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Modeling dye-sensitized solar cells: Understanding the mechanism, improving the efficiency

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Modeling Dye-Sensitized Solar Cells:

Understanding the mechanism, improving the efficiency

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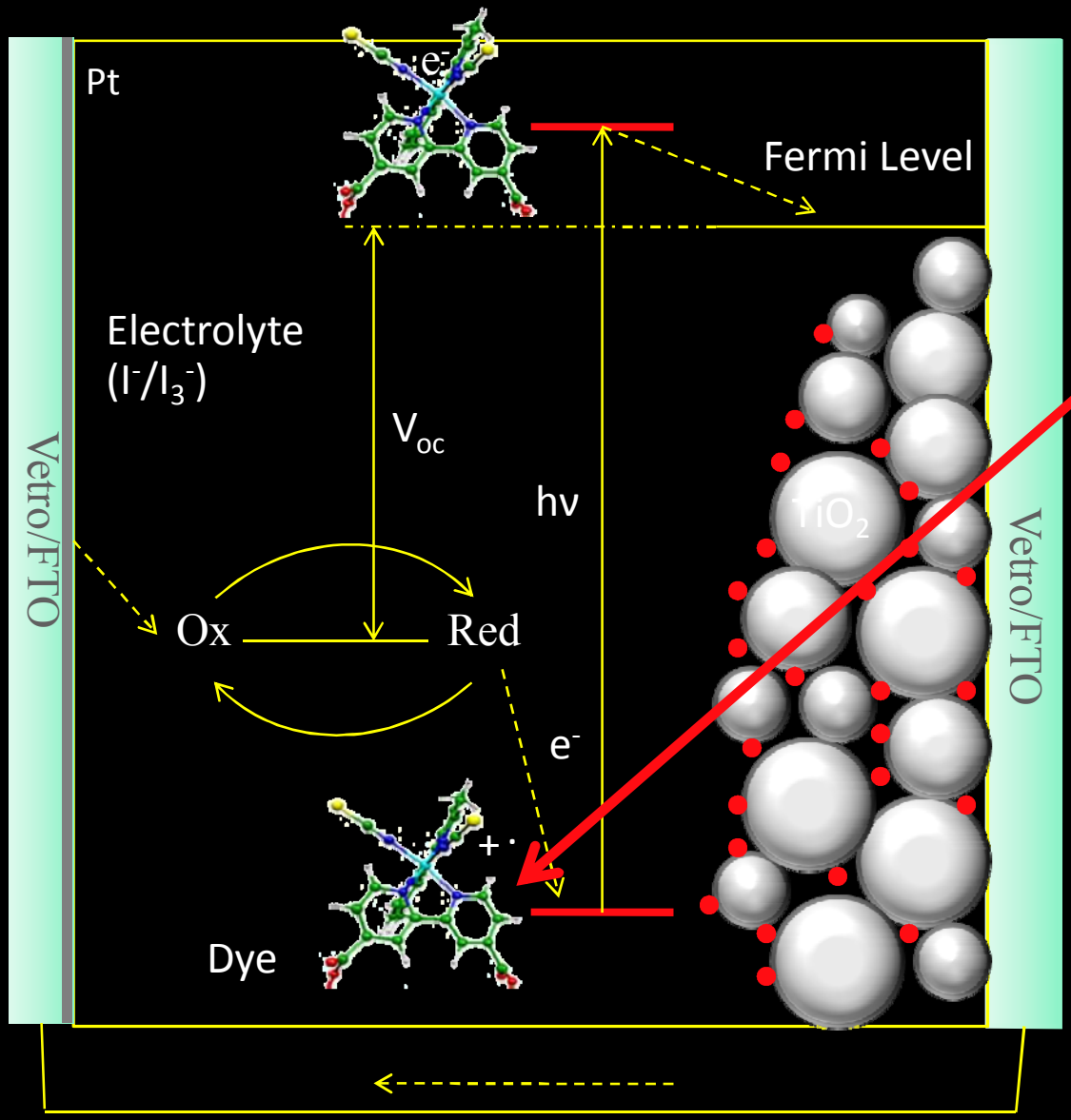
DSC: Principles of operation



In DSCs TiO_2 nanoparticles are sensitized with a light-harvesting sensitizer and are typically surrounded by a liquid electrolyte.

The dye-sensitizer captures photons and an electron/hole pair is generated.

The electron is injected into conduction band of TiO_2 and then flows into the external circuit.

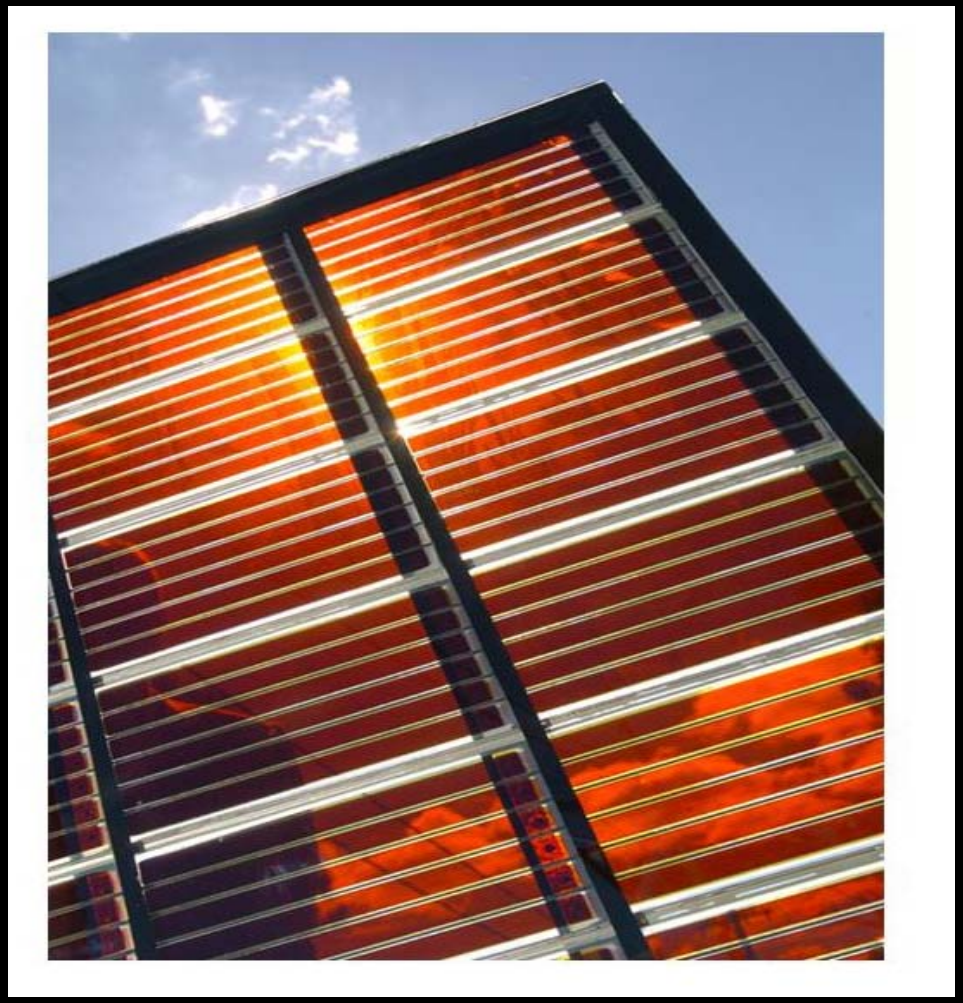
The oxided dye is regenerated by the redox couple in the electrolyte.

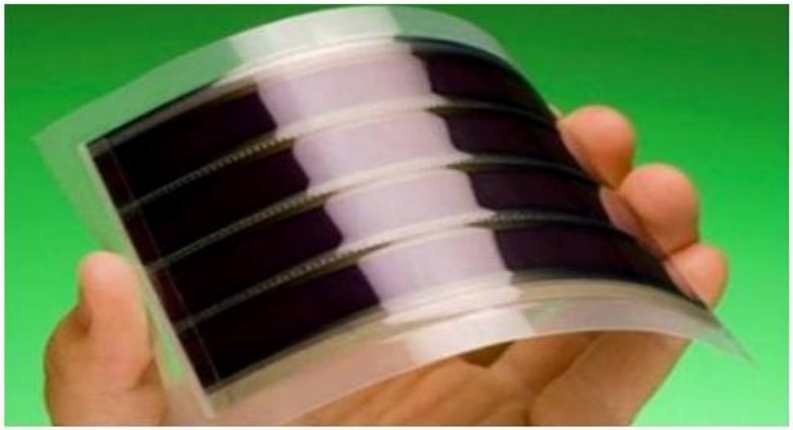
Photocurrent: rate of electron injection (I= dq/dt)

Photovoltage: Position of the conduction band.

M. Grätzel, *Nature*, 2001, **414**, 338

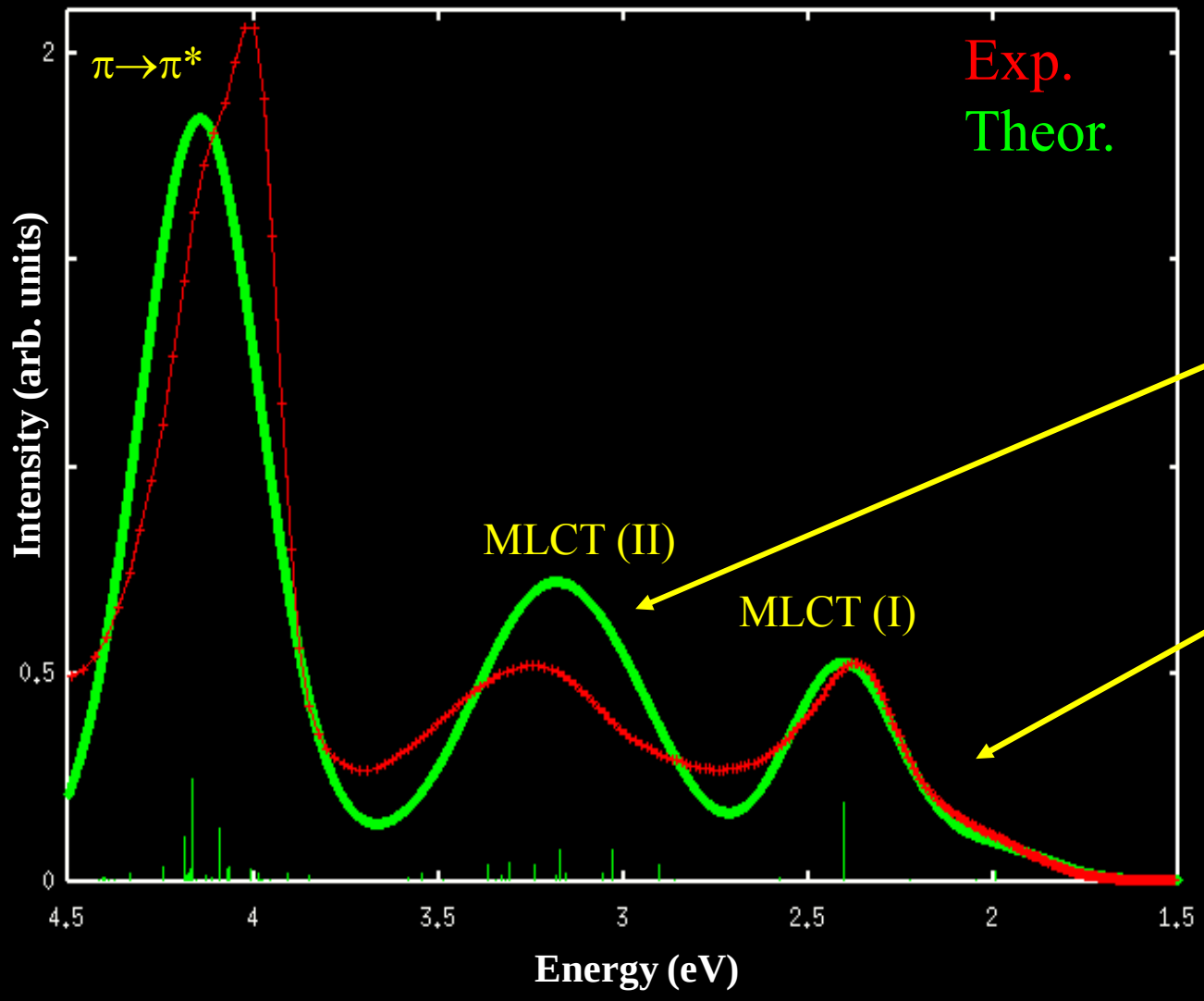
Dye-Sensitized Solar Cells: Flexible, colorful, transparent PVs

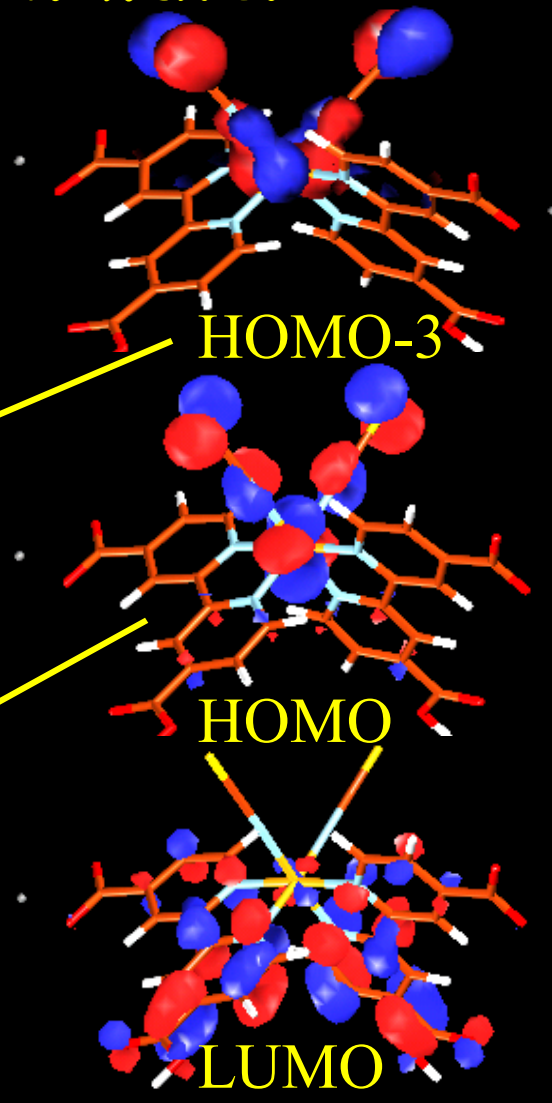




DYESOL-TATA (UK) / FUJIKURA (JPN)

Absorption spectrum of N719 in water:

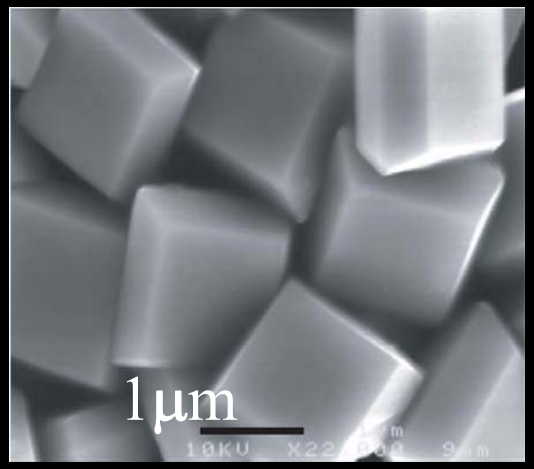


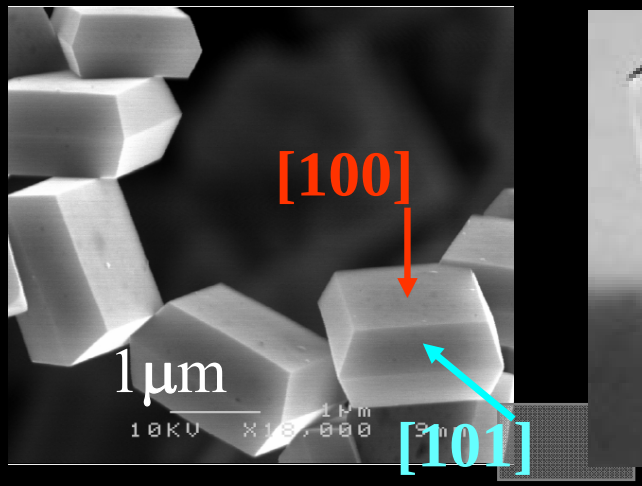


S. Fantacci, F. De Angelis, A. Selloni
F. De Angelis, S. Fantacci, A. Selloni
F. De Angelis, S. Fantacci, M.K. Nazeeruddin
F. De Angelis,. S. Fantacci, M. Grätzel et al.

***J. Am. Chem. Soc.* 2003, *125*, 4381.**
***Chem. Phys. Lett.* 2004, *389*, 204.**
***Chem. Phys. Lett.* 2005, *415*, 115.**
***J. Am. Chem. Soc.* 2005, *127*, 16835.**

Anatase TiO_2 nanocrystals





H. G. Yang et al. Nature 453, 2008, 29

Catal. Today 85, 2003,932

Truncated tetragonal bipyramidal shape:

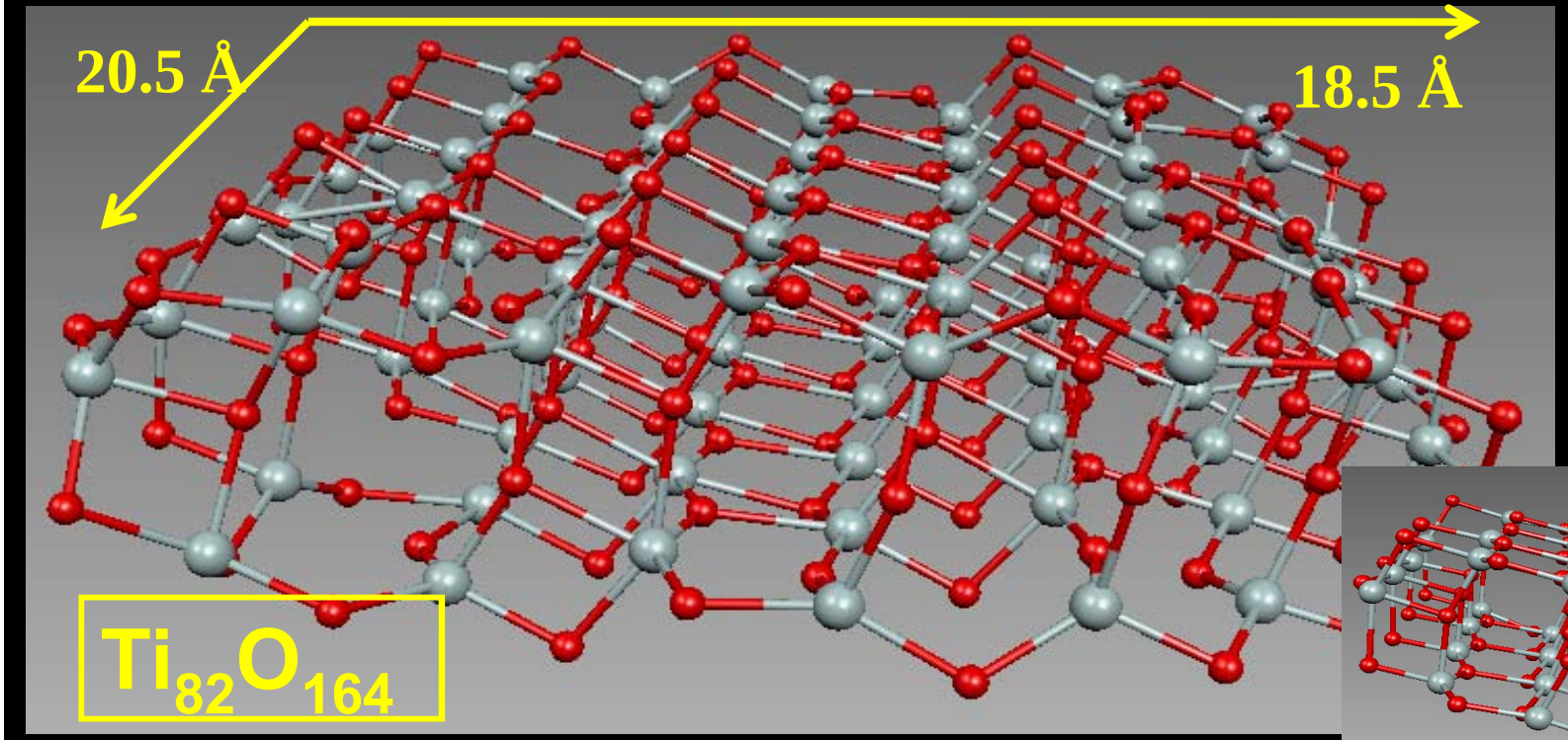
two flat, square surfaces are [001] facets and eight isosceles trapezoidal surfaces are [101] facets.

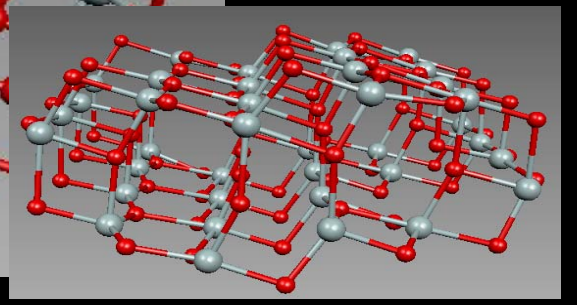
The [101] is the most thermodynamically stable surface, while the [001] is more reactive for dissociative adsorption of reactant molecules.

High surface area and large reactive surface → higher photocatalytic activities.

Modeling of TiO_2 nanoparticles:

Stoichiometric anatase $(TiO_2)_{38}$ and $(TiO_2)_{82}$ clusters of 1 and 2 nm dimensions exposing (101) surfaces



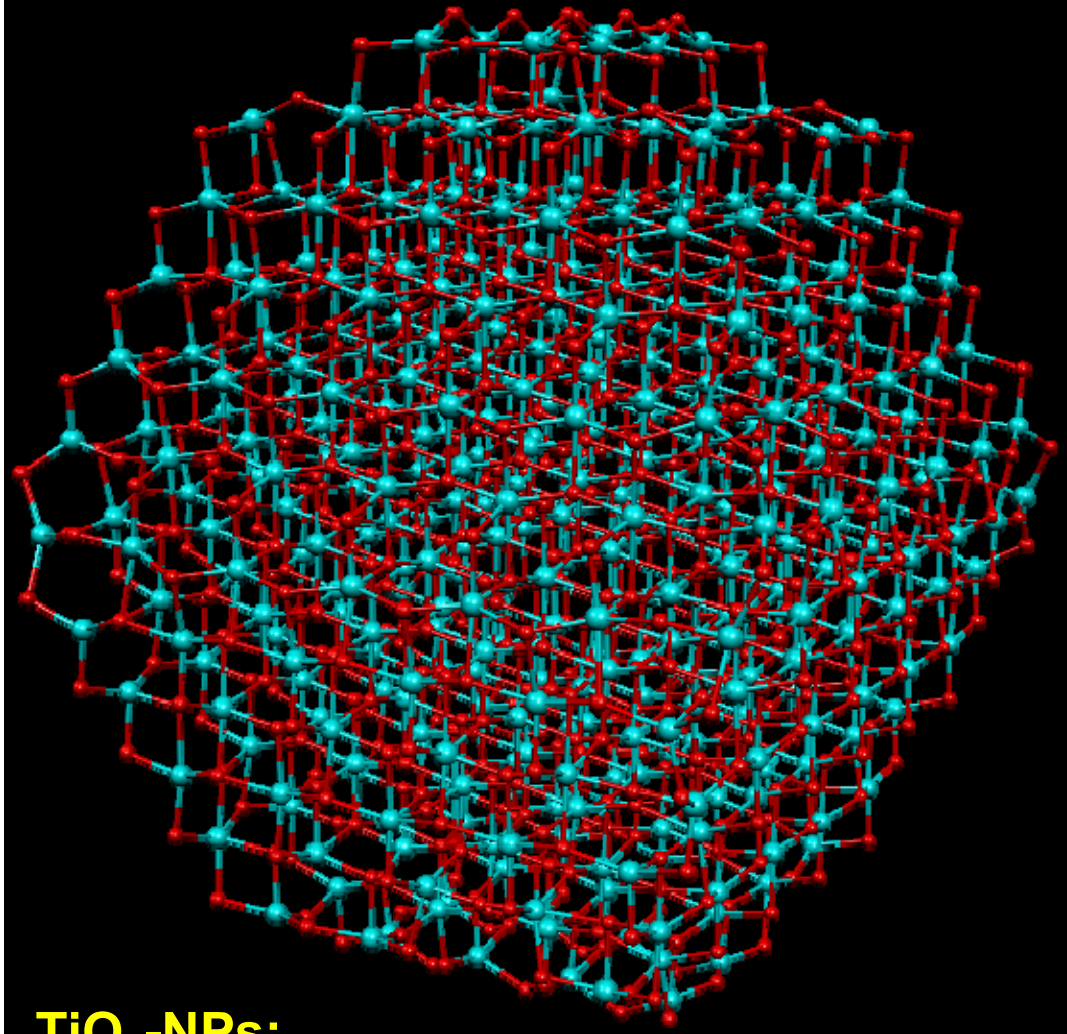


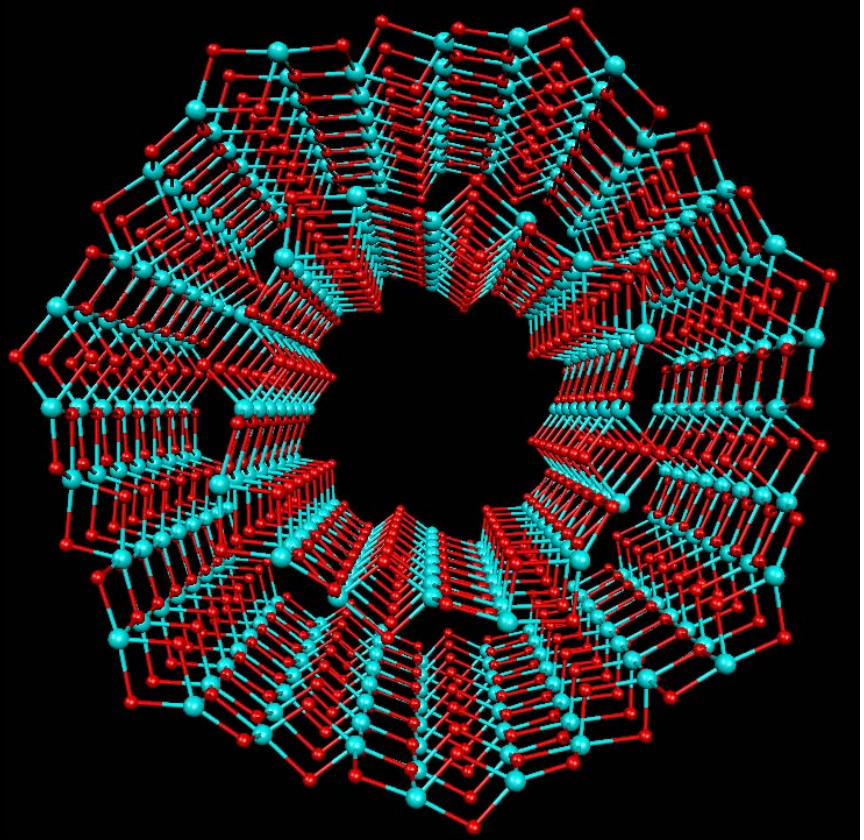
	B3LYP/3-21g*	B3LYP/DZVP
TD-DFT gap in water	3.20/3.41 eV	3.13/3.35 eV

Experimental gap in acqueous solutions: 3.20 – 3.30 eV

F. De Angelis, A. Tilocca, A. Selloni ***J. Am. Chem. Soc.*** **2004, *126*, 15024**

Realistic models of TiO_2 NTs and NCs





TiO_2-NPs:

Origin of sub-band gap states?

