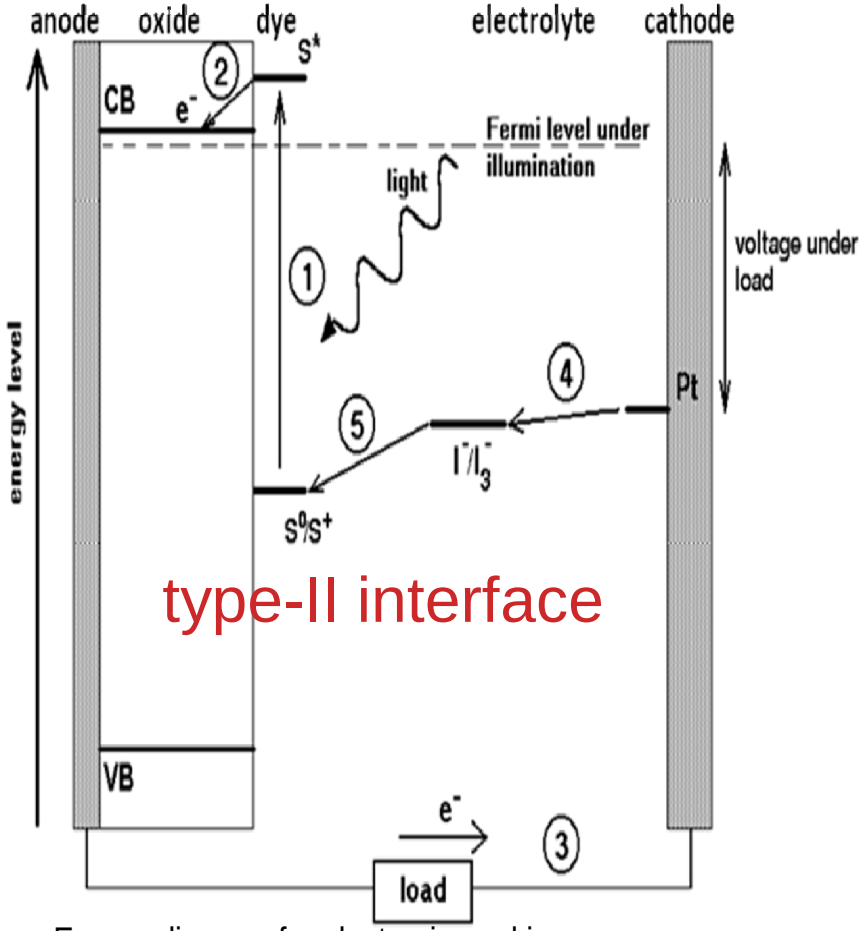
CNRNANO
ISTITUTO NANOSCIENZE CONSIGLIO NAZIONALE DELLE RICERCHE

# dye sensitized solar cells

Metal-oxide nanoparticles (especially $TiO_2$, ZnO, $SnO_2$) may be sensitized to harvest visible radiation in working solar cells, upon molecular dye functionalization →
GRAETZEL or DYE SENSITIZED SOLAR CELLS (DSSCs)*

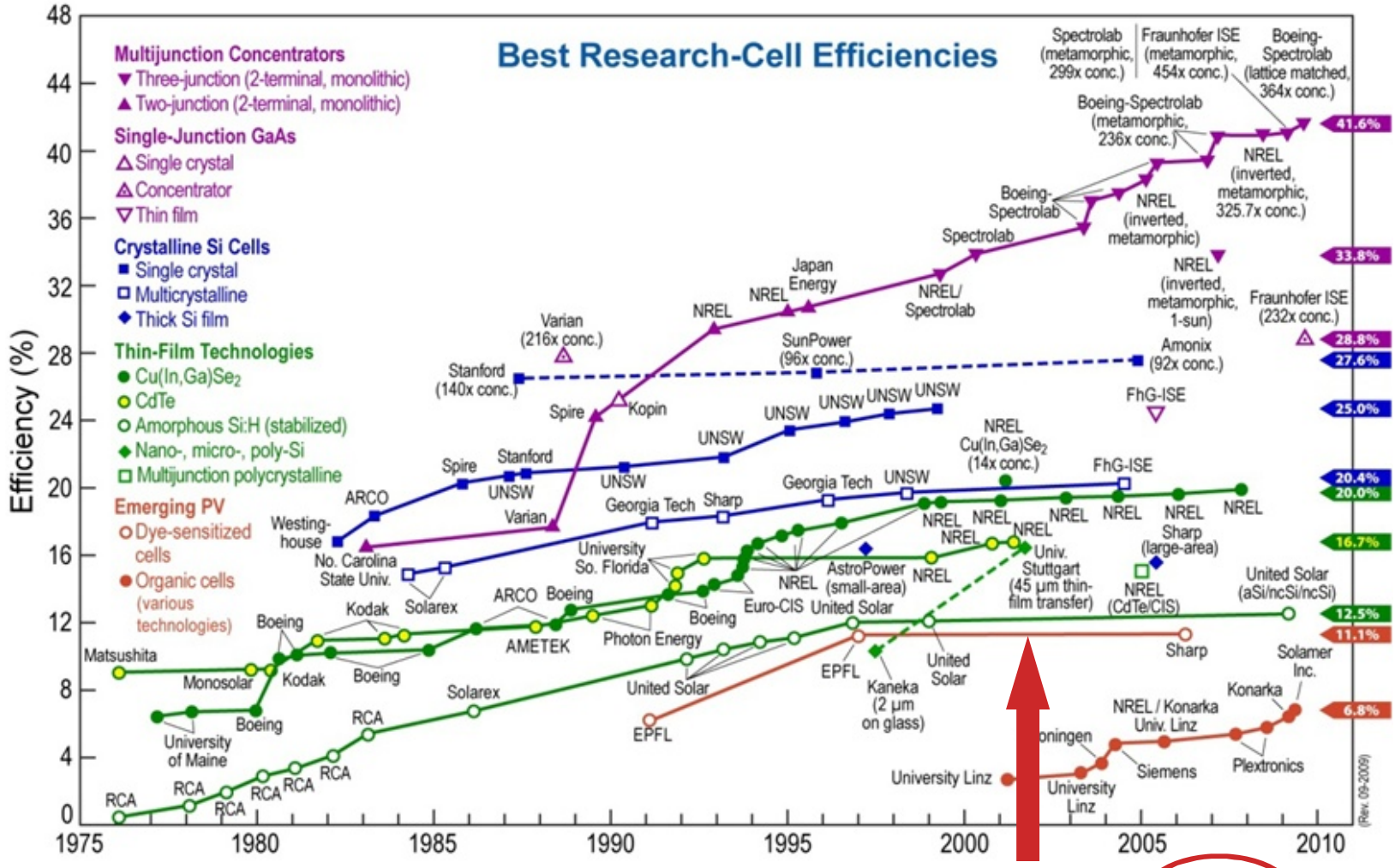



Energy diagram for electronic working process.

* O'Regan and Graetzel Nature 1991

# reported efficiencies




No progressive evolution in DSSC efficiencies $\eta = \frac{I_{max}}{I_{in}} = \frac{i_{sc} V_{oc} FF}{I_{in}}$

# basic processes

PROCESSES TO CONTROL/OPTIMIZE

- INTERFACE FORMATION
- LIGHT ABSORPTION
- CARRIER GENERATION
- ELECTRON TRANSPORT
- HOLE TRANSPORT
- RECOMBINATION
- CHARGE TRANSFER AT EXTERNAL CONTACTS
- SERIES RESISTANCE

NO MICROSCOPIC CONTROL OF THESE PROCESSES AT THE NANOSCALE

# (long term) goal for theory

GOAL: **Our aim** is *not* the direct enhancement of the DSSC efficiency, but the theoretical assessment of a representative DSSC model from **first principles**, with the net interest in the microscopic understanding of the mechanisms that rule the **optically active site** and of the fundamental interactions with the rest of the cell (electrolyte, external contacts, etc).

PROBLEM: NO **unique theoretical approach** to simulate the optoelectronic processes in a working DCCS, from first principles

Several skills are required !!!

# ab initio methods

PROPOSED TECHNIQUES

Ground state configurations & dynamics

→ GGA-DFT + total energy and forces (ground state)

→ ab initio molecular dynamics (Car-Parrinello) at finite temperature

www.quantum-espresso.org

Excited states

→ optical spectra – *turbo*-TDDFT

→ band-alignment, excitonic spectra – GW+BSE

→ atomic evolution of excited state – Ehrenfest dynamics

Vibrational spectra (IR, Raman) and heat propagation

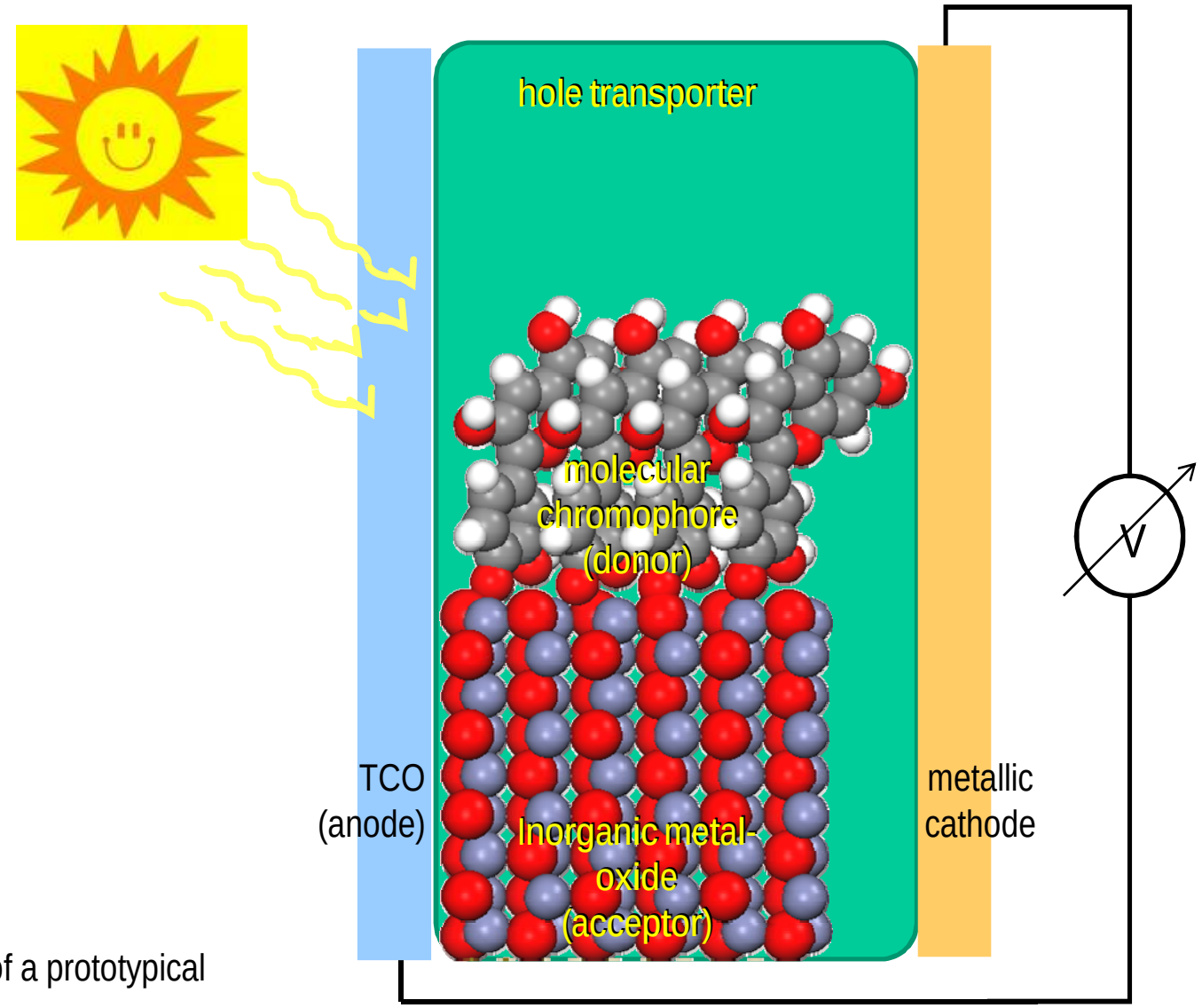
→ density functional perturbation theory

Electron Transport

→ DFT-Landauer for two terminal model devices

www.wannier-transport.org

# model system




Scheme of a prototypical DSSC

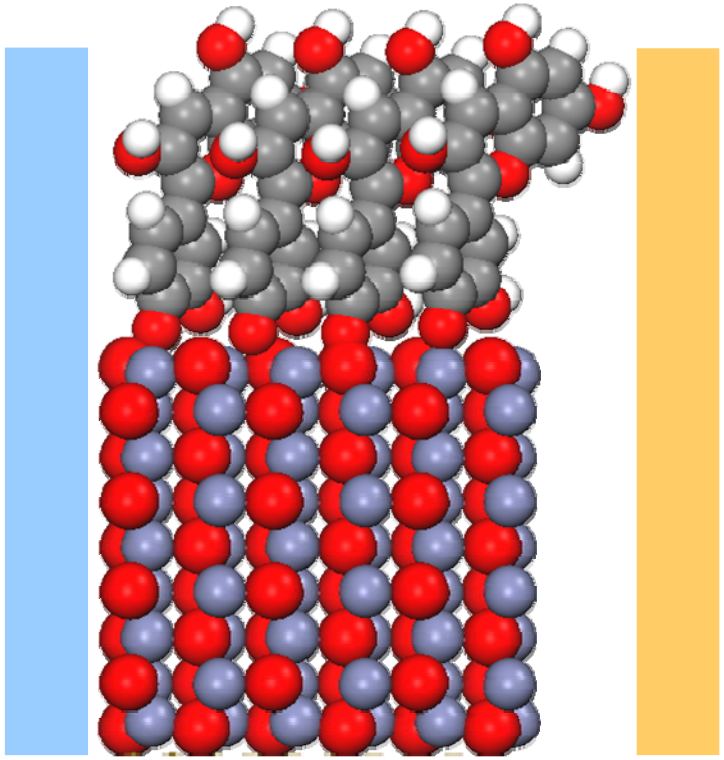
# model system

dye/metal-oxide/TCO
hybrid interfaces

Dye →
natural anthocyanin
(cyanin)

Substrate →
non-polar ZnO ($10\bar{1}0$)
surface

TCO →
Al doped ZnO (AZO)



# model system – hybrid interfaces

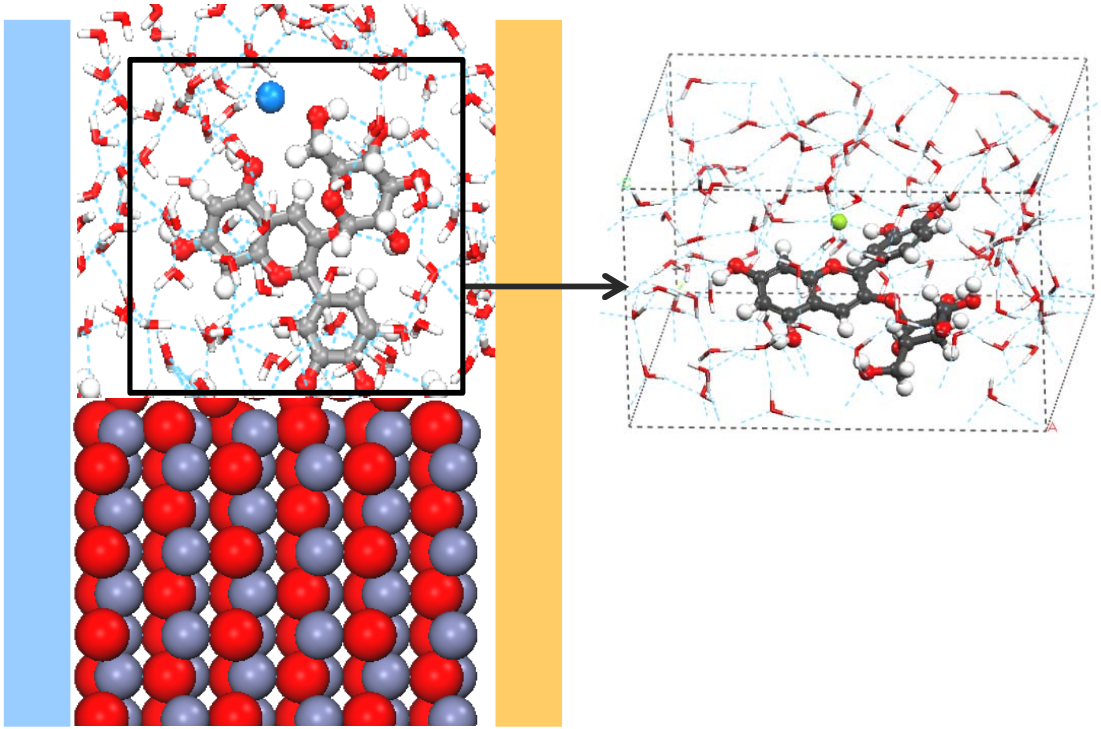
WARNING!

