Modeling Dye-Sensitized Solar Cells:

Understanding the mechanism, improving the efficiency

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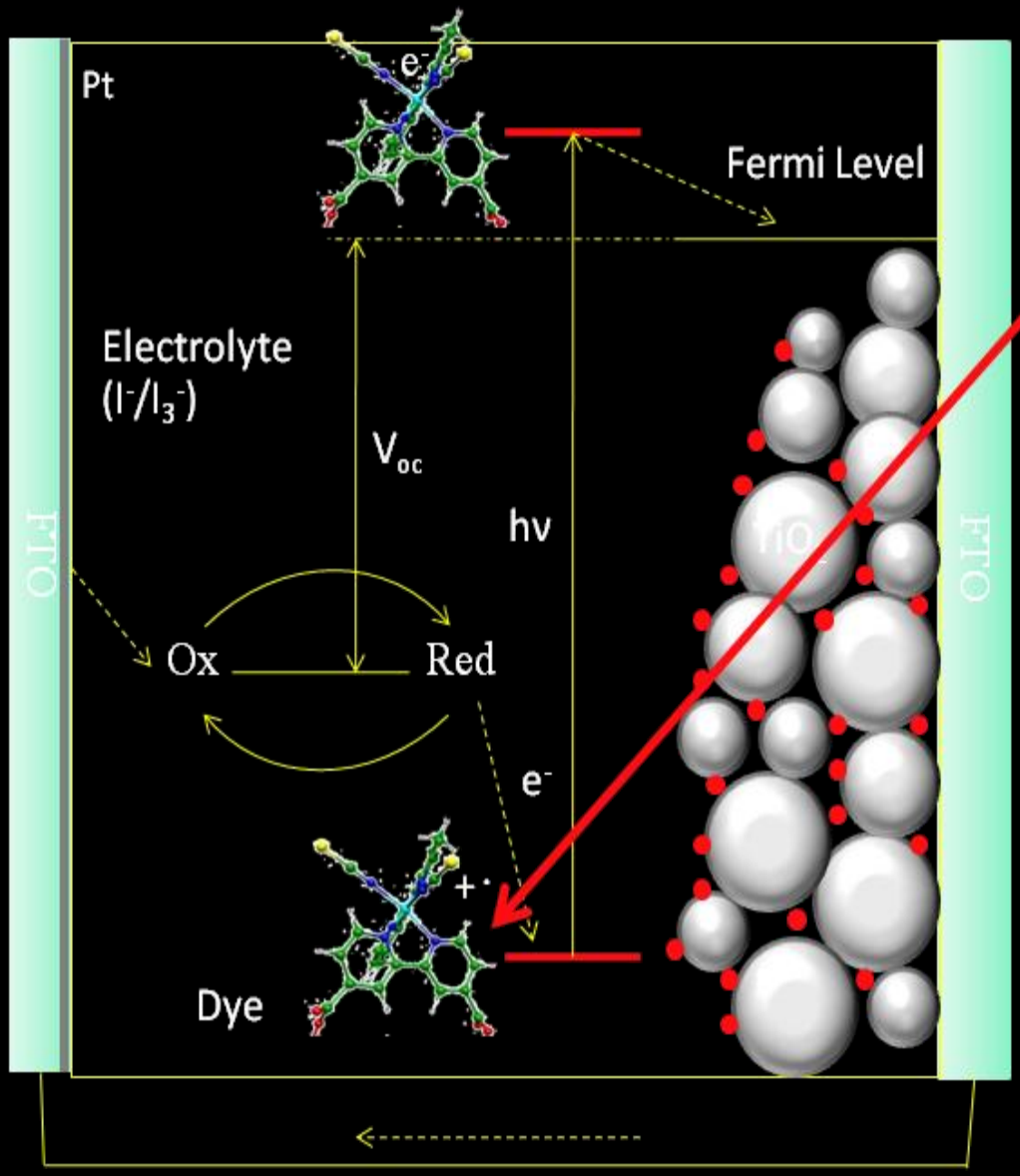
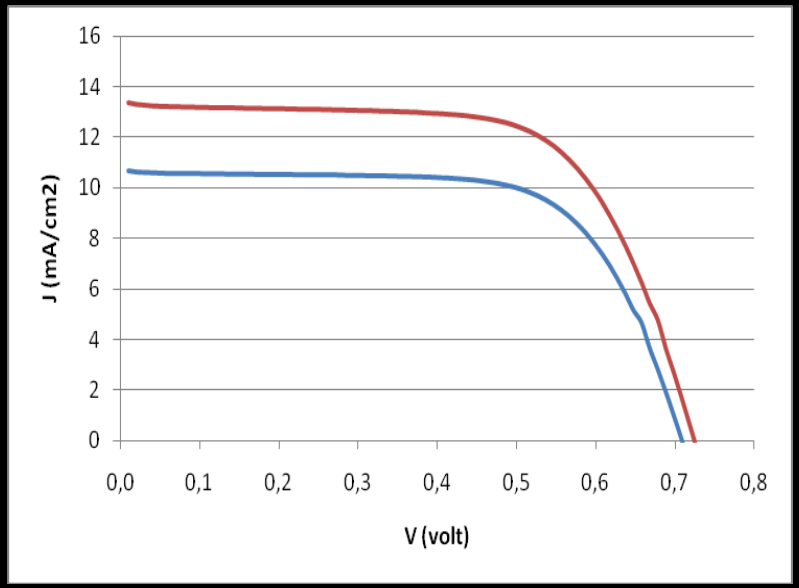
operational mechanism



I-V curve



Efficiency =
Jsc x Voc x FF/ Is

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

OUTLINE

Materials:

- **Dyes (QM)**
- **Semiconductors (QM+MS)**
- **Electrolytes (QM)**

Processes:

- **Adsorption/Absorption of Dyes@TiO_2**
- **Dyes@TiO_2 in solution environment**
- **FRET-based DSCs**
- **Recombination in Cobalt electrolyte DSCs**

F. De Angelis, S. Fantacci, ***Coord. Chem. Rev*** **2011, 17, 1093.**

The goal: modeling DSC devices

• **Large dimensions : realistic models usually require dealing with a few hundred atoms (oversimplified models are often inaccurate)**

•**Complexity : complex potential energy surfaces with several minima; dealing with transition metals (electronic correlation)**

•**Optical properties: need an accurate description of the excited states**

•**Dynamical aspects : need to perform ab initio molecular dynamics simulations**

Theoretical and computational approach

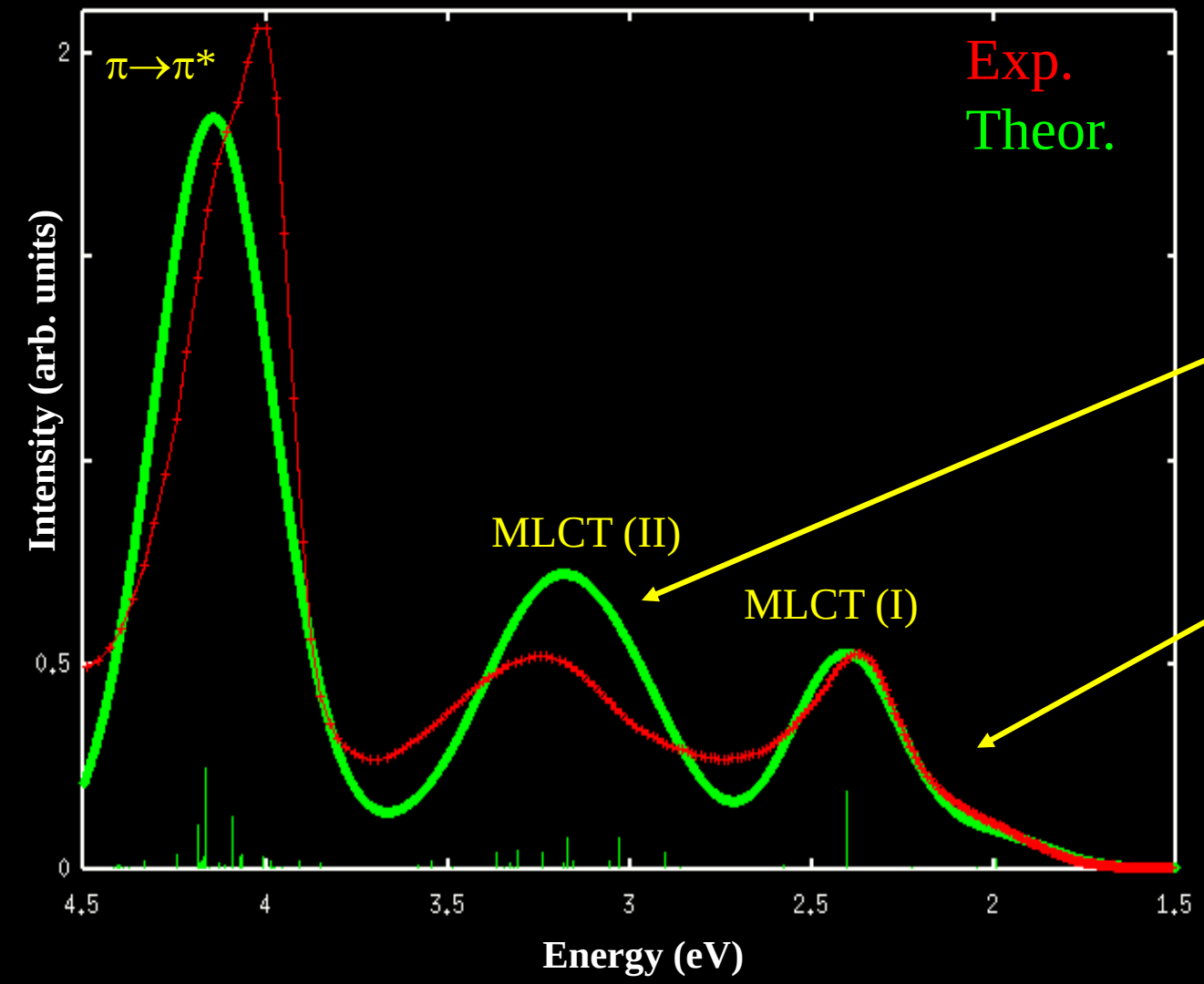
- Geometry optimizations of extended systems, in condensed phase, for both ground and excited states **(DFT + DFTB)**
- Ab initio molecular dynamics **(Car-Parrinello)**
- UV-vis absorption and emission spectra **(TDDFT-ab initio)**
- Inclusion of solvation effects **(explicit or PCM)**

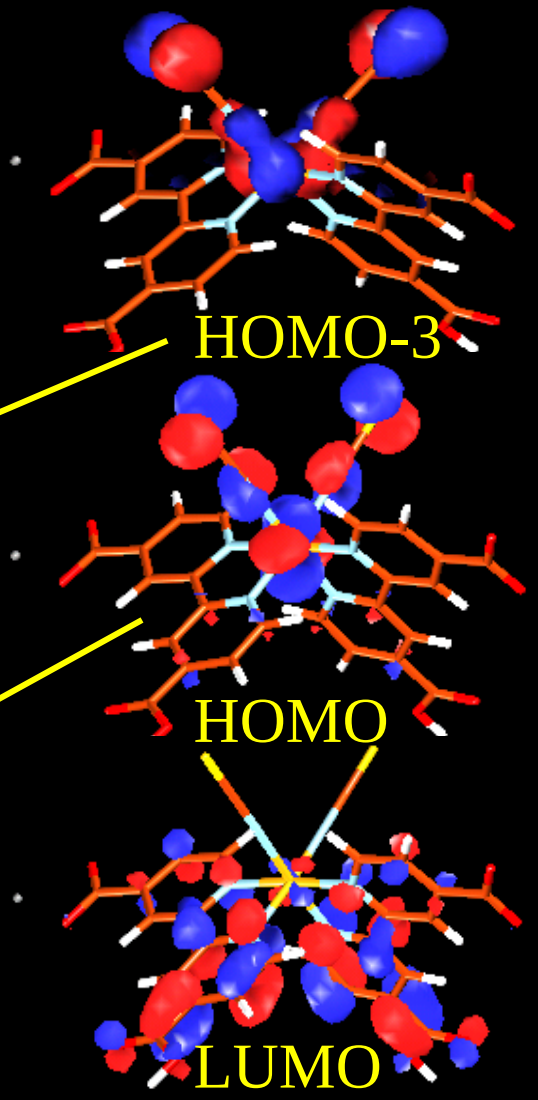
F. De Angelis, S. Fantacci, A. Sgamellotti, ***Theor. Chem. Acc.*** **2007, 17, 1093.**