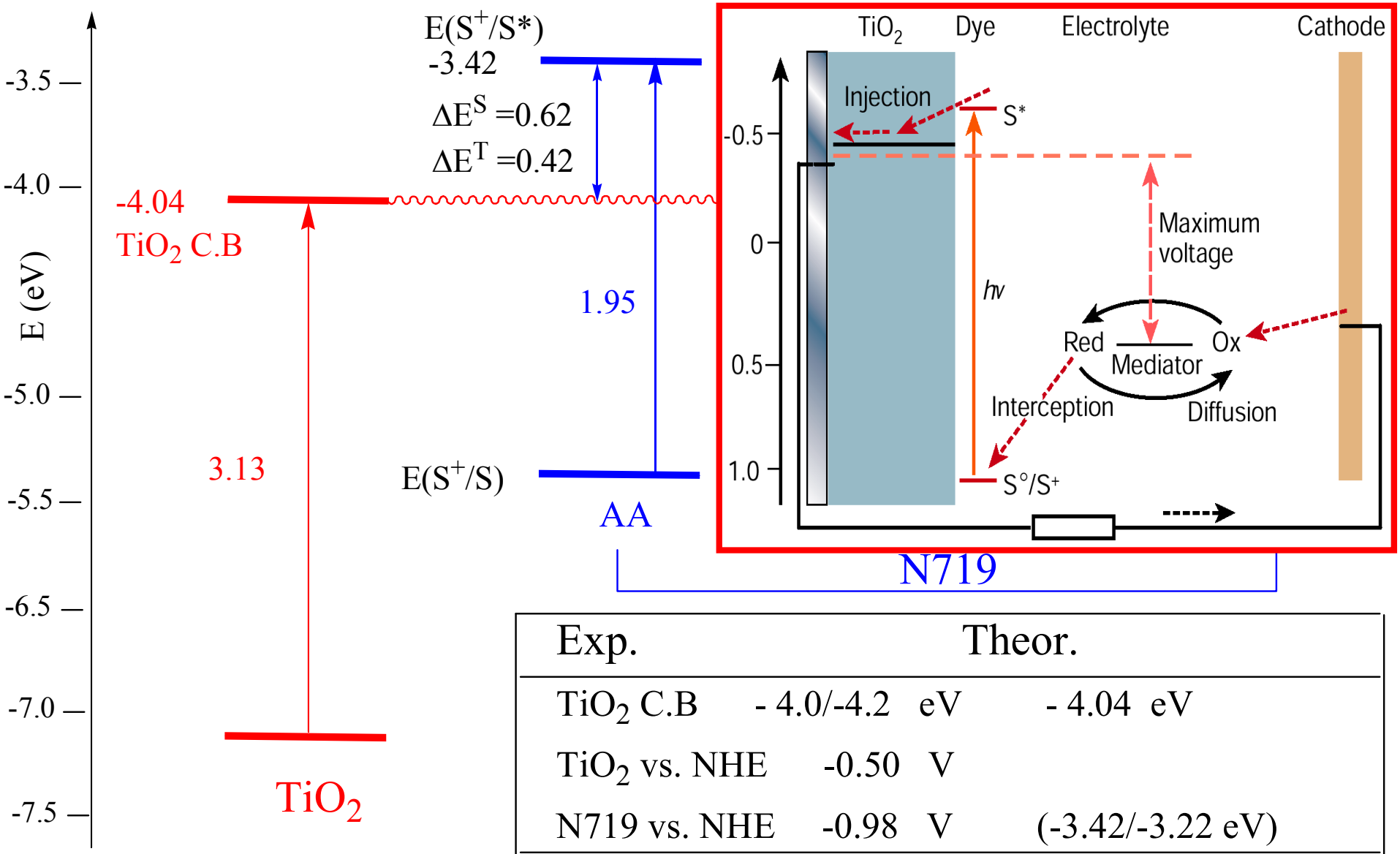
Work in progress

Single and Multi-Wall TiO_2-NTs:

Adsorption mode

F. Nunzi, F. De Angelis, ***J. Phys .Chem***. C, **2010**

Alignment of excited state potentials:

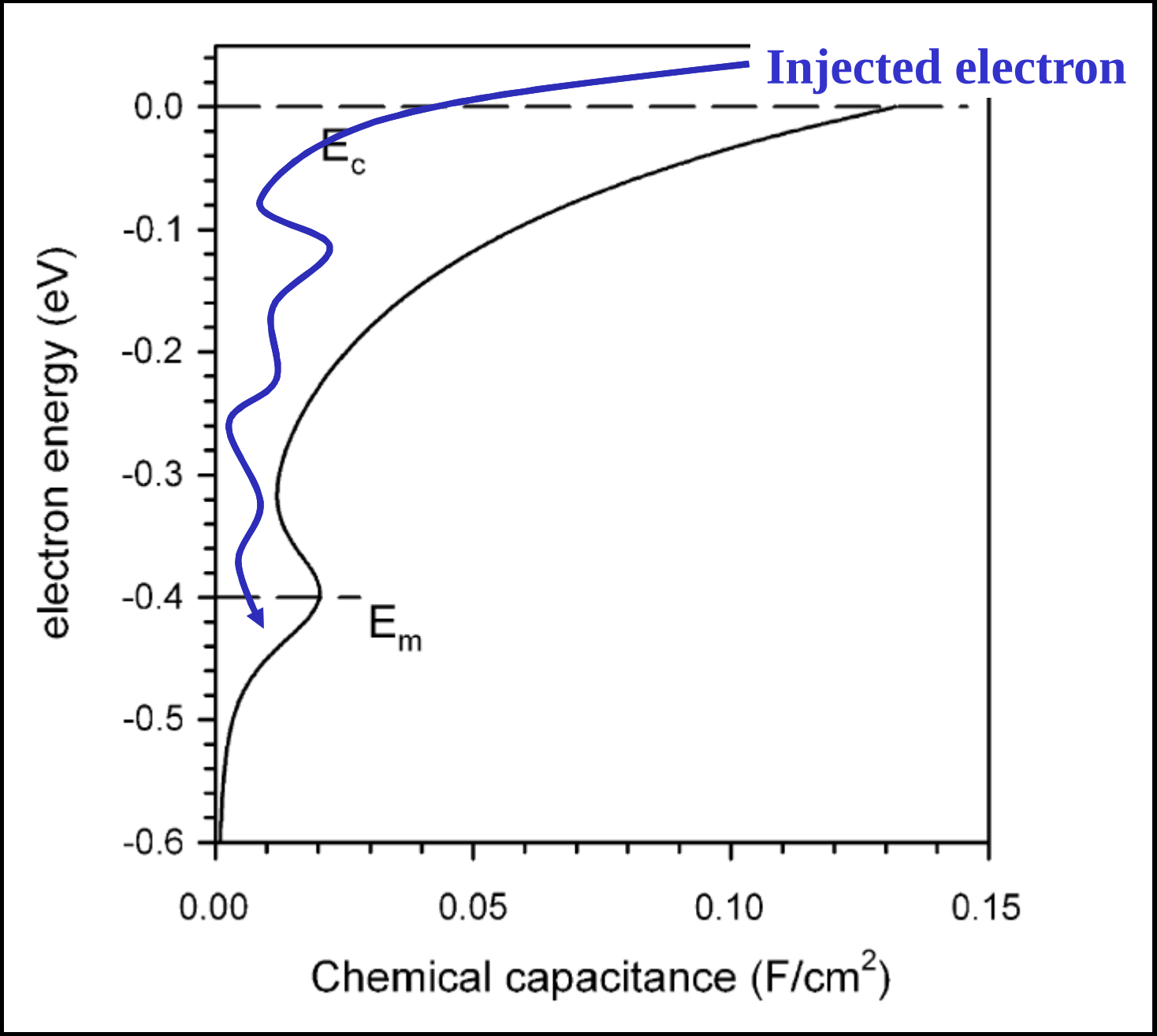


Exp.		Theor.
TiO_2 C.B	- 4.0/-4.2 eV	- 4.04 eV
TiO_2 vs. NHE	-0.50 V	
N719 vs. NHE	-0.98 V	(-3.42/-3.22 eV)

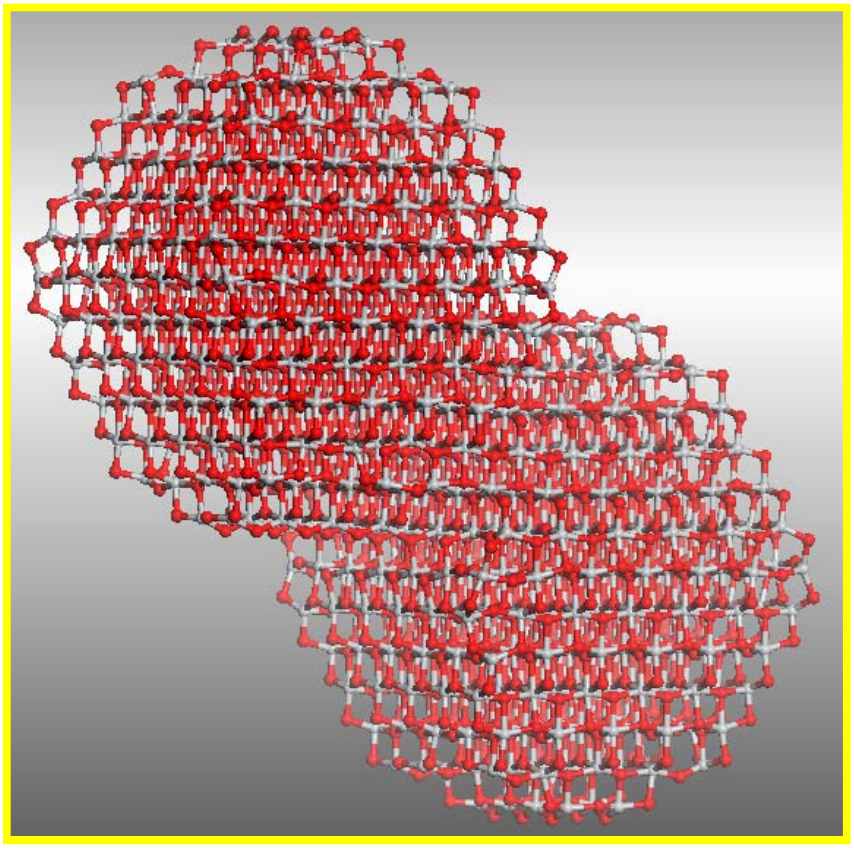
ΔE =0.48 V ΔE^T =0. 435 eV

F. De Angelis, S. Fantacci, A. Selloni, *Nanotechnology*, **2008**, *19*, 424002.

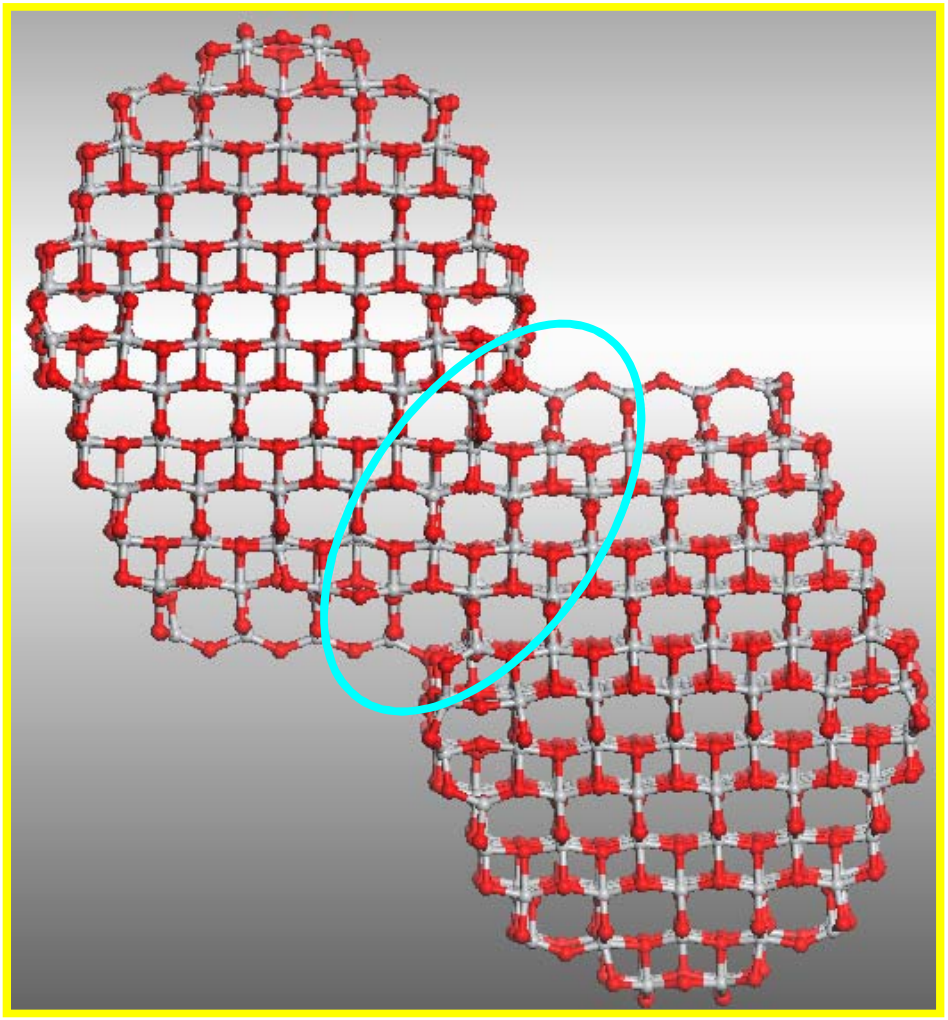
Trap states in TiO_2



THE INTERACTION OF TWO TiO_2 NANOCRYSTALS $(TiO_2)_{367}$ THROUGH THE [101]-[101] SURFACES:

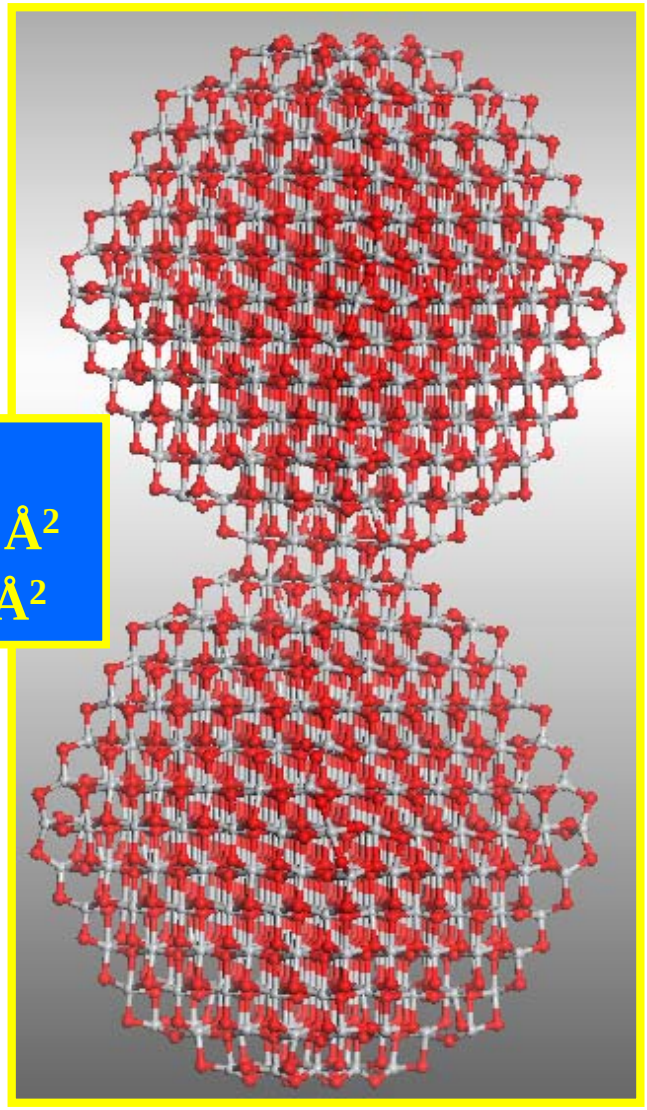


We computed an interaction energy of 27.5 eV.

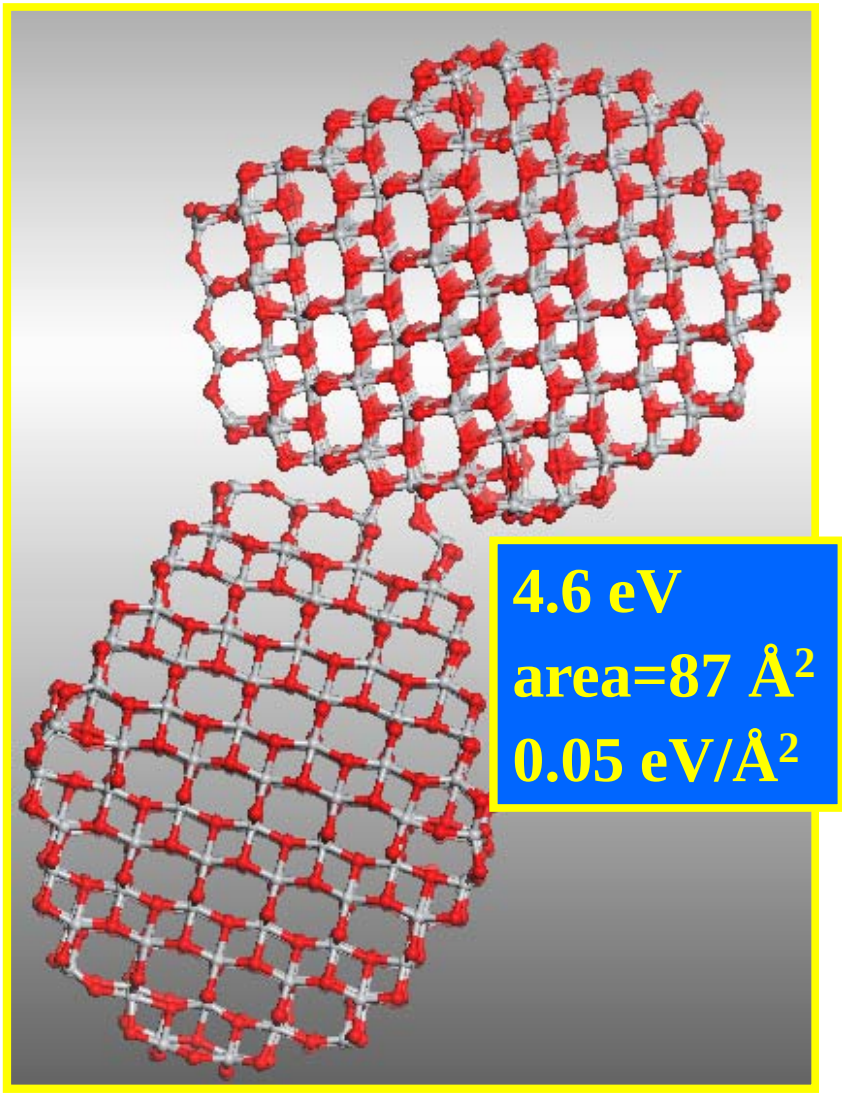


Estimating a contact surface area of 201 $Å^2$ at the interface, we calculate an energy interaction per area of **0.14 eV/ $Å^2$**.

THE INTERACTION OF TWO TiO_2 NANOCRYSTALS $(TiO_2)_{367}$ THROUGH THE [001]-[001] and [101]-[001] SURFACES:

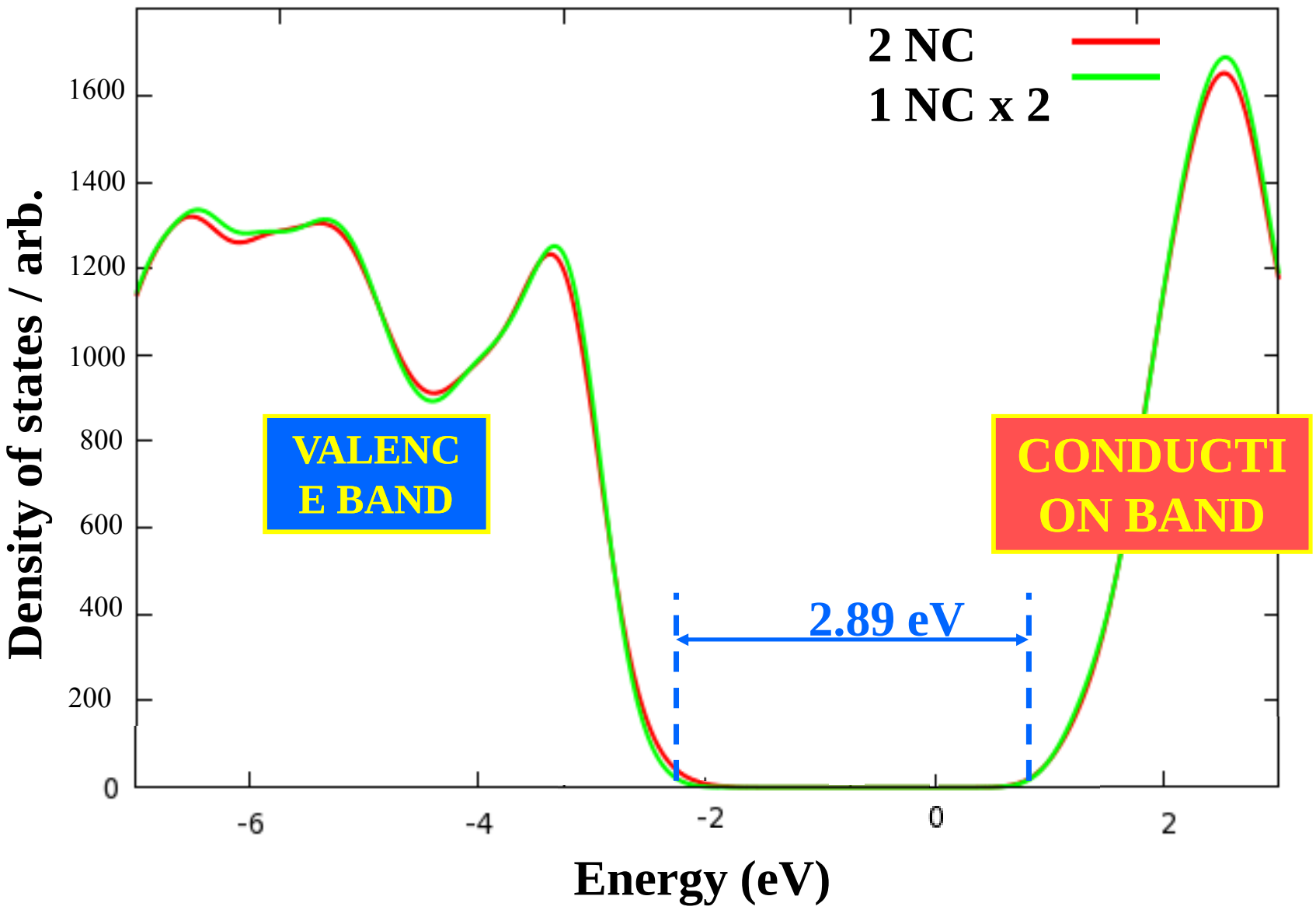


7.1 eV
area=87 Å^2
0.08 eV/Å^2

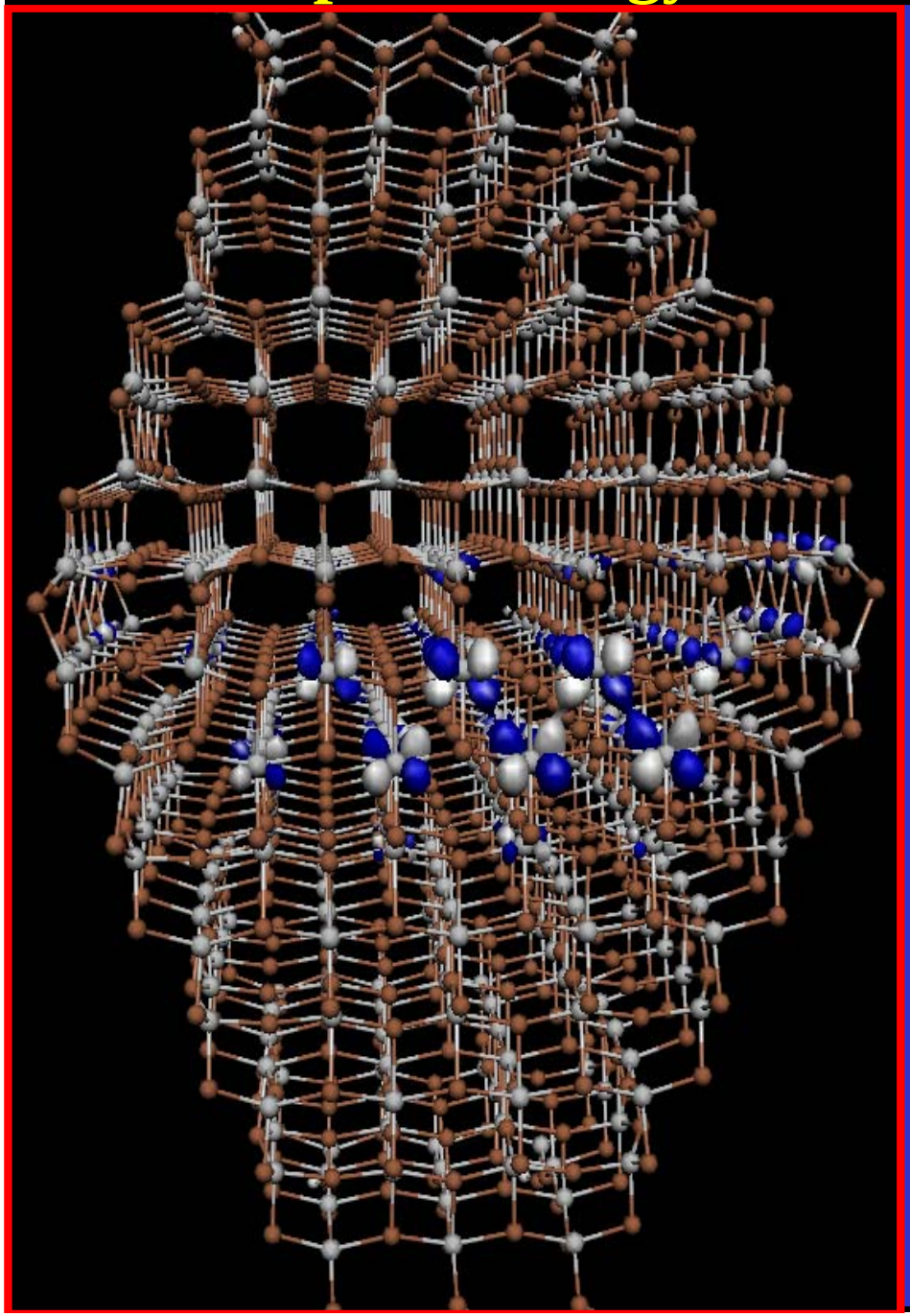


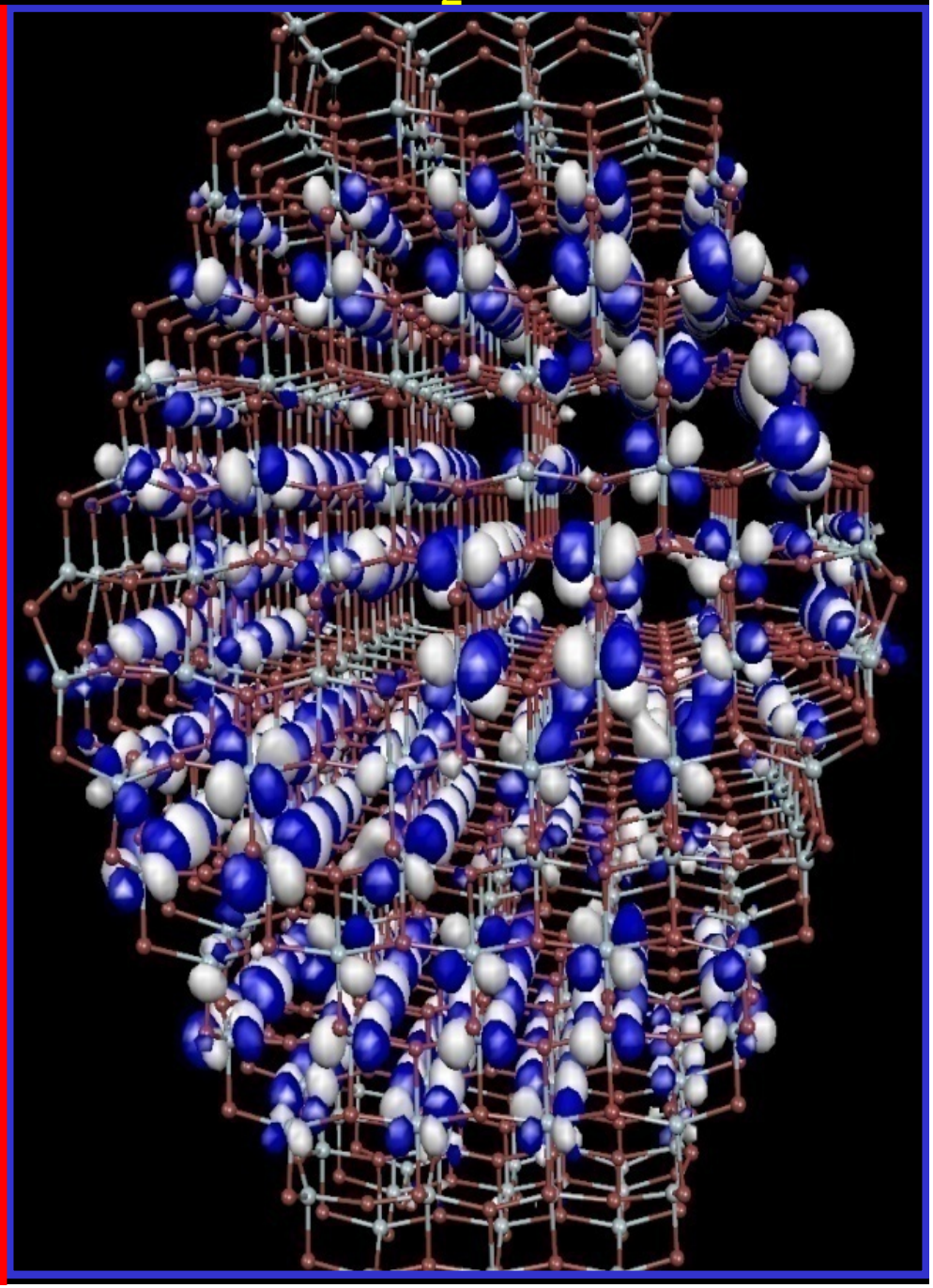
4.6 eV
area=87 Å^2
0.05 eV/Å^2

DOS FOR TWO TiO_2 NANOCRYSTALS [101]-[101]