1) In biological systems, natural dyes exist ONLY in liquid (typically water) solution

2) Most experiments are made in humid environments

The presence of liquid solvent and counterions may modify both the properties of the molecule and the coupling with the surface.

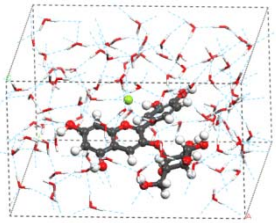
# zooming in the cell

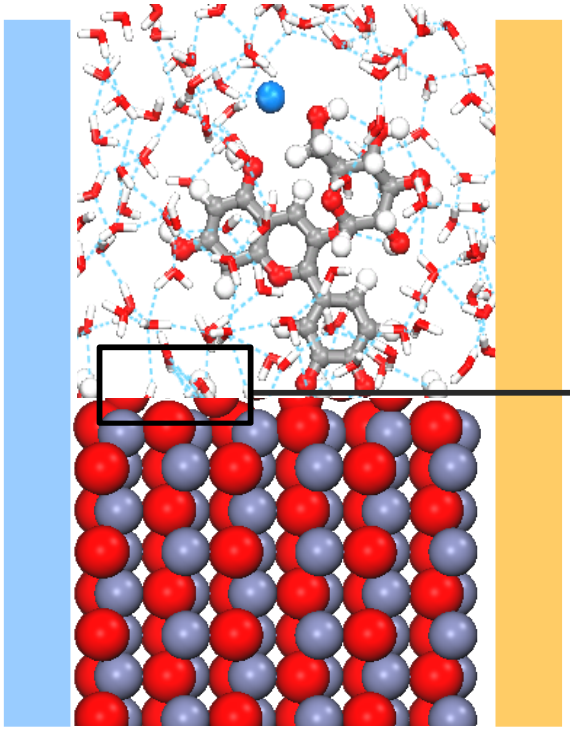


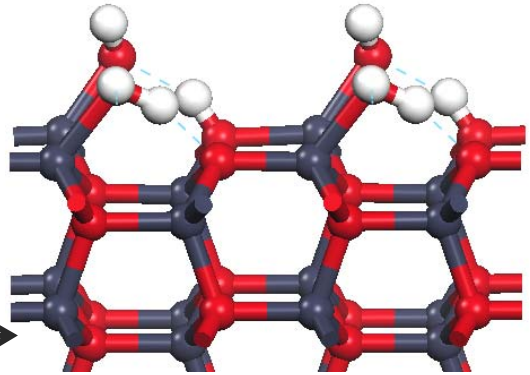
## Optoelectronic properties of the dye in solution

A. Calzolari, et al, JPCA 113 8801 (2009)
A. Calzolari, et al. JCP 132, 114304 (2010)
O.B. Malcioglu,et al, JACS **133**, 15425 (2011)

# zooming in the cell



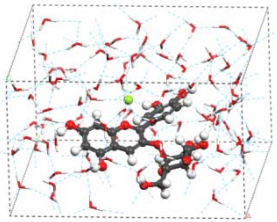


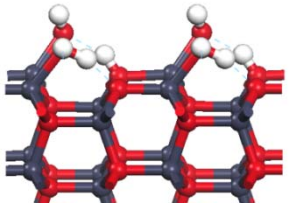


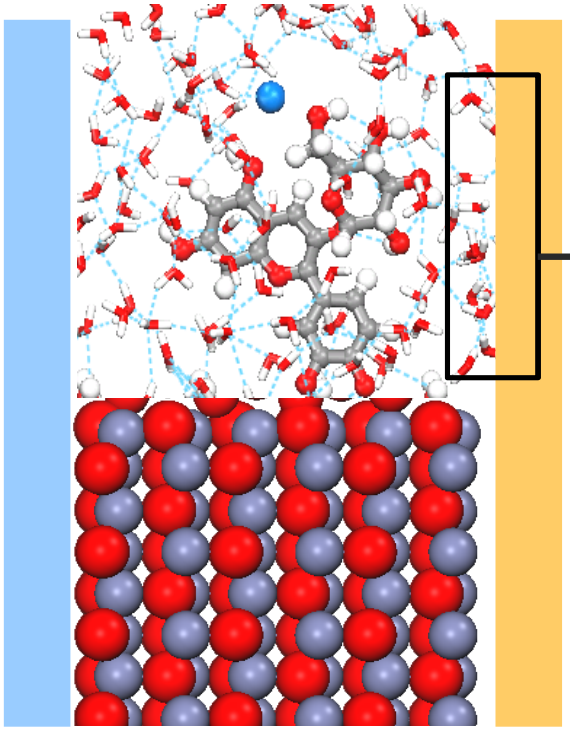
Early stage water adsorption on non-polar ZnO surface

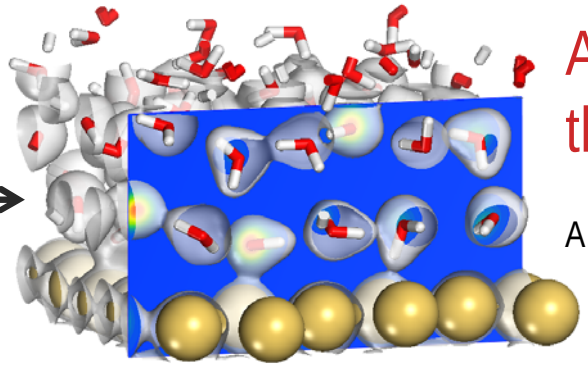
A. Calzolari, et al, JPCC **113**, 289 (2009)

# zooming in the cell





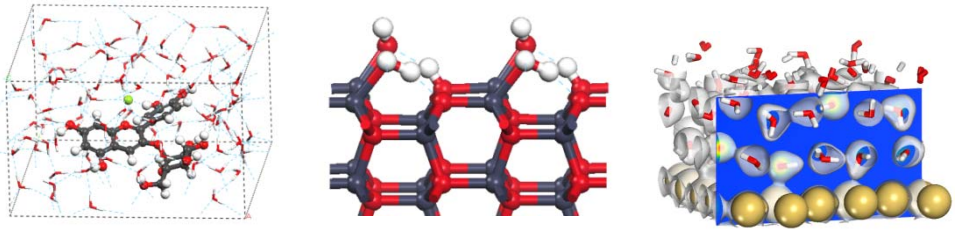


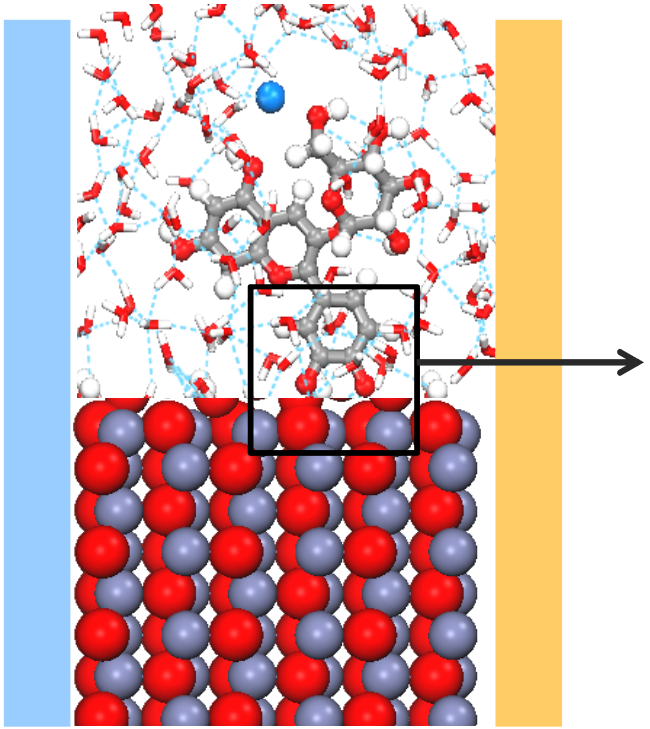


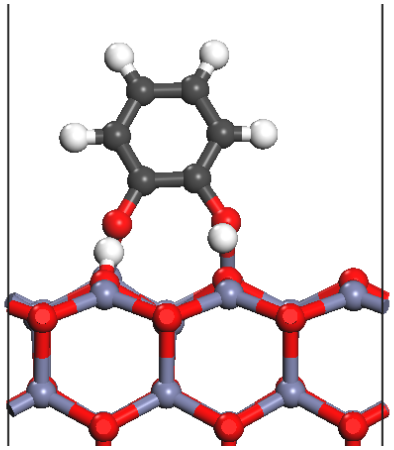
## Anomalous Wetting Layer at the Au(111) Surface

A. Calzolari, et al, JPC Lett. 2, 2582 (2011)

# zooming in the cell



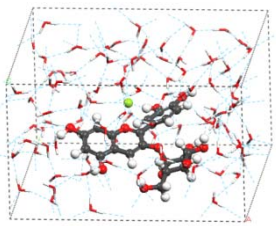
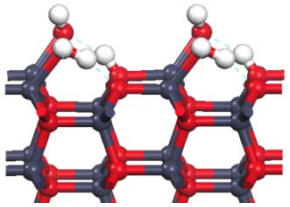
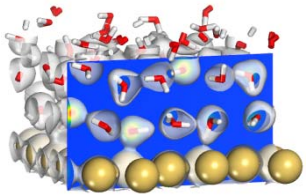
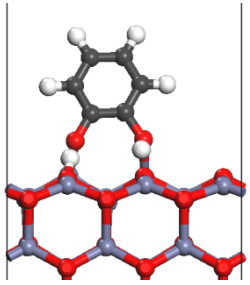


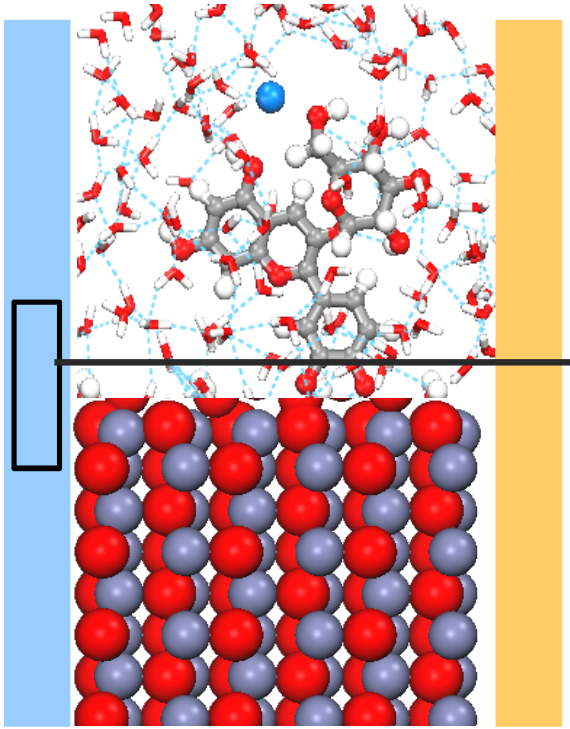


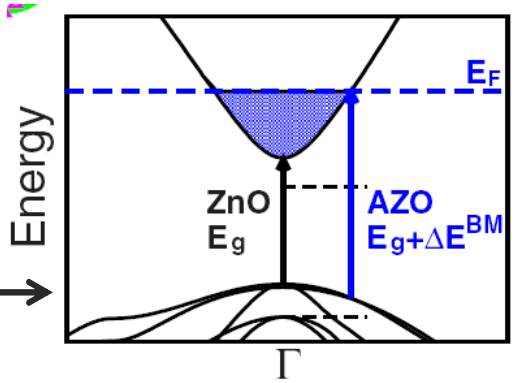
## Chromophore adsorption on non-polar ZnO surface

A. Calzolari, et al, JACS **133**, 5893 (2011)

# zooming in the cell

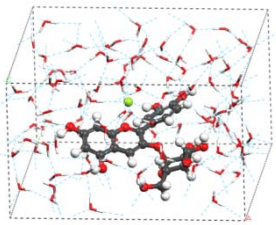


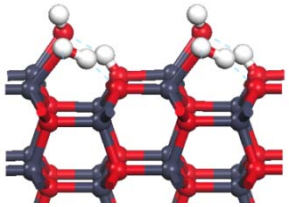


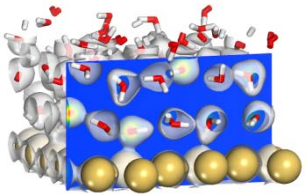

## Optoelectronic properties of Al doped ZnO (AZO)

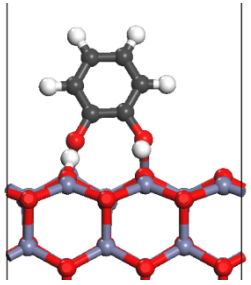
M. Bazzani, et al, APL 98 121907 (2011)

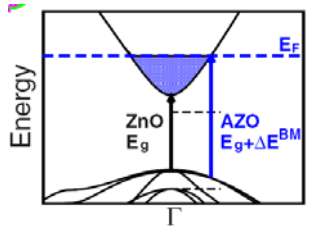
# zooming in the cell

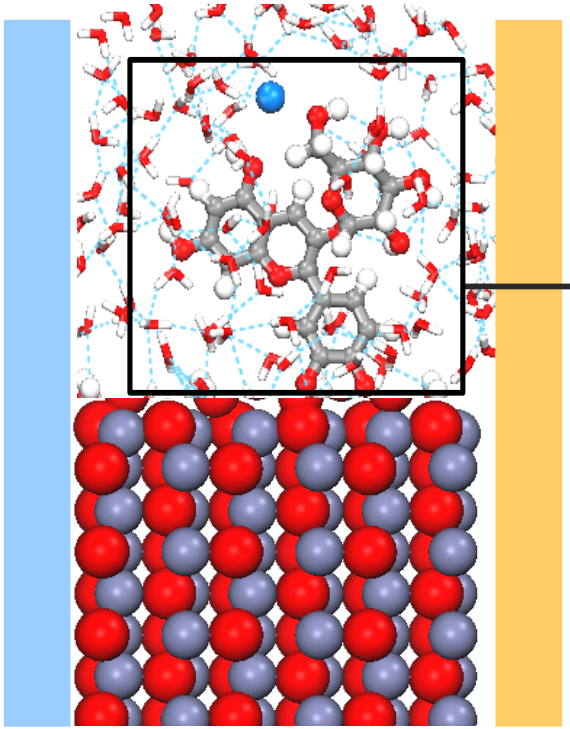


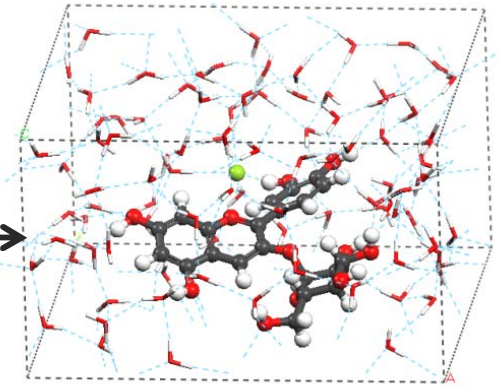










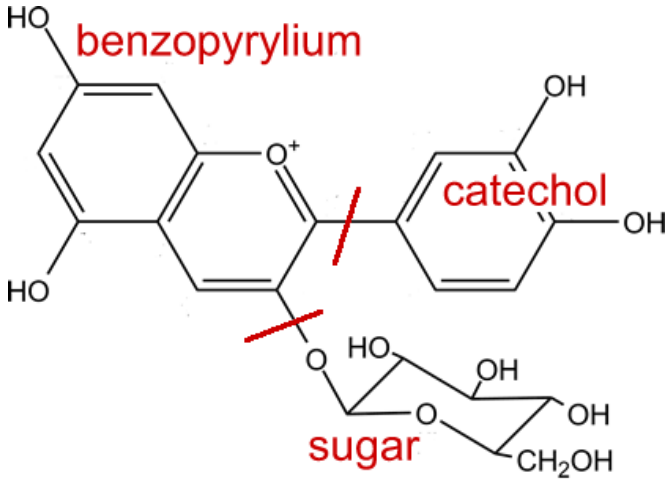
## Optoelectronic properties of the dye in solution


A. Calzolari, et al, JPCA 113 8801 (2009)
A. Calzolari, et al. JCP 132, 114304 (2010)
O.B. Malcioglu,et al, JACS **133**, 15425 (2011)

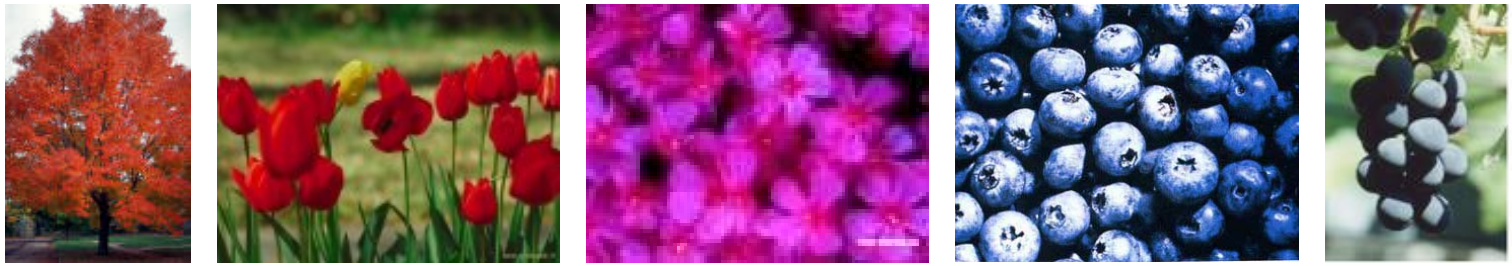

example 1

# introduction

- CYANIN (cyanidin-3-glucoside) is a natural **water-soluble** anthocyanin, positively **charged** in the ground state configuration (**flavylium cations**)




- Cyanins are main NATURAL DYES - from red to blue– in plants, flowers and fruits



- further properties:
  absorption of UV and visible radiation / antioxydant activity in cells / metal ions
  **chelators** (e.g. Al, Zn) **self-assembly** and **stacking** configurations →
  Food industry, pharmaceutical, medical, solar cell applications

# cyanin – gas phase*

IS THE SPECTRAL POSITION OF THE LOWEST ENERGY TRANSITIONS ENOUGH TO SIMULATE THE MAIN OPTICAL PROPERTIES OF THE MOLECULE???