Part I

Dyes

Ru-dyes: Absorption spectra

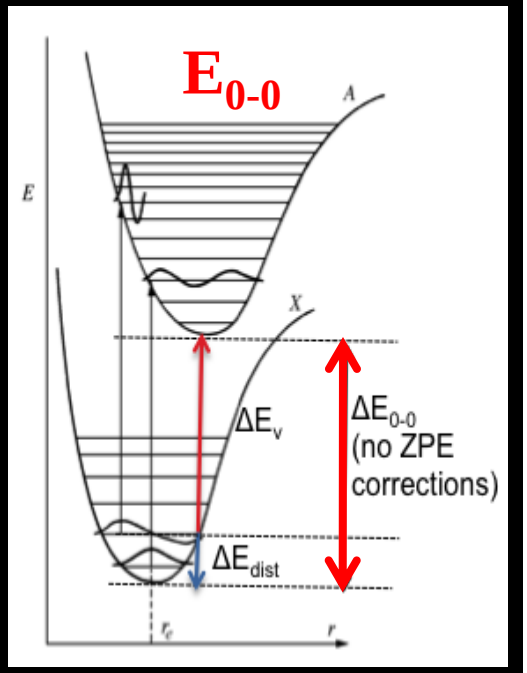




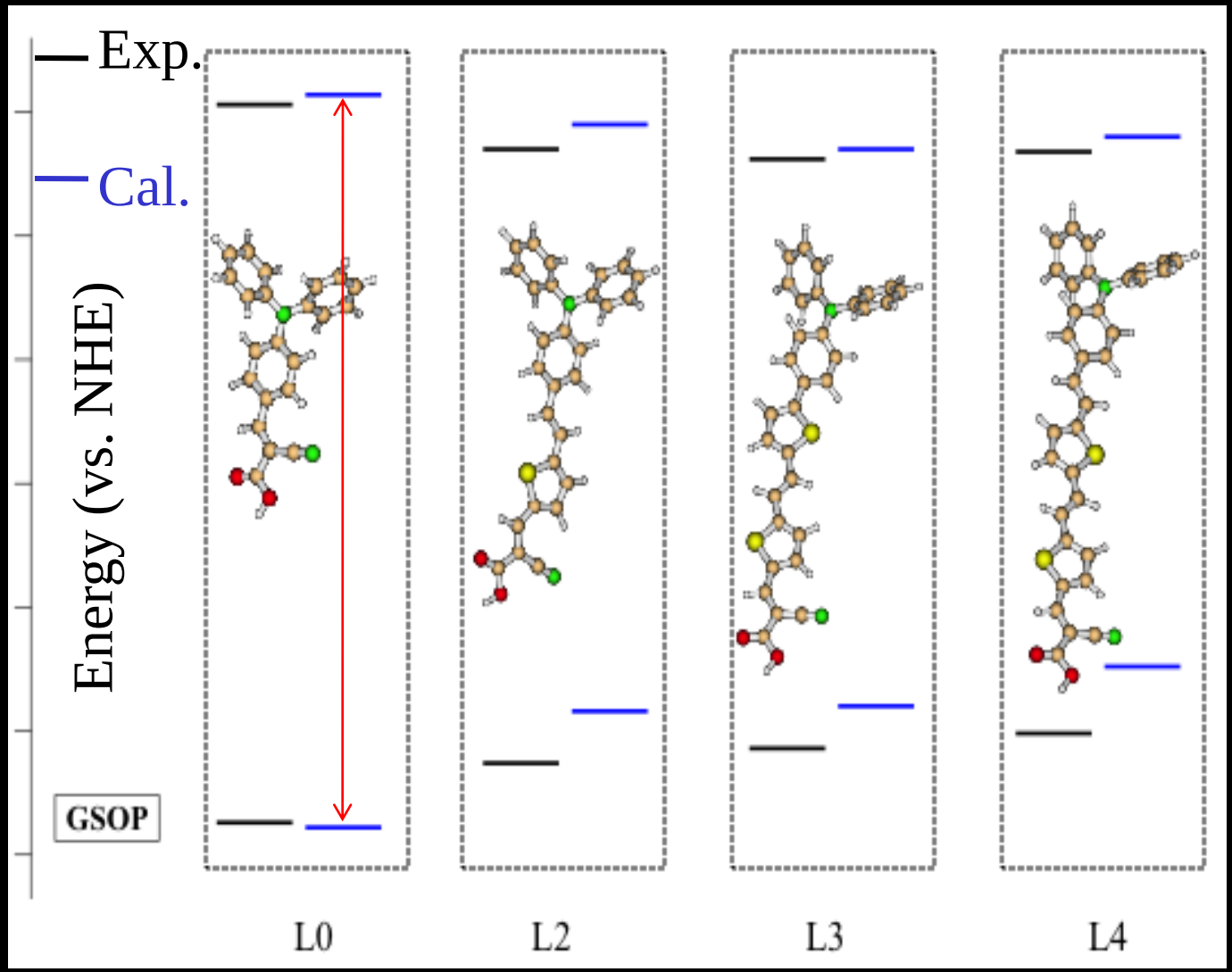
S. Fantacci, F. De Angelis, A. Selloni — ***J. Am. Chem. Soc.*** **2003, *125*, 4381.**
F. De Angelis, S. Fantacci, A. Selloni — ***Chem. Phys. Lett.*** **2004, *389*, 204.**
F. De Angelis, S. Fantacci, M.K. Nazeeruddin — ***Chem. Phys. Lett.*** **2005, *415*, 115.**
F. De Angelis,. S. Fantacci, M. Grätzel et al. — ***J. Am. Chem. Soc.*** **2005, *127*, 16835.**

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

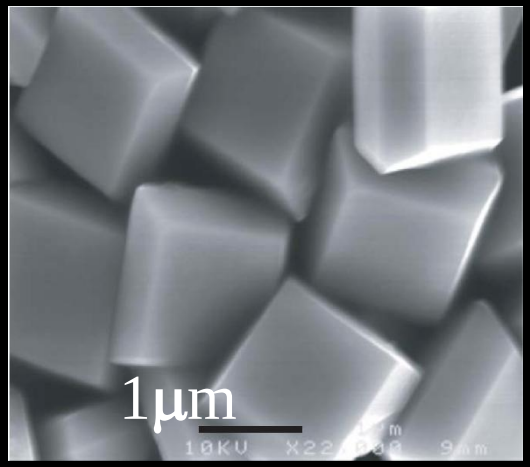


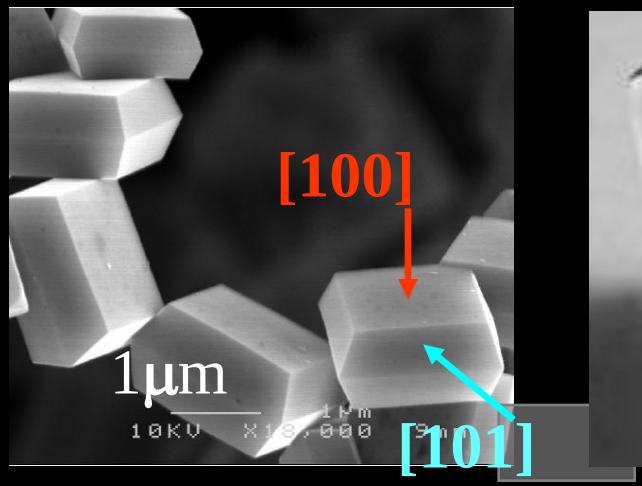
M. Pastore, F. De Angelis ***J. Phys. Chem. C*** **2011**.

Part II

Semiconductors

Anatase TiO_2 nanocrystals

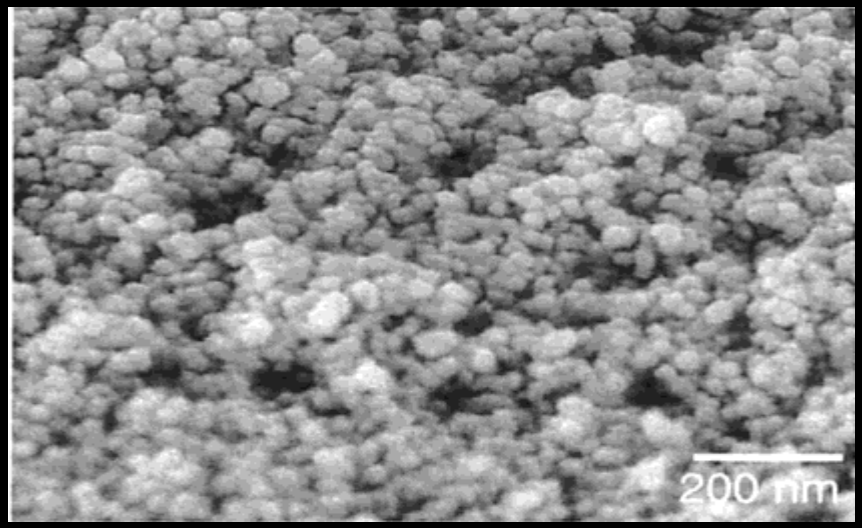




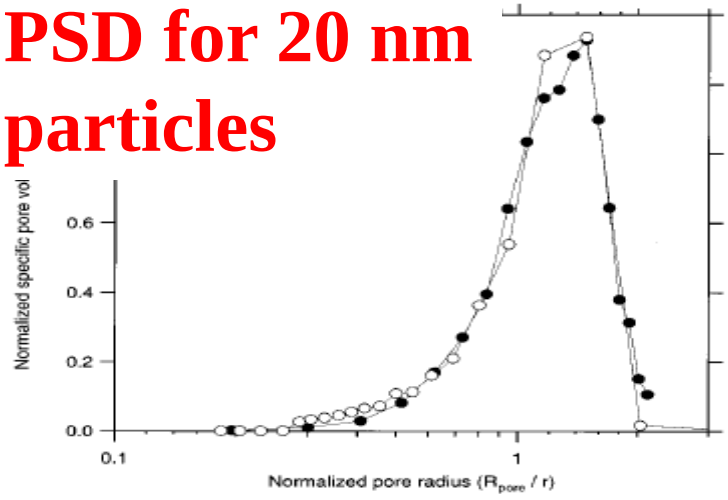
H. G. Yang et al. Nature 453, 2008, 29

Catal. Today 85, 2003,932

Mesoporous film of anatase TiO_2 nanocrystals:

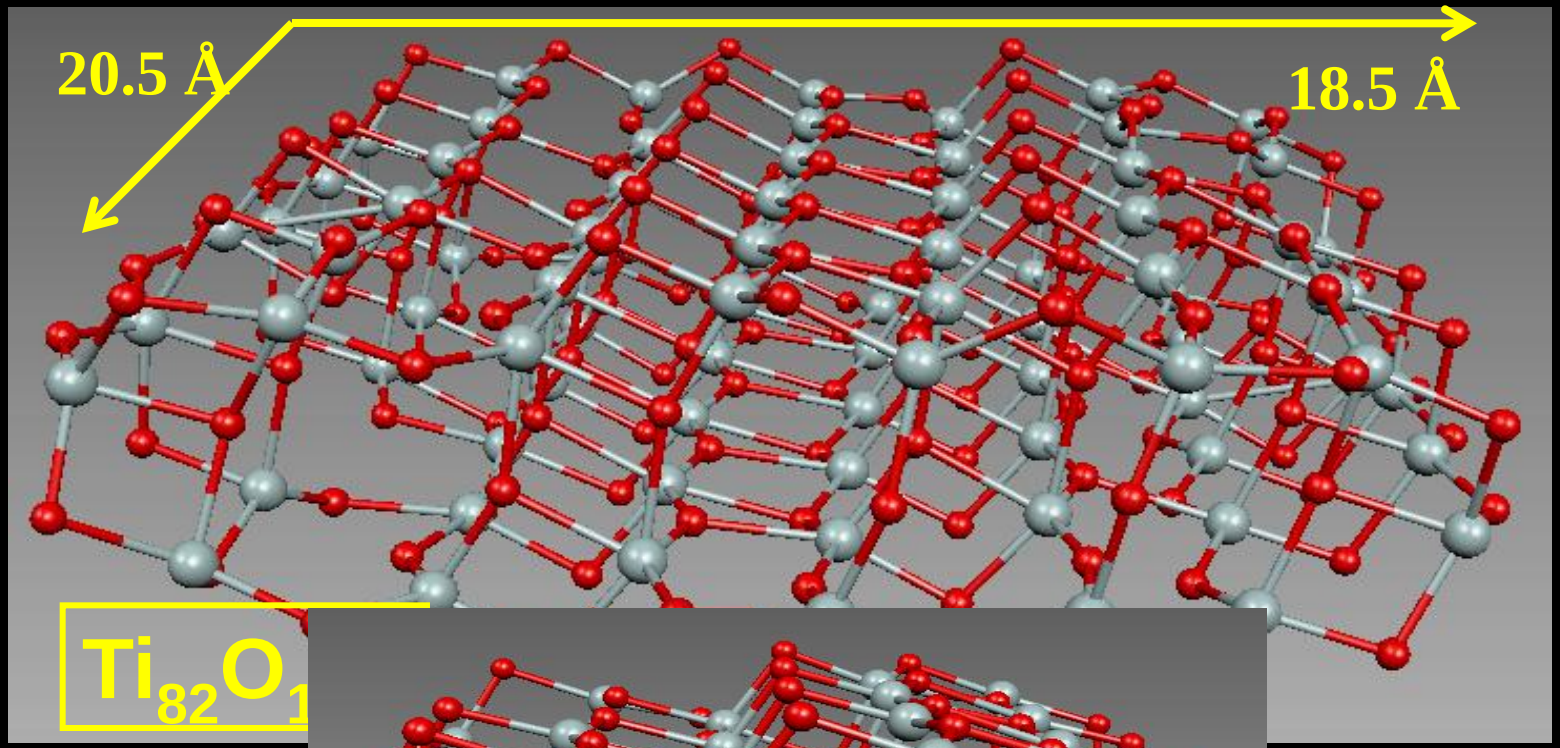


PSD for 20 nm particles



Modeling of TiO_2 nanoparticles:

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

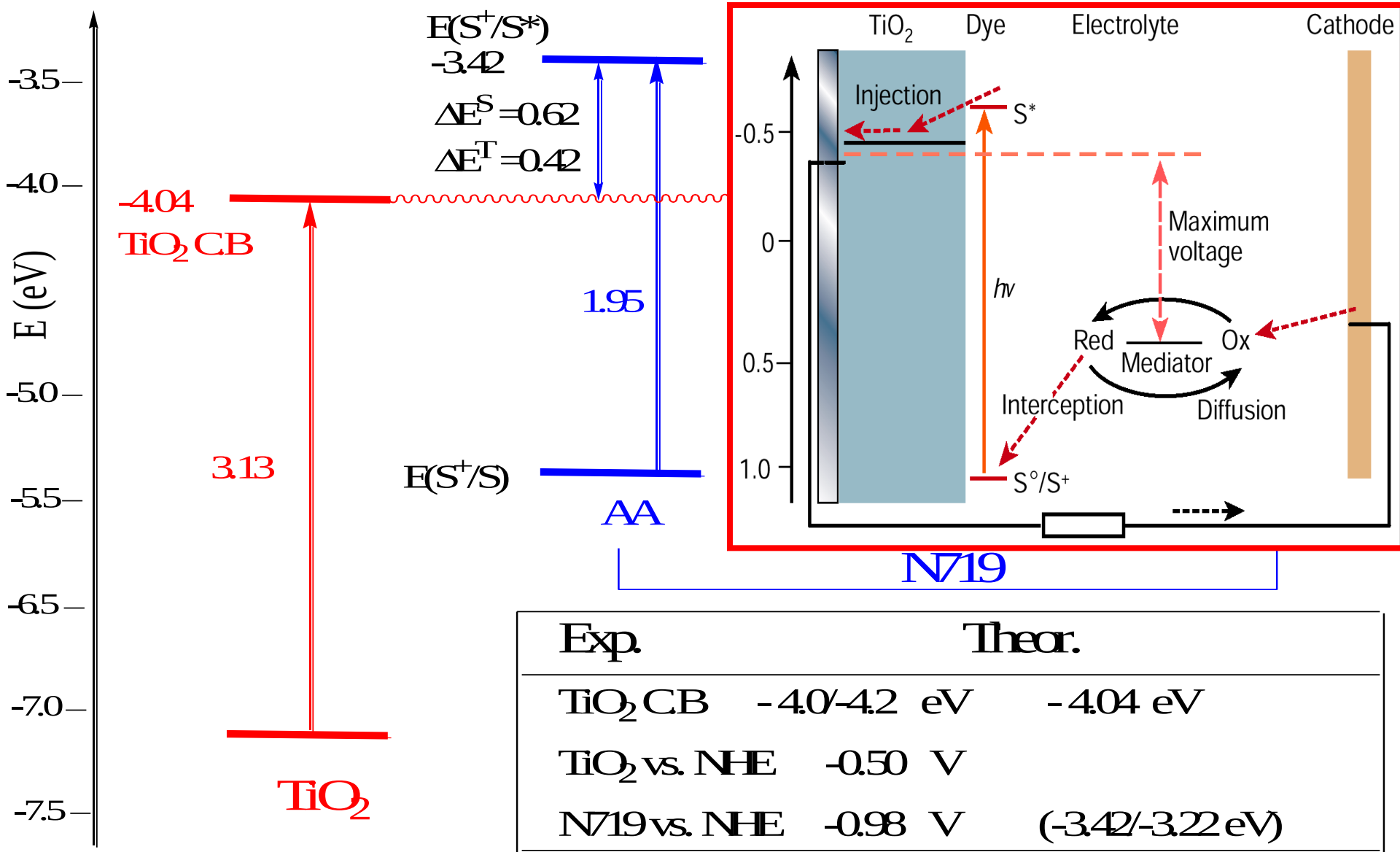


TD-DFT gap in **B3LYP/DZVP 3.13/3.35 eV**

Experime **3.20 – 3.30 eV**

F. De An **04, *126*, 15024**

Alignment of excited state potentials:

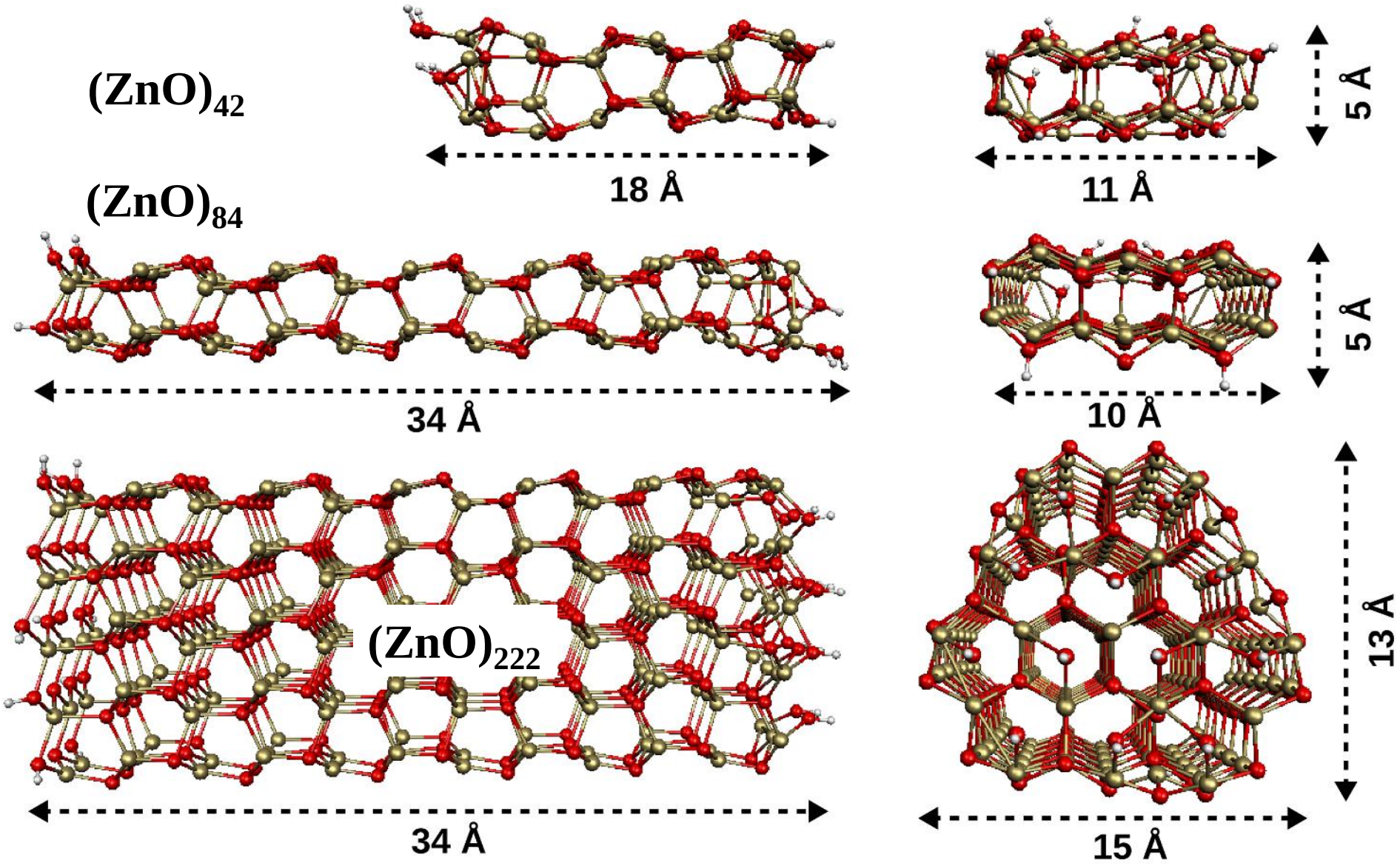


Exp.		Theor.
TiO_2 C.B	-4.0/-4.2 eV	-4.04 eV
TiO_2 vs. NHE	-0.50 V	
N719 vs. NHE	-0.98 V	(-3.42/-3.22 eV)

$\Delta E = 0.48$ V $\quad \Delta E^T = 0.435$ eV

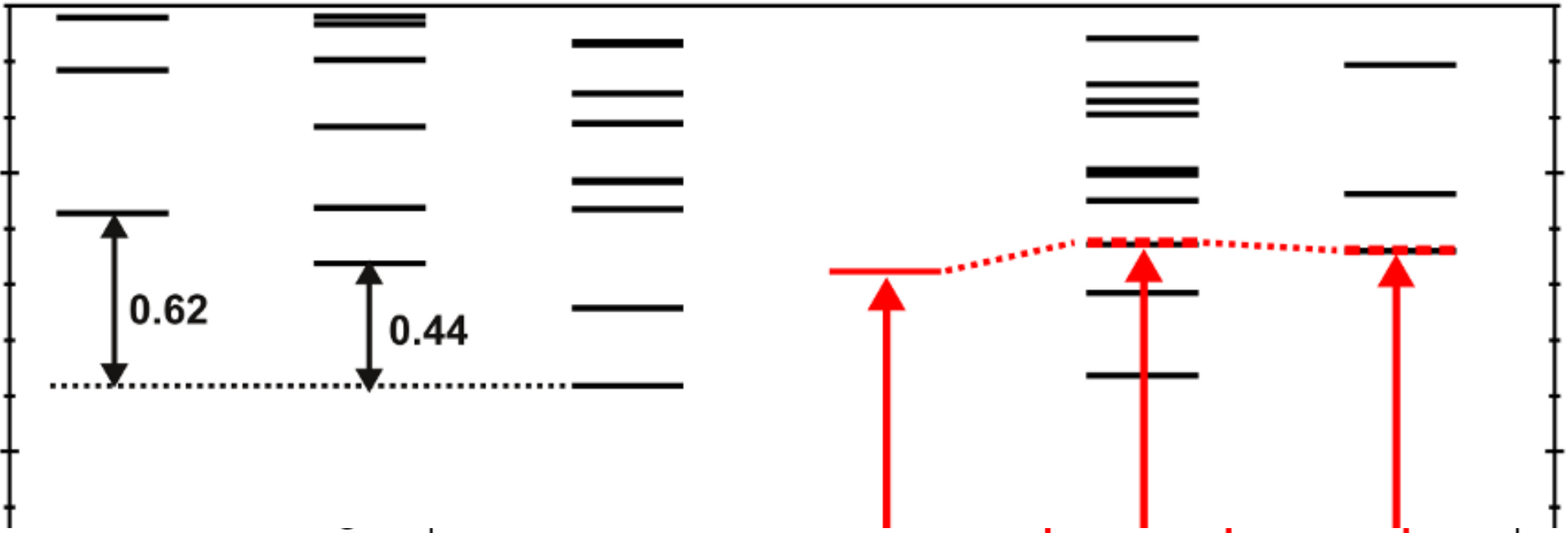
F. De Angelis, S. Fantacci, A. Selloni, *Nanotechnology*, **2008**, *19*, 424002.