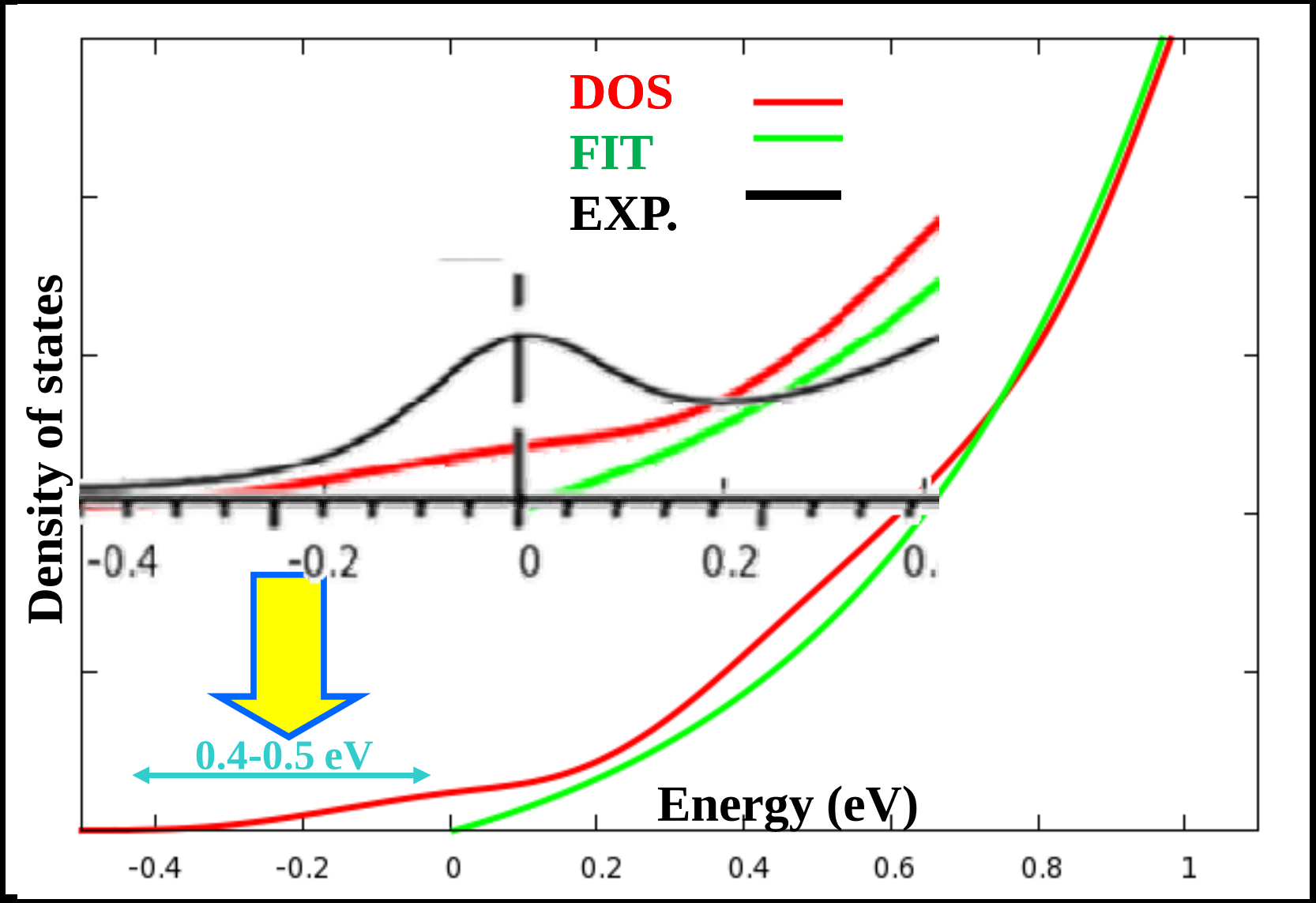


Space /energy distribution in a TiO_2 NC



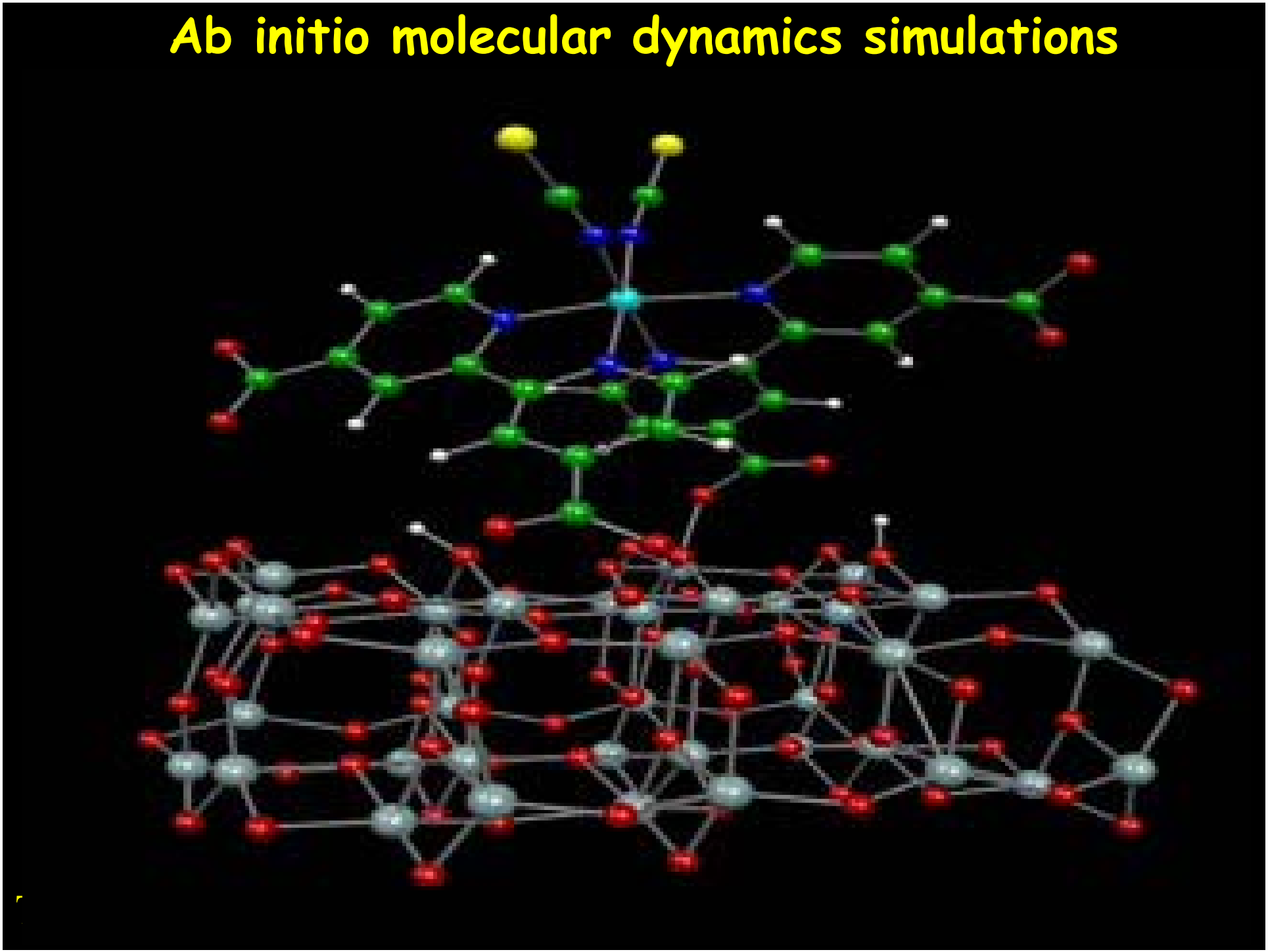


DOS FOR A SINGLE TiO_2 NANOCRYSTAL



SURFACE STATES OF INDIVIDUAL TiO_2 NANOCRYSTALS INTRODUCE SUB BAND-GAP STATES IN THE DOS

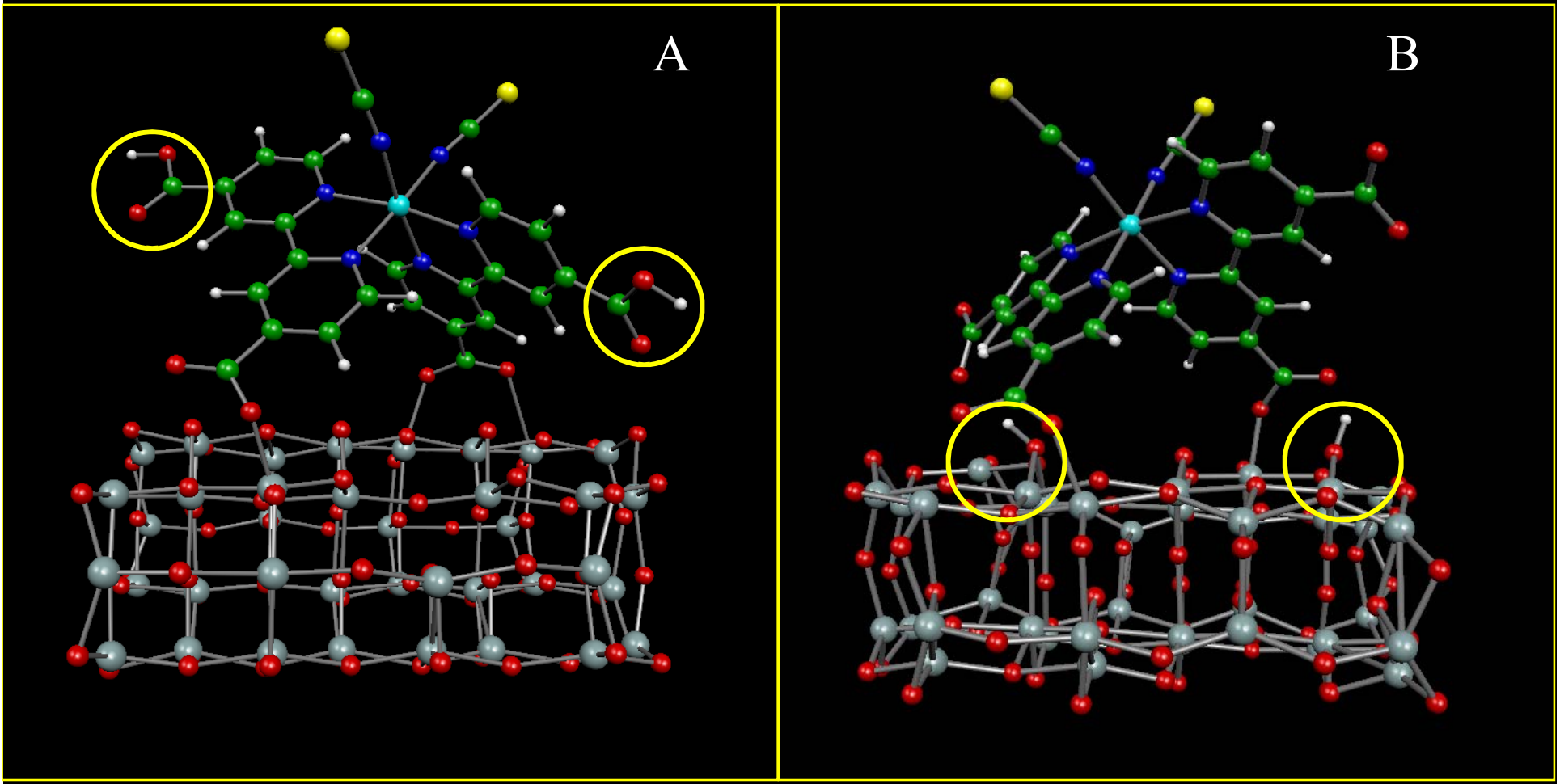
Ab initio molecular dynamics simulations



N719 adsorbed on TiO_2:

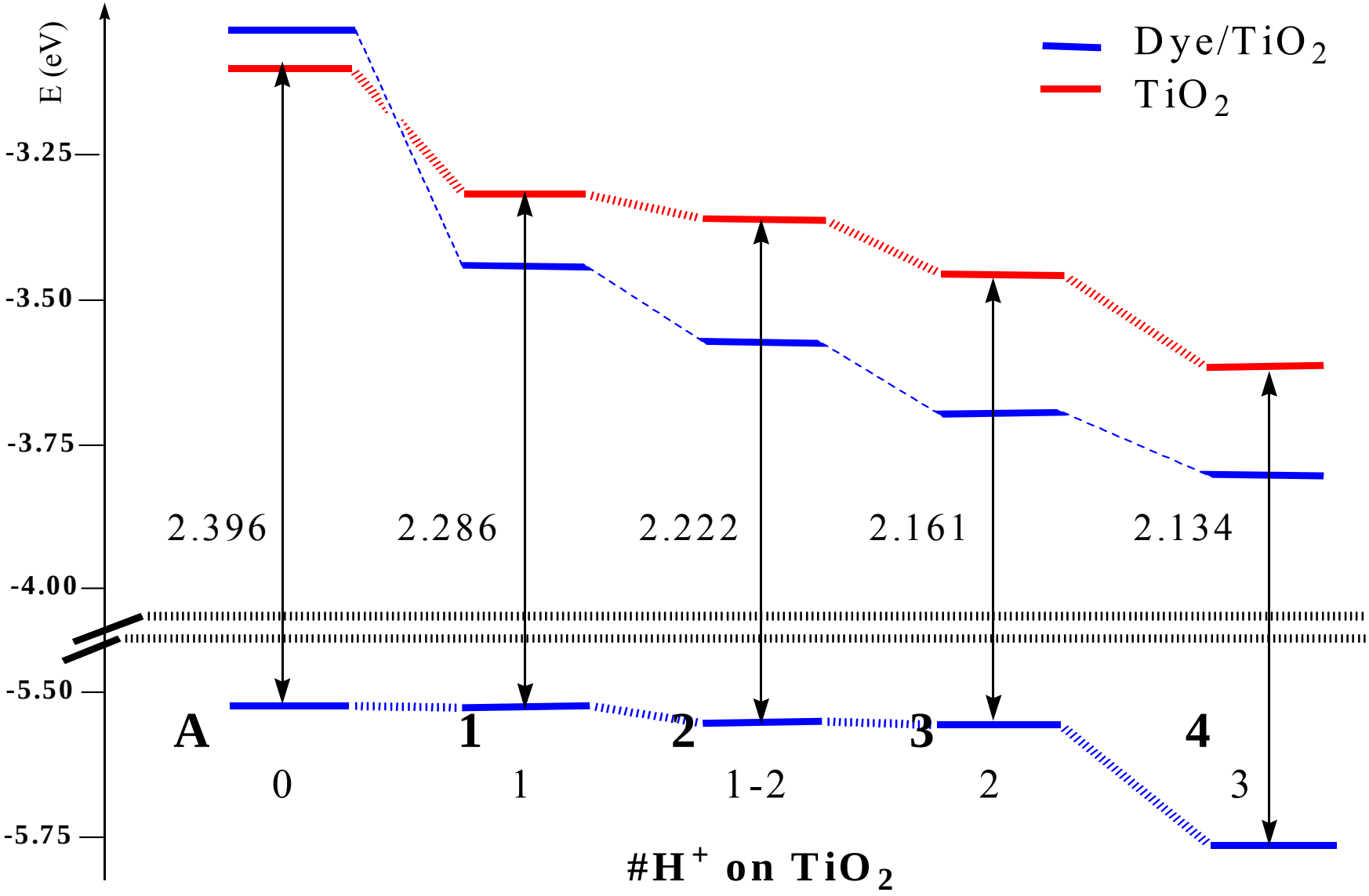
Two prototypical configurations of N719/TiO_2 were examined

The two protons are located on the dye (A) or on the TiO_2 (B)



F. De Angelis, S. Fantacci, A. Selloni, M. Grätzel ***J. Am. Chem. Soc.*** *2007, 129, 14156.*

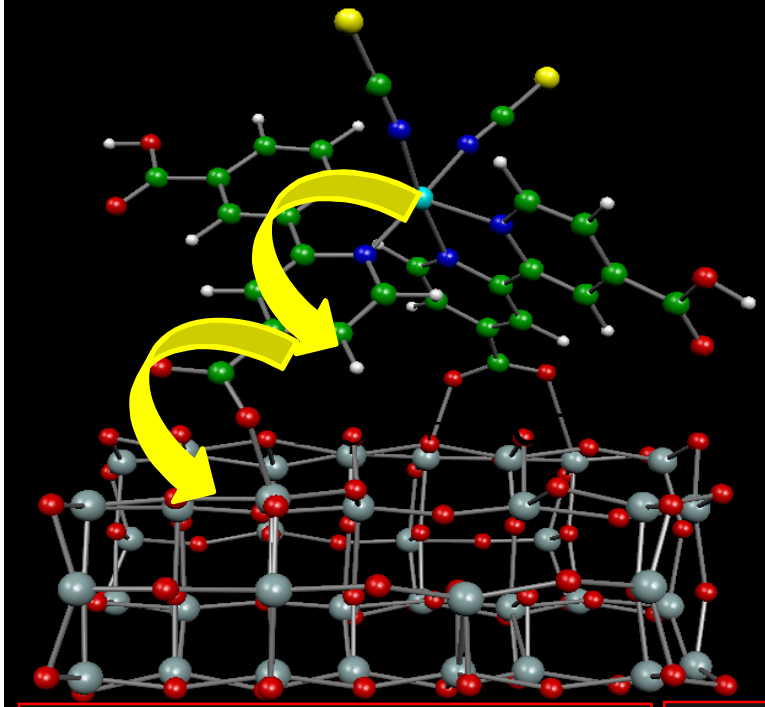
Electronic structure / number of H^+ on TiO_2

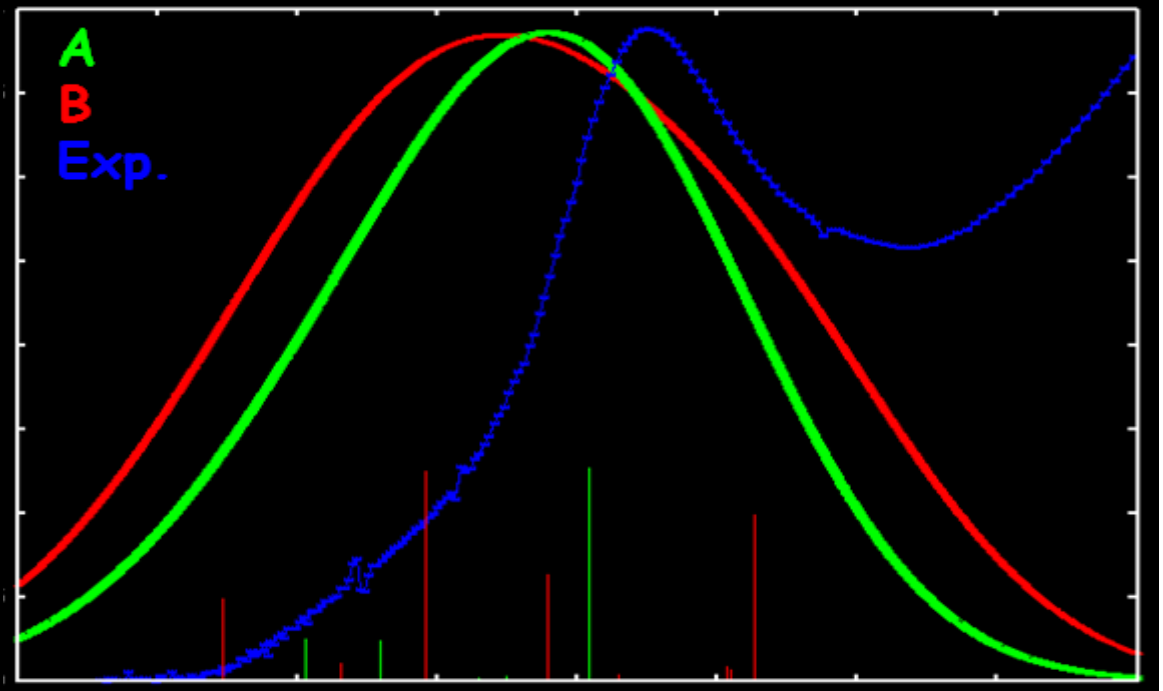


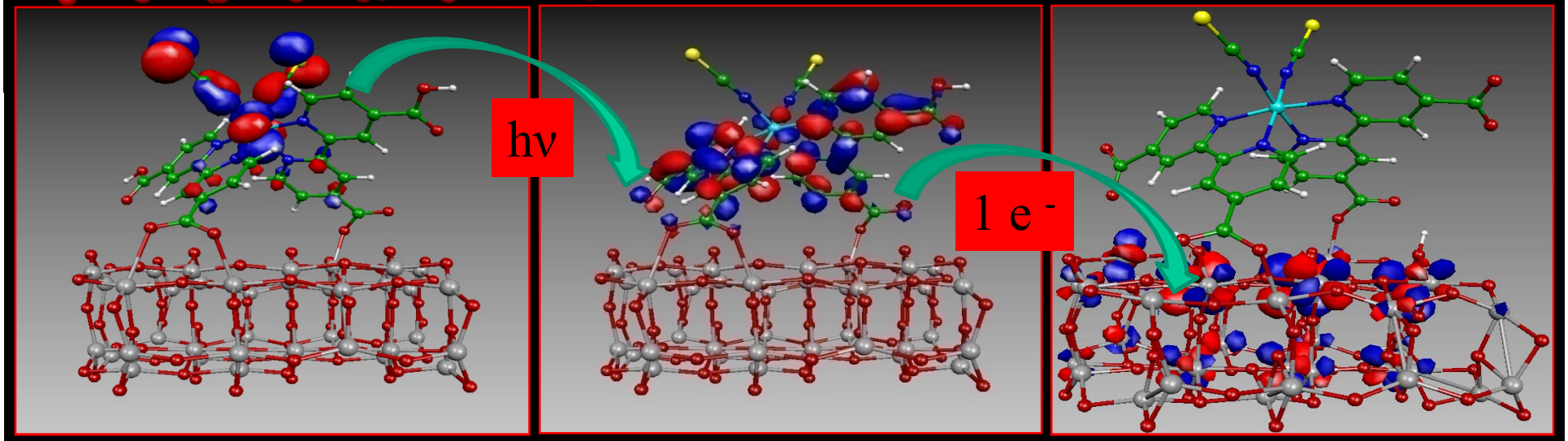
Increasing the protons on TiO_2 lowers the C.B. (and therefore V_{OC})

Md. K. Nazeeruddin, R. Humphry-Baker, P. Liska, M. Grätzel, *J. Phys. Chem. B,* **2003**, 107, 8981.