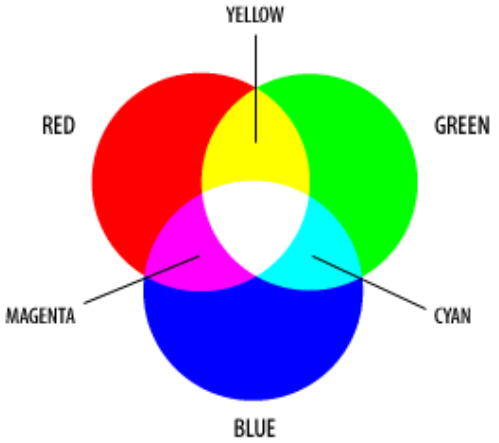
WHAT ABOUT COLOR??

* A. Calzolari, et al., JPCA **113** 8801 (2009)

# ab initio colorimetry

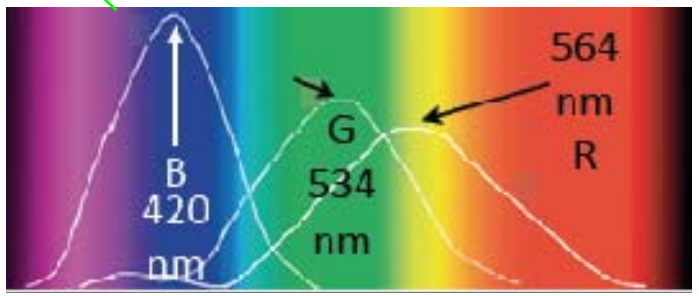
color perceived by human eye

$$\mathrm{rgb} = N \int I_T(\lambda)\,\mathrm{RGB}(\lambda)\,d\lambda$$

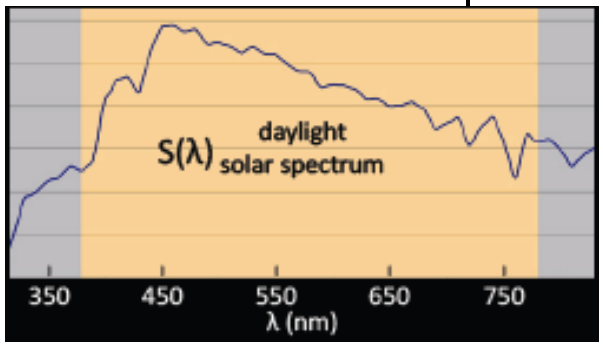



transmitted radiation

$$I_T(\lambda) = I_0(\lambda)\,\mathrm{e}^{-\kappa(\lambda)x}$$



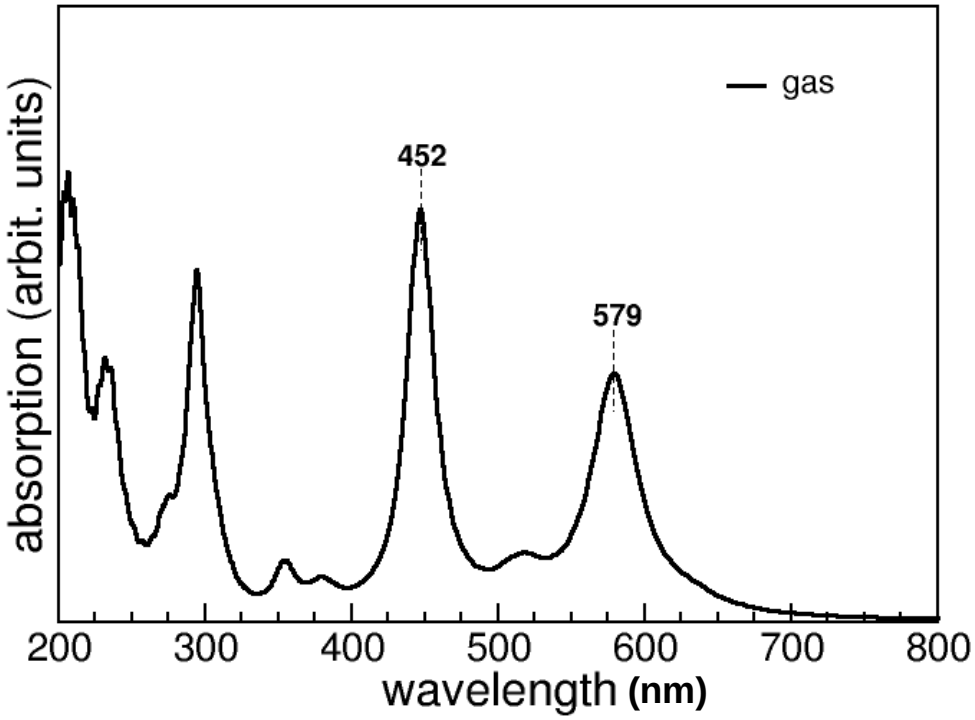

color matching functions (*tristimulus*)




incident radiation (*illuminant*)

absorption spectrum
(calculated)

# simulated color*

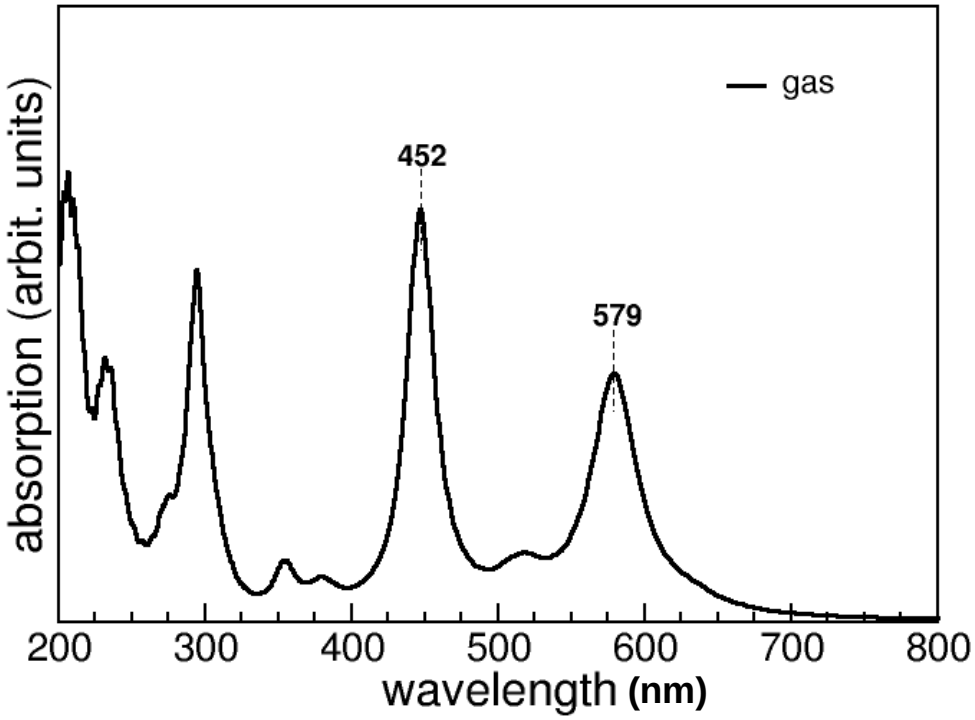



simulated color

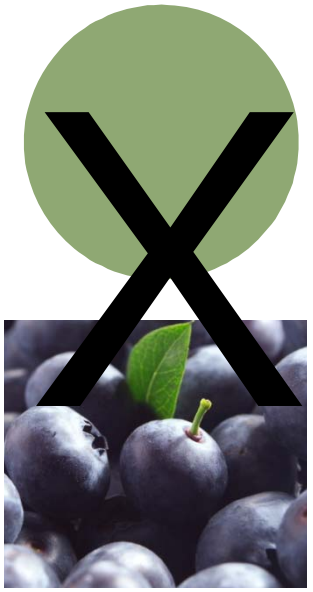
STATIC ABSORPTION SPECTRUM FOR ISOLATED MOLECULE DOES NOT REPRODUCE RED/PURPLE COLOR OBSERVED IN NATURAL SYSYEMS (e.g. berries, eggplants)

*O.B. Malcioglu, AC, R. Gebauer, D. Varsano S. Baroni, JACS **133**, 15425 (2011).

# simulated color*



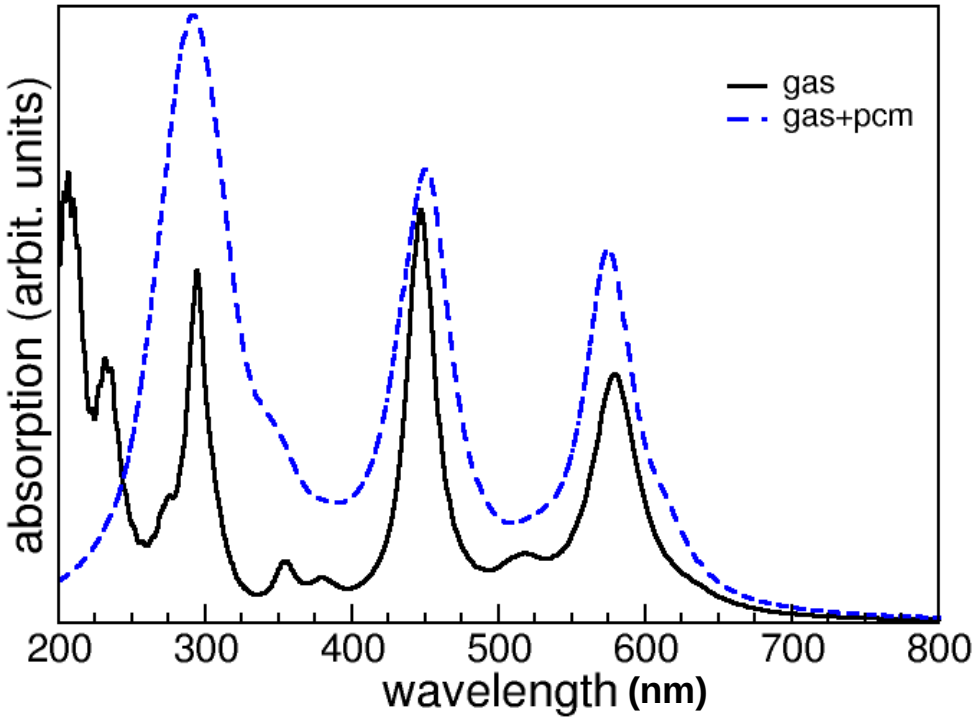

simulated color

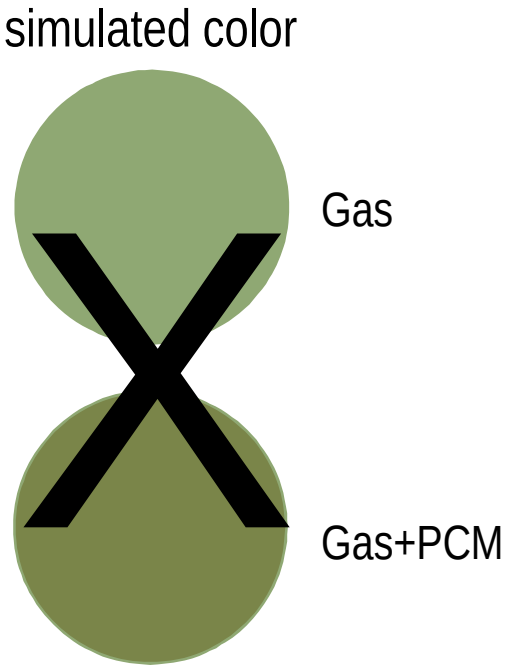


IN NATURAL SYSTEMS CYANINS ARE NOT IN THEIR GROUND STATE IN VACUUM, BUT ARE IMMERSED IN LIQUID SOLUTION (e.g. WATER) AND AT ROOM TEMPERATURE

*O.B. Malcioglu, AC, R. Gebauer, D. Varsano S. Baroni, JACS **133**, 15425 (2011).

# solvation effect - implicit solvent (PCM)*



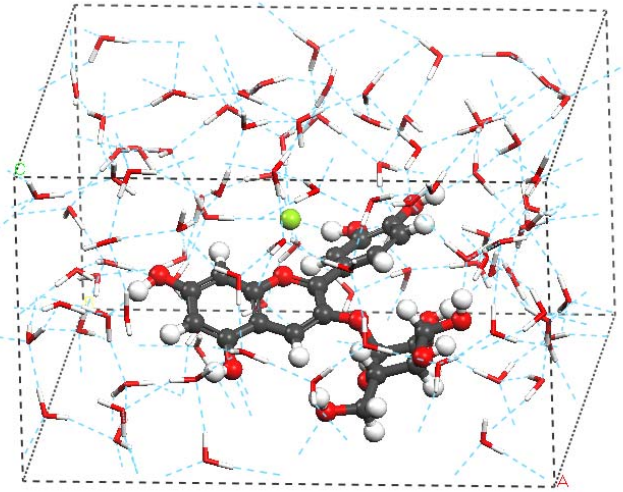



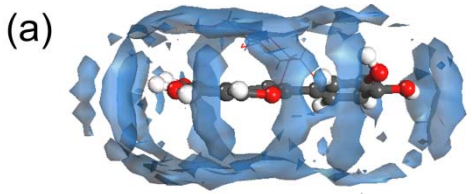

- *Polarizable continuum model* (PCM) + ground state geometry (gaussian 09)
- Slight batochromic (red shift) effect and hyperchromism
- NO drastic modification of the spectrum.

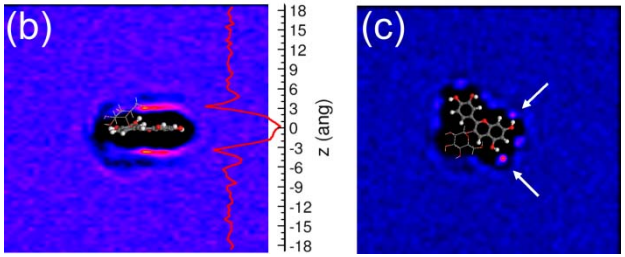
DARKER BUT STILL GREENISH COLOR

*O.B. Malcioglu, AC, R. Gebauer, D. Varsano S. Baroni, JACS **133**, 15425 (2011).