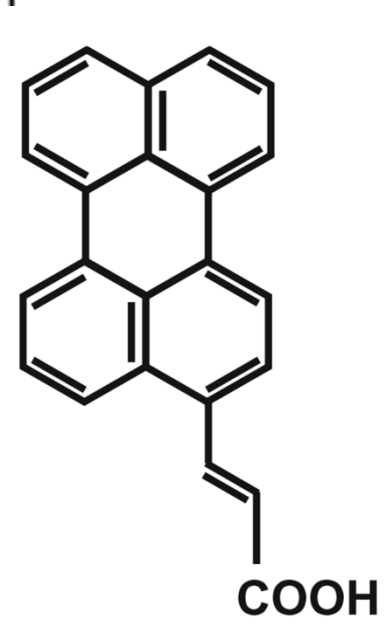
Modeling of ZnO nanostructures:

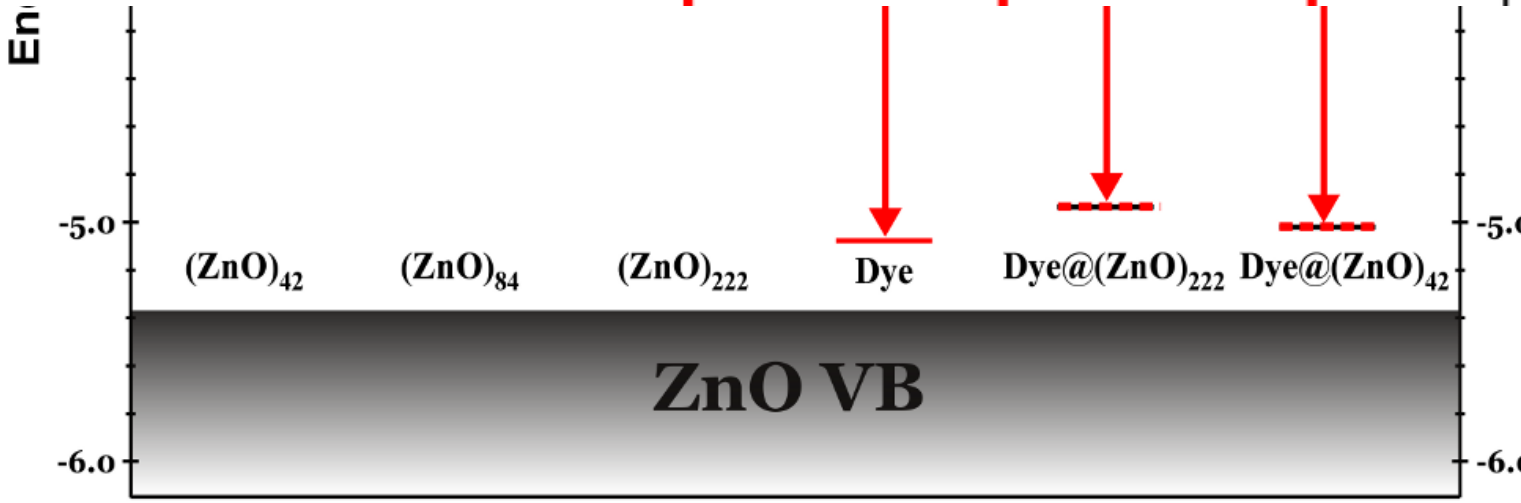


F. De Angelis, L. Armelao, ***PhysChemChemPhys* 2011**
J.M. Azpiroz, E, Mosconi, F. De Angelis ***J. Phys. Chem.* 2012**

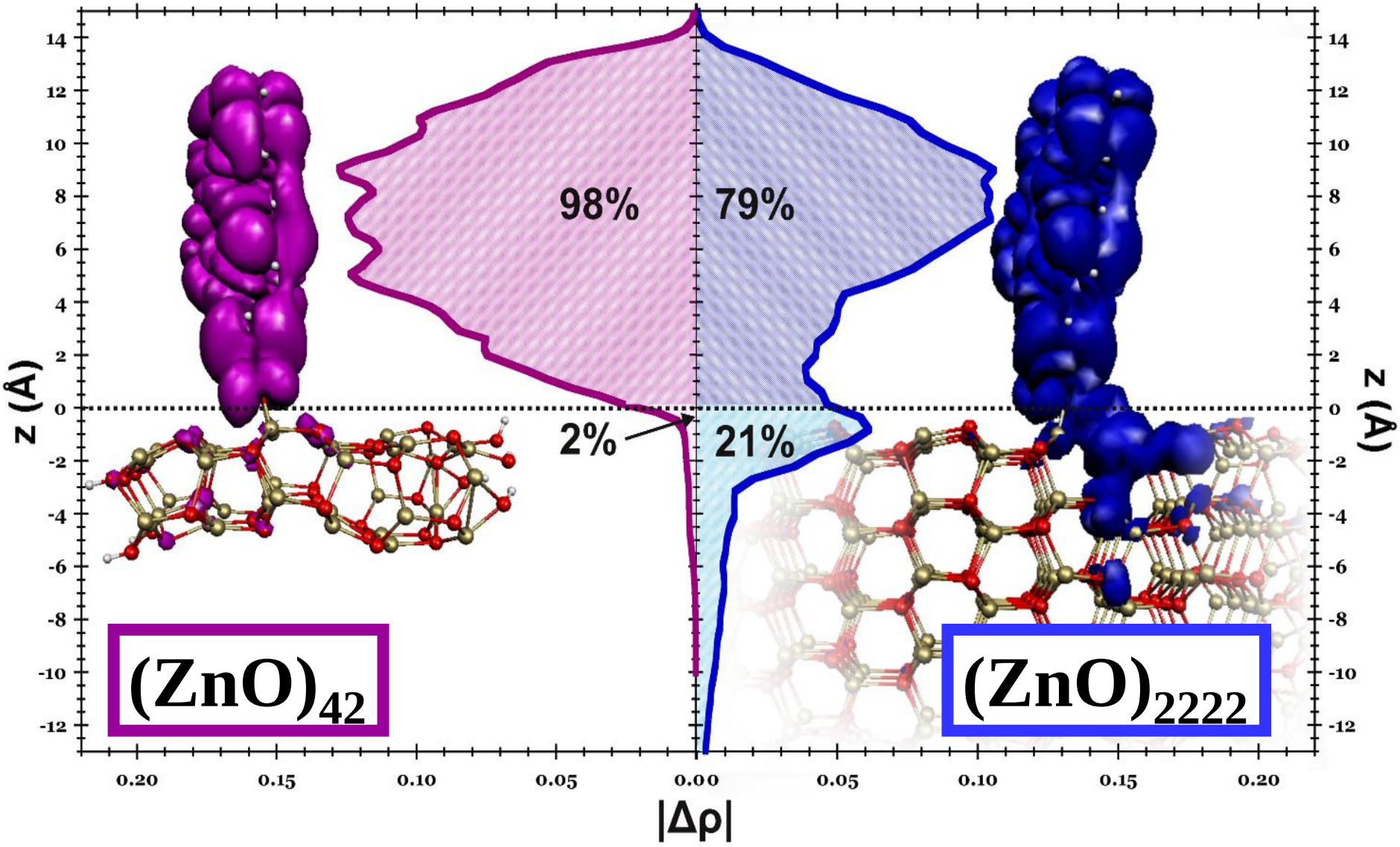
Modeling organic dyes adsorbed on ZnO





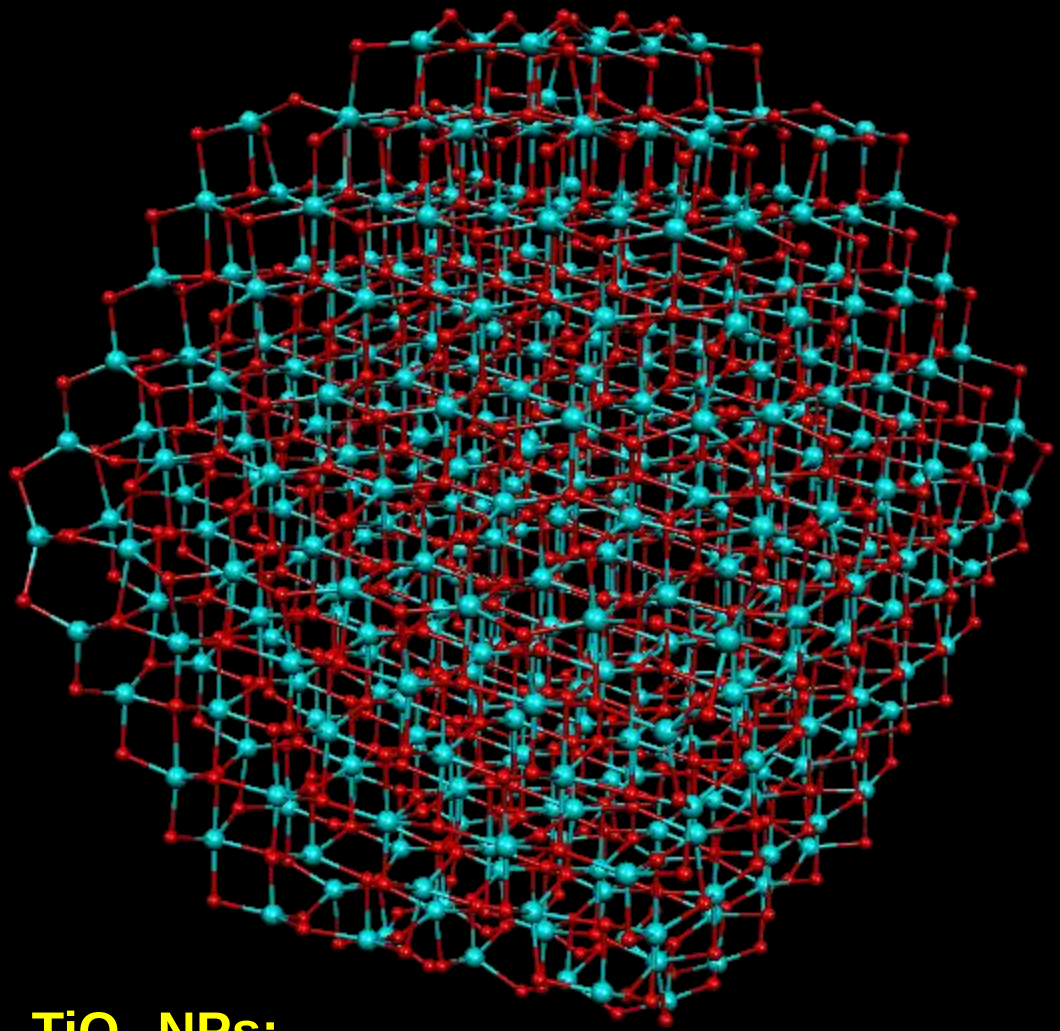


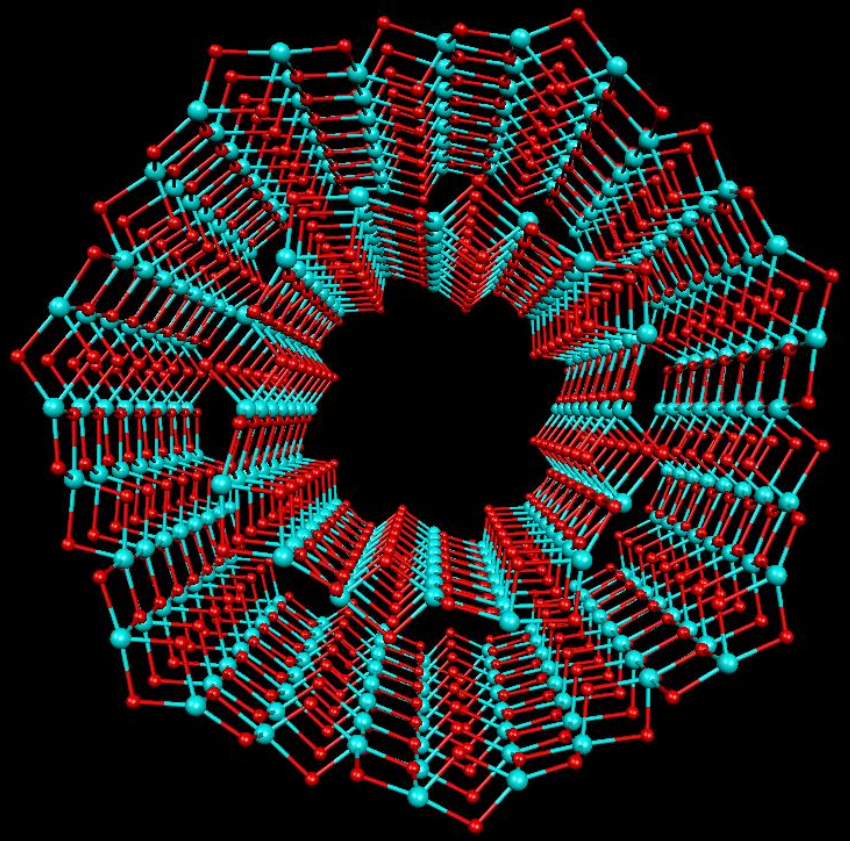
Dye/ZnO excited state mixing changes with semiconductor dimensions



A. Amat, F. De Angelis **PCCP 2012.**

Realistic models of TiO_2 NTs and NCs





TiO_2-NPs:

Origin of sub-band gap states?