Charge generation and injection mechanisms:



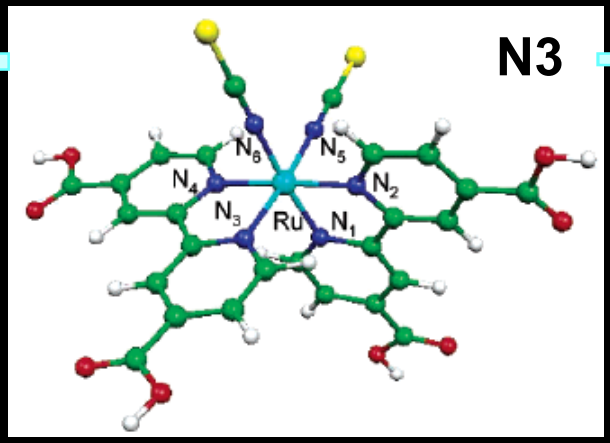




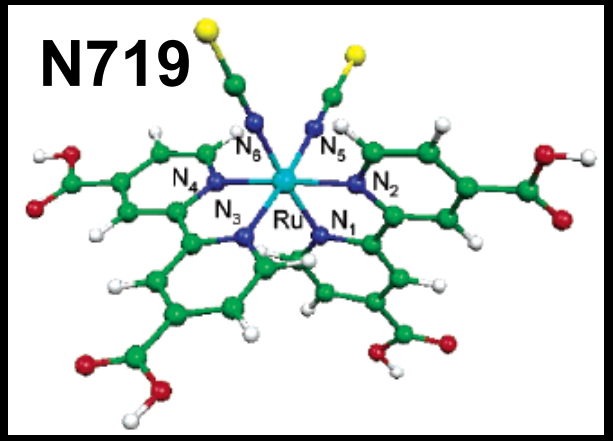
F. De Angelis, S. Fantacci, A. Selloni, M. Grätzel ***J. Am. Chem. Soc.*** *2007, 129, 10320.*

Tuning the properties of Ru(II) TiO_2 sensitizers

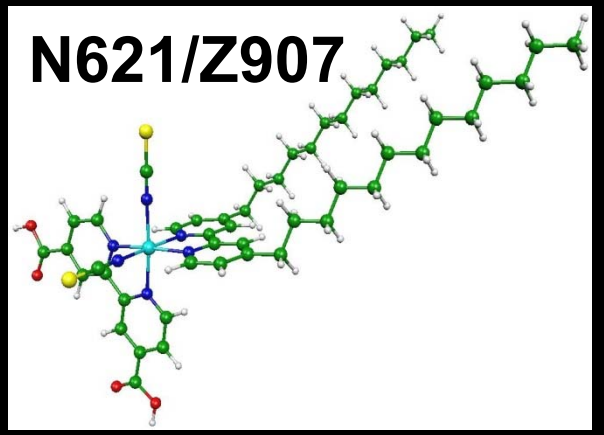
Control of protonation/ conuterions



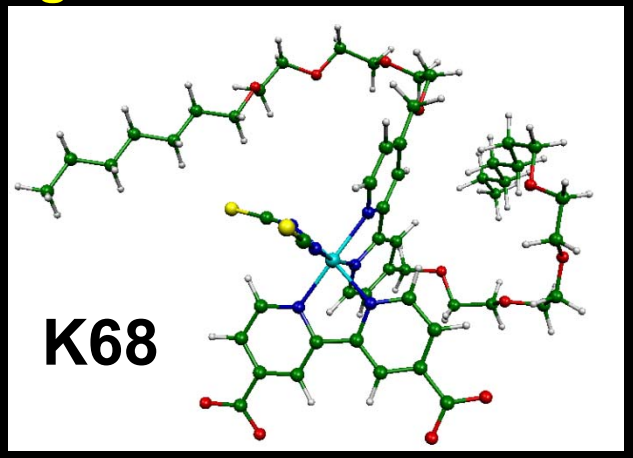
Stability/ Charge separation

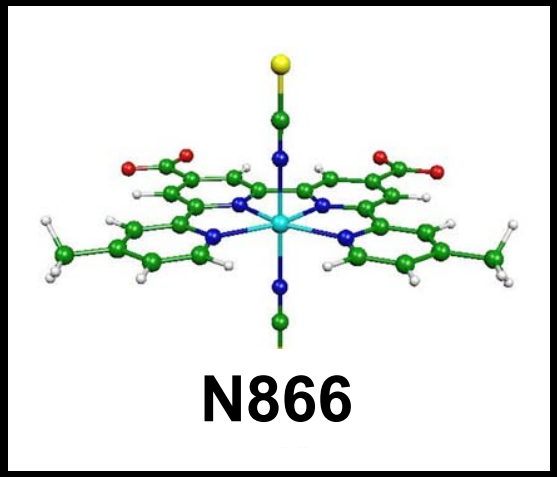


Ion-coordinating ligands

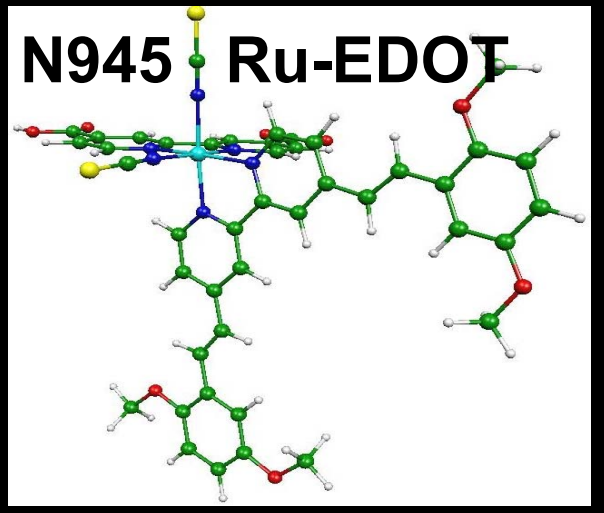


Improved light harvesting





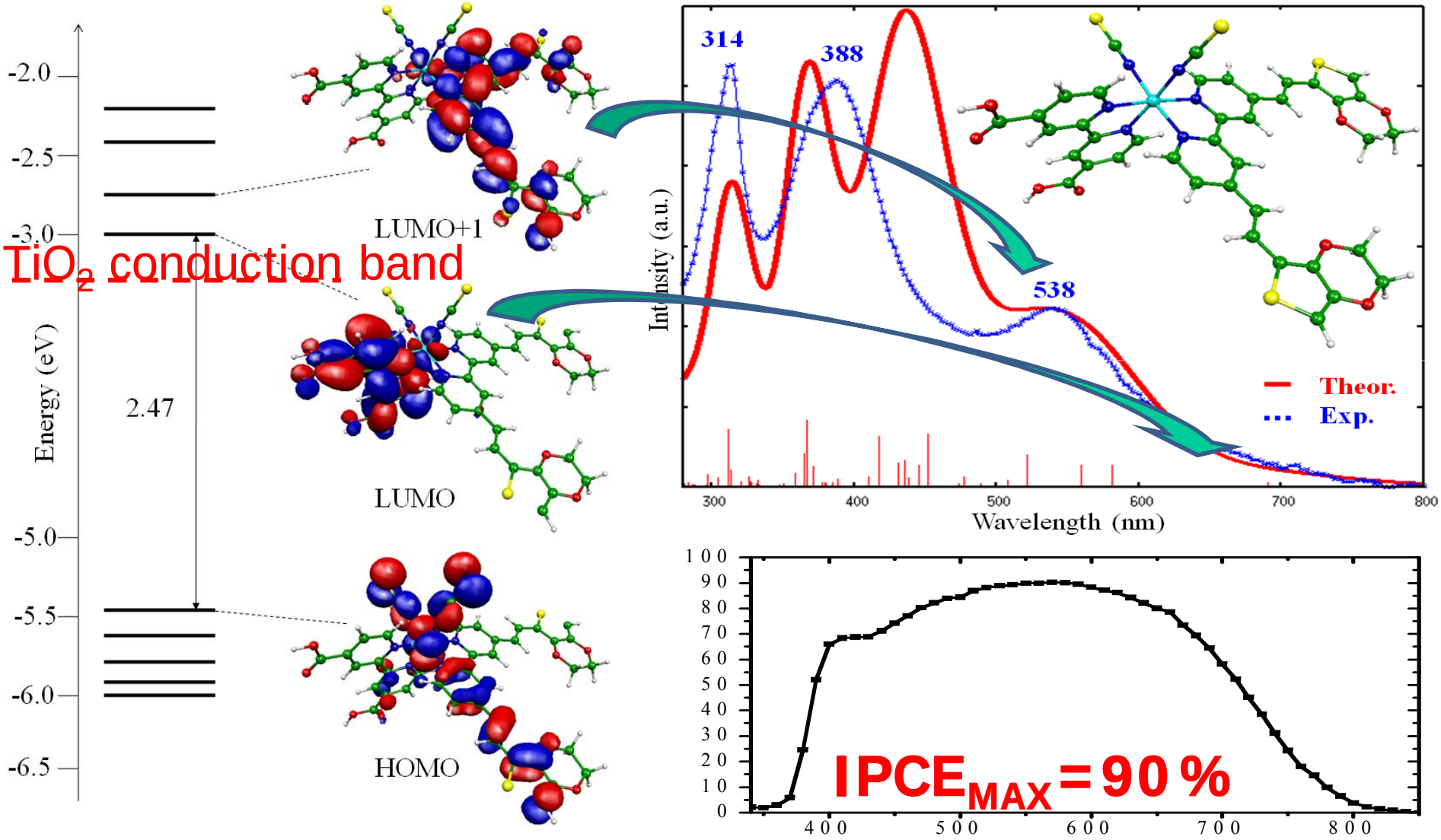
Quaterpyridil ligands
Trans isomers



Heteroleptic Ru(II) sensitizers: Ru-EDOT

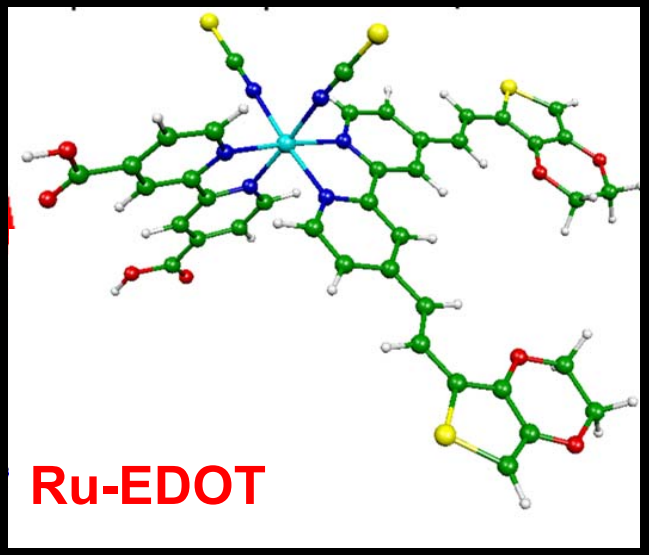
High molar extinction coefficient ⇩ **High spectral response in the red**

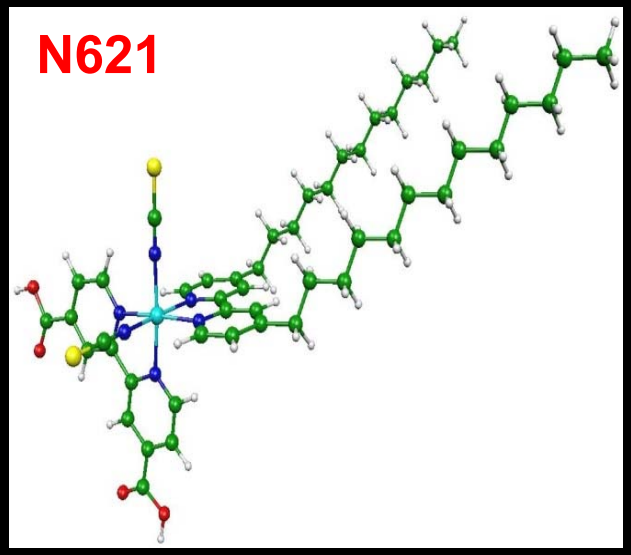
Improved photovoltaic performances

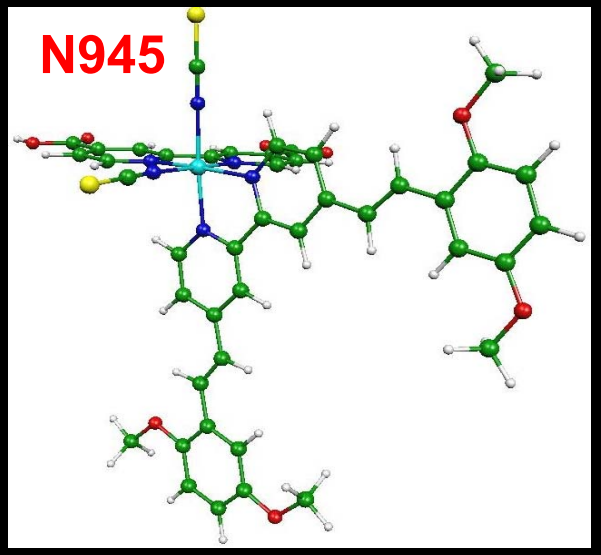


A. Abbotto, F. De Angelis, S Fantacci, M. Grätzel et al. *Chem Commun.* **2008,** 5318.

Heteroleptic Ru(II) TiO_2 sensitizers





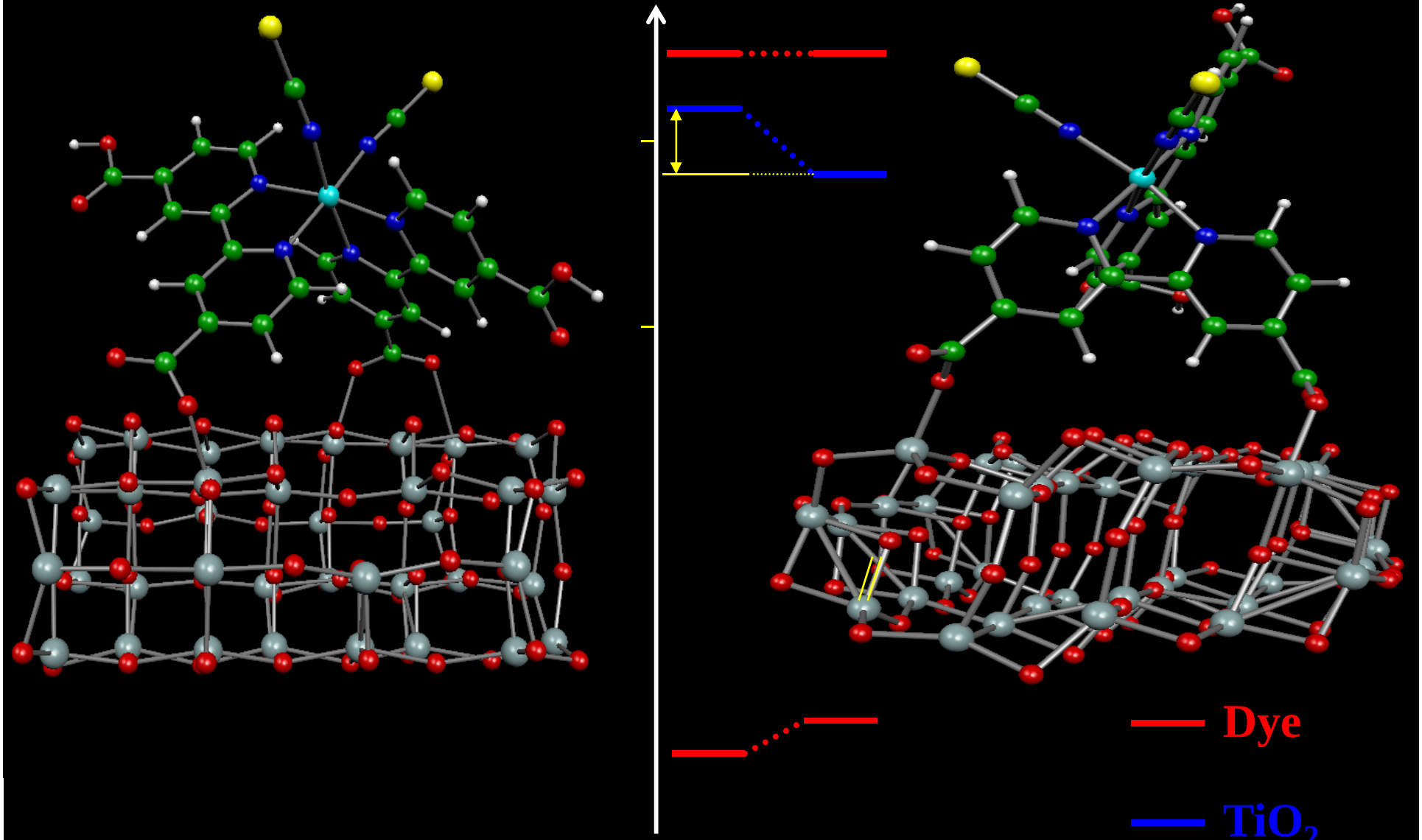


Sensitizer	Number of protons	Current mA/cm^2	Potential (mV)	Fill Factor	Efficiency at 1.5 AM
N719	2	16.66	846	0.73	10.28
N621	1	16.22	766	0.70	8.69
K19	1	16.40	768	0.73	9.19
N945	1	17.25	759	0.73	9.55
Ru-EDOT	2	19.1	663	0.72	9.11

A considerable reduction of the open circuit potential (ca. 180 mV) and therefore of the overall efficiency is observed with heteroleptic sensitizers

F. De Angelis, S. Fantacci, A. Selloni, M. Grätzel, M.K. Nazeeruddin ***Nano Lett.*** **2007, 7, 3189.**

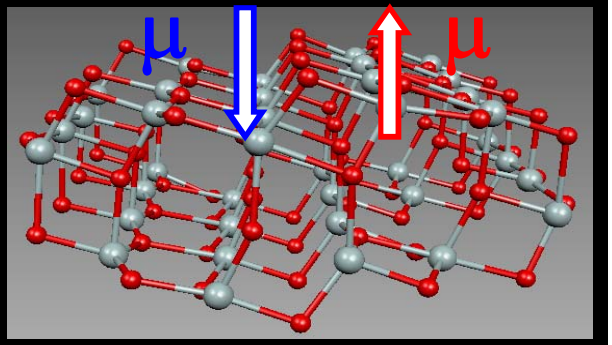
Adsorption of Homoleptic/Heteroleptic dyes on TiO_2

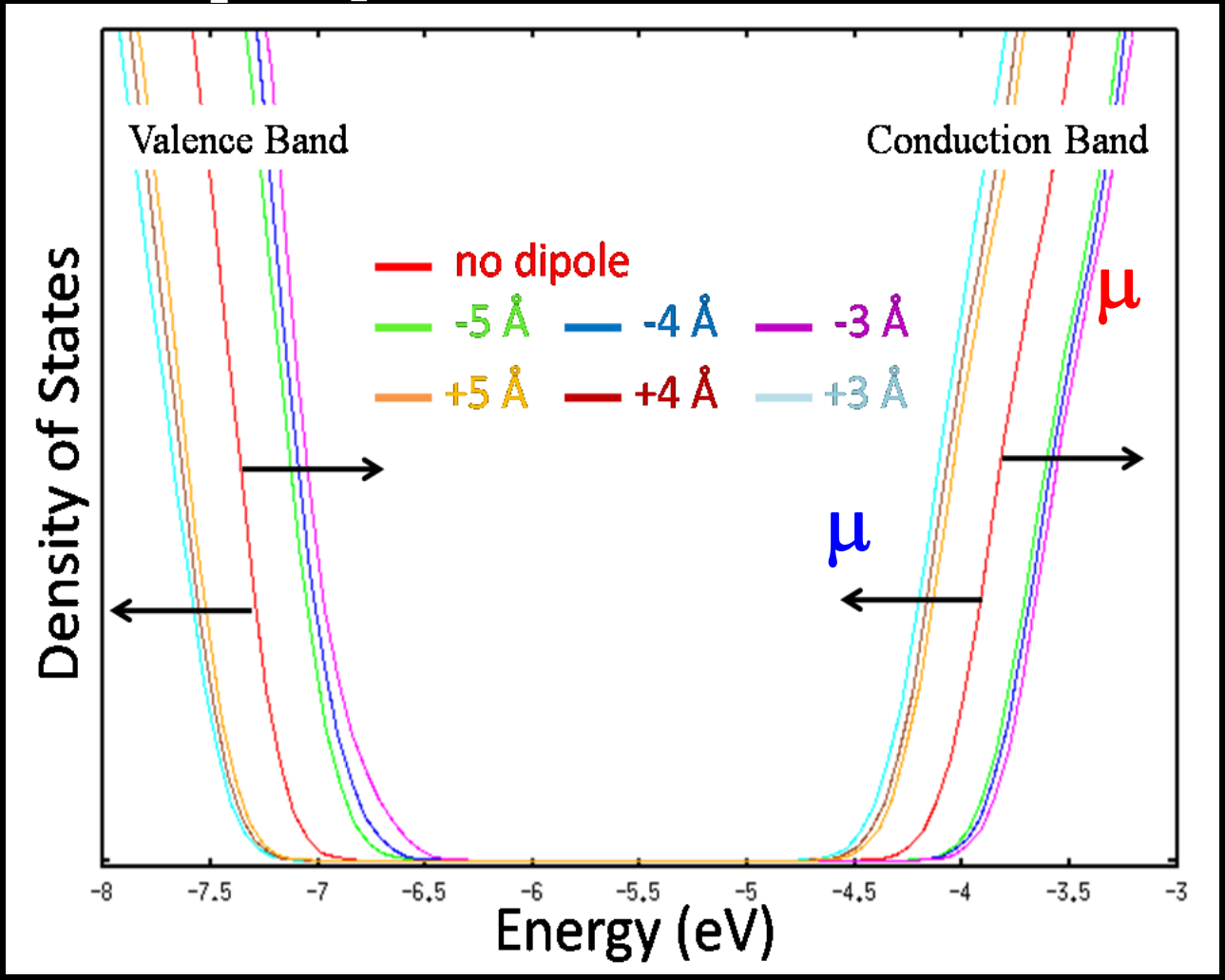


F. De Angelis, S. Fantacci, A. Selloni, M. Grätzel, M.K. Nazeeruddin ***Nano Lett.*** **2007, 7, 3189.**

Effect of a dipole (30 D) on the TiO_2 c.b.:

The sensitizer dipole and adsorption alters the TiO_2 c.b. position



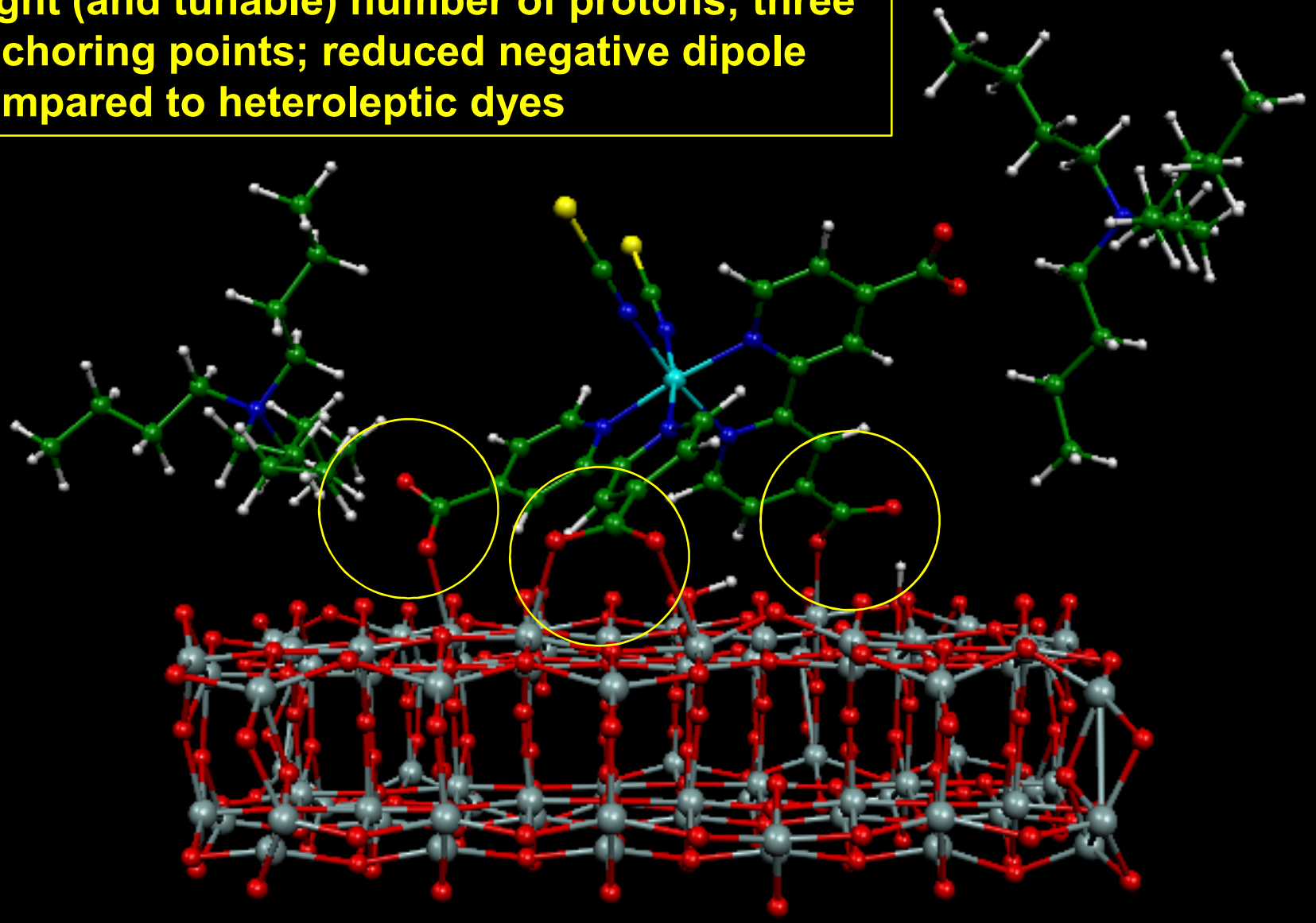


Sensitizer	Dipole components		
	μ_x	μ_y	μ_z
N719 **a**	-10.7	4.7	**-23.1**
N719 **b**	---	---	---
N719 **c**	-17.1	3.4	-29.0
N621	-16.8	1.8	**-30.1**

F. De Angelis, S. Fantacci, A. Selloni, M. Grätzel, M.K. Nazeeruddin ***Nano Lett.*** **2007, 7, 3189.**

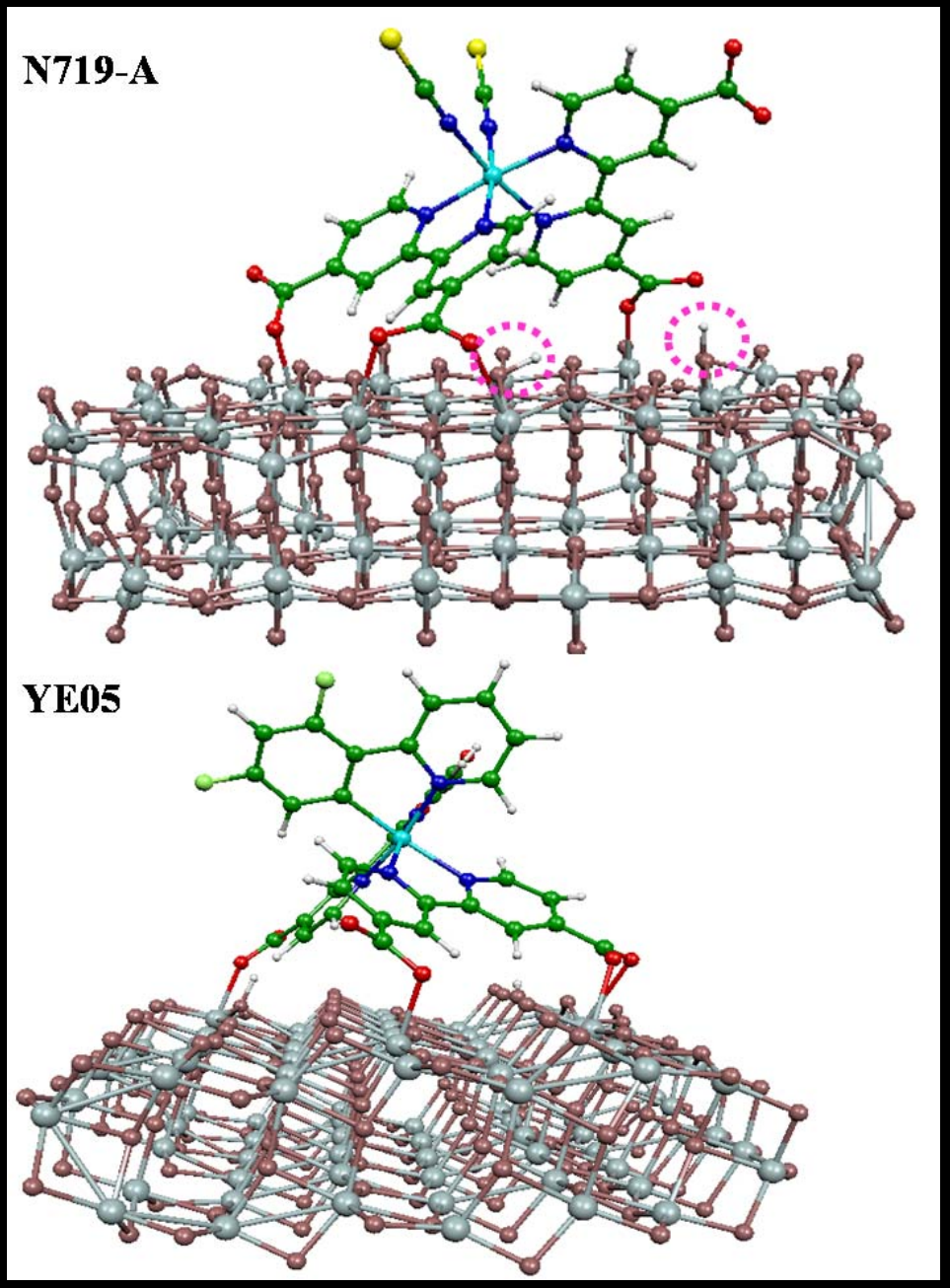
The success of N719: Adsorption geometry