# solvation effect – explicit solvent at RT






SDF of oxygen atoms of the solvent wrt the benzopyrylium ring

globally neutral system

→ 1 cyanin (cation)

→ 1 $Cl^-$ (counter ion)

→ solvent (95 $H_2O$ molecules)

technical details

- $\mu$=340 au, $\delta$t=0.075 fs, $\Gamma$-only

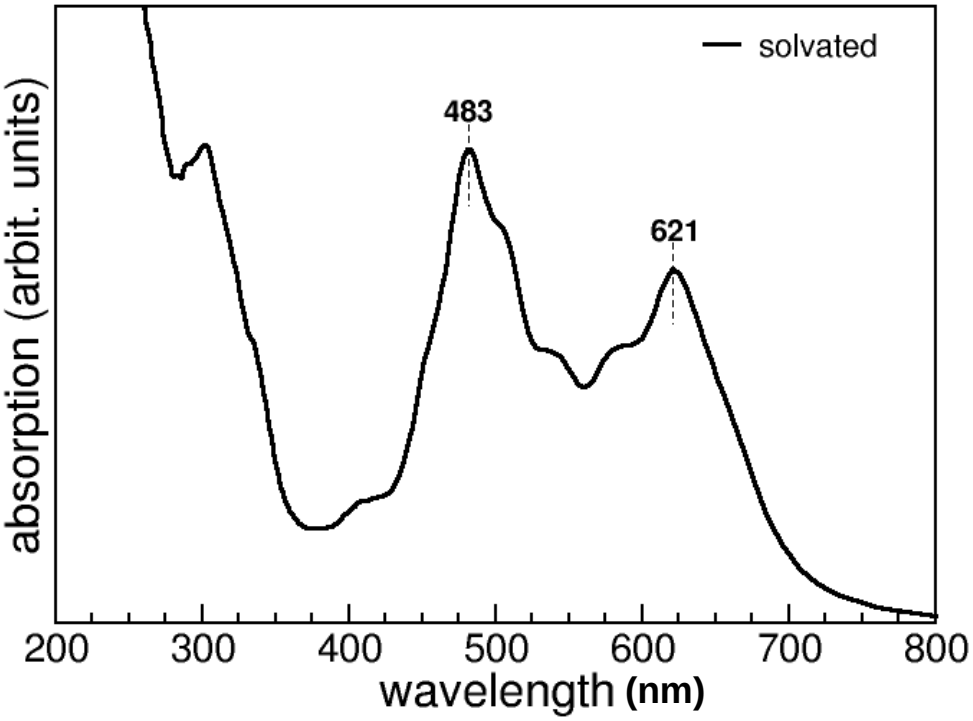
288 atoms (939 valence electrons) → large system for *ab initio* simulations

- 3.5 ps of thermal equilibration at T=300K + 20 ps of production time (microcanonical ensemble)

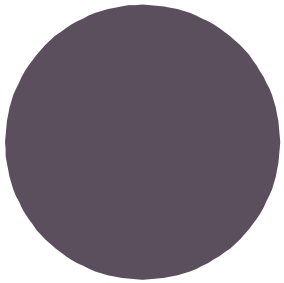
Hydration properties and electronic structure of solvated cyanin

A. Calzolari et. al JCP **132**, 114304 (2010)

# time averaged spectra – explicit solvent at RT*




simulated color



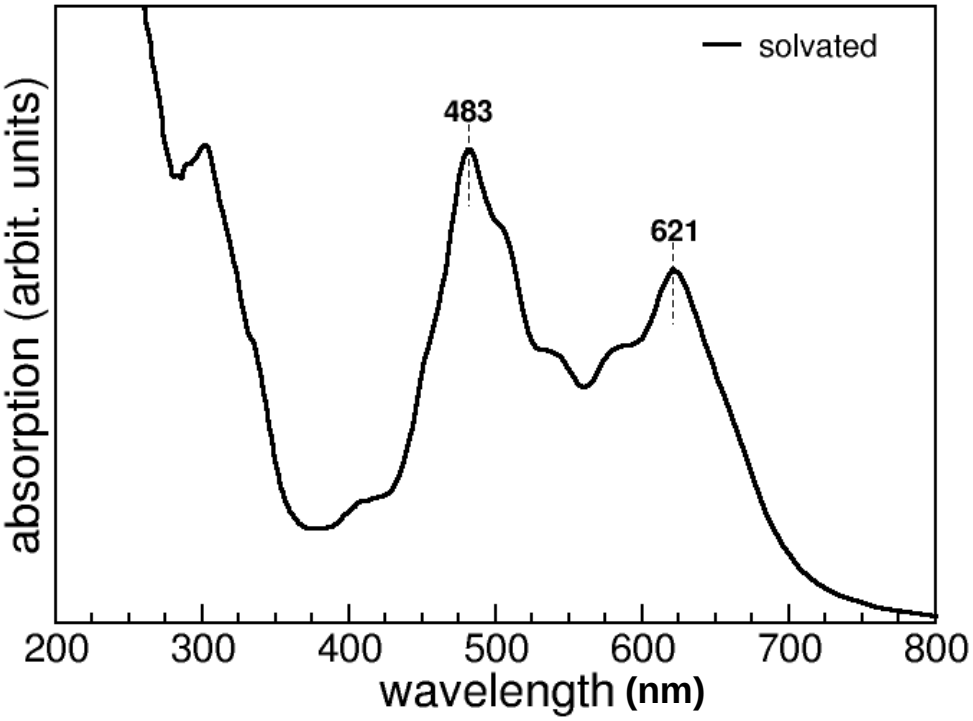
Solvated

- Fully solvated molecule → **broader absorption band** ($\lambda$ = 400-700 nm), characterized by two main peaks at $\lambda$ =621 nm and $\lambda$ =483 nm and several shoulders in the middle
- Single snapshot spectra differ in the number of peaks and maxima position

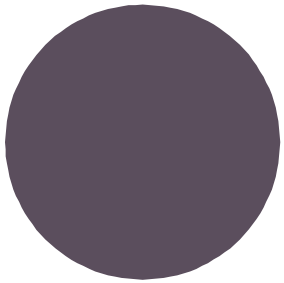


*O.B. Malcioglu, AC, R. Gebauer, D. Varsano S. Baroni, JACS **133**, 15425 (2011).

# time averaged spectra – explicit solvent at RT*




simulated color



Solvated

- Thermal dynamics changes the optical properties of molecule in liquid solution → Thermal effects cannot be neglected in solar cells
- Good light absorption properties → CYANIN SUITABLE FOR DSSCs (??)

*O.B. Malcioglu, AC, R. Gebauer, D. Varsano S. Baroni, JACS **133**, 15425 (2011).

# DSSCs using cyanin/$TiO_2$

Table 1 List of the natural dyes used and photoelectrochemical properties of $TiO_2$/natural dye cells.

| | Dye | Dye content (%) | Additives[a] (%) | $\lambda_{max}$[b] (nm) | $\lambda_{thd}$[b] (nm) | LHE[c] (%) | IPCE[c] (%) | APCE[c] (%) | $I_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | F.F. (%) | $\eta$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (i) | Red cabbage | 36 | CA(2), GS(62) | 547(571) | 647(707) | 61 | 25 | 41 | 4.70 | 0.525 | 61 | 1.51 |
| (ii) | Cochineal | 80 | DX(20) | 492(480) | 582(702) | 39 | — | — | 6.00 | 0.397 | 52 | 1.24 |
| (iii) | Purple sweet patato | 43 | CA(7), DX(50) | 535(574) | 626(630) | 41 | — | — | 5.68 | 0.393 | 51 | 1.13 |
| (iv) | Curcumin | 100 | — | 427(485) | 507(621) | 58 | 16 | 28 | 5.35 | 0.410 | 50 | 1.10 |
| (v) | Kaoliang | 76 | SC(0.8), DX(23.2) | 497(495) | 588(607) | 37 | 19 | 51 | 3.64 | 0.452 | 61 | 1.00 |
| (vi) | Gardenia yellow | 60 | DX(40) | 441(438) | 512(520) | 34 | 15 | 44 | 3.20 | 0.570 | 49 | 0.90 |
| (vii) | Carthamus yellow | 40 | DX(60) | 406(432) | 481(650) | 29 | 11 | 38 | 1.90 | 0.465 | 68 | 0.60 |
| (viii) | Beet red | 80 | SA(8), SMP(1), DX(11) | 539(494) | 626(620) | — | — | — | 2.90 | 0.400 | 38 | 0.44 |
| (ix) | Monascus | 50 | DX(50) | 491(529) | 607(630) | 31 | — | — | 1.58 | 0.396 | 53 | 0.33 |
| (x) | Annatto | 10 | LA(90) | 455(438) | 538(608) | — | — | — | 2.45 | 0.294 | 38 | 0.27 |
| (xi) | Gardenia blue | 90 | LA(10) | 597(600) | 683(720) | 44 | 1.5 | 3.4 | 1.33 | 0.387 | 45 | 0.23 |
| (xii) | Lac | 100 | — | 478(498) | 588(636) | — | — | — | 1.56 | 0.349 | 39 | 0.21 |
| (xiii) | Cacao | 90 | DX(10) | 446(570) | 600(750) | 32 | 1.3 | 4.1 | 1.17 | 0.312 | 44 | 0.16 |
| (xiv) | Tamarind | 90 | DX(10) | 447(570) | 623(757) | 36 | 2.7 | 7.5 | 1.36 | 0.280 | 42 | 0.16 |
| (xv) | Spirulina | 66 | — | 616(666) | 680(750) | — | — | — | 0.89 | 0.363 | 40 | 0.13 |
| (xvi) | Strawberry | — | — | (534) | (707) | — | — | — | 2.86 | 0.405 | 53 | 0.61 |
| (xvii) | Blueberry | — | — | (590) | (742) | — | — | — | 4.29 | 0.360 | 34 | 0.52 |
| (xviii) | Coffee | — | — | (442) | (690) | — | — | — | 2.55 | 0.409 | 39 | 0.41 |
| (xix) | Grape | — | — | (550) | (692) | — | — | — | 1.81 | 0.427 | 43 | 0.33 |
| (xx) | Green tea | — | — | (445) | (660) | — | — | — | 0.98 | 0.412 | 47 | 0.19 |
| (xxi) | Lemon | — | — | (606) | (750) | — | — | — | 1.41 | 0.416 | 29 | 0.17 |
| (xxii) | Orange | — | — | (608) | (748) | — | — | — | 1.02 | 0.412 | 31 | 0.13 |

[a]; CA = citric acid, GS = glutinous starch syrup, DX = dextrin, SC = sodium carbonate, SA = sodium L-ascorbate, SMP = sodium metaphosphate, Their contents are indicated in parenthesis. [b]; Measured for aqueous solutions of natural dyes except for (iv) for which ethanol was used as solvent. In parenthesis are the values for the same dyes adsorbed on $TiO_2$ films. [c]; Measured at $\lambda_{max}$ of adsorbed dyes.

D. Zhang et al. Trans. Mater. Res. Soc. Jpn. 27, 811 (2002)

# DSSCs using cyanin/ZnO

Table 2 Photoelectrochemical properties of ZnO/natural dye cells.

| Dye | $\lambda_{max}$* (nm) | $\lambda_{thd}$* (nm) | LHE (%) | IPCE (%) | APCE (%) | $I_{sc}$ (mA/cm$^2$) | $V_{oc}$ (mV) | *F.F.* (%) | $\eta$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| (i) | 592 | 701 | 54 | — | — | 0.55 | 286 | 31 | 0.050 |
| (ii) | 588 | 700 | 40 | — | — | 0.049 | 38 | — | — |
| (iii) | 523 | 649 | 46 | — | — | 0.12 | 170 | 33 | 0.0068 |
| (iv) | 433 | 601 | 52 | 3.0 | 5.8 | 0.92 | 273 | 28 | 0.070 |
| (v) | 430 | 615 | 43 | — | — | 0.47 | 282 | 33 | 0.051 |
| (vi) | 433 | 500 | 27 | 0.9 | 3.3 | 0.29 | 307 | 63 | 0.057 |
| (vii) | 429 | 550 | 31 | — | — | 0.69 | 353 | 43 | 0.10 |
| (viii) | 493 | 621 | 46 | — | — | 0.12 | 136 | 29 | 0.014 |
| (ix) | 523 | 648 | 44 | — | — | 0.69 | 323 | 51 | 0.11 |
| (x) | 437 | 608 | 28 | — | — | 0.64 | 285 | 41 | 0.075 |
| (xi) | 596 | 692 | 48 | 3.2 | 6.7 | 0.97 | 286 | 45 | 0.13 |
| (xii) | 543 | 730 | 50 | — | — | 0.22 | 276 | 32 | 0.019 |
| (xiii) | 459 | 650 | 41 | 0.6 | 1.5 | 0.19 | 254 | 29 | 0.014 |
| (xiv) | 458 | 800 | 13 | 1.0 | 7.7 | 0.17 | 153 | 31 | 0.0081 |
| (xv) | 632 | 734 | 34 | — | — | 0.26 | 299 | 39 | 0.030 |
| (xviii) | 530 | 700 | 51 | — | — | 0.55 | 149 | 27 | 0.022 |

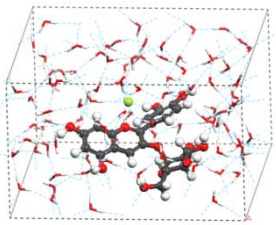
*: Measured for the dyes adsorbed on ZnO. Dyes were adsorbed from aqueous solutions except for (i) and (iv) for which ethanolic solutions were used.

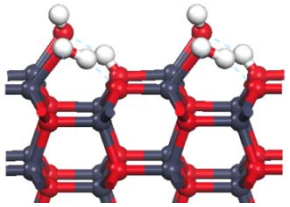
D. Zhang et al. Trans. Mater. Res. Soc. Jpn. 27, 811 (2002)

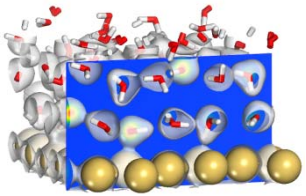
# DSSCs using cyanin/ZnO

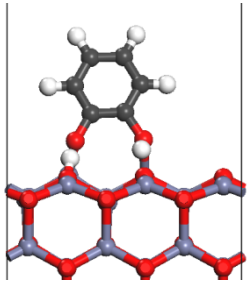
despite the good absorption properties of the dye
the efficiencies of these cells are very low (< 1%)

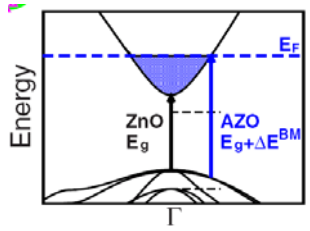
# zooming in the cell

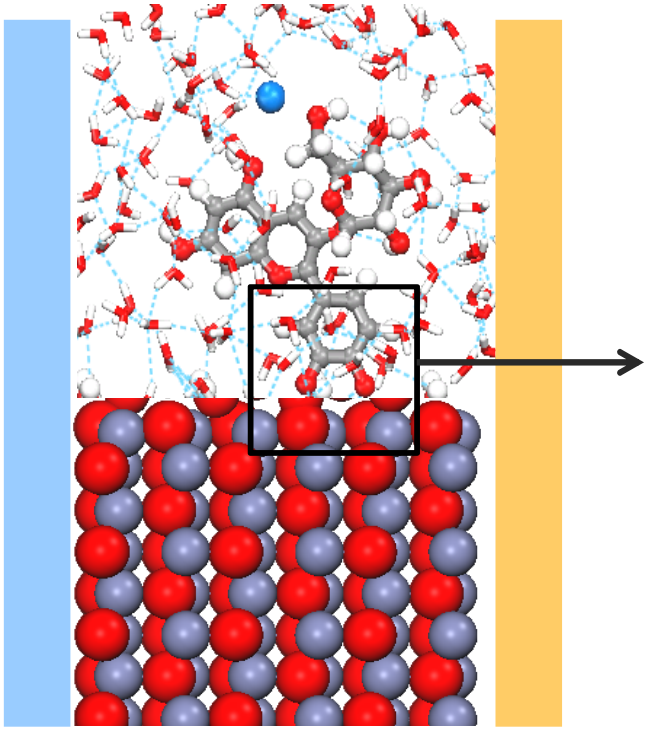


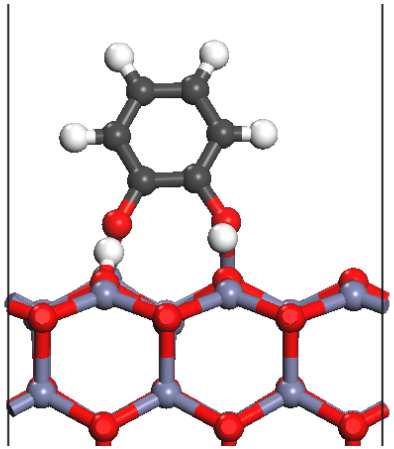










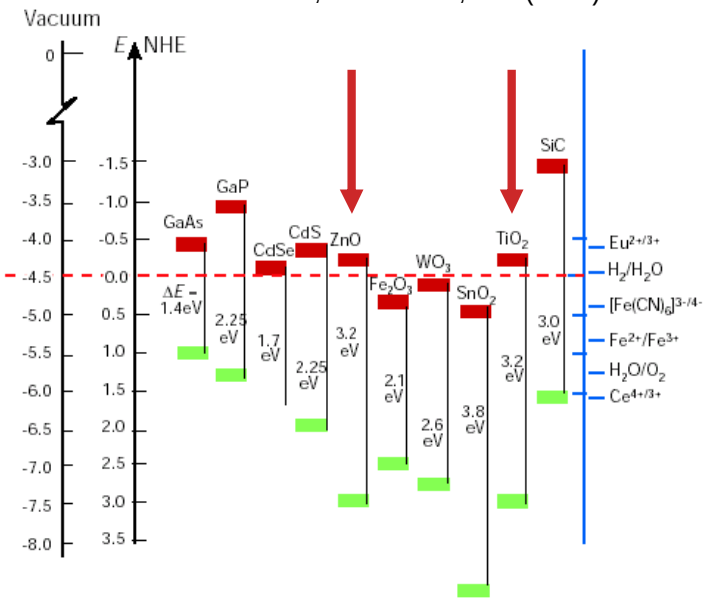
Chromophore adsorption on non-polar ZnO surface