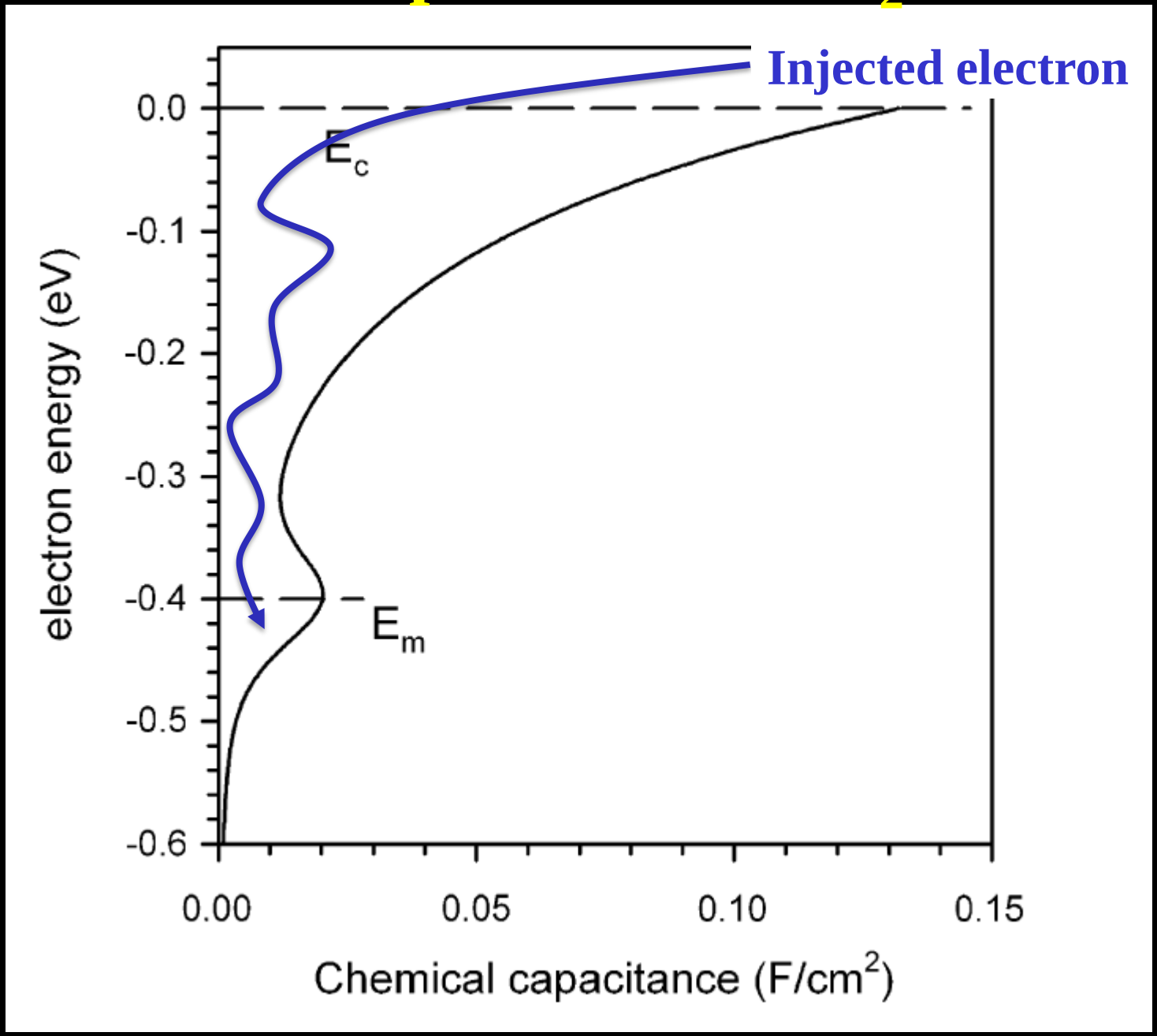
Work in progress

Single and Multi-Wall TiO_2-NTs:

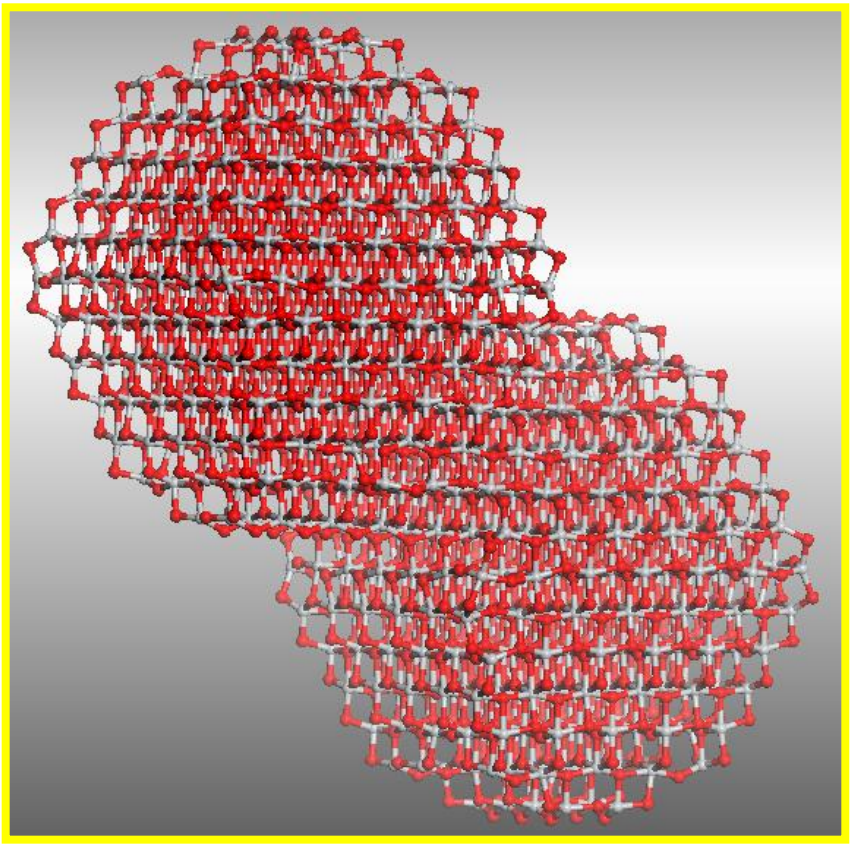
Adsorption mode

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

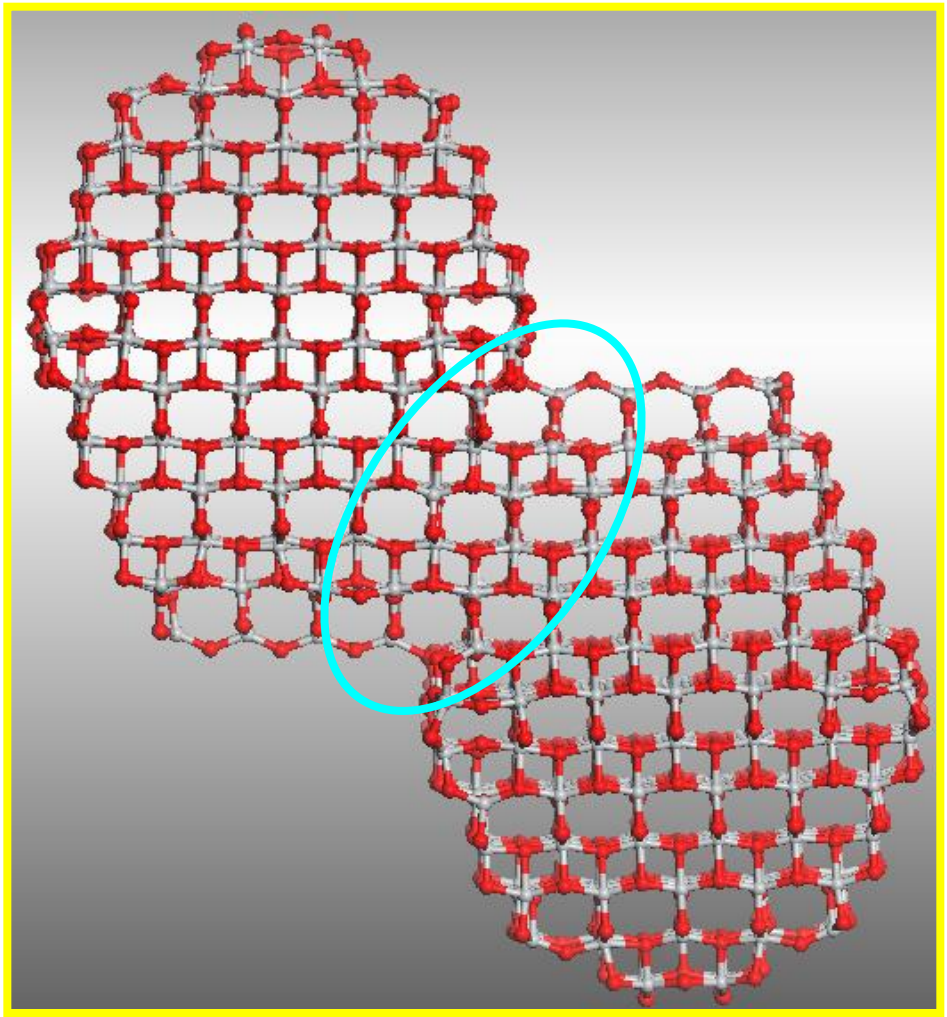
Trap states in TiO_2



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

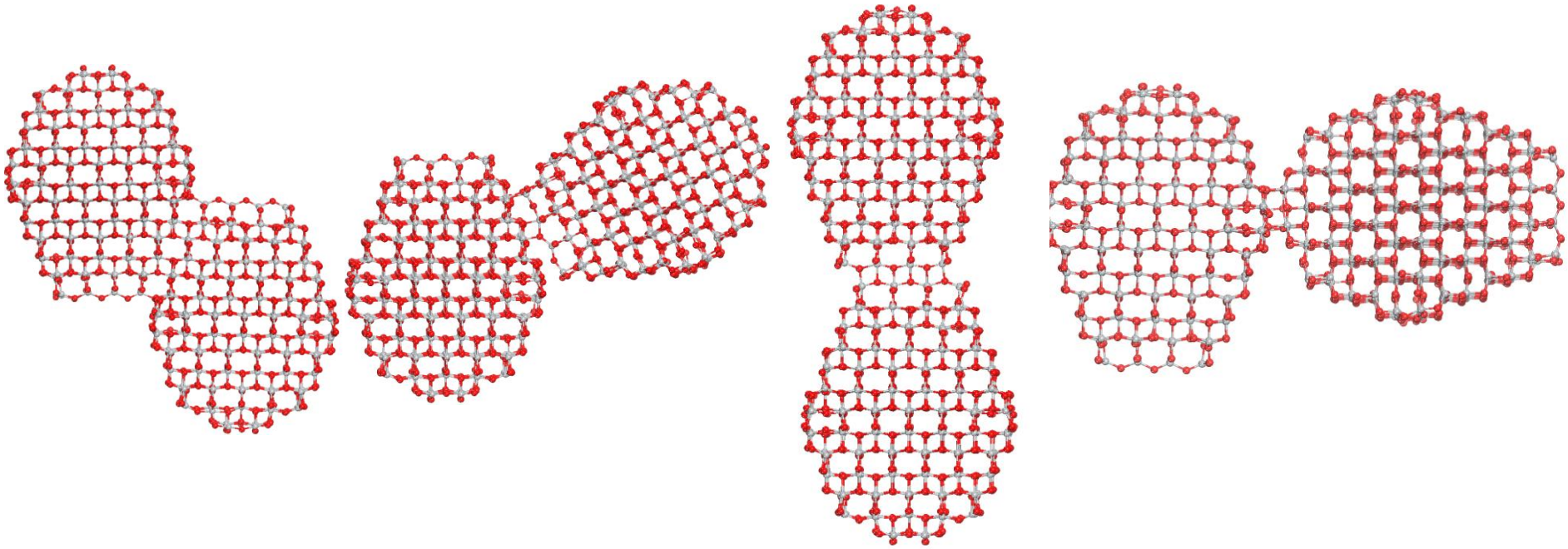


We computed an interaction energy of 27.5 eV.