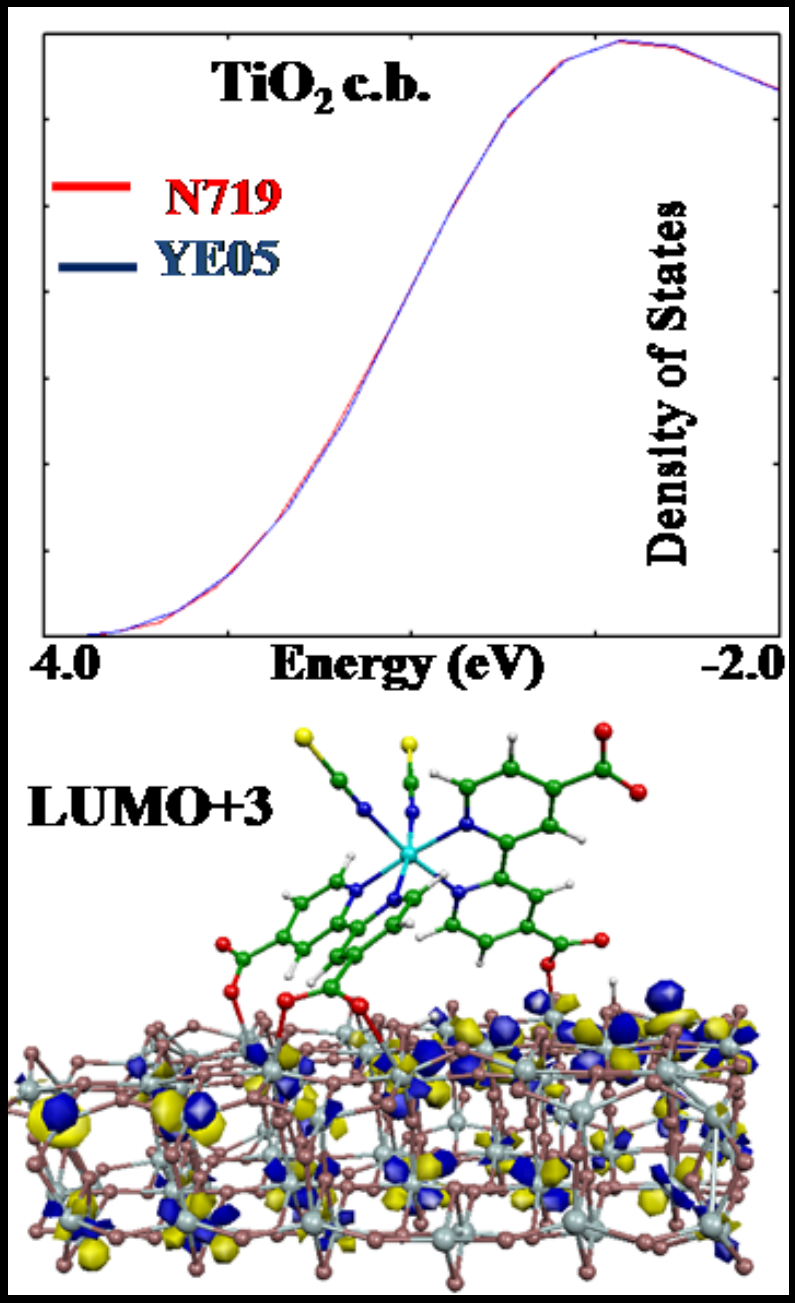
Right (and tunable) number of protons; three anchoring points; reduced negative dipole compared to heteroleptic dyes



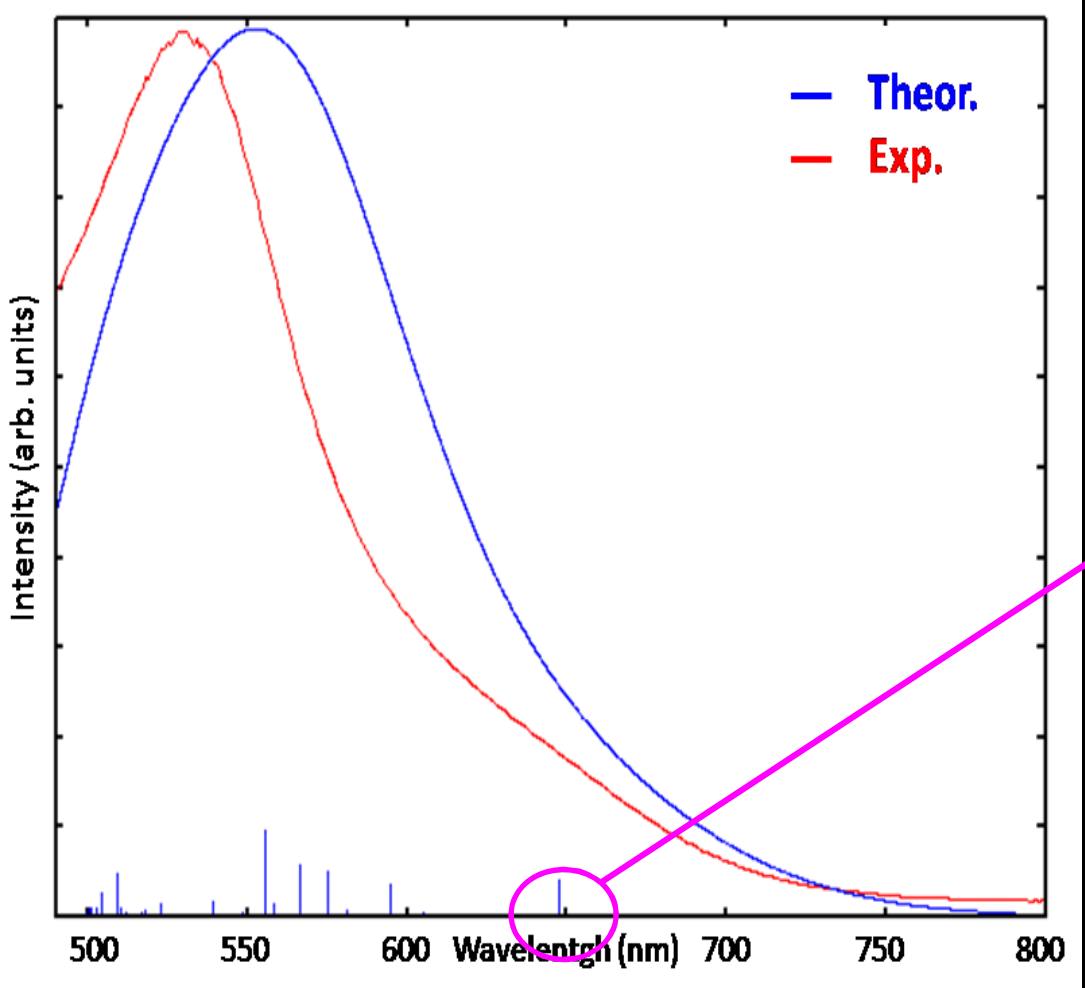
F. De Angelis, S. Fantacci, M. Grätzel, ***J. Phys .Chem***. C, 2010.

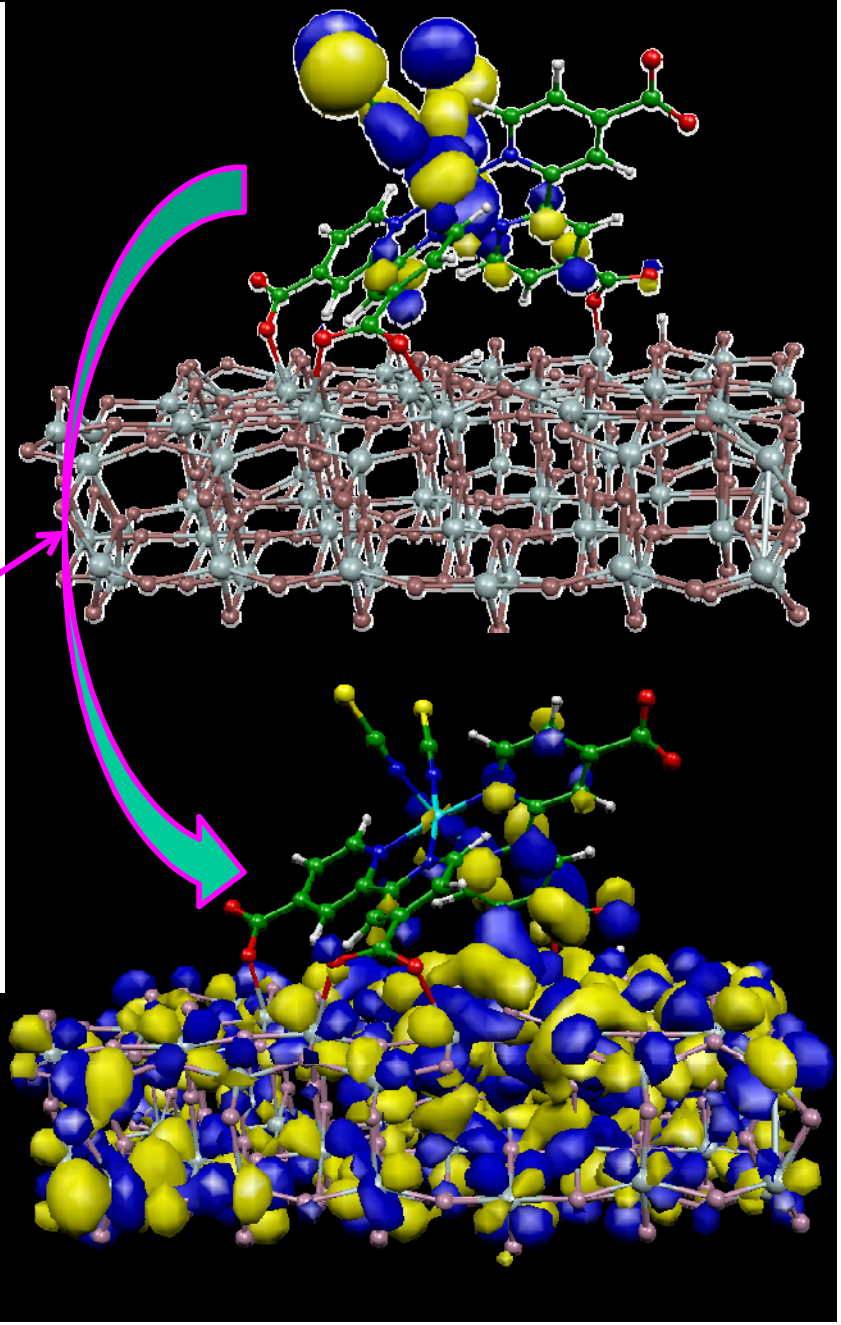
Adsorption geometry: Influence on the TiO_2 c.b.





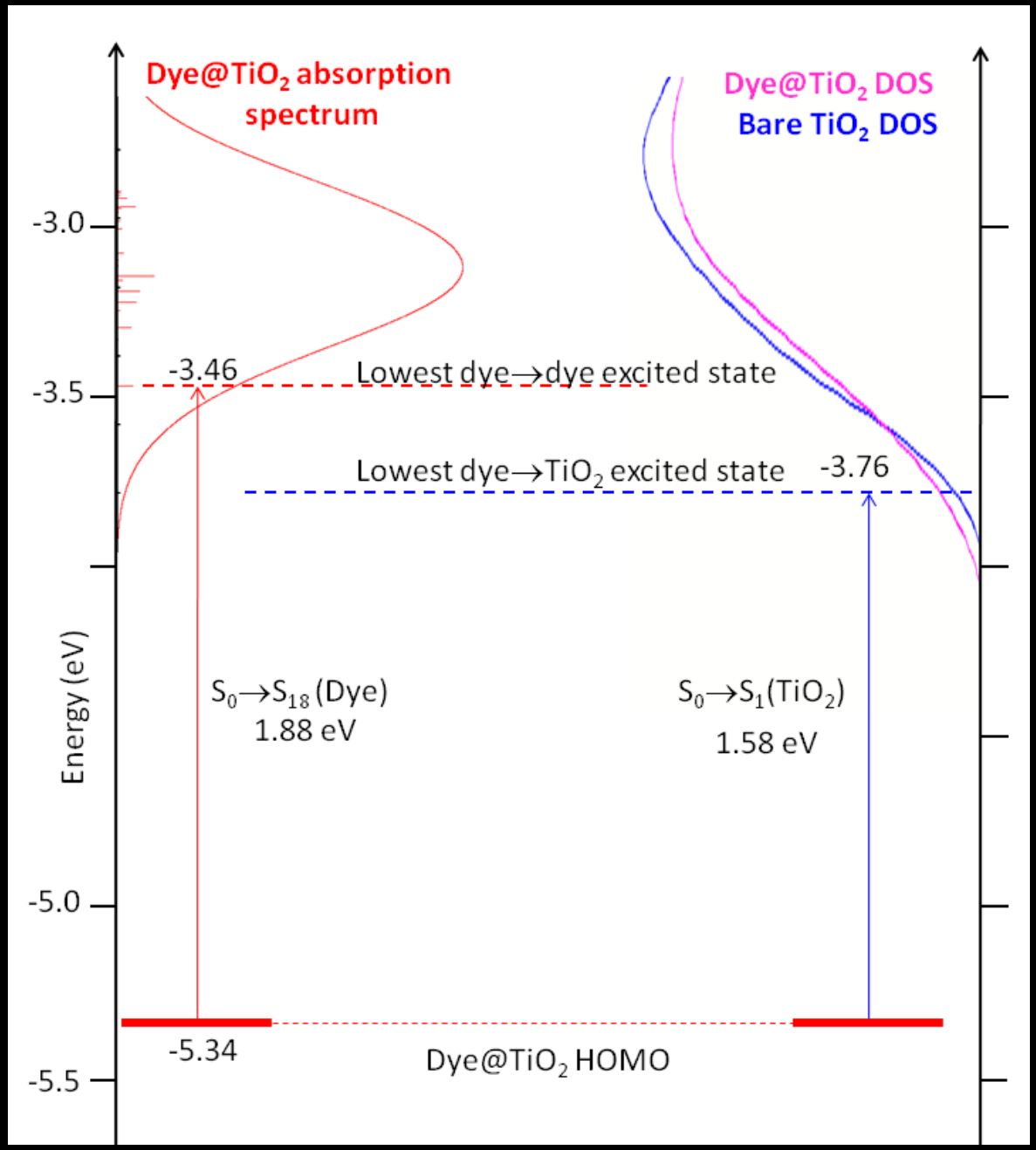
COMPARISON OF THE CALC. AND EXP. ABSORPTION SPECTRA OF N719@TIO$_2$ AND ASSIGNMENT OF THE LOWEST INTENSE TRANSITION





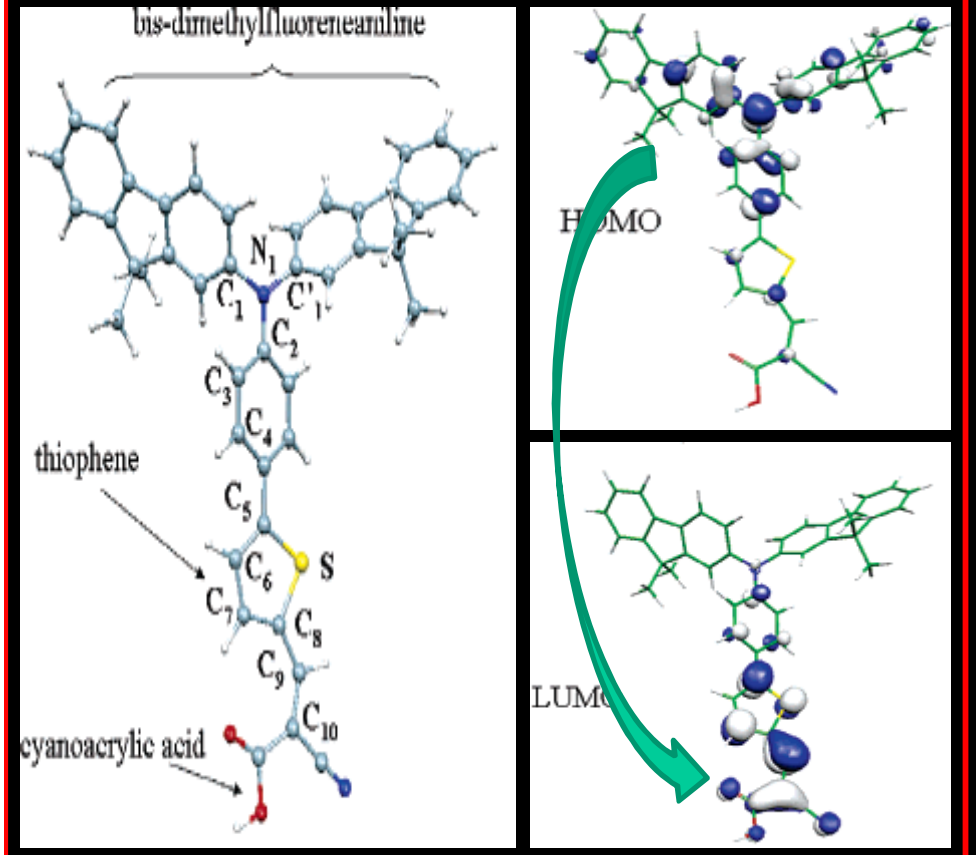
The lowest intense transition has a strong excited state delocalization into the TiO2, suggesting a strong coupling and an almost instantaneous electron transfer following light absorption.

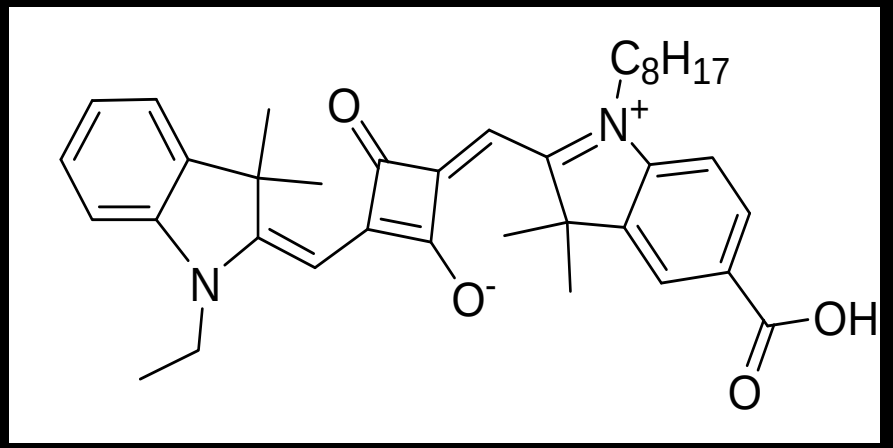
ALIGNMENT OF THE N719@TiO_2 ABSORPTION SPECTRA AND ENERGY LEVELS

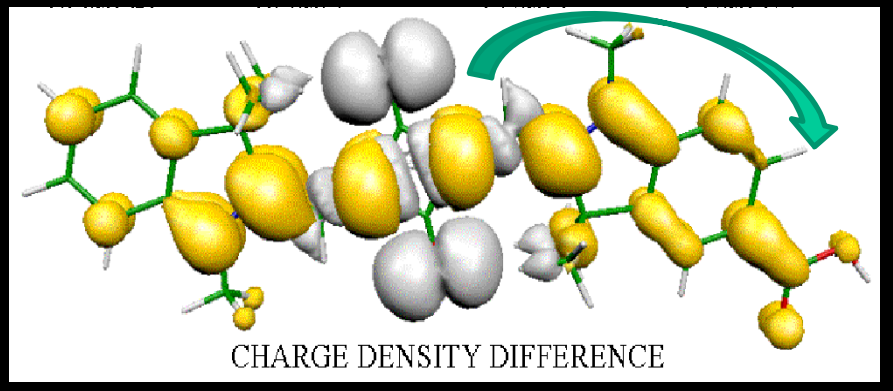


F. De Angelis, S. Fantacci, M. Grätzel, ***J. Phys .Chem***. C, 2011.

DSSCs based on organic dye-sensitizers:





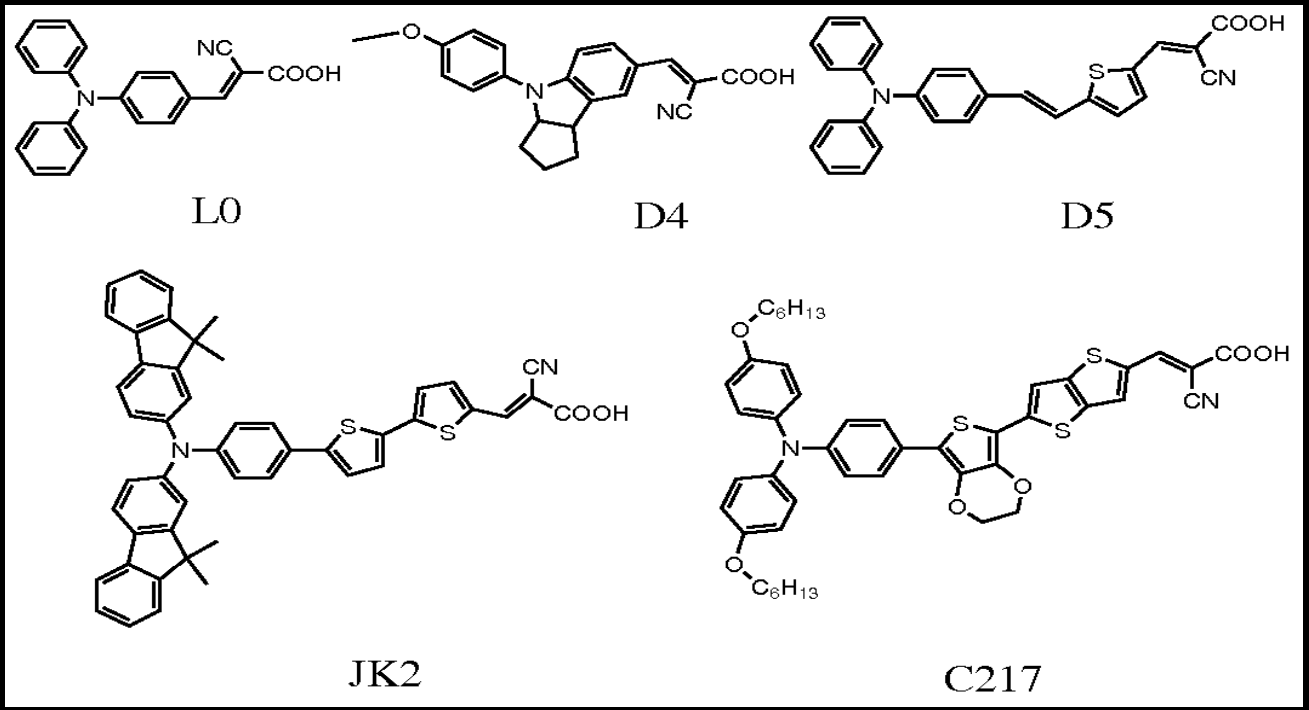


η=8.1 %

η=4.5%

- S.Kim, F. De Angelis, S. Fantacci, M. Grätzel, et al. ***J. Am. Chem. Soc.*** **2006, 128, 16701.**
- J.-H. Yum, F. De Angelis, M. Grätzel, et al. ***J. Am. Chem. Soc.*** **2007, 129, 10320.**
- D.P. Hagberg, F. De Angelis, M. Grätzel, et al. ***J. Am. Chem. Soc.*** **2008, 130, 6259.**
- M. Pastore, F. De Angelis, M. Grätzel, et al. ***J. Phys. Chem. C.*** **2010, in press.**

Electronic structure of standalone organic dyes :



Dye	Solvent	λ_{max} (nm)	E_{exc} (eV)
D4	Ethanol	390	3.18
L0	Ethanol	386	3.21
	Acetonitrile	373	3.32
D5	Ethanol	441	2.81
	Methanol+Acid	474	2.62
	Acetonitrile	427	2.90
C217	Chloroform	551	2.25
JK2	Ethanol[7]	436	2.84

Benchmark of quantum methods for organic dyes :

		TDDFT			Wavefunction methods			
Dye	**Λ**	**B3LYP**	**MPW1K**	**C-B3LYP**	**CCSD**	**NEVPT2**	**RI-CC2**	**CASSCF**
D4	0.52	3.10	3.46	3.48	3.53	3.64	3.16	4.24
L0	0.51	2.99	3.40	3.45	3.59	3.49	3.16	4.26
D5	0.47	2.23	2.70	2.97	-	-	2.72	-
C217	0.38	1.96	2.50	2.64	-	-	2.50	-
JK2	0.35	1.99	2.60	2.78	-	-	2.68	-

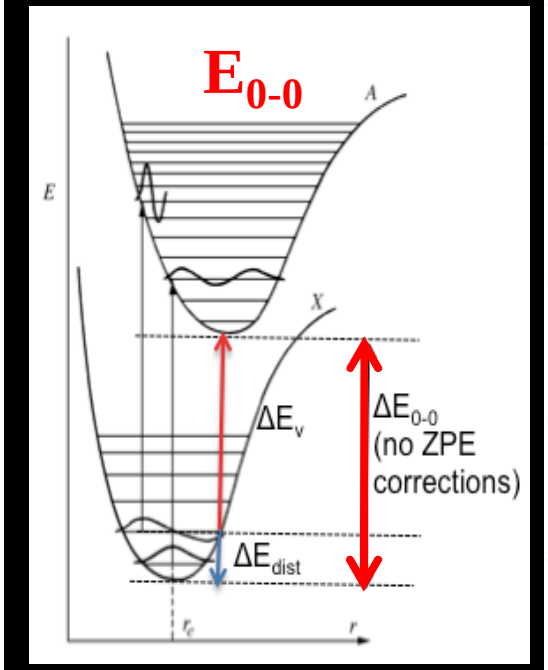
TDDFT well behaves when increasing the dye CT

Dye	**MPW1K**				**B3LYP**				**Exp.**
	protonated		deprotonated		protonated		deprotonated		
	E_{exc}	F	E_{exc}	f	E_{exc}	f	E_{exc}	f	E_{exc}
D4	3.17	1.250	3.51	1.139	2.81	1.053	3.07	0.935	3.18
L0	3.15	1.075	3.46	0.661	2.73	0.886	2.89	0.469	3.21-3.32
D5	2.48	1.673	2.86	1.740	2.00	1.201	2.38	1.129	2.62-2.90
C217	2.32	1.924	2.67	2.148	1.74	1.065	2.15	1.543	2.25
JK2	2.45	1.549	2.81	1.714	1.82	0.767	2.26	0.880	2.84

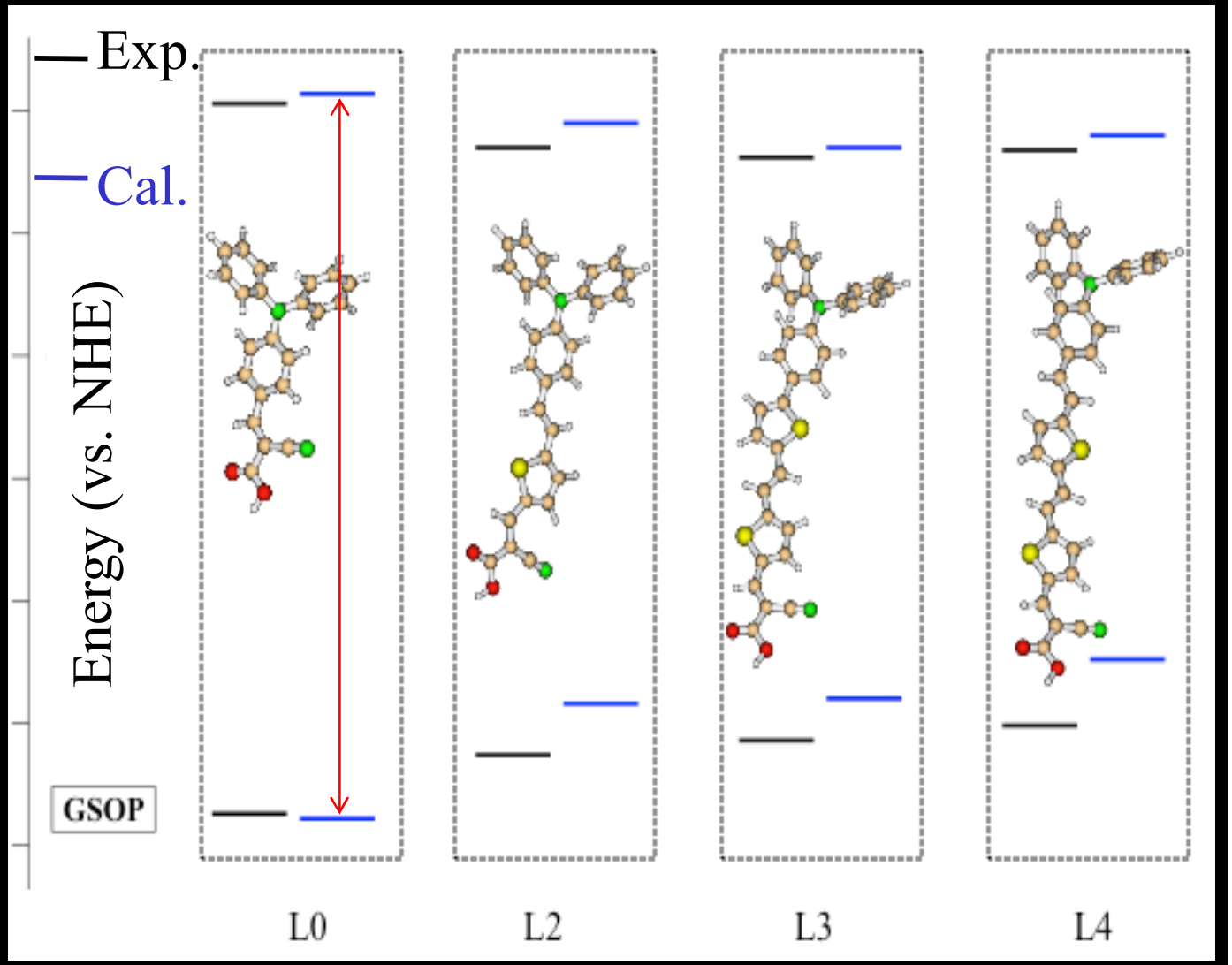
•M. Pastore, F. De Angelis, M. Grätzel, et al. J*. **Phys. Chem. C.*** **2010.**