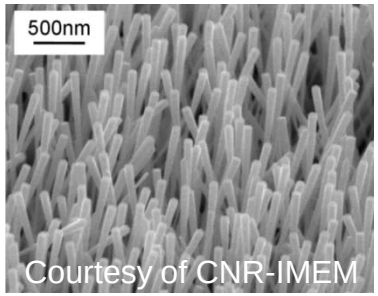
A. Calzolari, et al, JACS **133**, 5893 (2011)

example 2

# ZnO – general properties

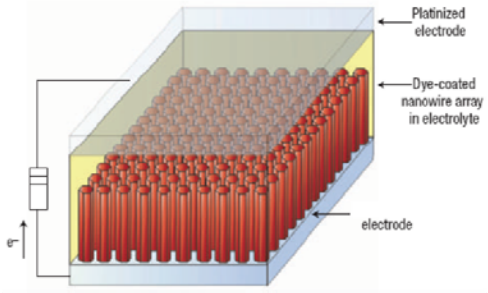
M. Graetzel, Nature 414, 338 (2001)




Experimental SEM image of ZnO nanopillars

Scheme of a DSSC based on ZnO nanowires.



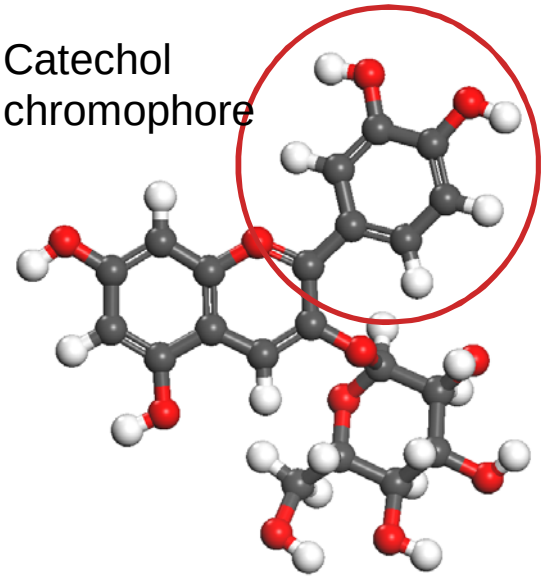

M. Law, *et al*., Nat. Mater. 4, 455 (2005)

ZnO appealing properties for optoelectronic applications

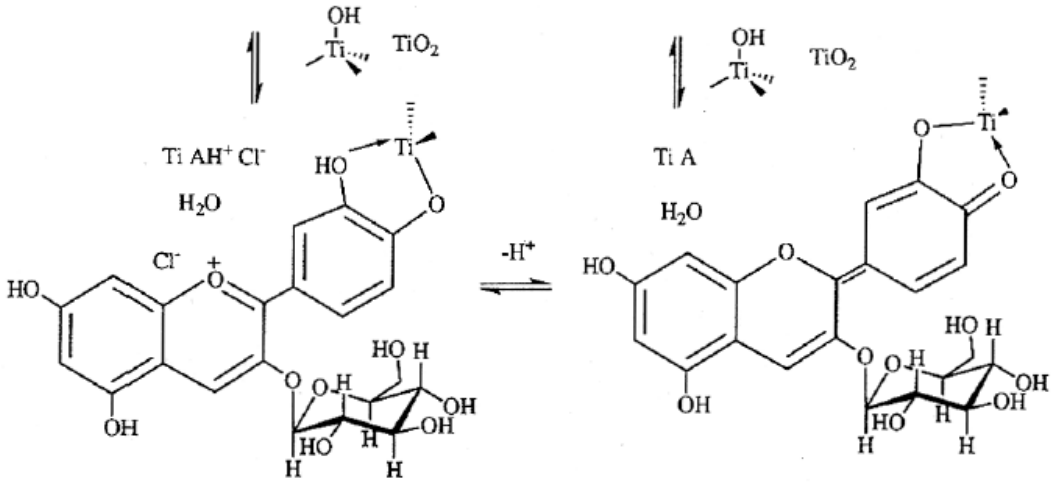
- High thermal conductivity, efficient luminescence and strong excitonic effects even at room temperature.
- High electrical conductivity → ZnO has band properties similar to $TiO_2$
- Easily grown in ordered array of nanostructures such as wires and tetrapods, that may be applied in new optoelectronic devices
- Many devices proposed: LED, field emitters, lasers, sensors, solar cells...

# chromophore adsorption on $TiO_2$ substrate

Catechol chromophore



Experiments suggest adsorption on $TiO_2$ nanoparticles through catechol binding at Ti metal sites

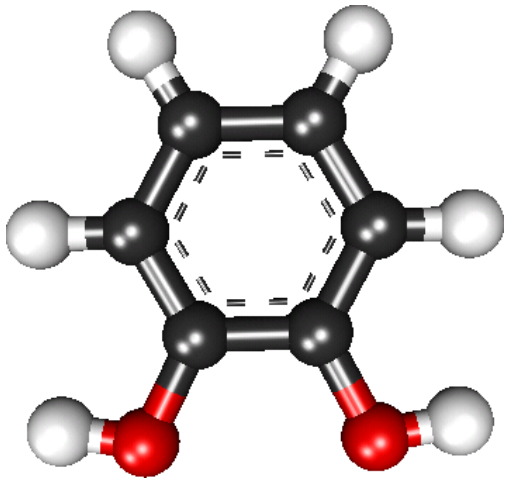



N.J. Chepery et al. JPCB, 101, 9342 (1997)
Meng, S.; Ren, J.; Kaxiras, E. *Nano Lett.* **2008**, *8*, 3266.
Hao, S.; et al J. *Sol. Energy* **2006**, *80*, 209.

ZnO($10\bar{1}0$) has different spatial and stoichiometric metal distribution on surface wrt $TiO_2$ → OH-OH distance in catechol fits the surface dimer separation (i.e. Zn-Zn)

# catechol/ZnO – goal for theory

UNDERSTANDING THE BASIC PHYSICAL PROPERTIES OF THE PROTOTYPICAL CATECHOL/ZnO INTERFACE



CATECHOL (1,2-dihydroyphenyl)

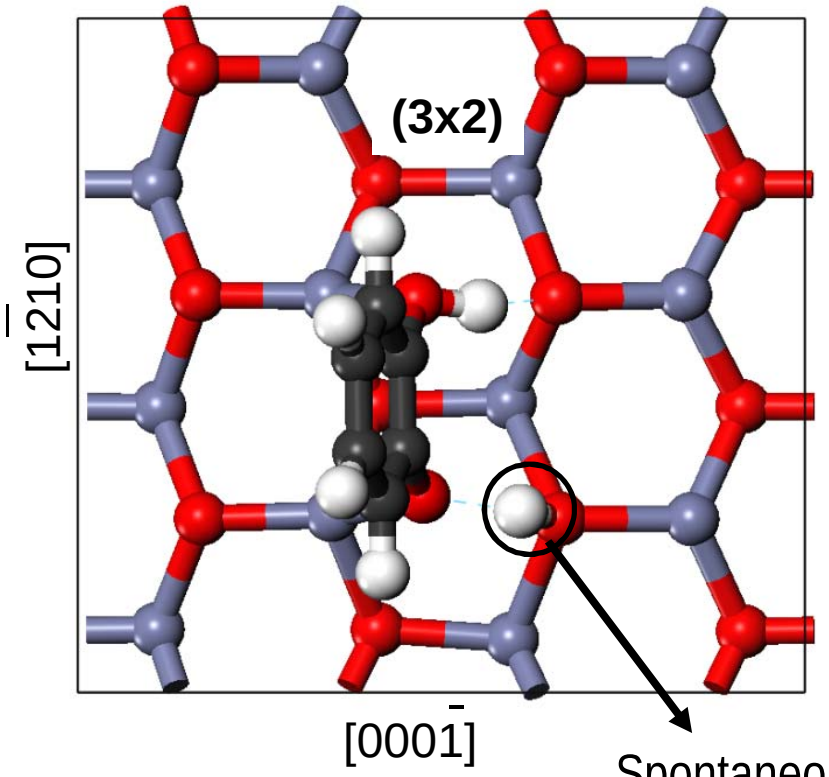
it is simultaneously a linker for molecular binding and an efficient chromophore.

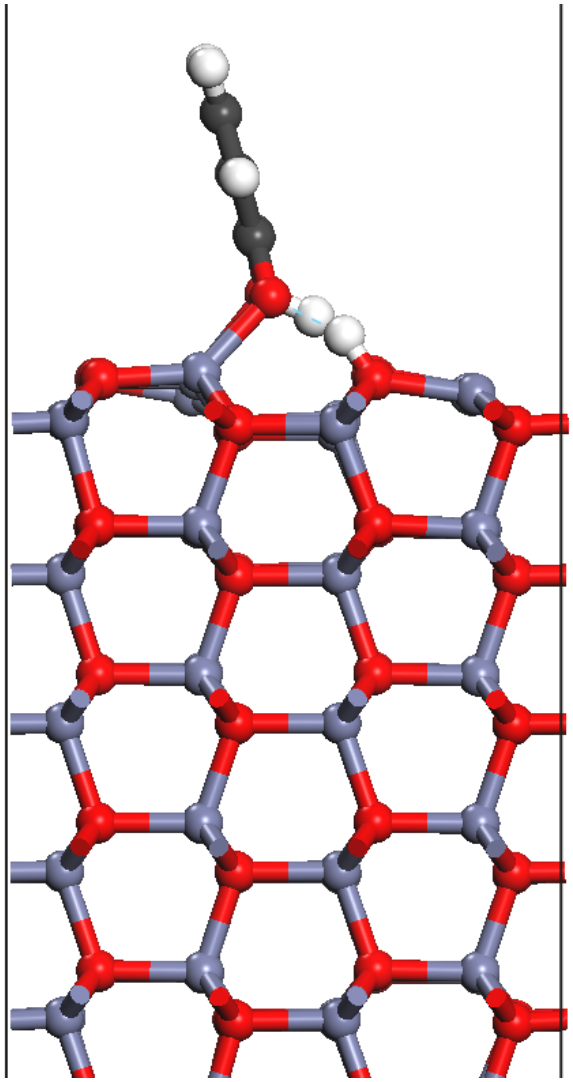
[Li, S.-H.; et al. JACS 131, 980 (2009)]
[Li, S.-H.; et al. JACS 133, 7816 (2011)]

→ prototypical sensitizer for ZnO and $TiO_2$

[K. Maeda et al. JACS 127, 8286 (2005).]
[L.G. Rego et al. JACS 125, 7989 (2003)]
[W. Duncan, OV Prezhdo, JPCB, 109, (2005)]

# catechol/ZnO – structural properties



Catechol@ZnO(10-10)-(3x2)
- spontaneous H dissociation
- bidentate bonding at two Zn sites
- formation of 2 H-bonds with surface

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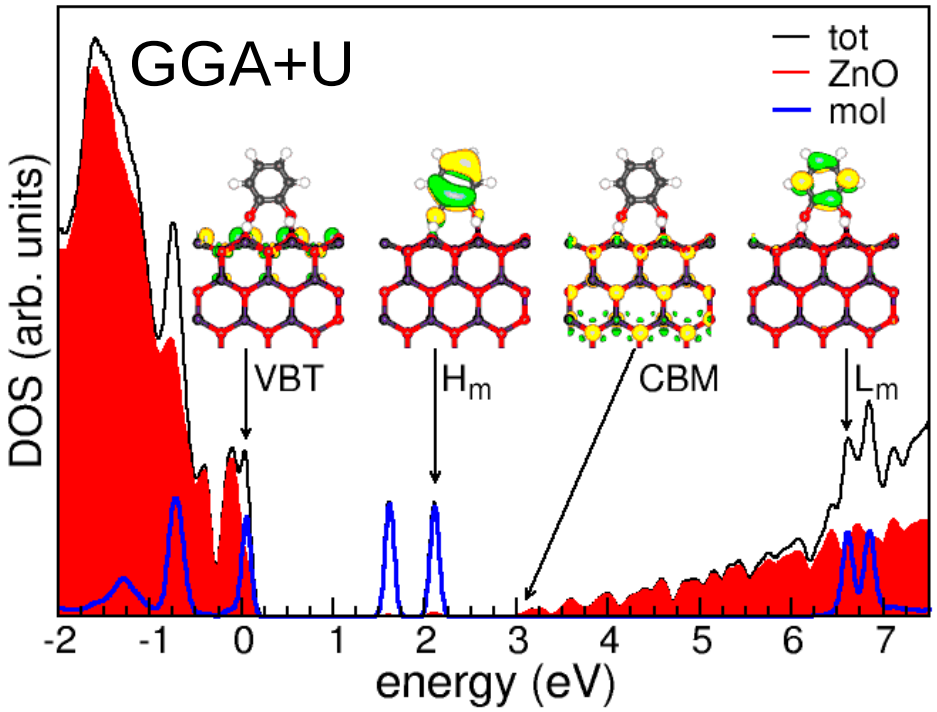
A. Calzolari, A. Ruini, A. Catellani, JACS **2011** 133, 5893.

# catechol/ZnO – electronic properties




-Valence band top (VBT) and the conduction band minimum (CBM) of the surface remains similar to the clean case

-Zn-O binding orbitals are detected at lower energy (ca. -1.5 eV) in the valence band → **dative charge transfer** from Zn dimer atoms to catechol oxygens.

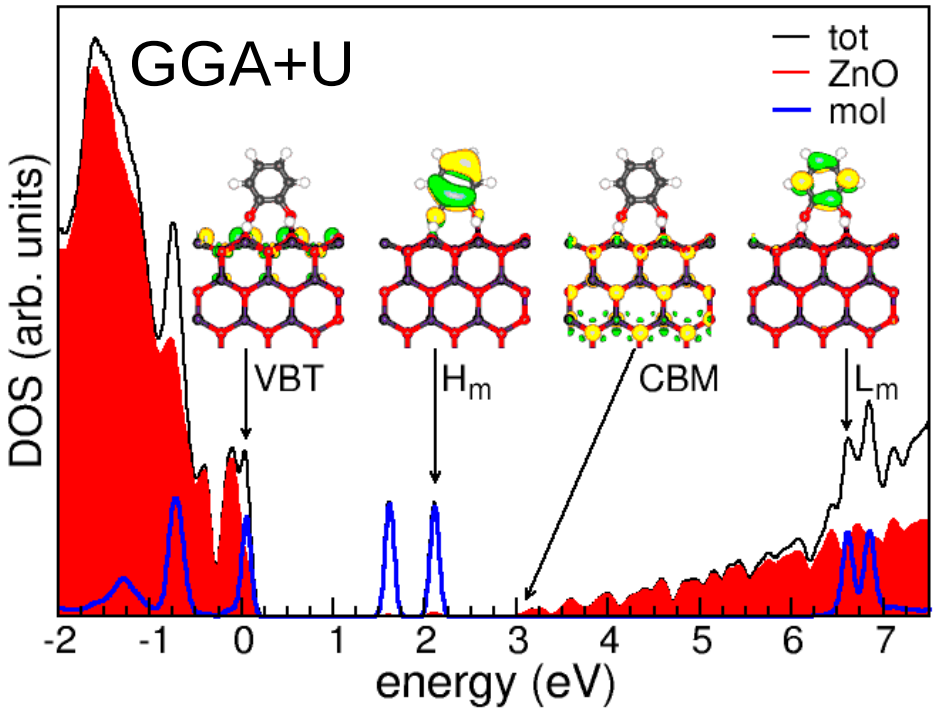
- The gap area → the presence of two **occupied molecular states**, which derive from the HOMO (H*m*) and HOMO-1 orbitals of the radical catechol. Corresponding LUMO state (L*m*) of the dye is set at higher energy (~6.5 eV) in the conduction band.