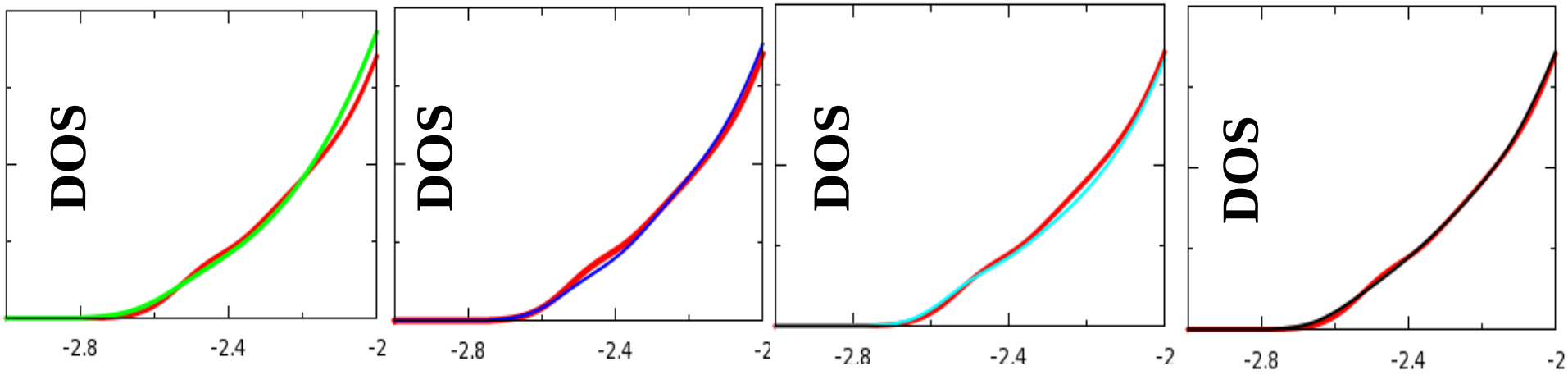


Estimating a contact surface area of 201 $Å^2$ at the interface, we calculate an energy interaction per area of **0.14 eV/ $Å^2$**.

THE INTERACTION OF TWO TiO_2 NANOCRYSTALS :

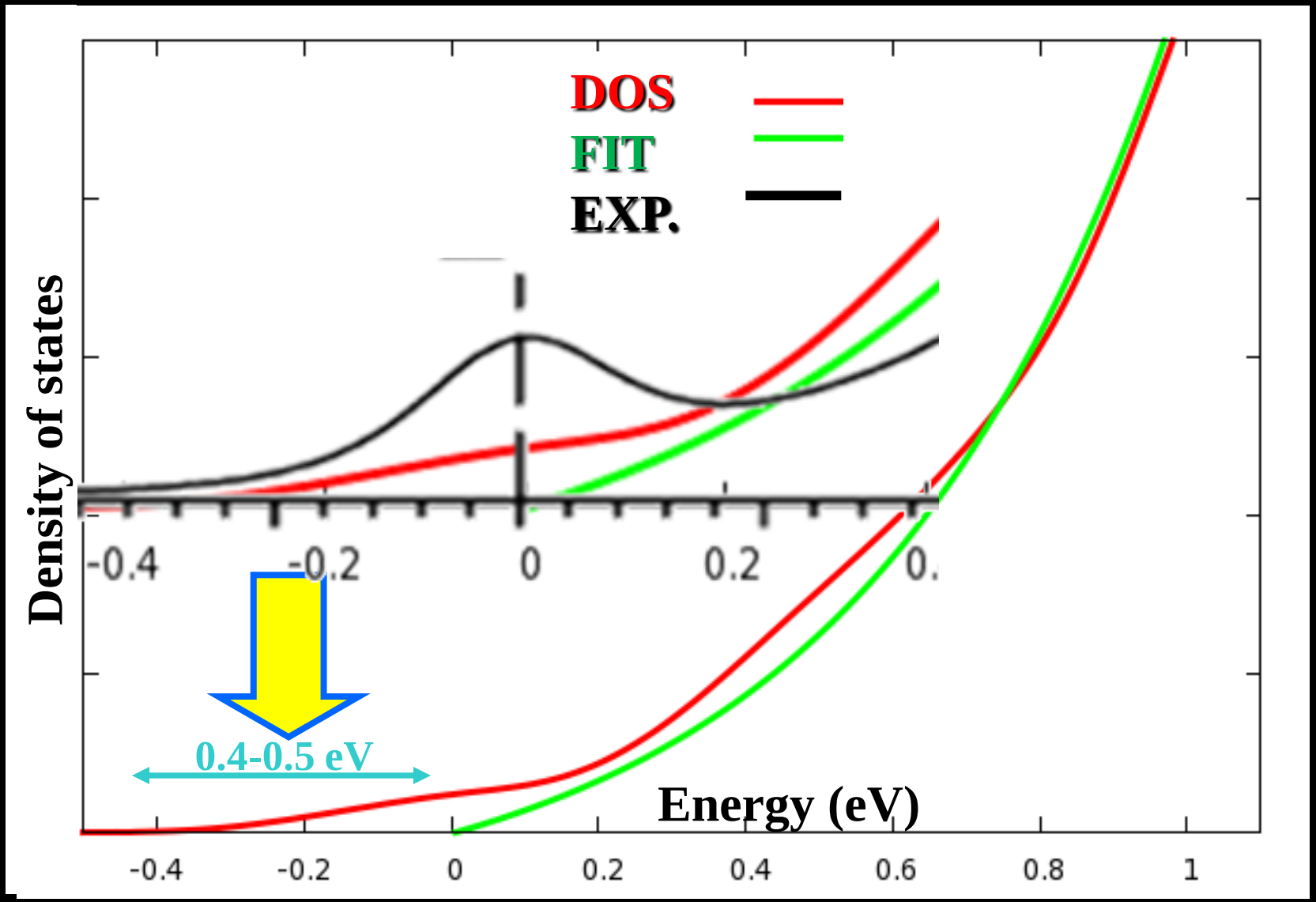


101/101 **101/001** **001/001** **100/001**



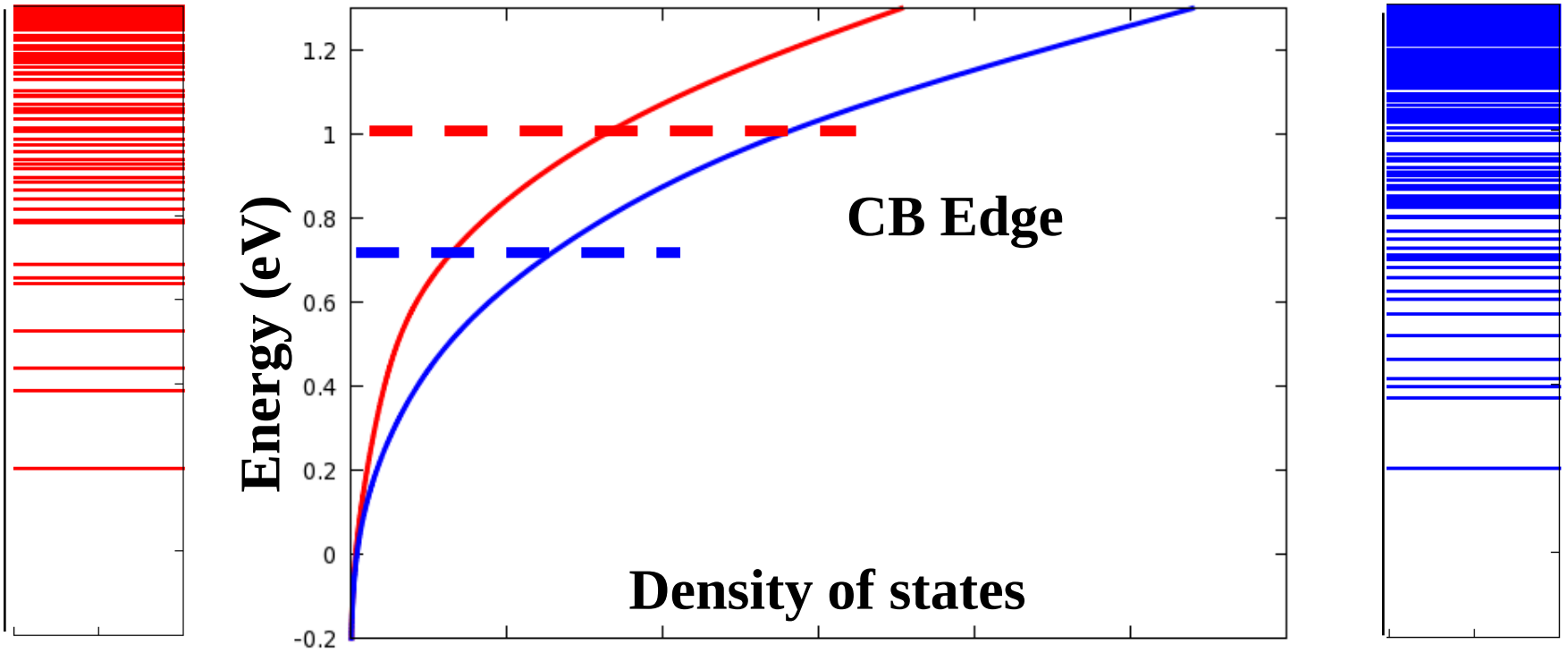
NO TRAP STATES AT THE GRAIN BOUNDARIES!

DOS FOR A SINGLE TiO_2 NANOCRYSTAL

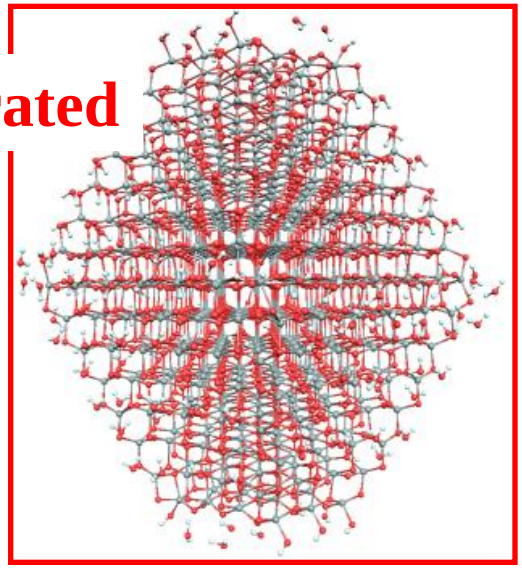


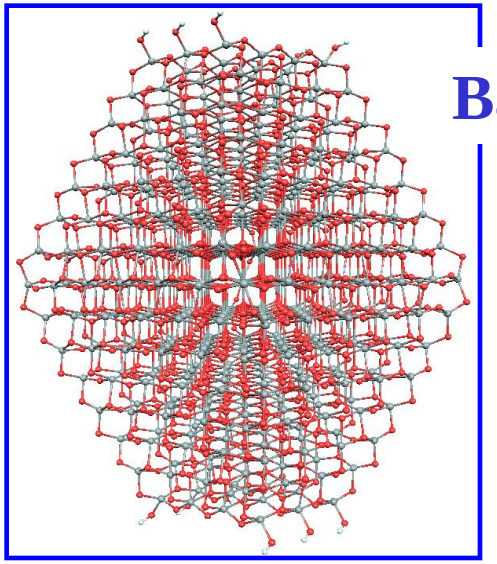
SURFACE STATES OF INDIVIDUAL TiO_2 NANOCRYSTALS INTRODUCE SUB BAND-GAP STATES IN THE DOS