TDDFT prediction of the ground and excited state oxidation potential of organic dyes

ESOP=GSOP + $E_{0\text{-}0}$

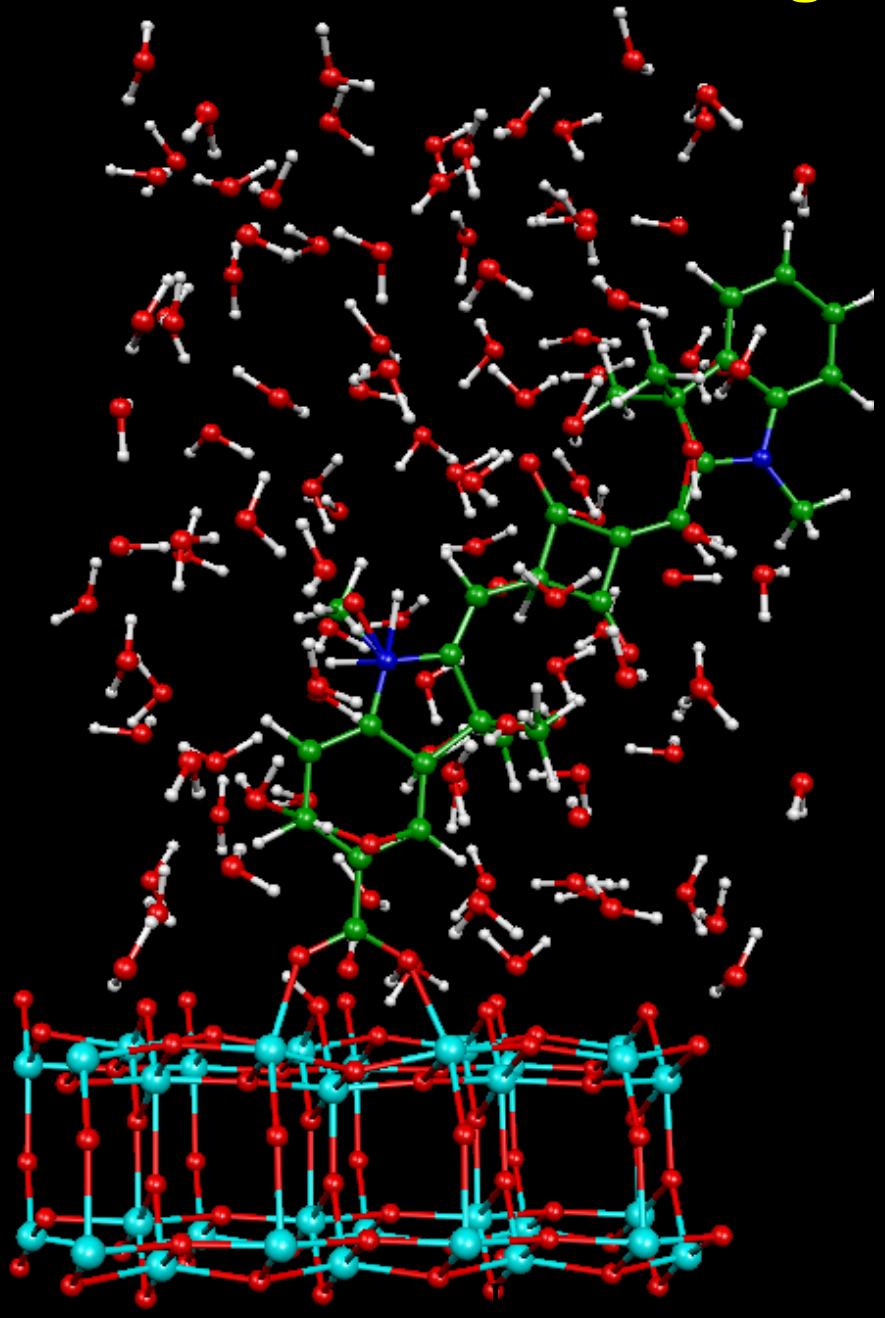


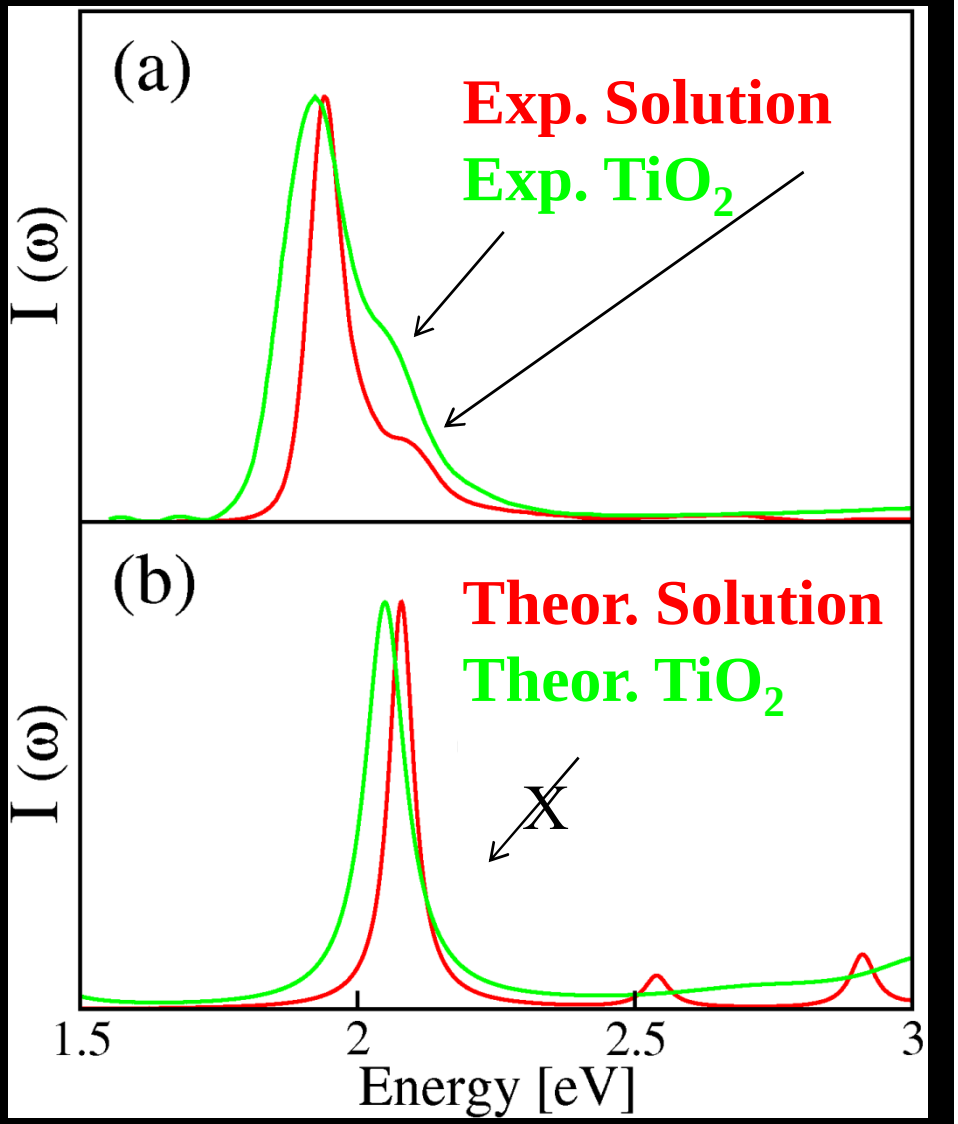
CALCULATE
THE GSOP ***AND*** THE
EXCITED STATE
GEOMETRY



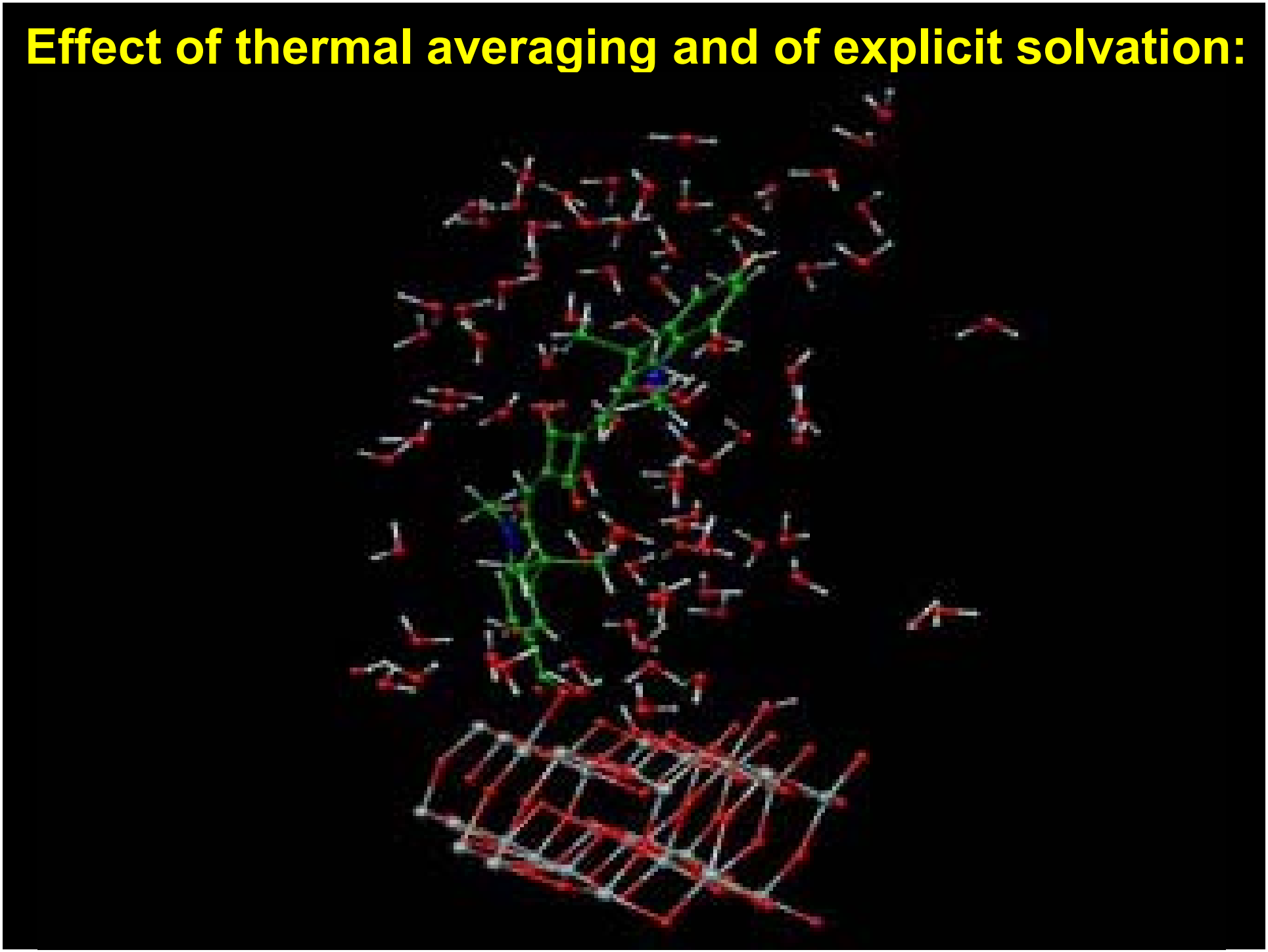
M. Pastore, F. De Angelis ***J. Phys. Chem. C* 2011**.

Effect of thermal averaging and of explicit solvation:

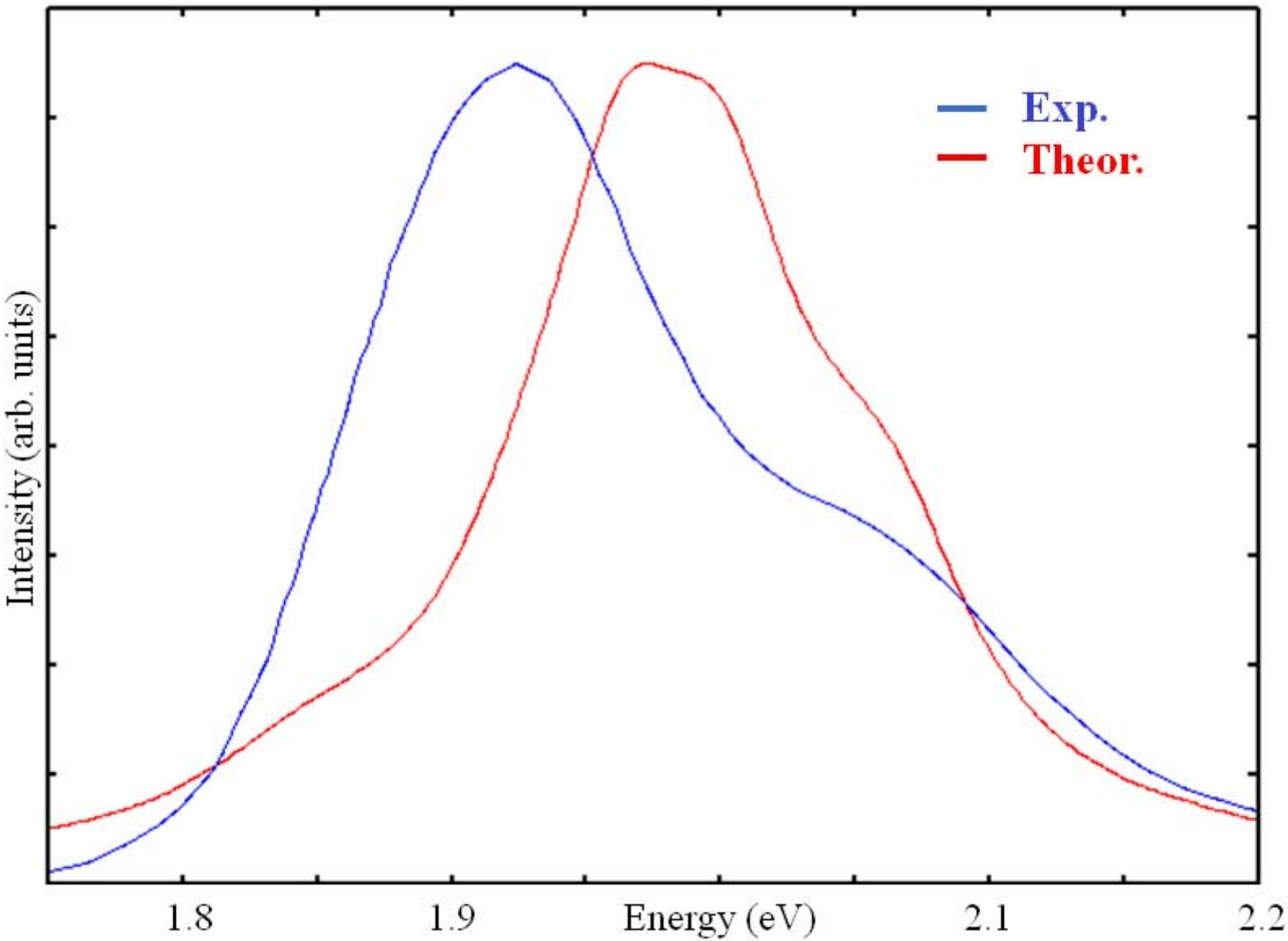




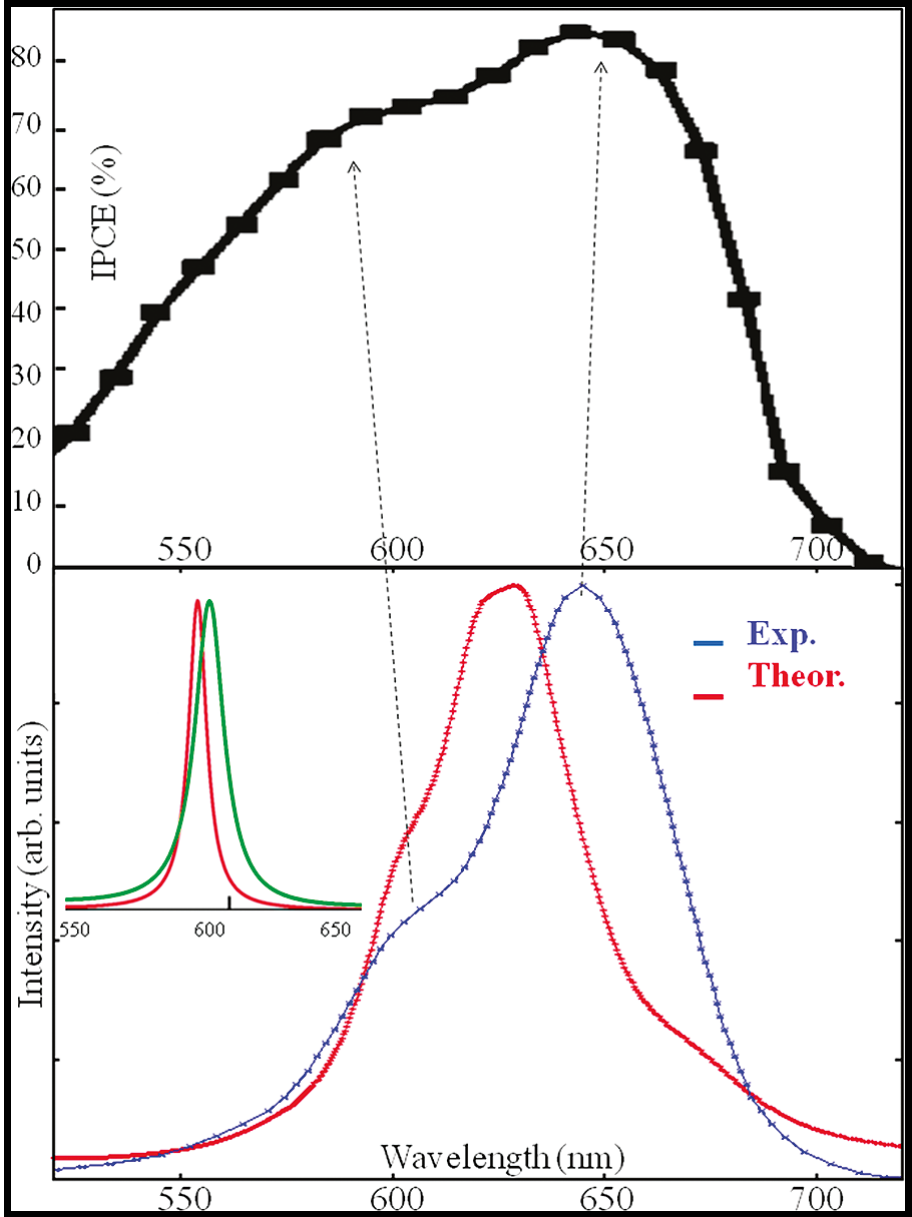
Effect of thermal averaging and of explicit solvation:

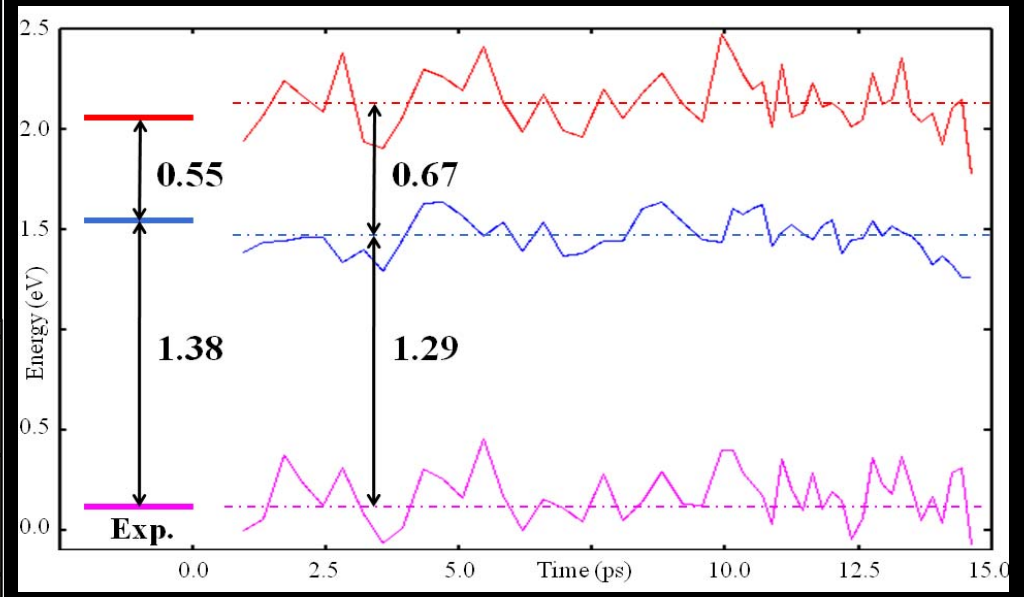


Solution thermally averaged absorption spectum:



Effect of thermal averaging and of explicit solvation

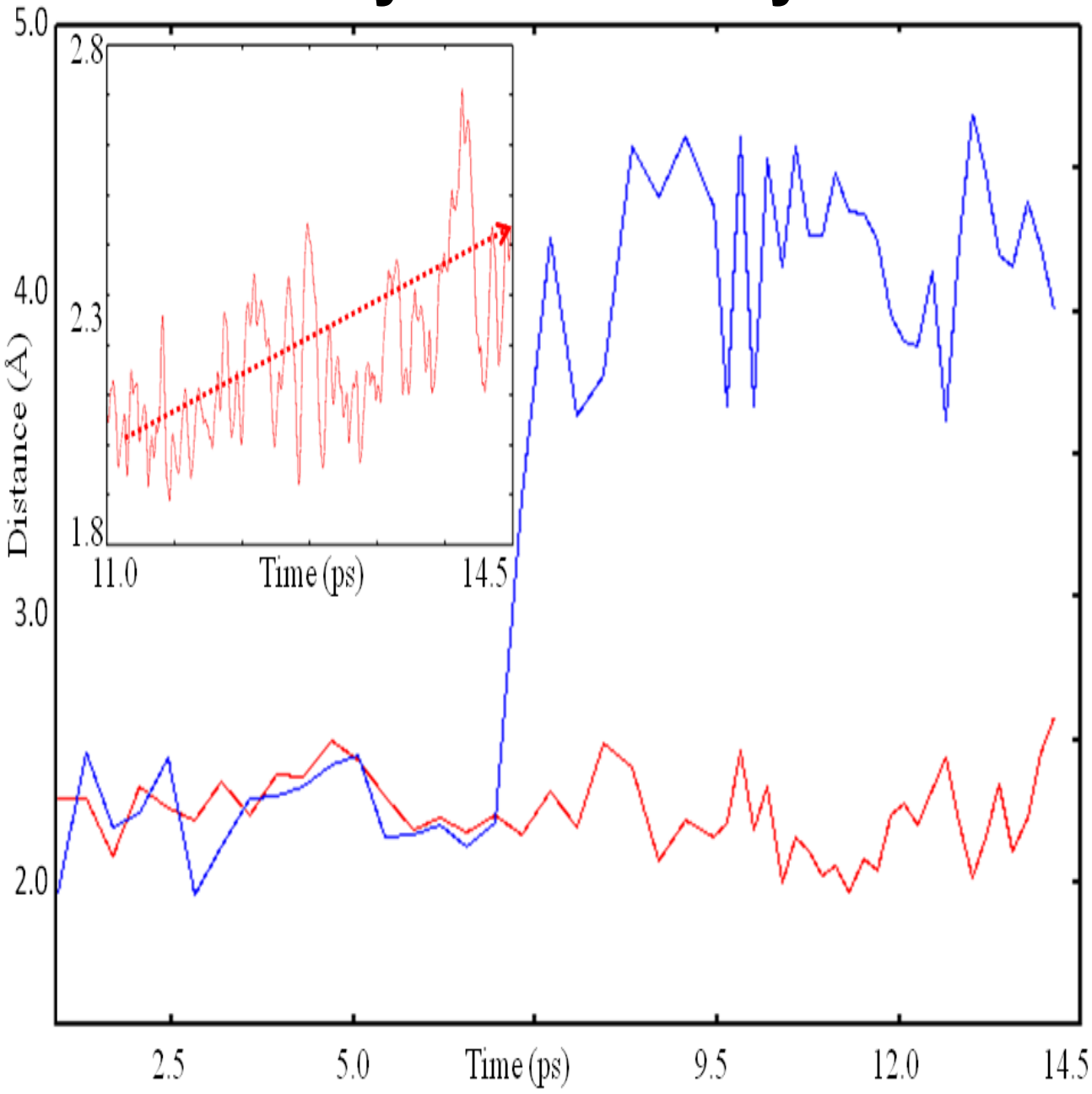


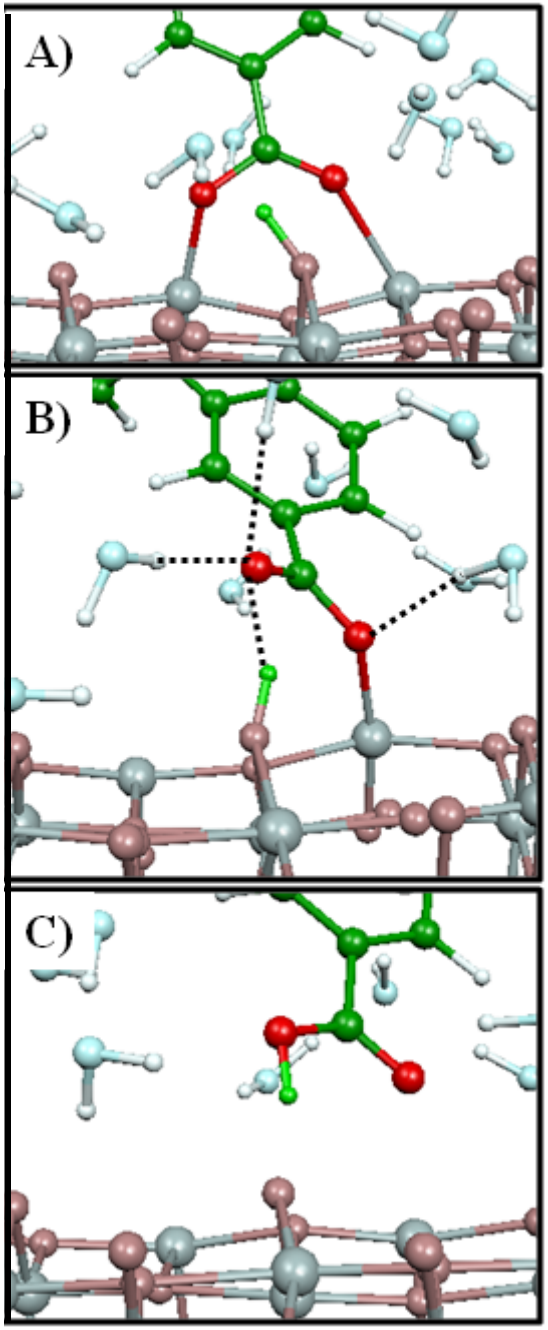


Alignment of energy levels

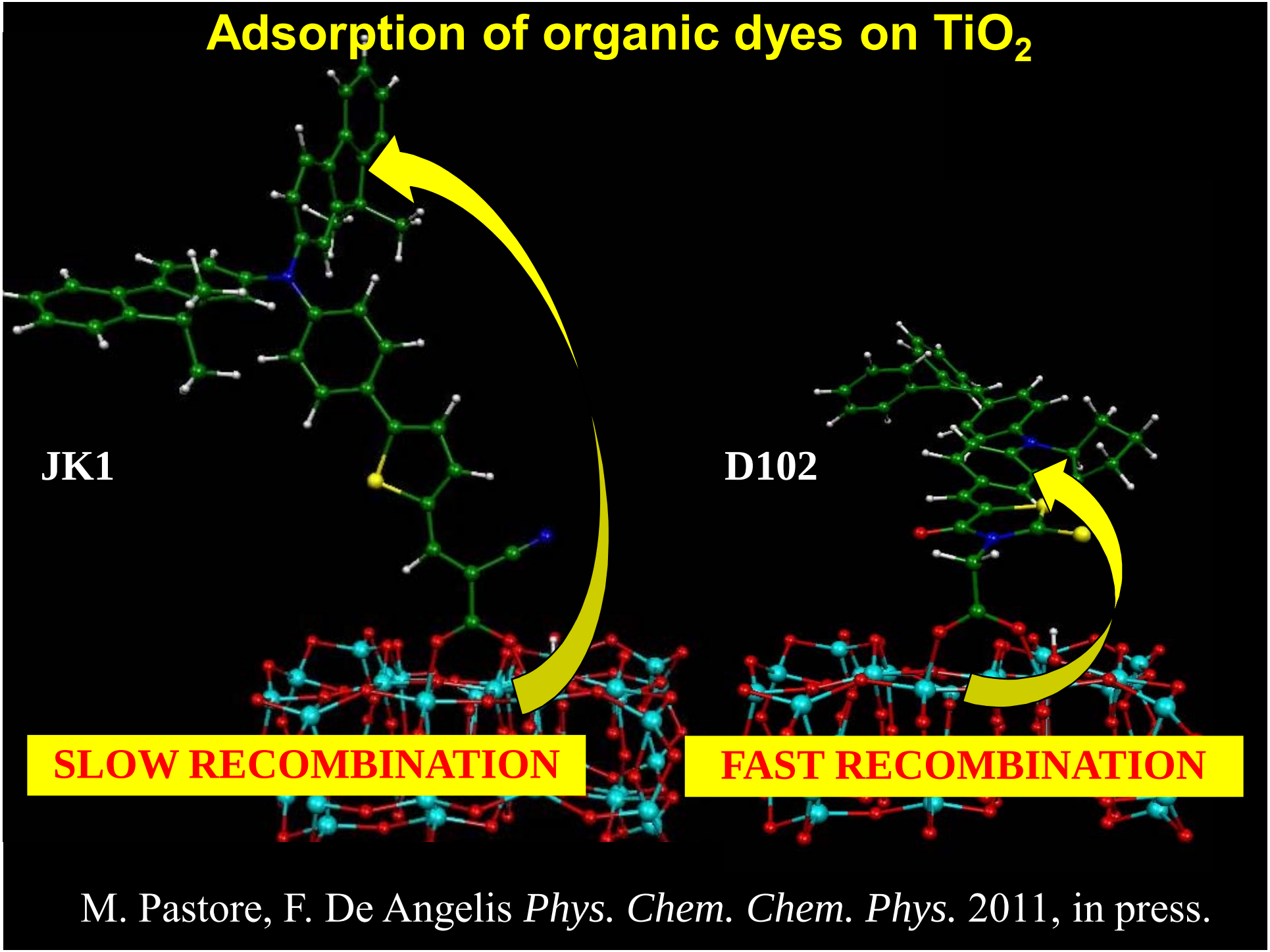
F. De Angelis, S. Fantacci, R. Gebauer. *J. Phys. Chem. Lett.* **2011**.