-The resulting effective gap of the interface (H*m*-CMB) is reduced to 0.9 eV, which is consistent with an optical excitation in the visible range, as observed in the experiments

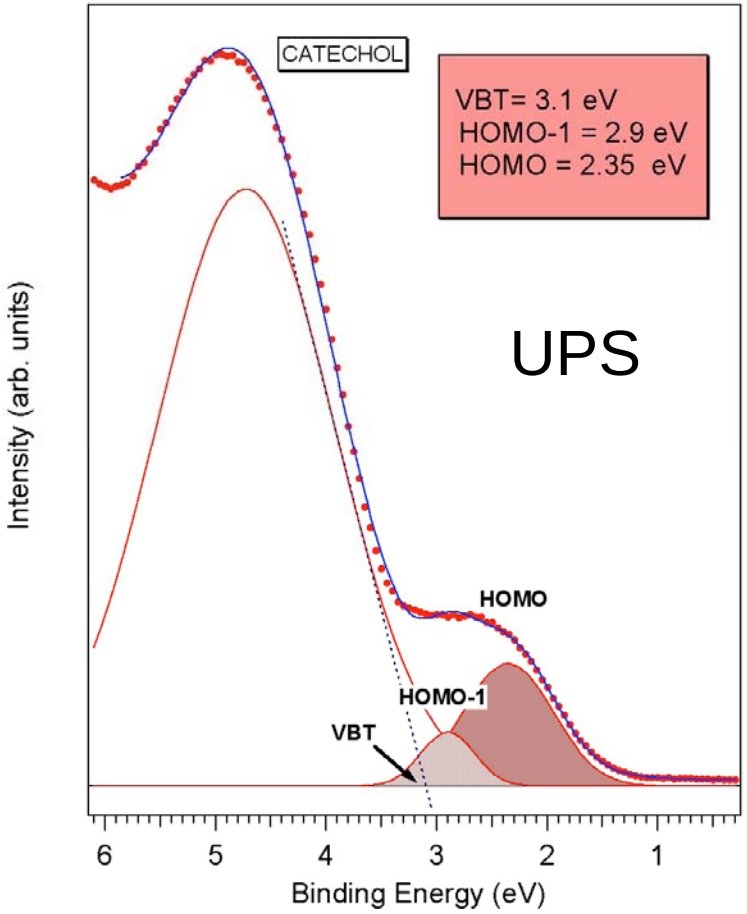


A. Calzolari, A. Ruini, A. Catellani, JACS **2011** 133, 5893.

# catechol/ZnO – electronic properties

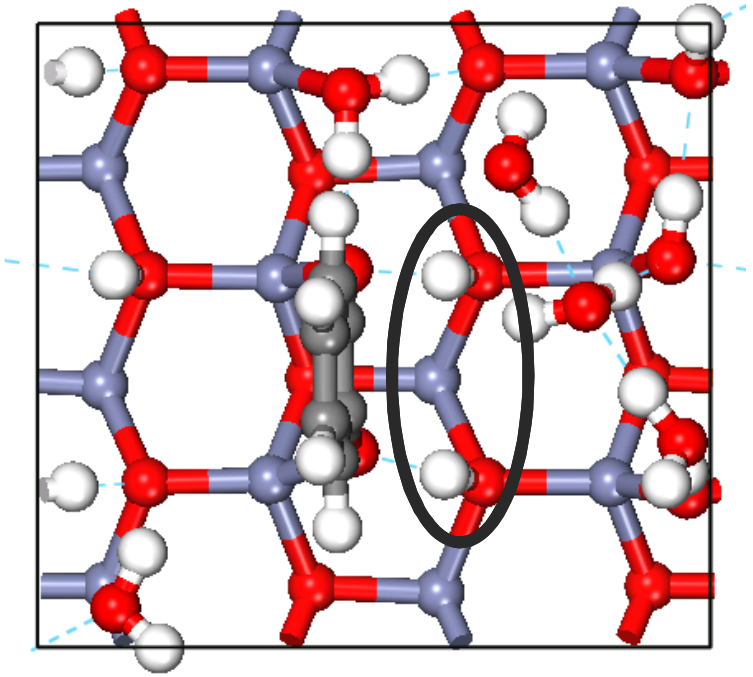


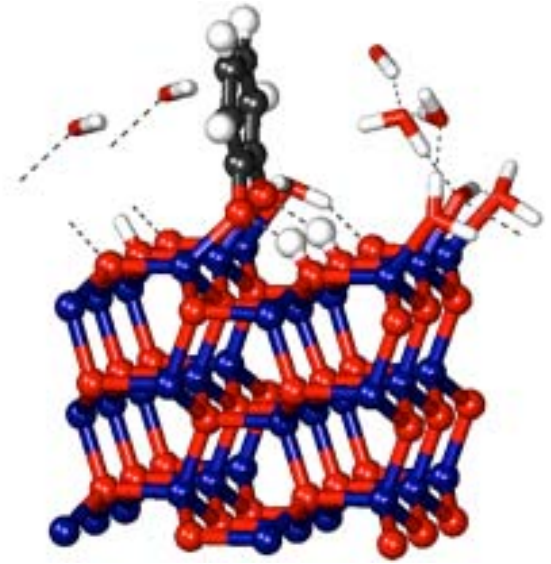

Presence of molecular state in the ZnO gap confirmed by photoemission results

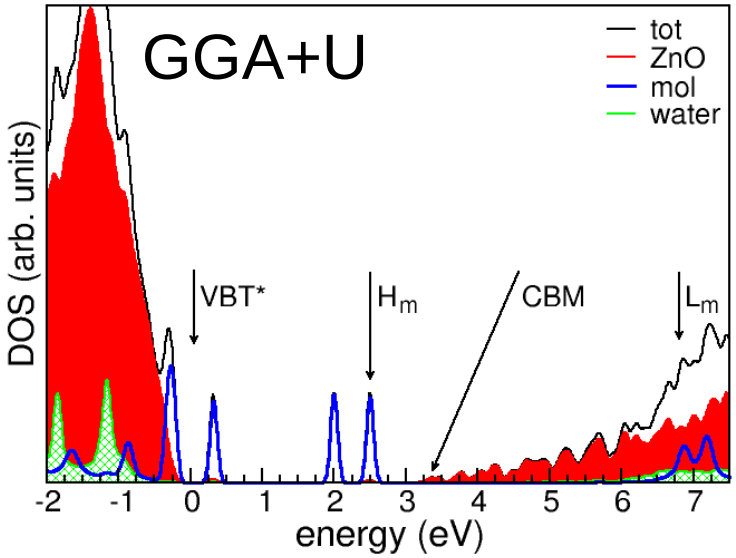



Courtesy of V. De Renzi et al. (2011)
UniMoRe & CNR-NANO-S3
Modena

# codeposition of catechol + water @ ZnO








Effect of water
- Double de-protonation
- Surface dimer saturation
- Shift of molecular state in ZnO gap

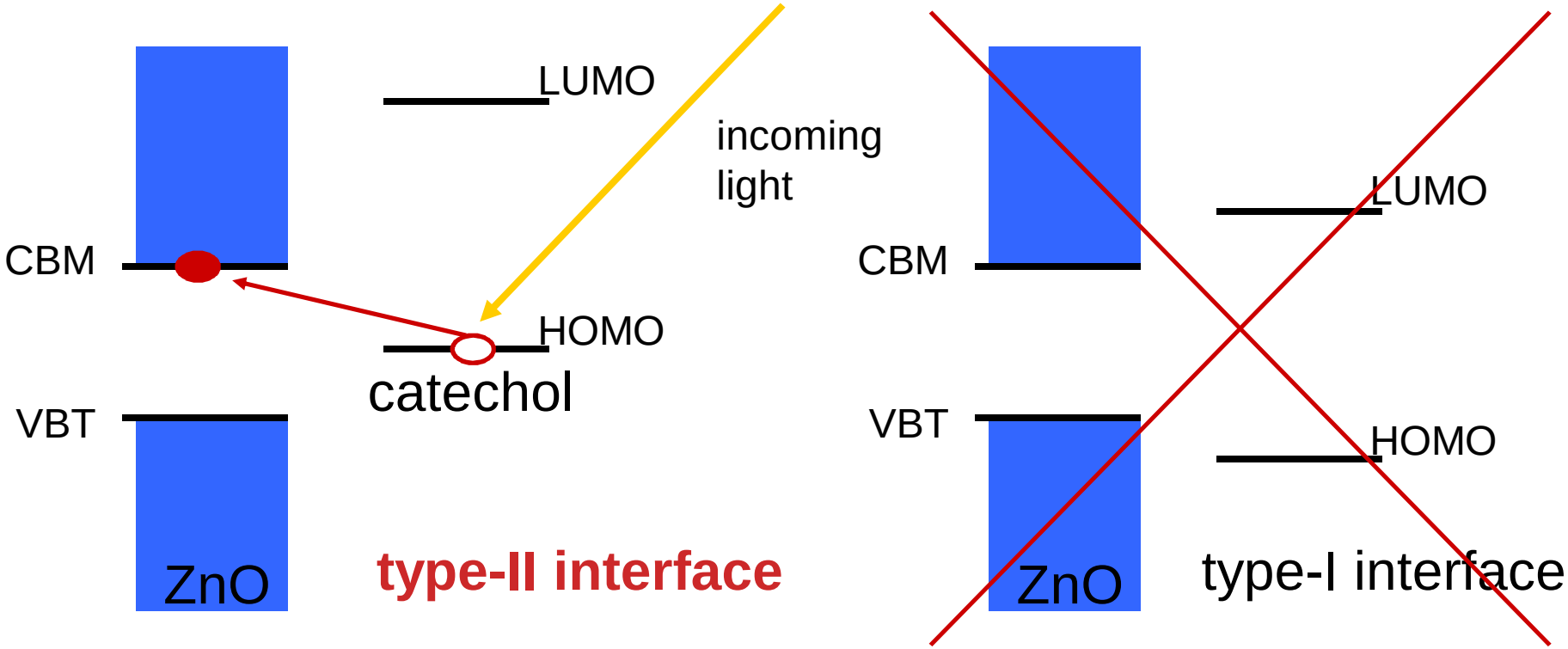
→

Modification of surface acidity



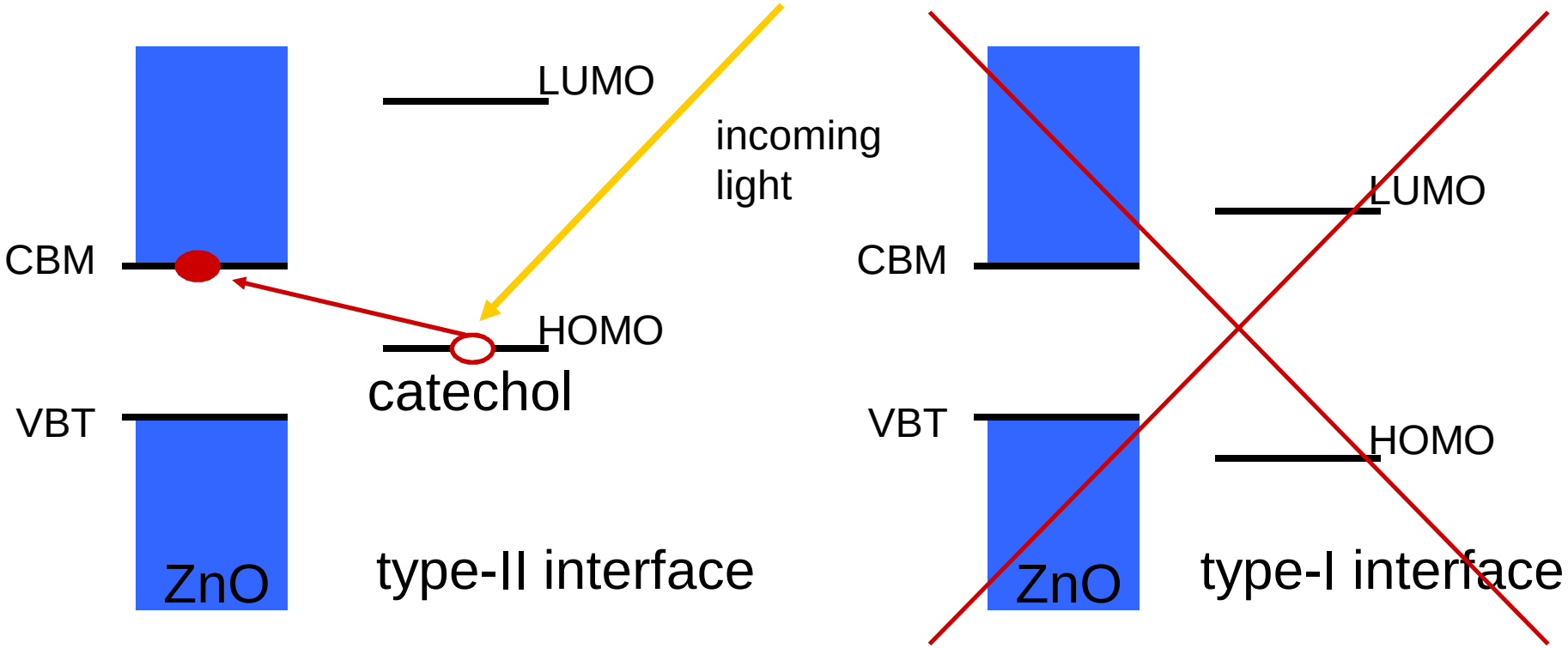
A. Calzolari, A. Ruini, A. Catellani, JACS **2011** 133, 5893.

# catechol/ZnO – summary




Adsorption of catechol translates the intrinsic optical properties of ZnO to those of a staggered type-II interface, which is able to absorb light across the UV-vis range and may separate electrons and holes across the interface, fast injecting photoelectrons from the dye to the metal-oxide.

# catechol/ZnO – summary




Open questions:

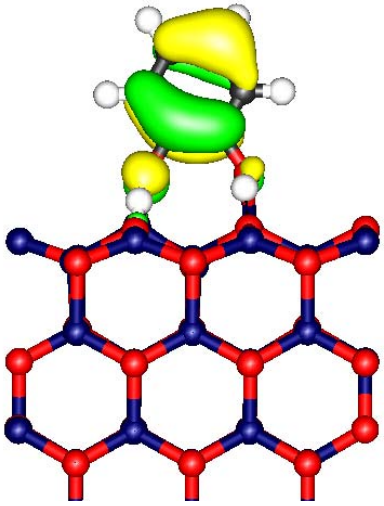
- What pins the molecular HOMO inside the ZnO gap → type-II interface?
- How can we modify energy position of the molecular orbitals, in order to modulate the band alignment of the interface?

# band alignment problem

OBSERVATION:

After adsorption the H*m* state is still a purely molecular state not affected by the interaction with the surface (binding states are~3.5 eV lower in energy).

→ The energy position of the catechol HOMO within the ZnO gap is mainly dictated by its intrinsic low ionization potential wrt the ZnO one



HOMO

Catechol HOMO has contributions on both anchor group and aromatic ring

How do they affect the energy position of HOMO state?