EFFECT OF SATURATING LIGANDS: 154 H2O - TiO_2



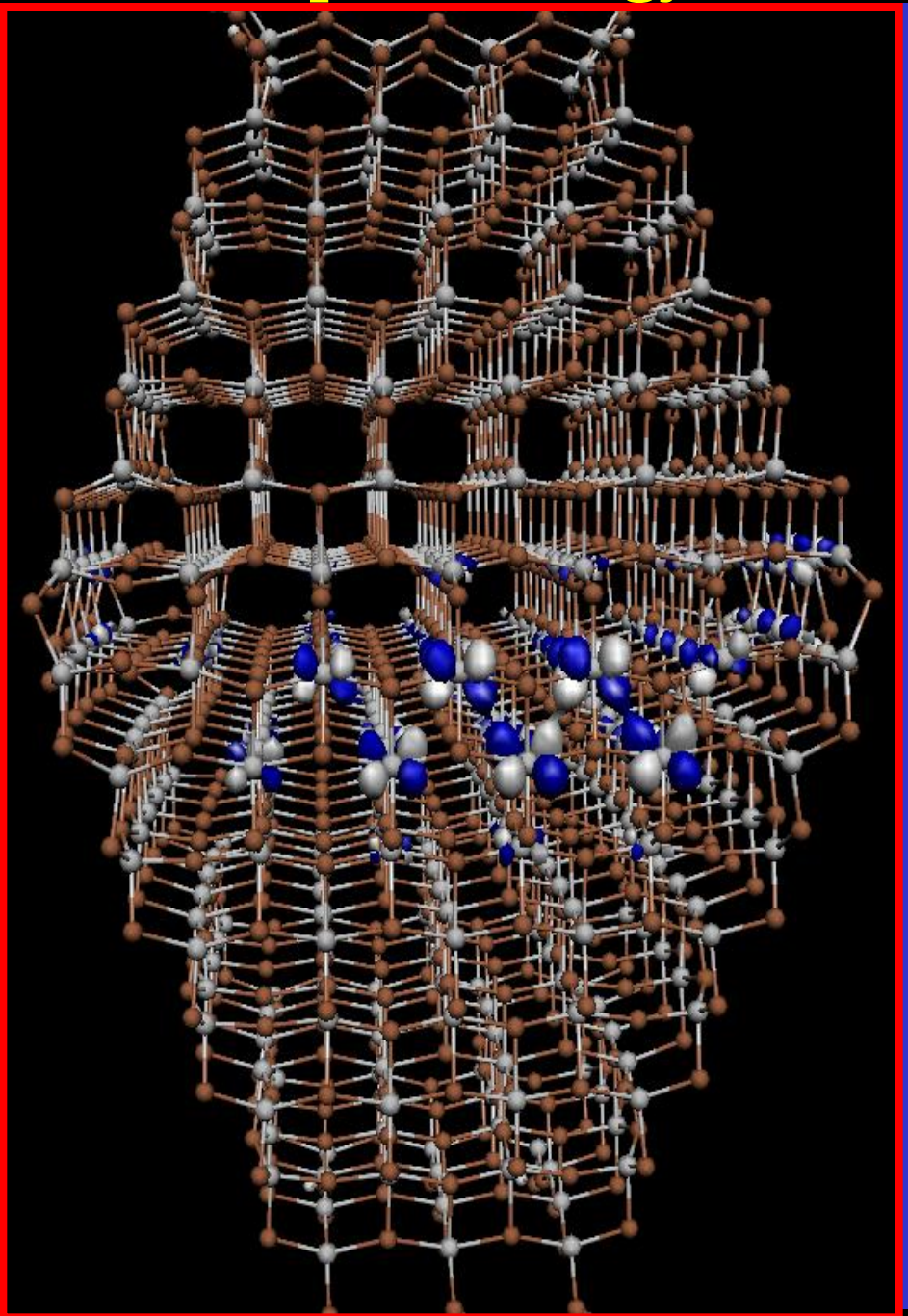
Water-saturated

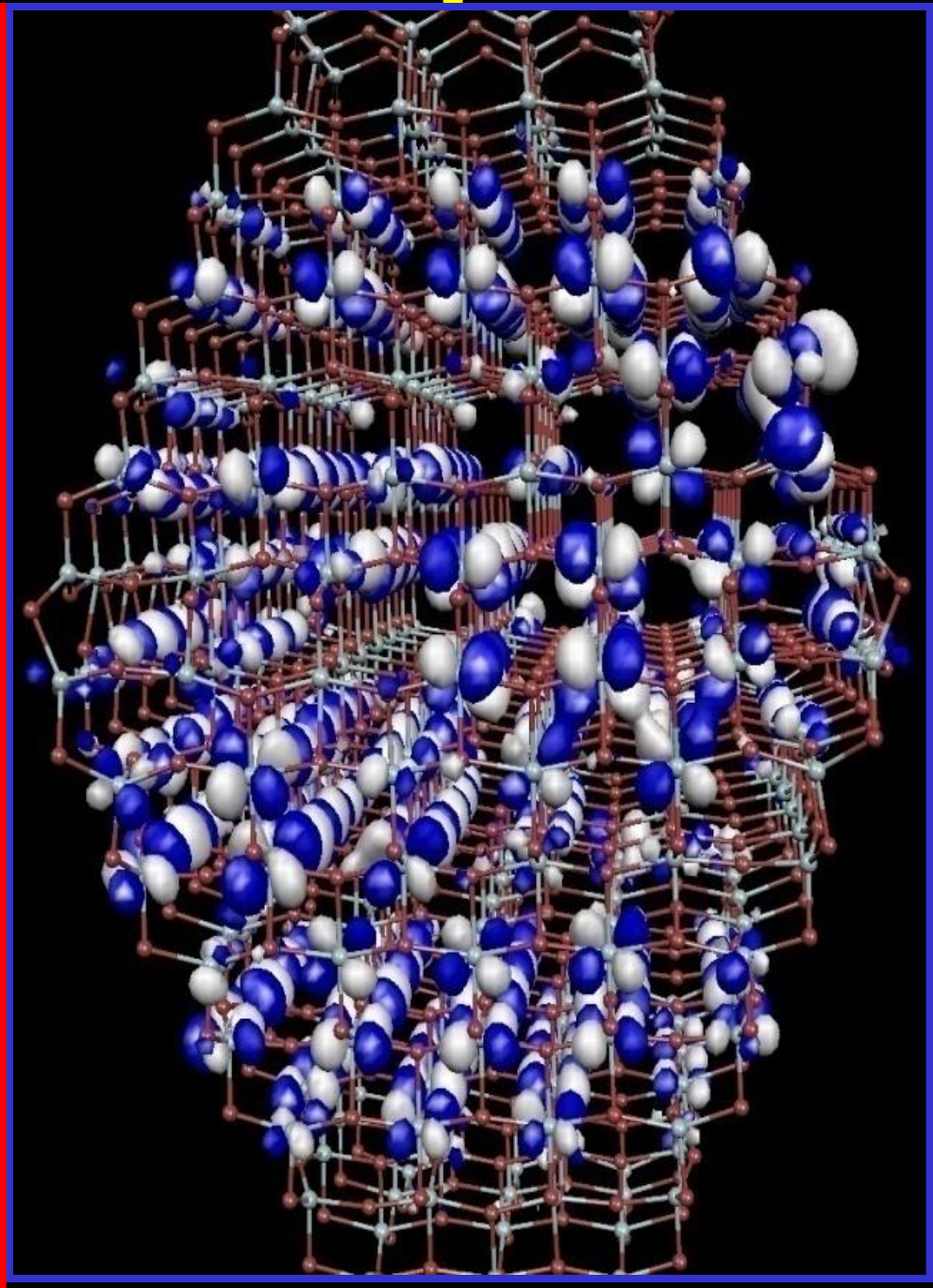




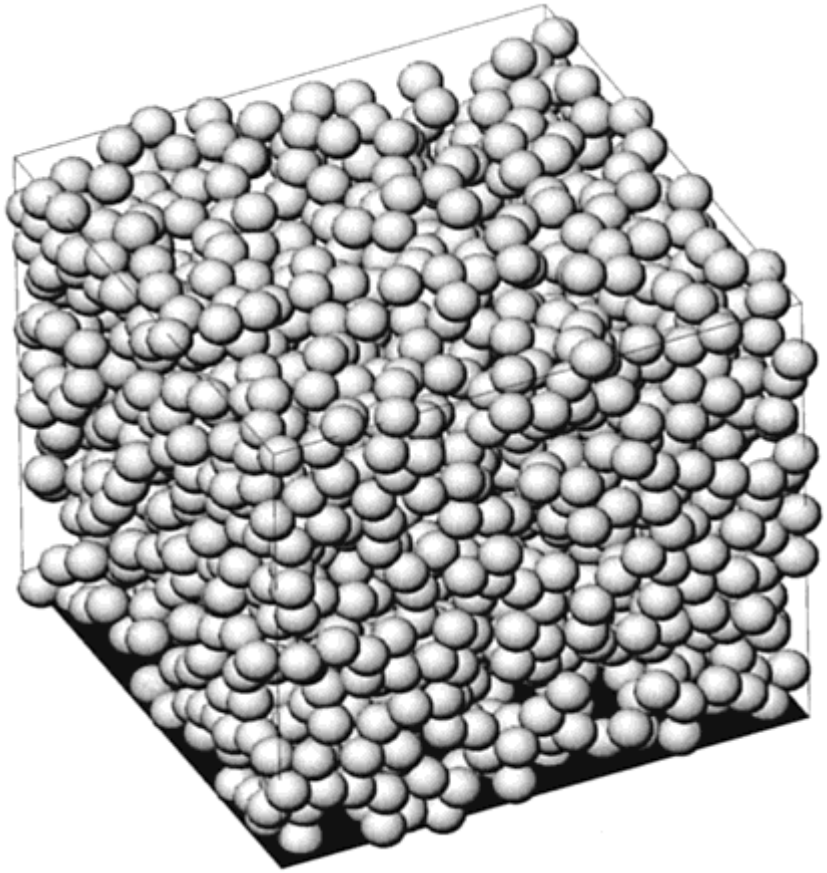
Bare TiO_2 NC

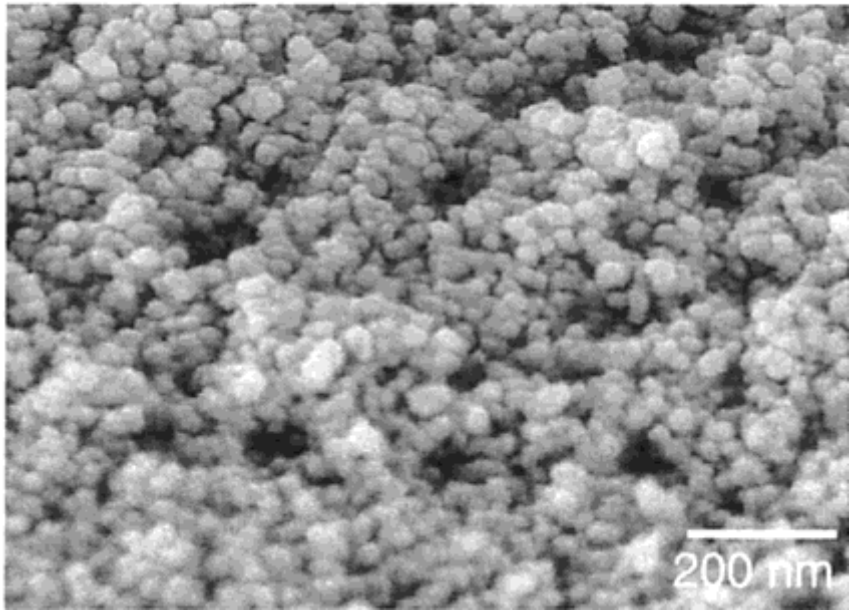
Space /energy distribution in a TiO_2 NC