Dynamics analysis:



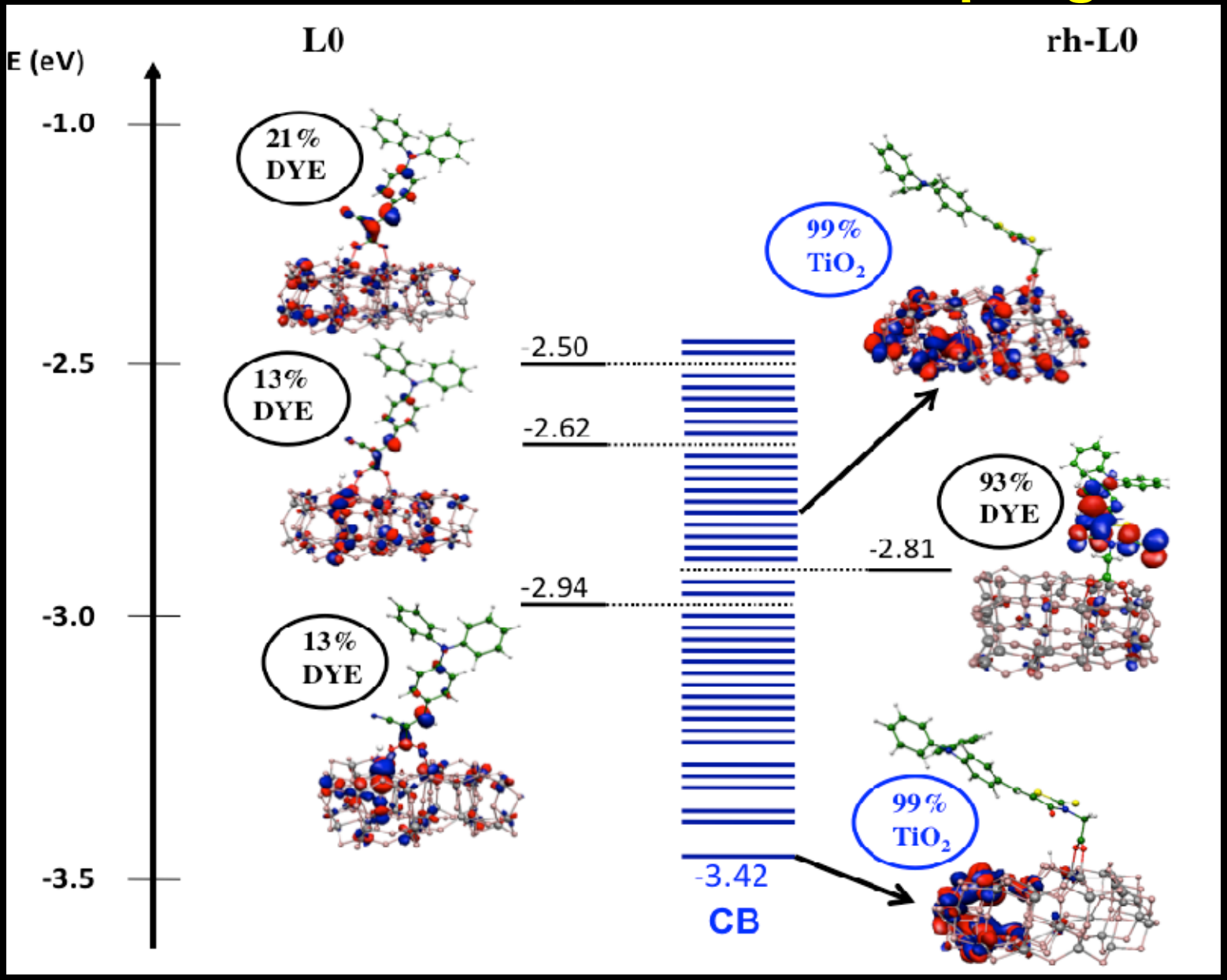


Adsorption of organic dyes on TiO_2



M. Pastore, F. De Angelis *Phys. Chem. Chem. Phys.* 2011, in press.

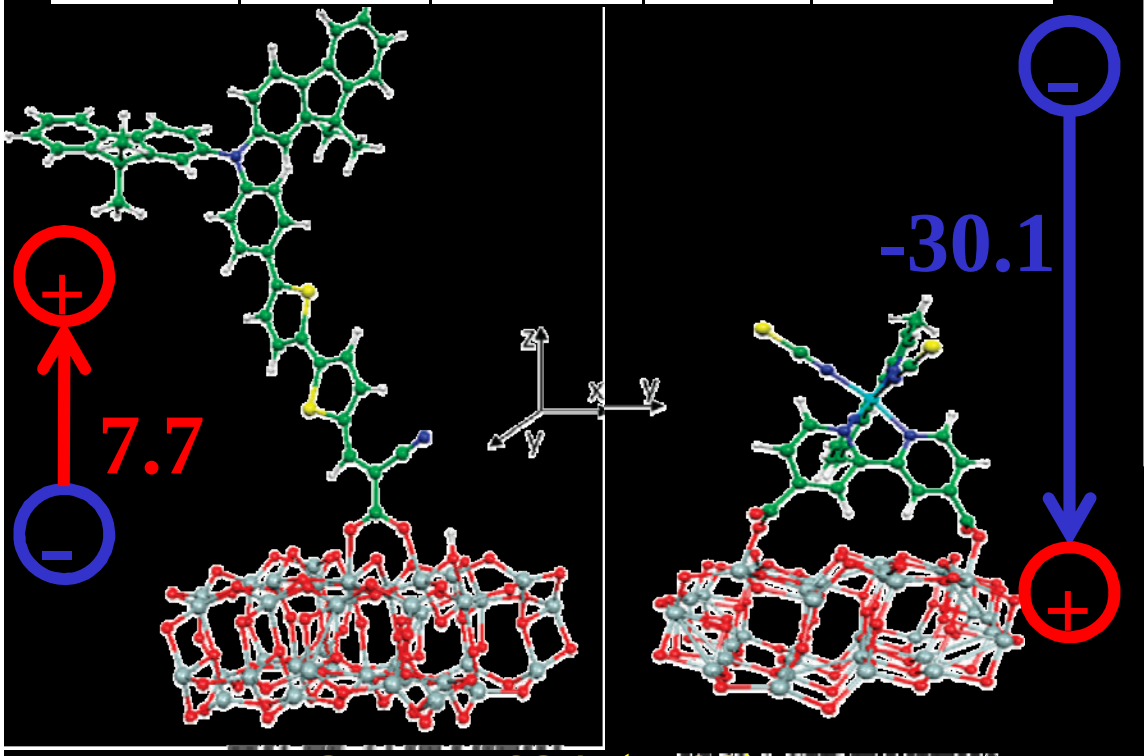
Similar structure, different coupling



M. Pastore, F. De Angelis *Phys. Chem. Chem. Phys.* 2011, in press.

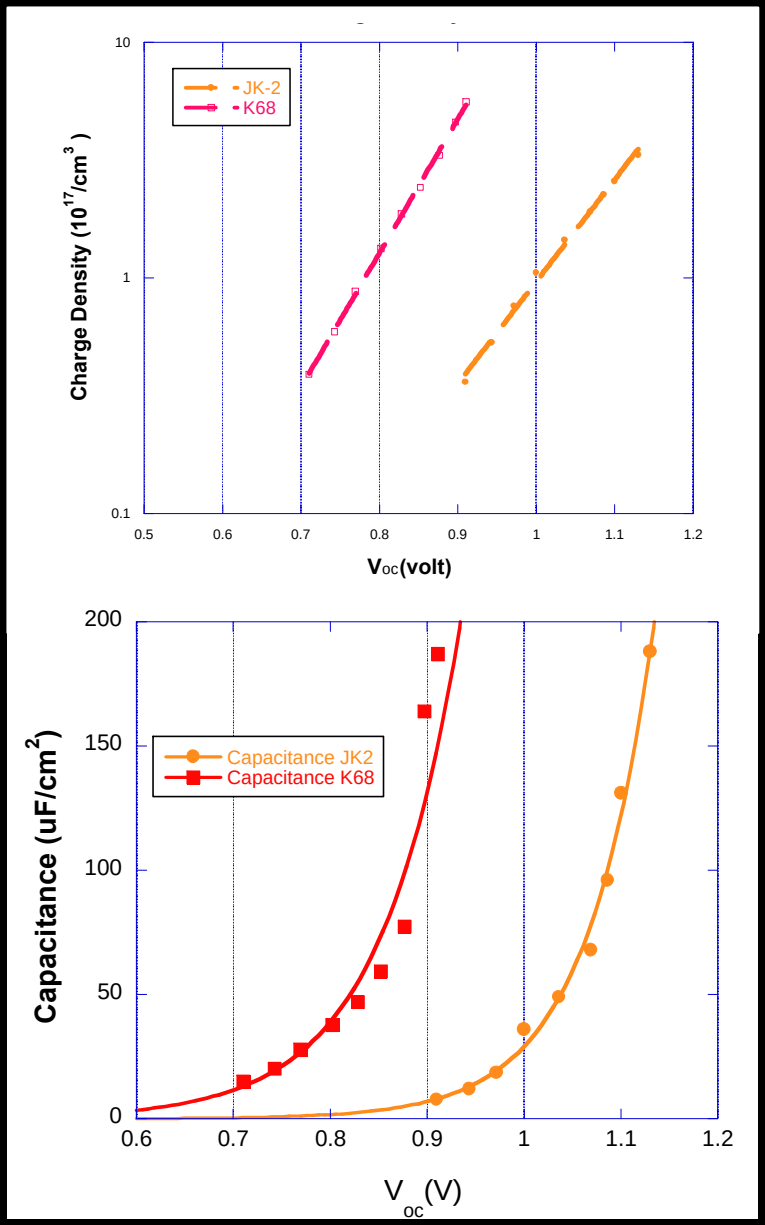
Sensitizer Dipole : Organic vs. Ru-dyes in SS-DSC

Dye	V_{oc}(mV)	J_{sc} (mA/cm^2)	FF(%)	Efficiency (%)
JK2	1087.5	3.85	67.7	3.17
K68	896.7	5.7	76.1	3.88



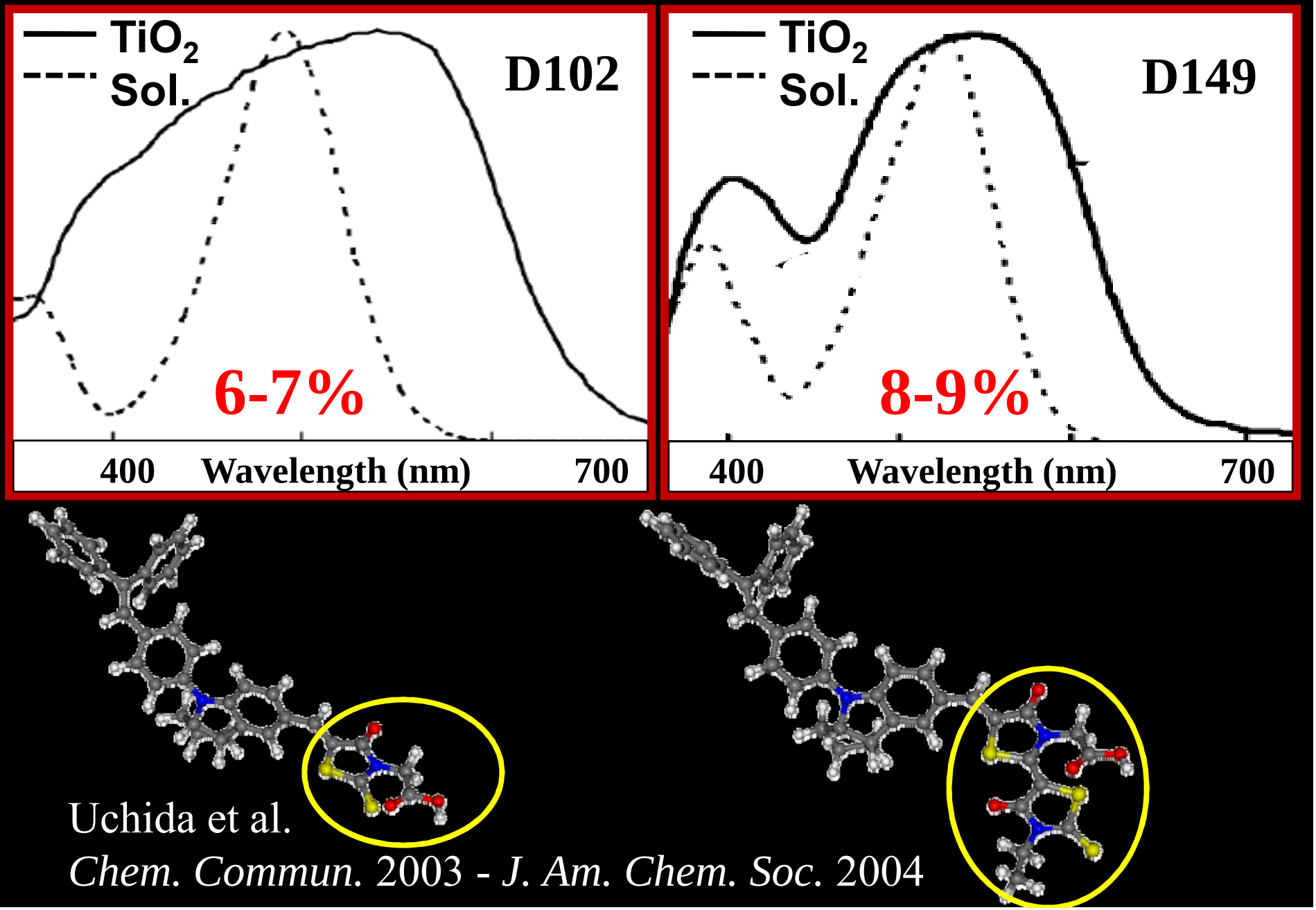
JK2 vs. N621 (K68)

Organic dyes have a positive dipole, shiting TiO2 c.b. at higher energy



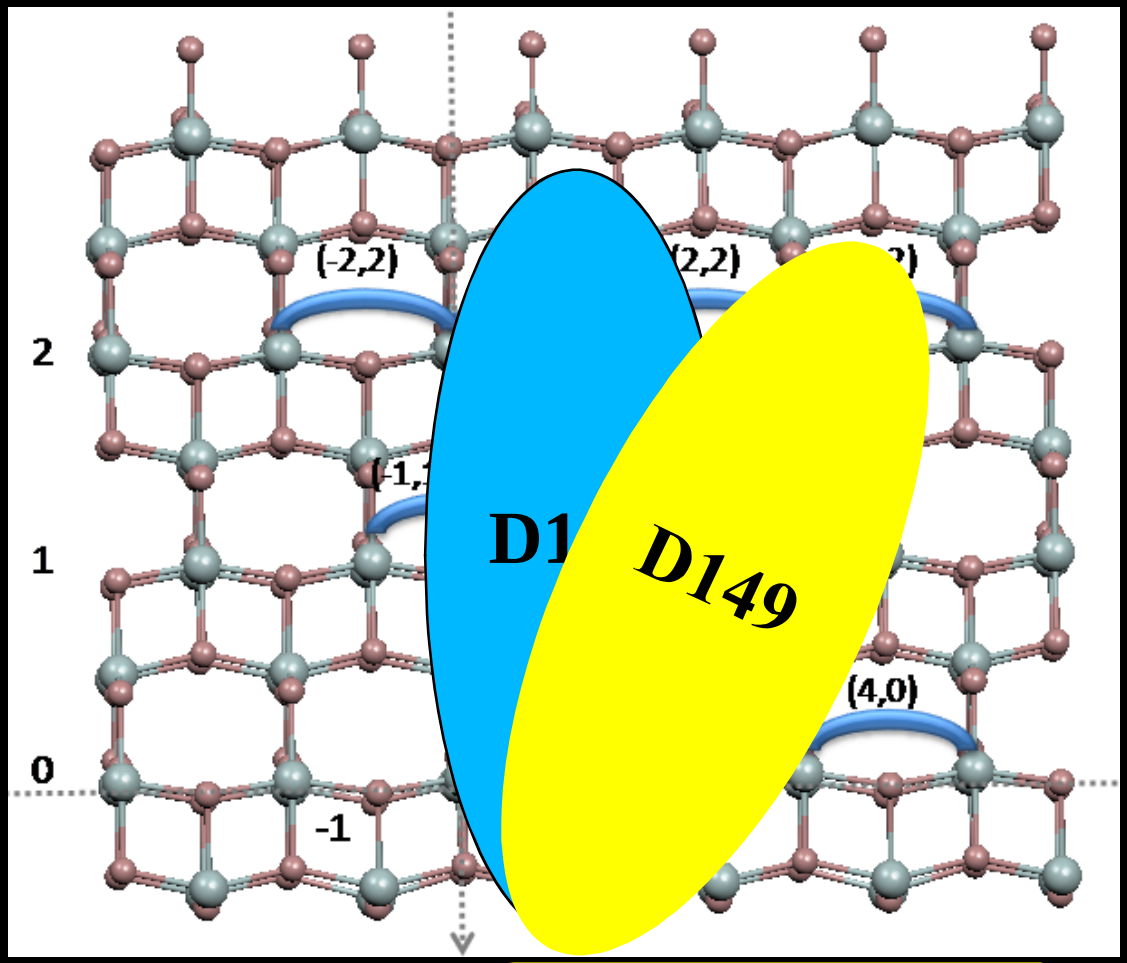
Chen, F. De Angelis, Md. K. Nazeeruddin, M. Grätzel, ***Nano Lett.*** **2009**, 9, 2489.

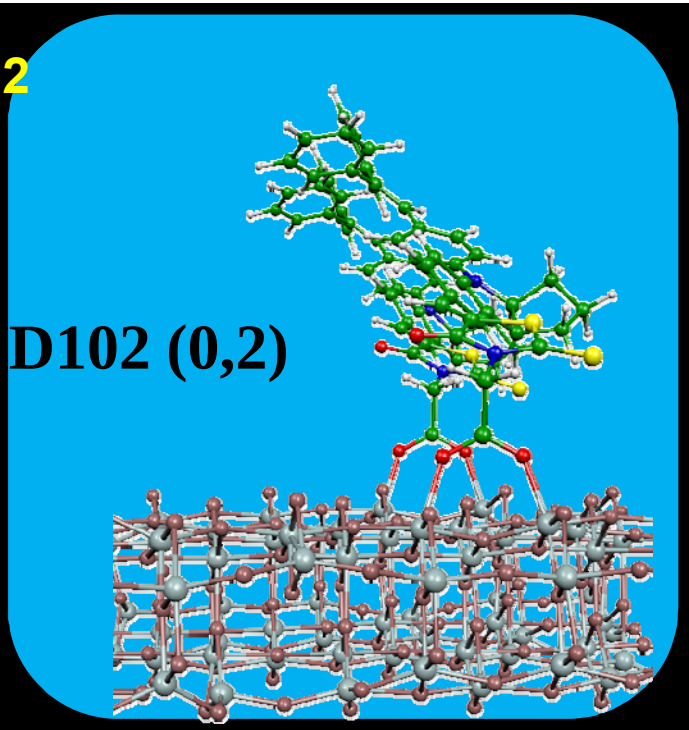
Indoline dyes: Dye Aggregation on TiO_2

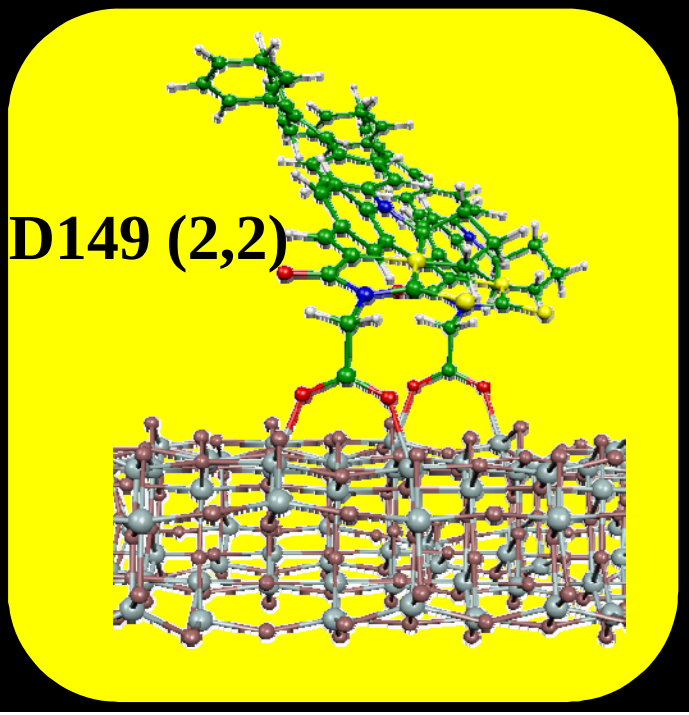


Uchida et al.
Chem. Commun. 2003 - *J. Am. Chem. Soc.* 2004

Aggregation of D102/D149 on TiO_2





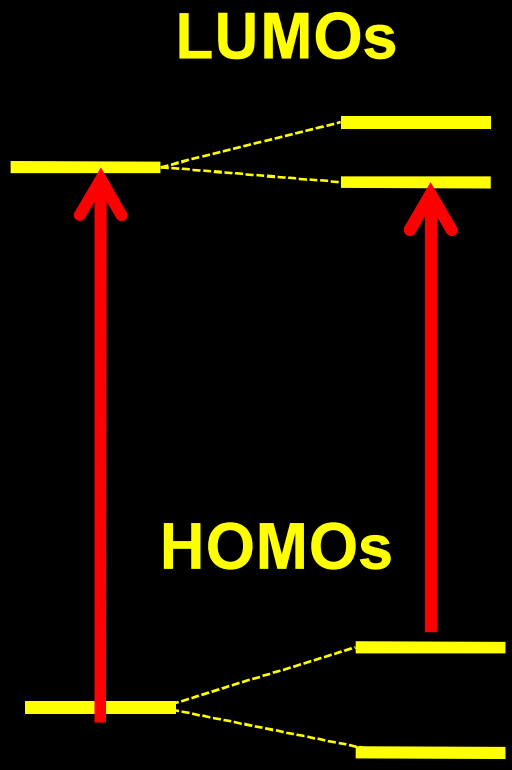


Interaction energies (kcal/mol)

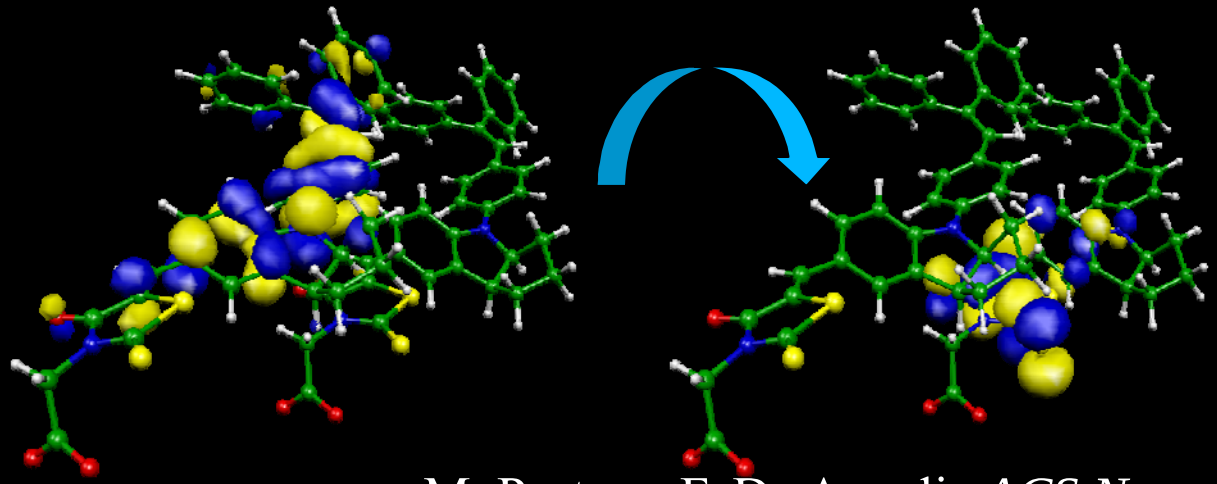
Dimer	D102	D149
(0,2)	0.0	4.5
(2,2)	3.9	0.0
(-1,1)	1.2	N/A

Aggregation on TiO_2: Electronic properties

	Monomer		Dimer			
Dye	Exc.	f	Exc.	f	Shift	Exp.
D102	2.11	0.82	**1.96** 2.10 2.18 2.28	**0.022** 1.016 0.537 0.001	0.15	0.22
D149	2.06	0.80	**1.97** 2.05 2.07 2.23	**0.007** 0.720 0.784 0.001	0.08	0.06