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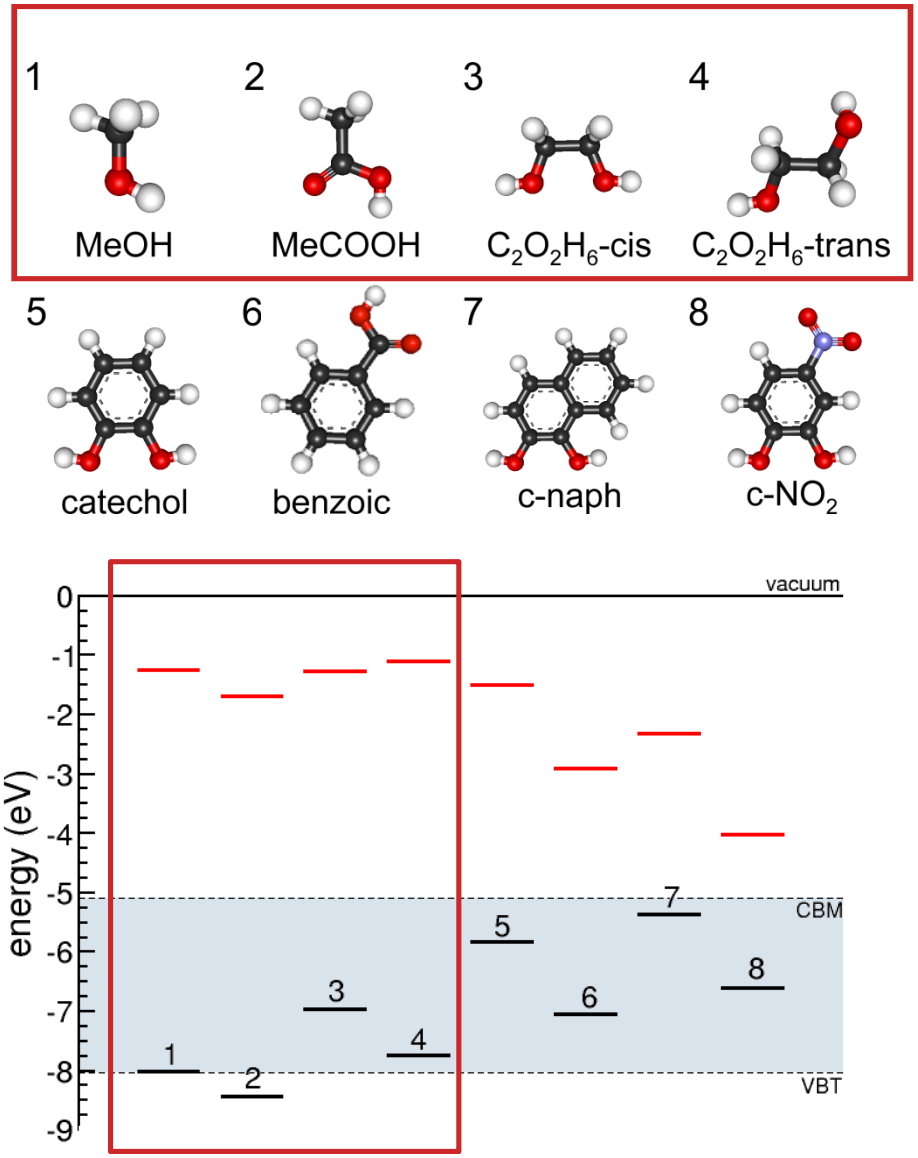
# band alignment problem

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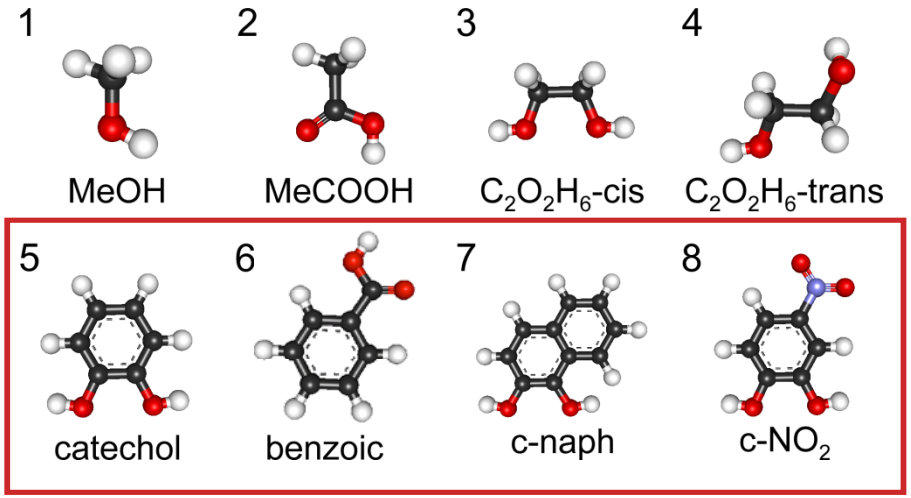
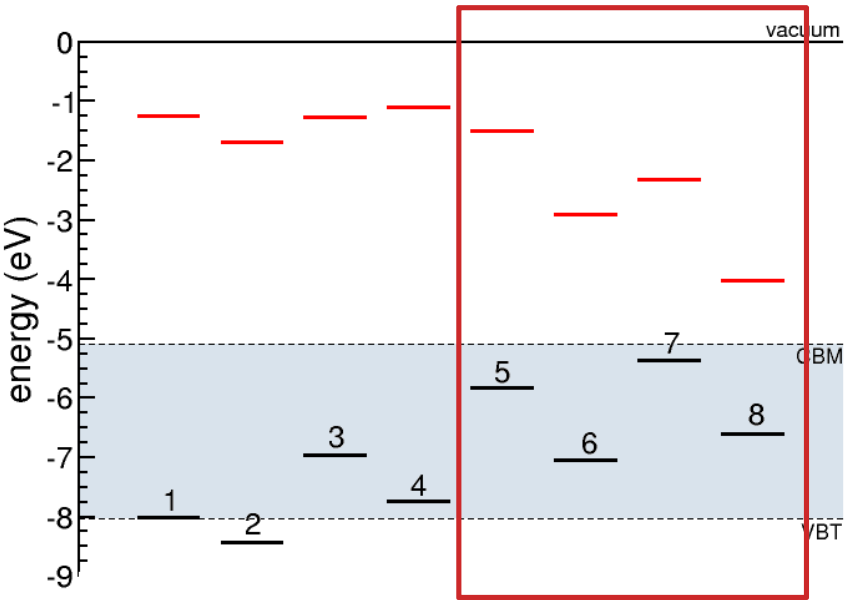
ANCHOR GROUPS

- 3 groups: -OH, COOH, $C_2O_2$
- Methanol and acetic acid do not introduce states in the ZnO gap

- $C_2O_2H_6$-cis fragment sets the HOMO level deep inside the ZnO gap → $C_2O_2H_6$-cis has two close lone pairs that repulse each other, reducing the ionization potential, i.e. shifting HOMO to higher energies.

# band alignment problem




A. Calzolari, A. Ruini, A. Catellani, JACS **2011** 133, 5893.

ANCHOR GROUPS

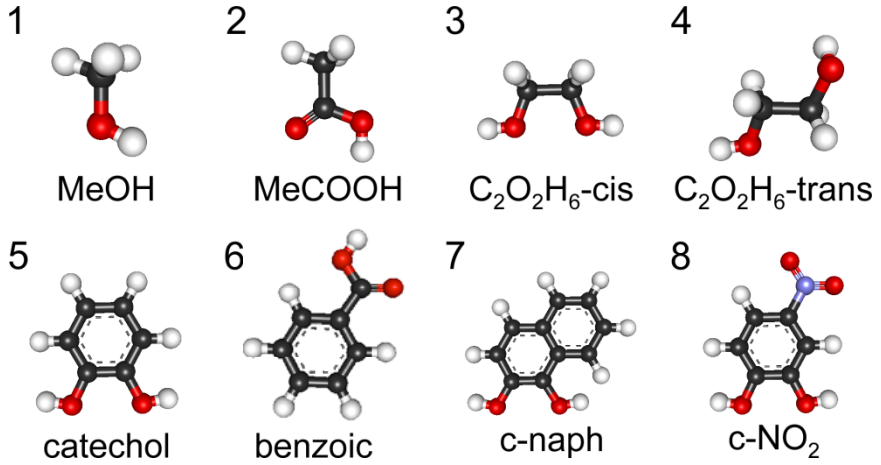
- 3 groups: -OH, COOH, $C_2O_2$
- Methanol and acetic acid do not introduce states in the ZnO gap

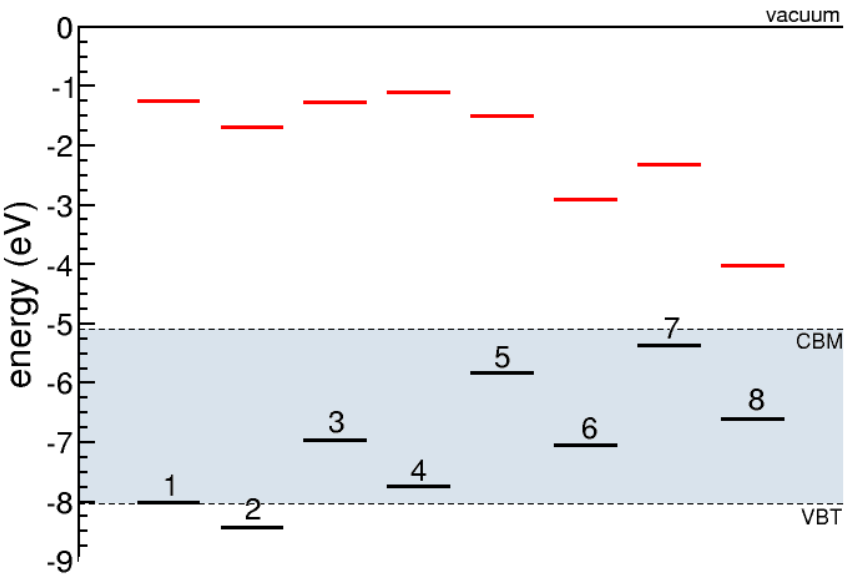
•$C_2O_2H_6$-cis fragment sets the HOMO level deep inside the ZnO gap → $C_2O_2H_6$-cis has two close lone pairs that repulse each other, reducing the ionization potential, i.e. shifting HOMO to higher energies.

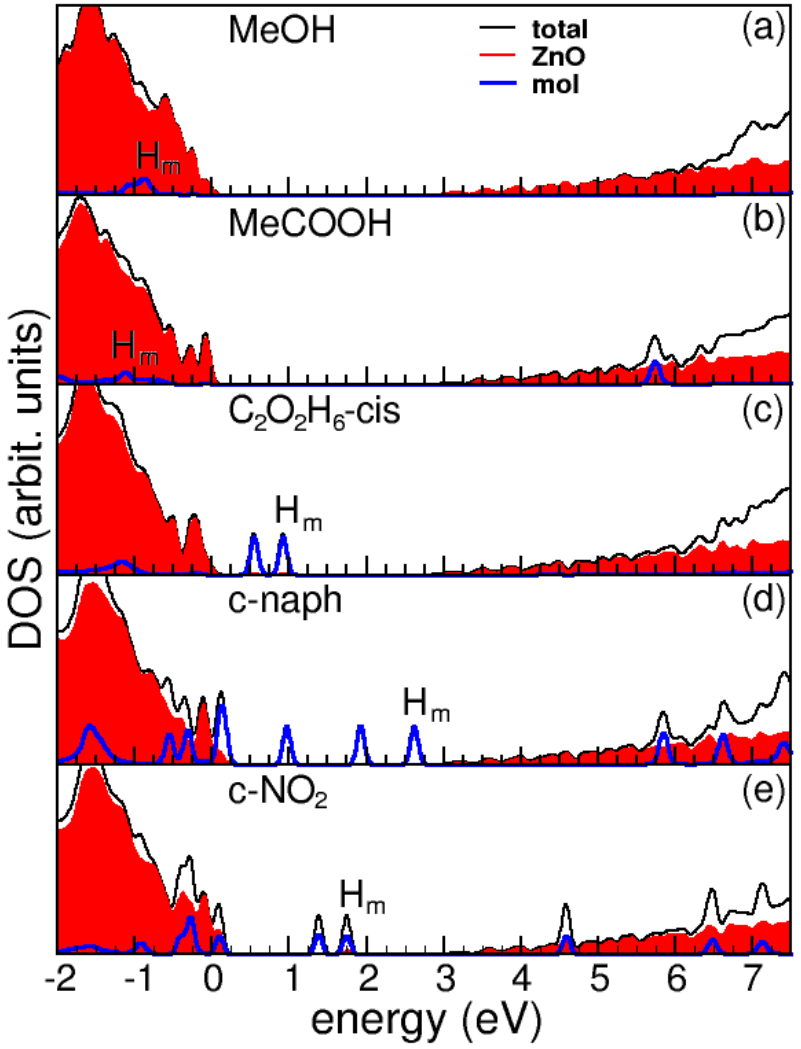
CONJUGATION

- Both conjugated chains and aromatic rings shift the HOMO to higher energies, even in the presence of COOH anchor group.
- Effects of anchor groups and charge conjugation sum almost linearly
- Inclusion of strong electron acceptor ($NO_2$) reduces the repulsion between oxygen of anchor groups shifting down the HOMO state.

# band alignment problem




Trend confirmed in full interfaces

A. Calzolari, A. Ruini, A. Catellani, JACS **2011** 133, 5893.

# band alignment problem

RATIONAL FOR THE BEST SUITED SURFACE FUNCTIONALIZATION

- In the case of applications that require a reasonably high $\Delta V$ voltages (e.g. solar cells) or p-like behavior, the inclusion of electron acceptor functional groups is preferred.

- On the contrary, in order to have n-like materials (e.g. transparent conducting oxides) or for devices working in the infrared regime, the inclusion of aromatic systems and/or electron donor groups is preferred.

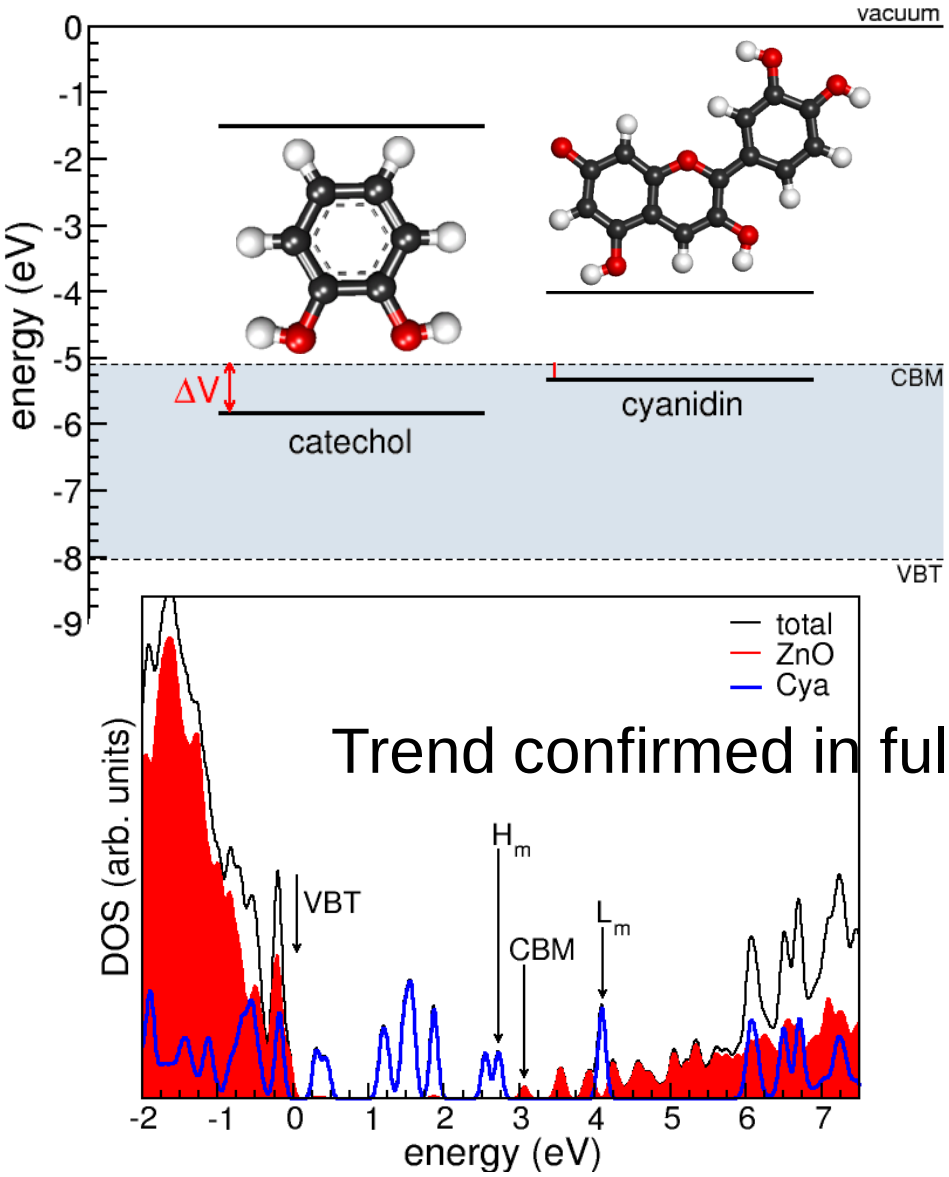
- A proper combination of the two allows for intermediate configurations.