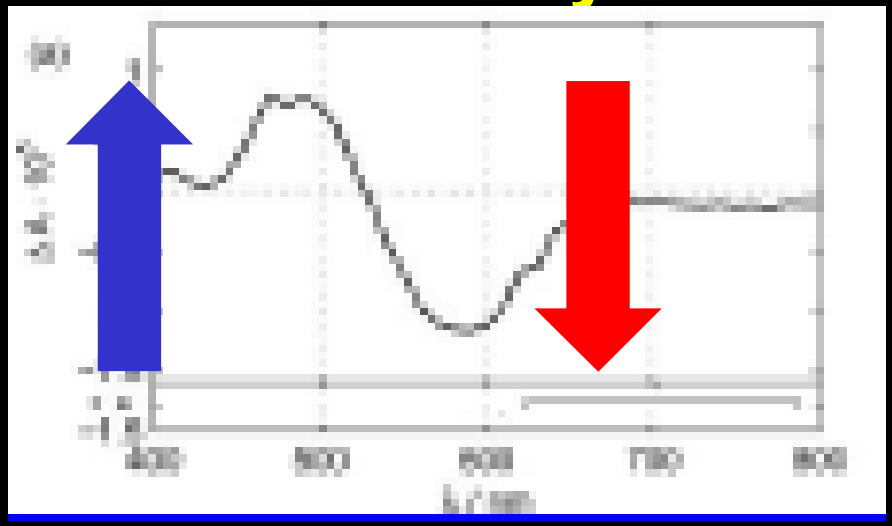
Excited states:



Monomer **Dimer**

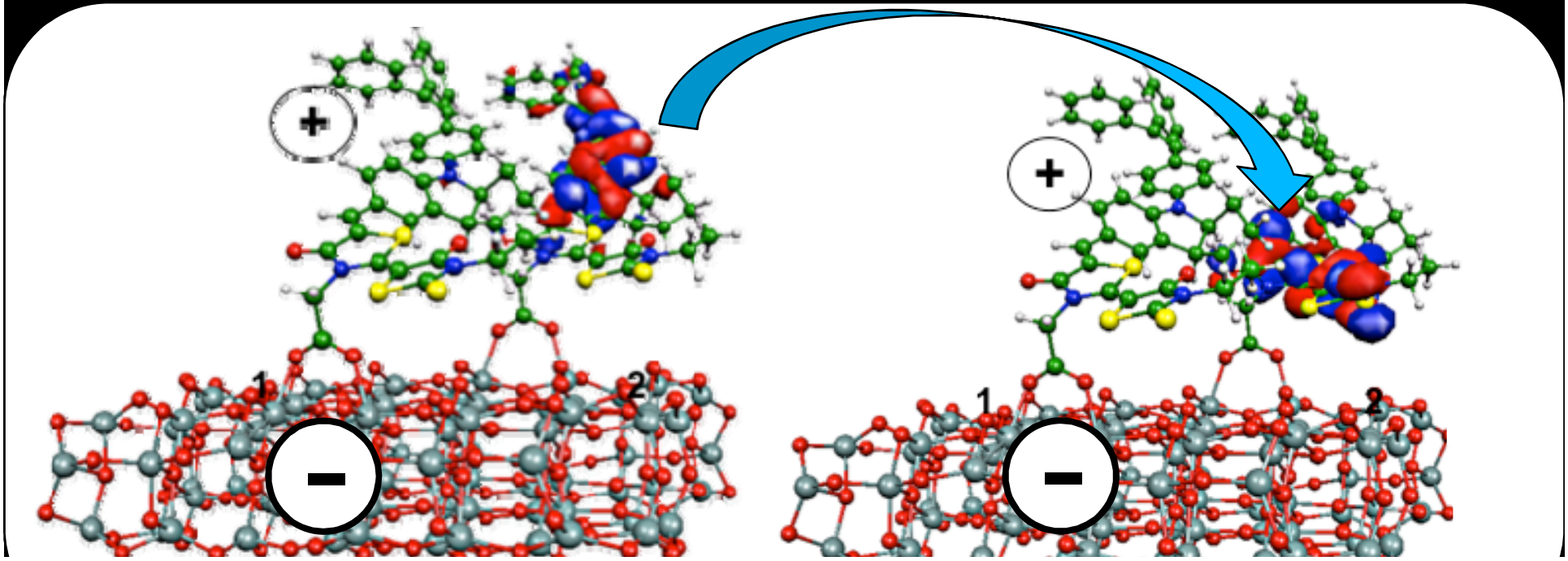
M. Pastore, F. De Angelis *ACS Nano*, **2010**, 4, 556.

Stark effects in dye-sensitized heterointerfaces



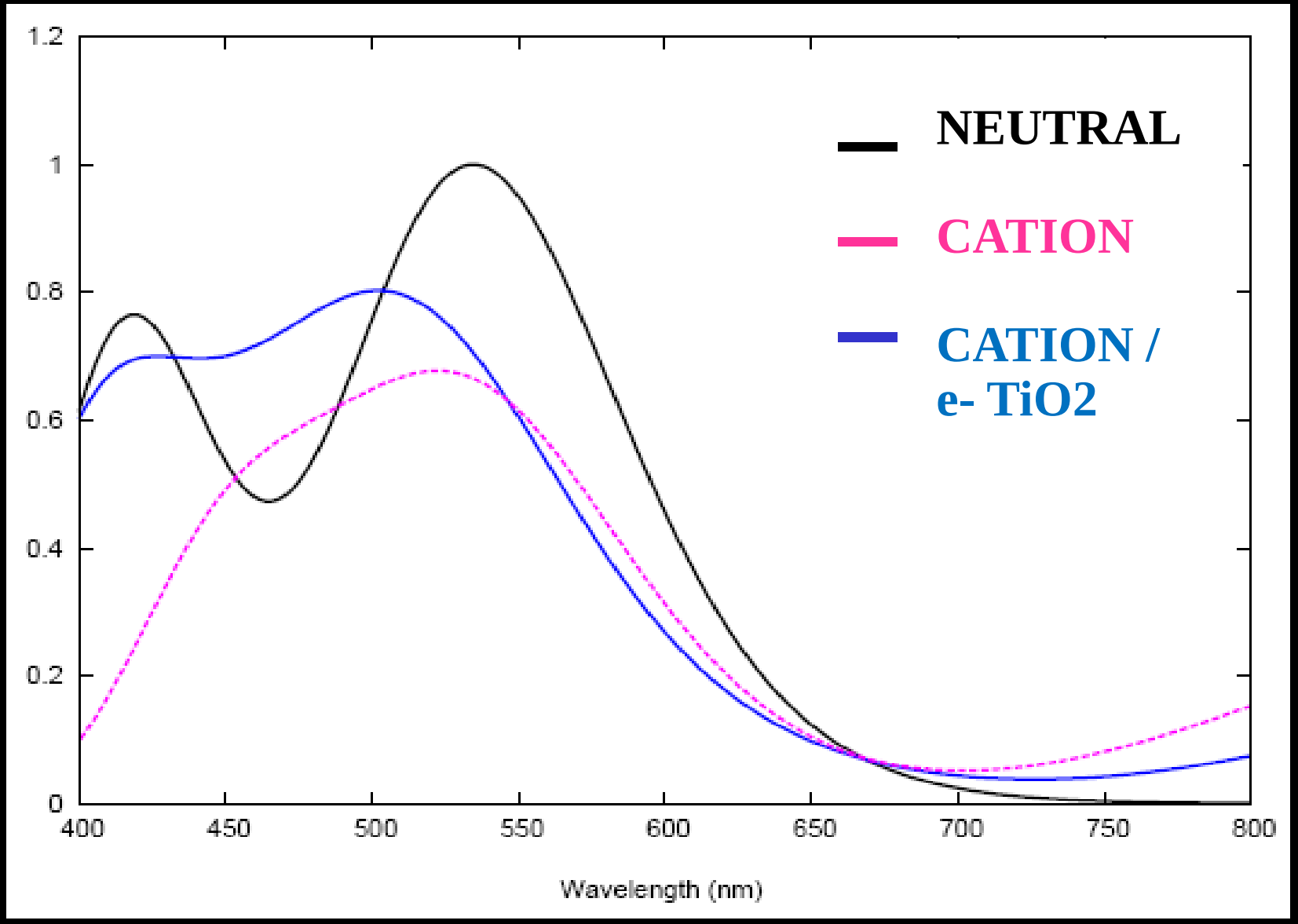
For D149 an absorbance blue-shifted has been measured when applying an electric field perdpendicular to the surface

Cappel et al. J. Am. Chem. Soc. 2010, 132, 9096 / Meyer et al. J. Am. Chem. Soc. 2010



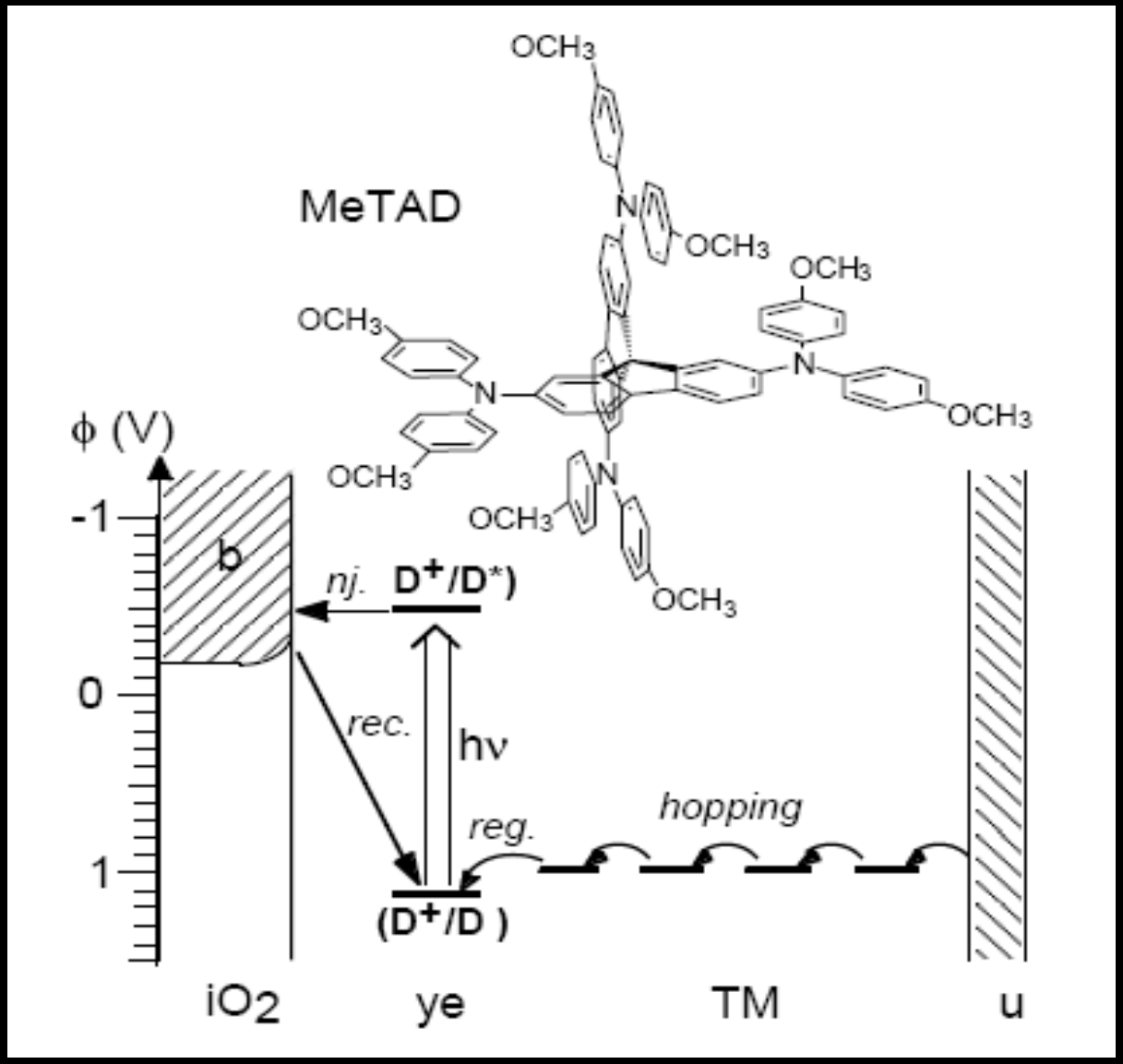
OUR MODEL: D149 DIMER ON TiO2 – 1 NEUTRAL – 1 OXIDIZED

Calculated absorption spectra



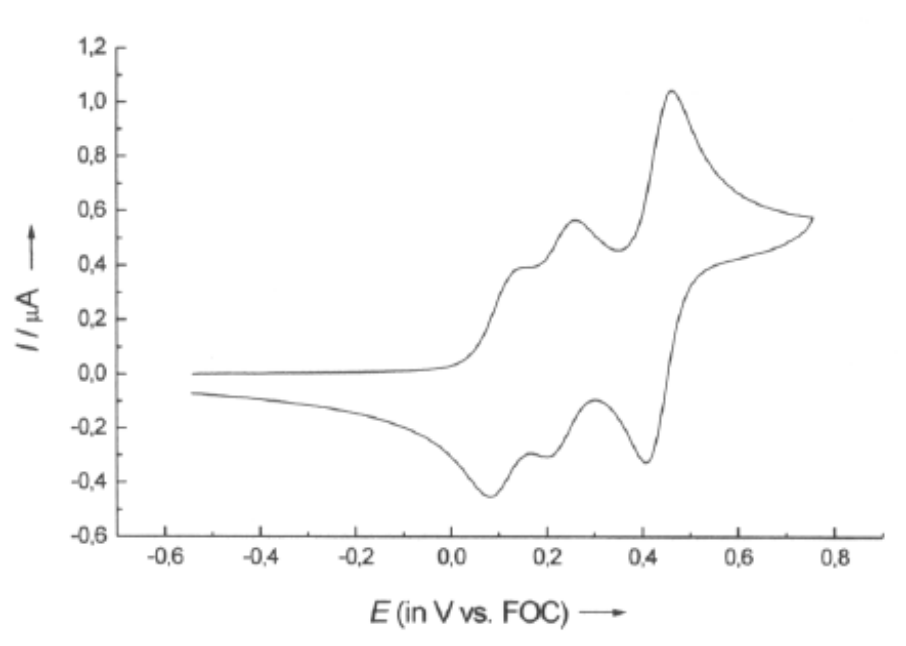
M. Pastore, F. De Angelis *J. Phys. Chem. Lett.* 201

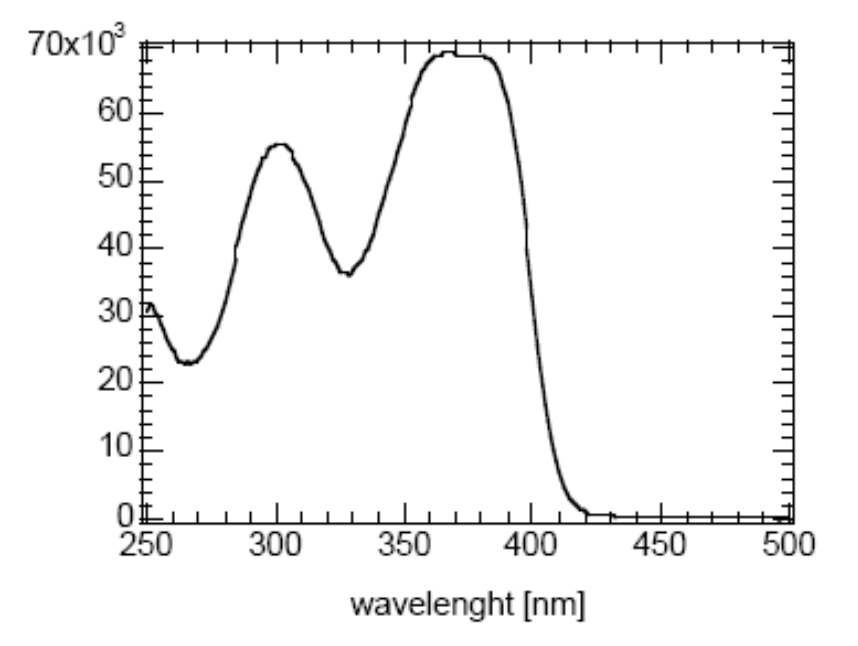
Solid State DSSC: Spiro-OMe-TAD



M. Grätzel et al. Nature 1998, 395, 583

Spiro-OMe-TAD: Electronic and optical properties

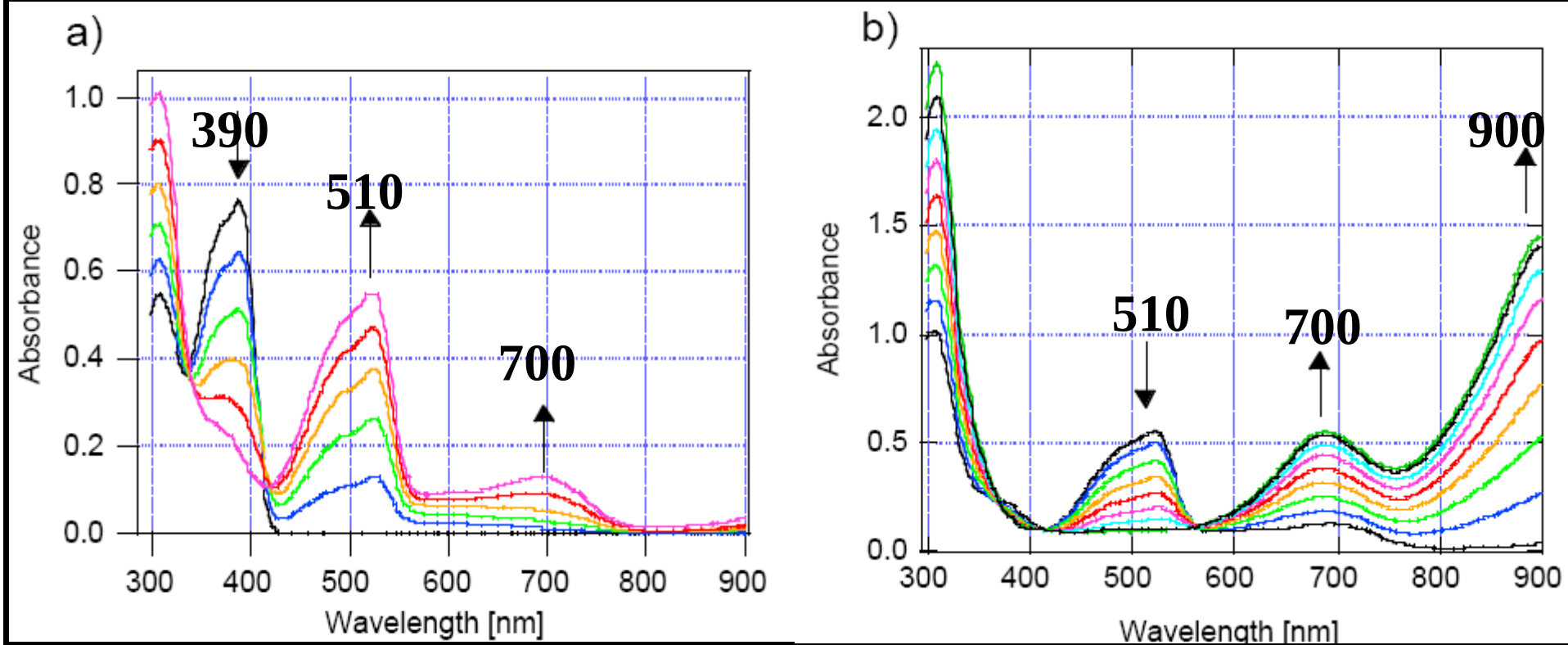




- Less positive oxidation potential than I^-/I_3^-
- The neutral form absorbs in the UV

U. Bach, PhD Thesis, EPFL, 2000

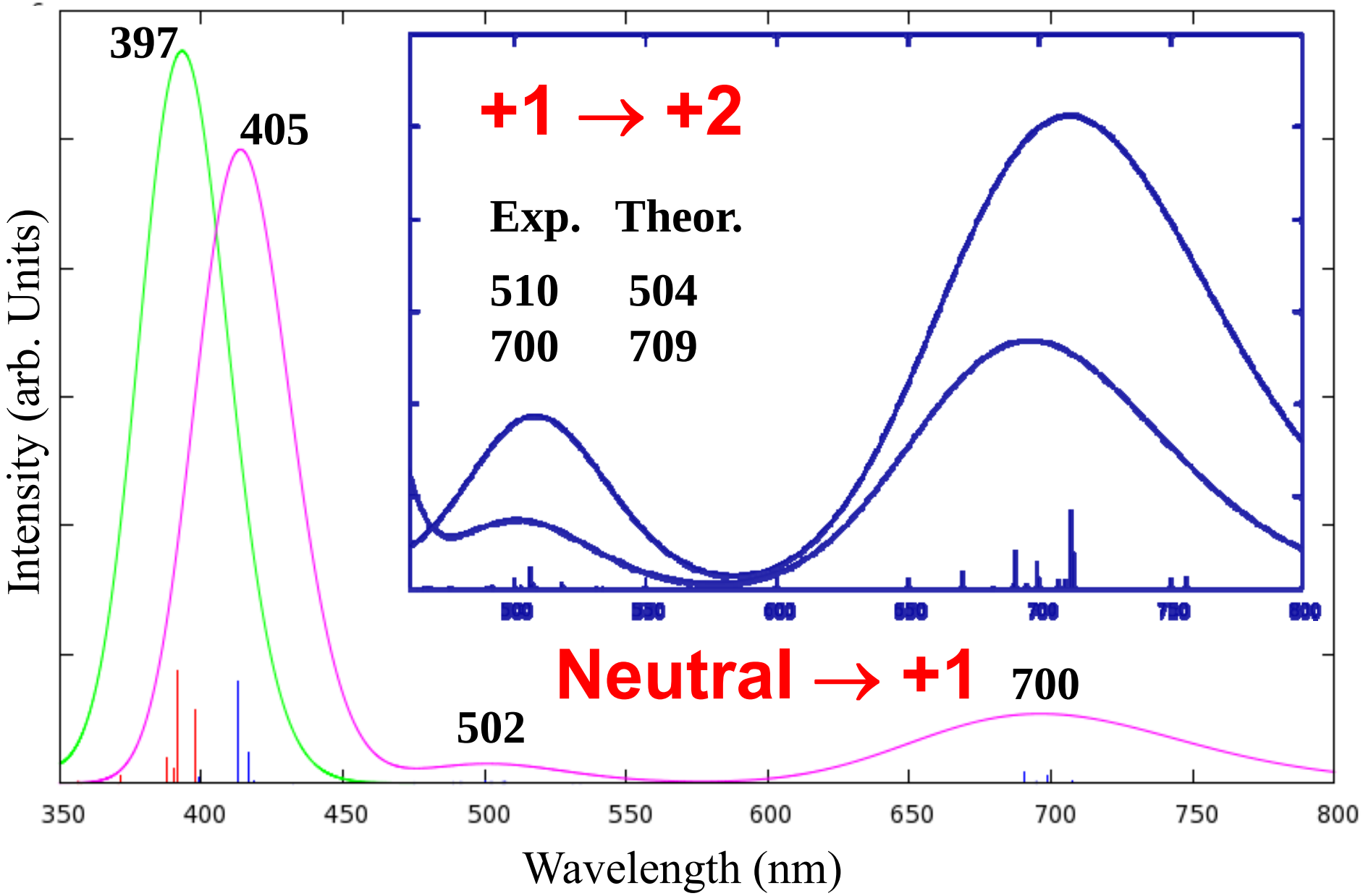
Spiro-OMe-TAD: Optical properties of the oxidized species



- The oxidized forms absorbs strongly in the Vis

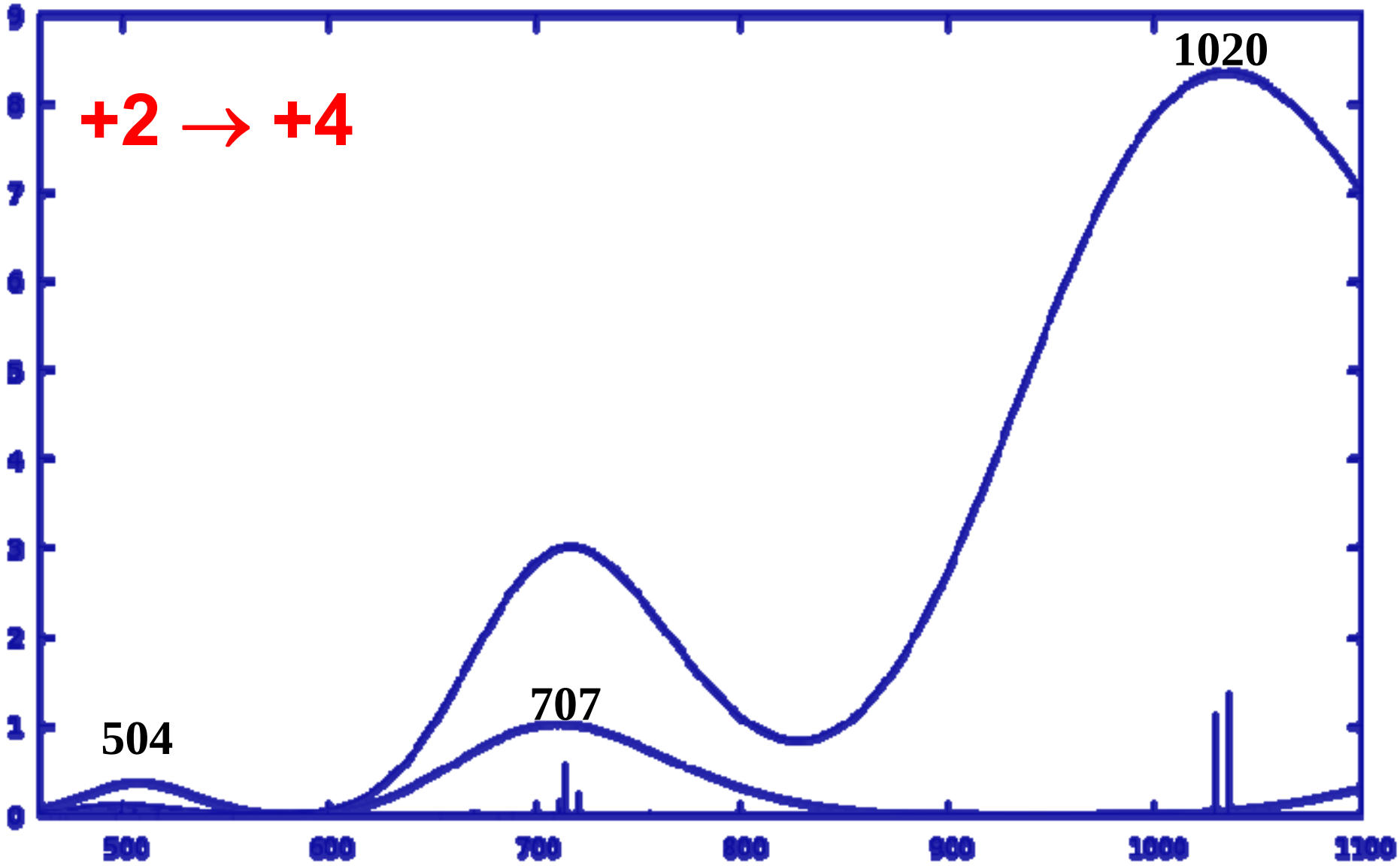
U. Bach, PhD Thesis, EPFL, 2000

Spiro-OMe-TAD: Simulated absorption spectra



S. Fantacci, F. De Angelis J. Phys. Chem. A, 2011, in press.

Spiro-OMe-TAD: Simulated absorption spectra



S. Fantacci, F. De Angelis J. Phys. Chem. A, 2011, in press.

HOPV group Perugia

ICTP / SISSA Collaboration:

R. Gebauer, S. Baroni

Experiments at EPFL:

•Md. K. Nazeeruddin, M. Grätzel

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MIUR PRIN 2008 CNR EFOR 2011 IIT-SEED 2009

ESF HOPV 2010 EU-FP7: NMP-2009 ENERGY-2010