To be confirmed by experiments in collaboration with
V. De Renzi et al (UniMORE and CNR-NANO-S3, Modena)



A. Calzolari, A. Ruini, A. Catellani, JACS **2011** 133, 5893.

# what can we expect in the case of cyanin?




Good light absorption

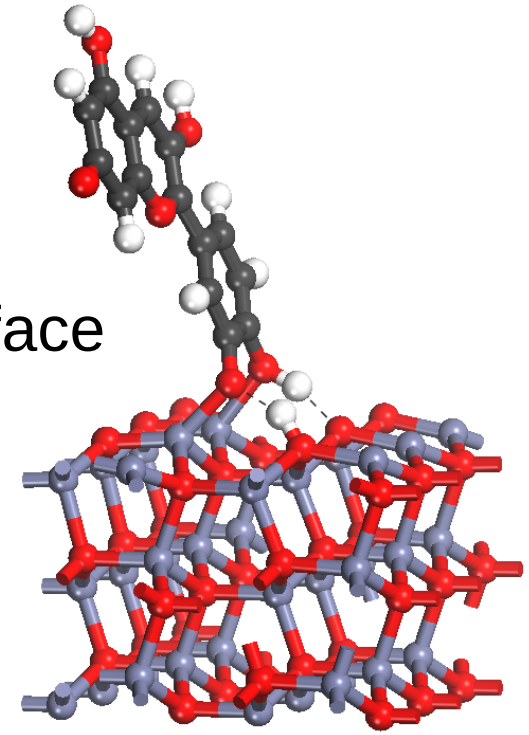
Type-II interface but

→ low extracted photovoltage ΔV

→ low efficiency

$$\eta = \frac{I_{max}}{I_{in}} = \frac{i_{sc} V_{oc} FF}{I_{in}}$$

Trend confirmed in full interface



A. Calzolari, A. Ruini, A. Catellani, preprint (2011).

# conclusions

- We characterized the **structural, electronic and optical properties** of the main components of the active part of a prototypical DSSC
  - molecular dye (cyanin)
  - metal-oxide substrate (ZnO)
  - TCO anode (Al:ZnO)

and their interaction with the surrounding **water environment**

- Single subsystems have intrinsic properties suitable for solar cell applications

- The formation of hybrid dye/substrate/TCO interfaces may change the intrinsic properties of the single subsystem

- Theoretical simulations as predicting tool for rationale DSSC design

# acknowledgments

Theory

Alice Ruini - CNR-NANO, Modena IT
Alessandra Catellani - CNR-IMEM, Parma IT
Stefano Baroni – SISSA, Trieste IT
Ralph Gebauer – ICTP, Trieste IT
Susanna Monti – CNR-IPCF, Pisa IT
Daniele Varsano – Universita' La Sapienza, Roma IT

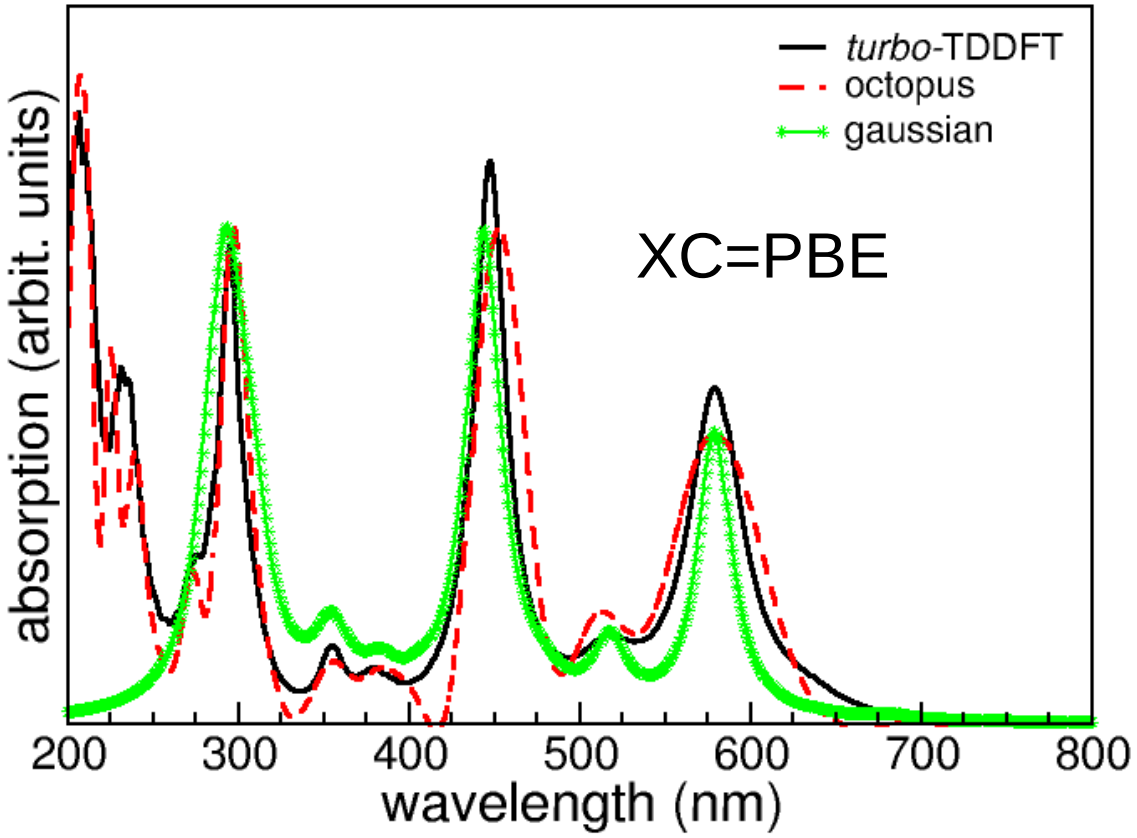
Experiments

Valentina De Renzi and Paola Luches – UniMoRe and CNR-NANO-S3, Modena IT
Itamar Willner - The Hebrew University of Jerusalem, Israel

!! POSTDOC POSITIONS AVAILABLE !!

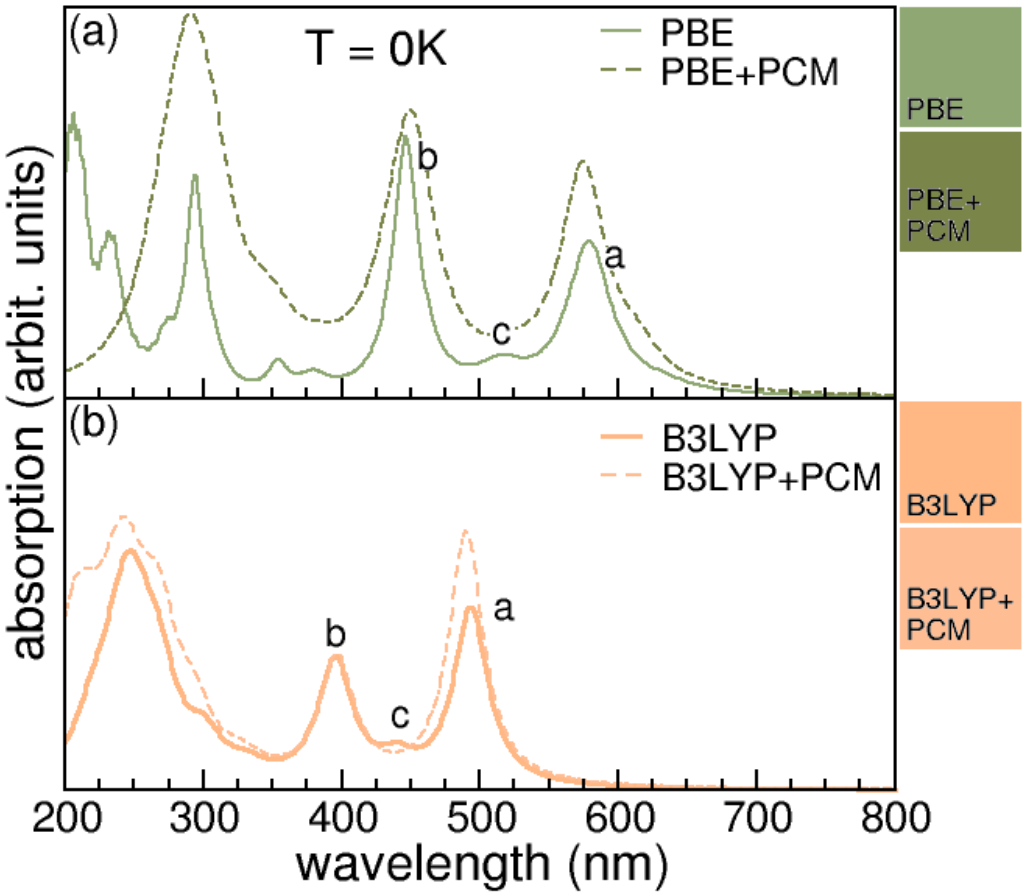
contact: arrigo.calzolari@nano.cnr.it

# benchmark tests

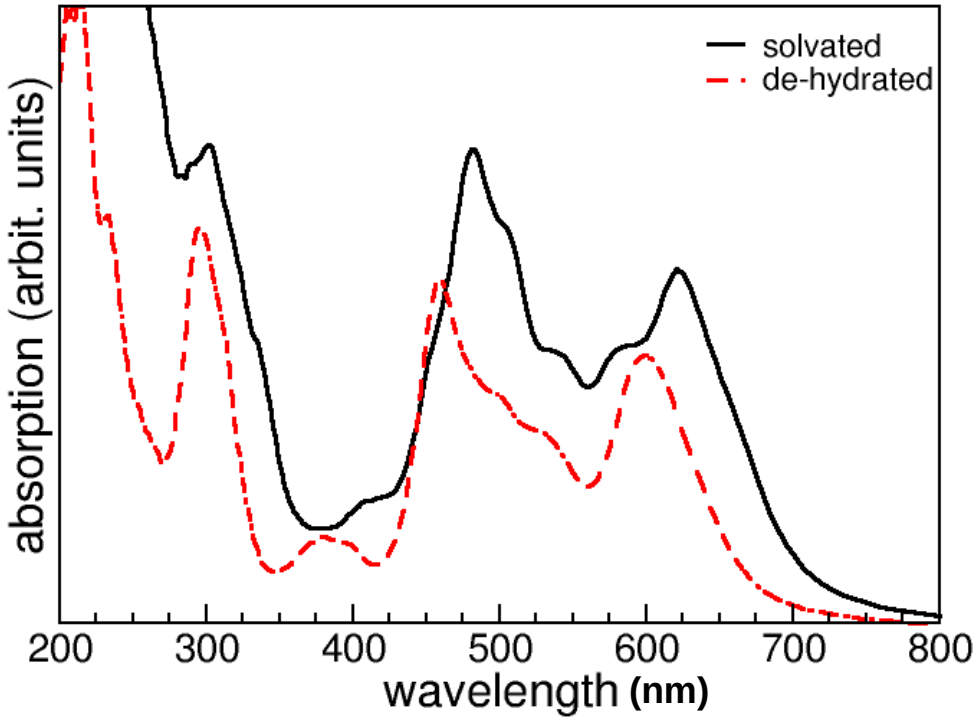



Absorption spectra for the cyanin molecule in the charged flavylium configuration, calculated in vacuum and zero temperature with different TDDFT codes, namely *turbo*-TDDFT, *octopus* and *gaussian09*.

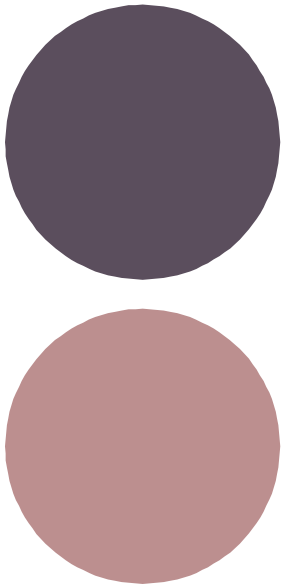
# Effect of XC functional



# time averaged spectra – de-hydrated system*




simulated color



Solvated

De-hydrated

- Same snapshots, NO water
- Same spectral features as fully solvated →

Dielectric Effect → bato- and hyper-chromism (similar to PCM)

Effect of thermal fluctuations → broadening of absorption spectrum

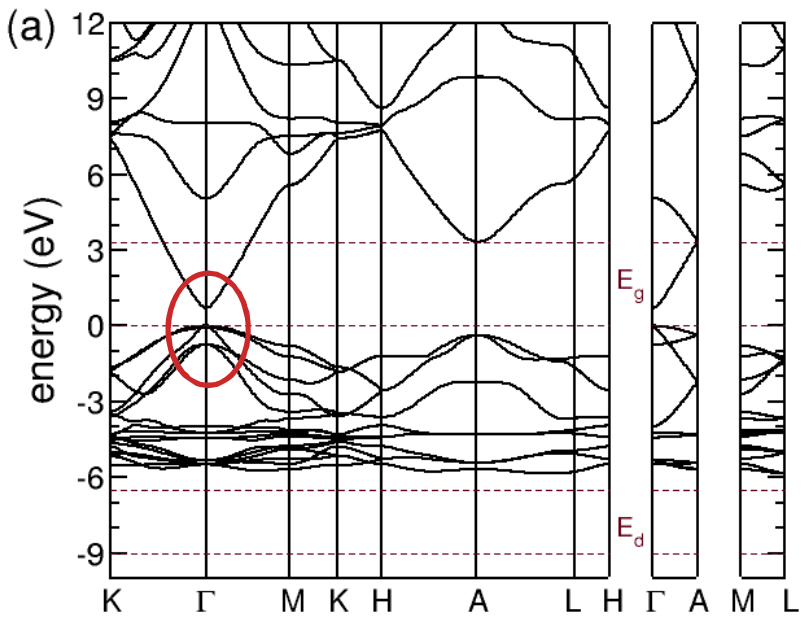
CNRNANO
ISTITUTO NANOSCIENZE CONSIGLIO NAZIONALE DELLE RICERCHE

*O.B. Malcioglu, AC, R. Gebauer, D. Varsano S. Baroni, JACS **133**, 15425 (2011).

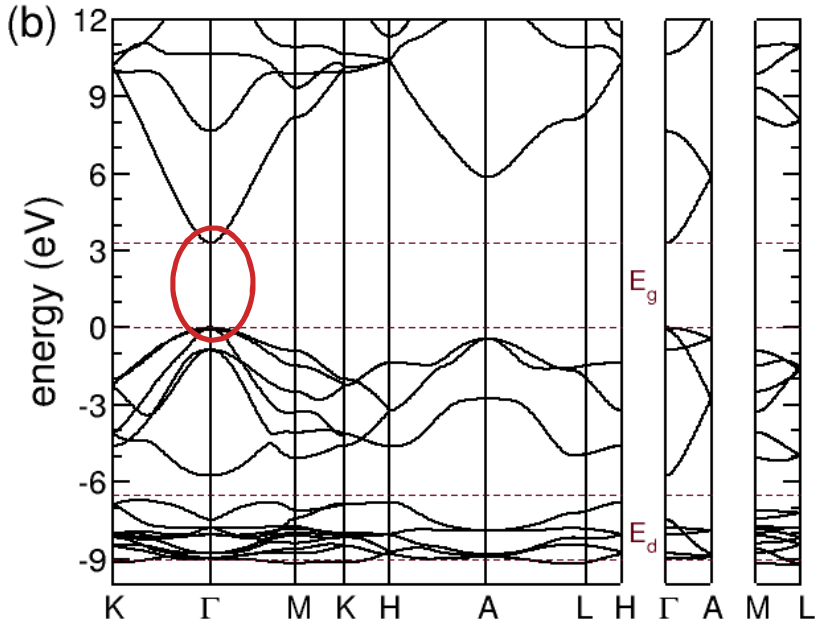
# gap opening

DFT+U* used to correct the bandgap of ZnO

U parameter fitted to reproduce the experimental bandstructure of ZnO bulk.
→ Gap comparison: $\Delta E_g$(exp) = 3.3 eV $\Delta E_g$(DFT) = 0.7 eV $\Delta E_g$(DFT+U) = 3.1 eV




DFT




DFT+U



*A. Janotti, D. Segev, C.G. Van de Walle, Phys. Rev. B 74, 045202 (2006)