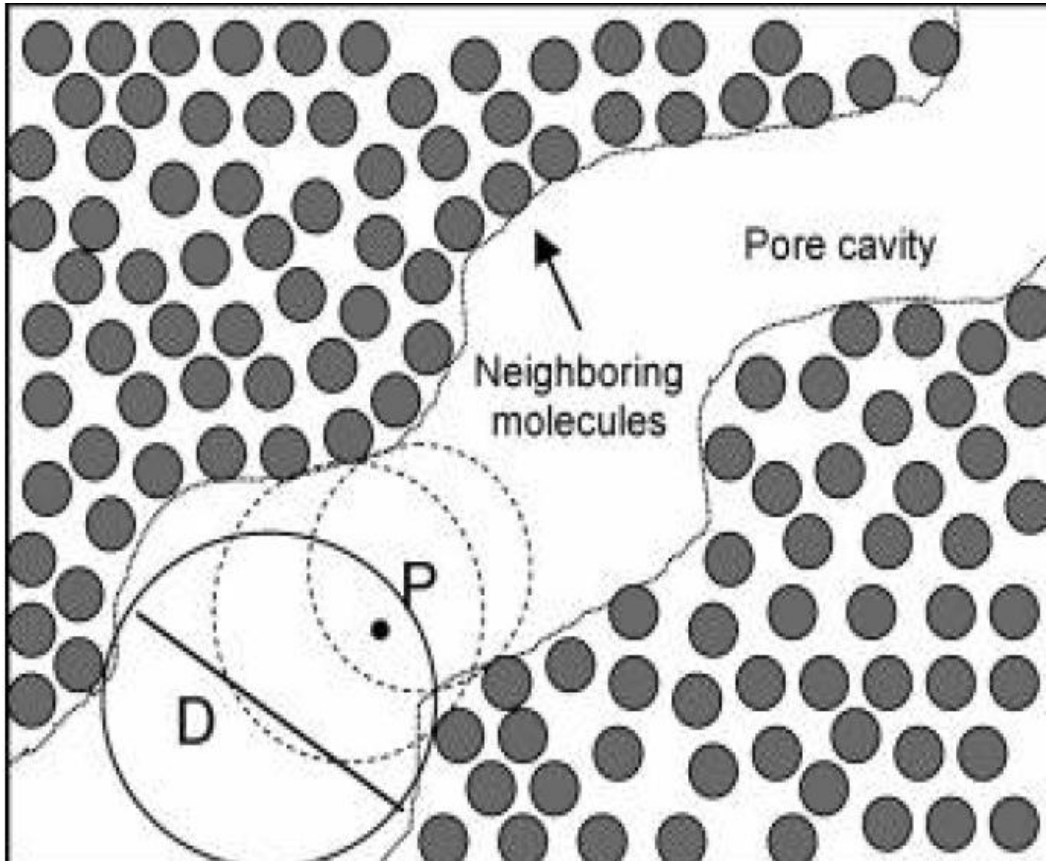
Simulating the mesoporous film: Sphere packing

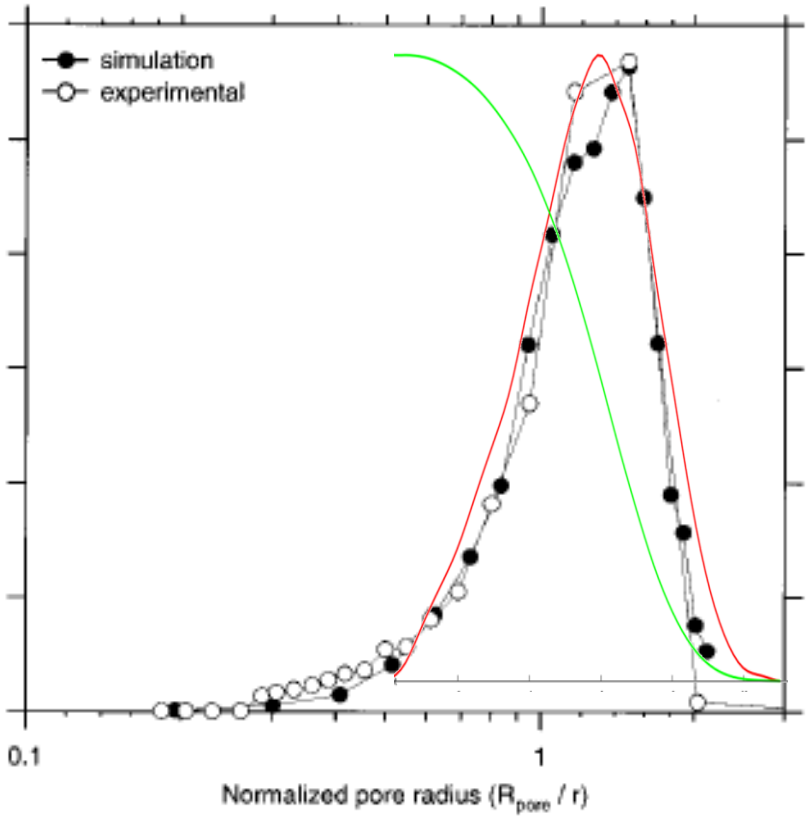




van de Lagemaat, Benkstein, Franck *J. Phys. Chem. B, Vol. 105, No. 50, 2001*

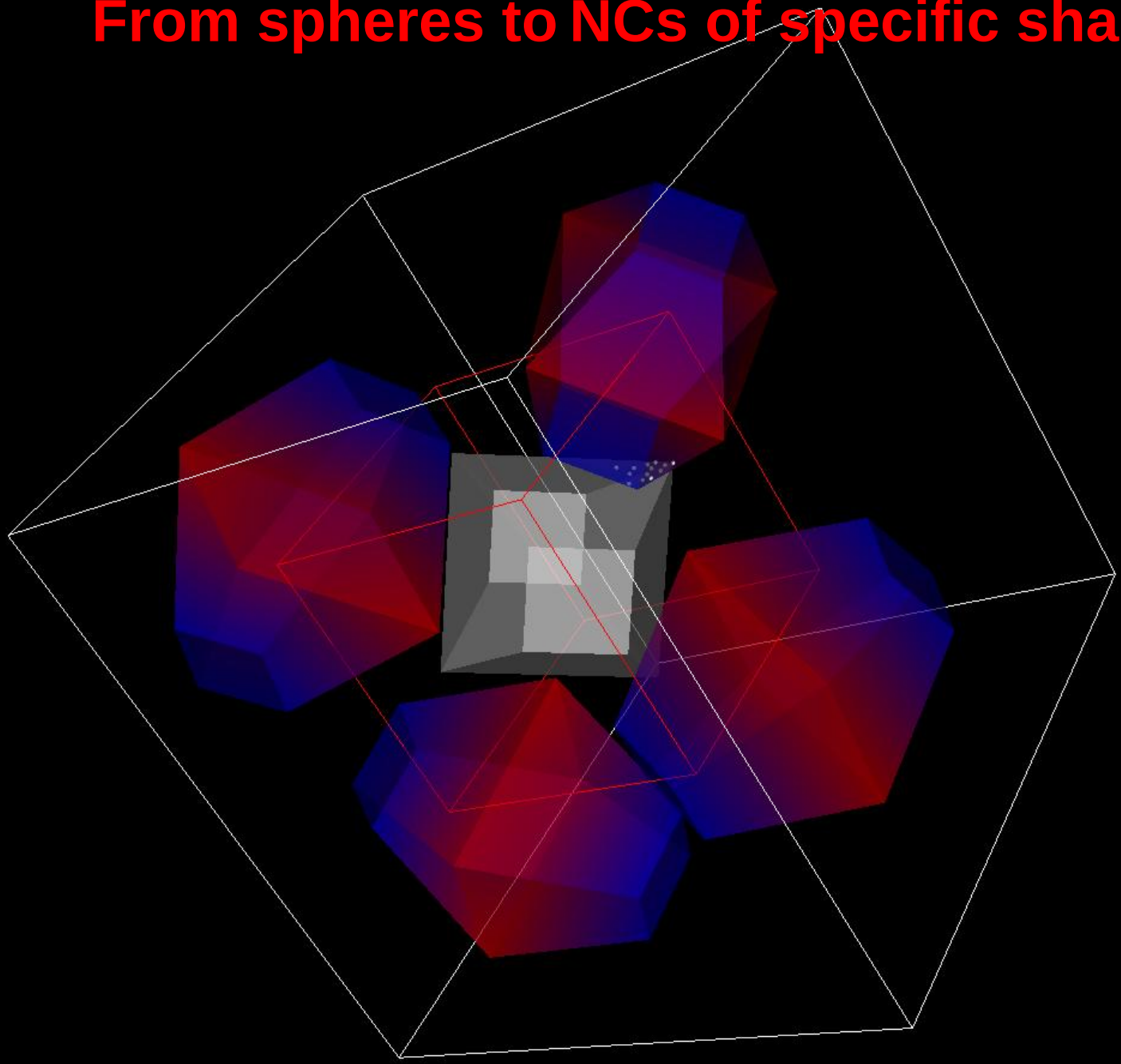
Pore Size Distribution (PSD) calculation



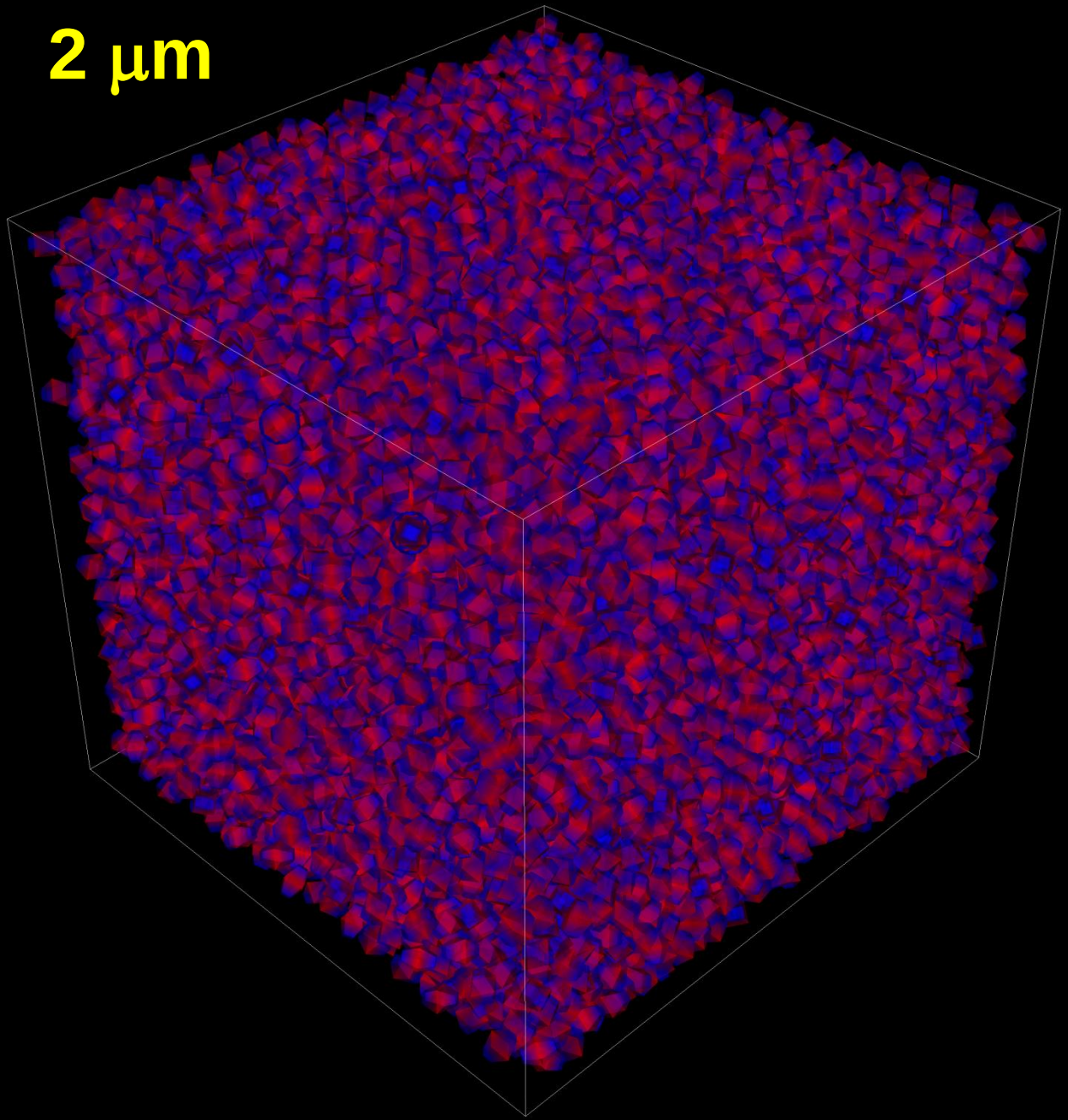


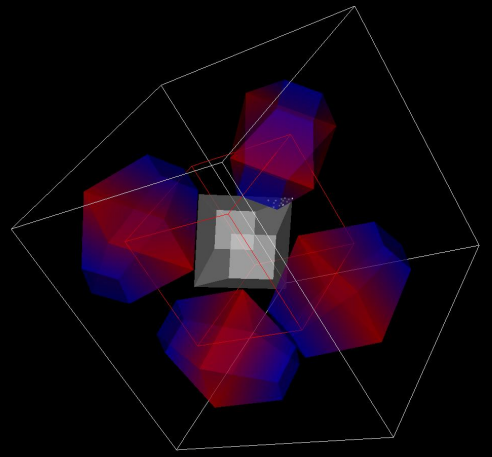
van de Lagemaat, Benkstein, Franck *J. Phys. Chem. B, Vol. 105, No. 50, 2001*

From spheres to NCs of specific shape



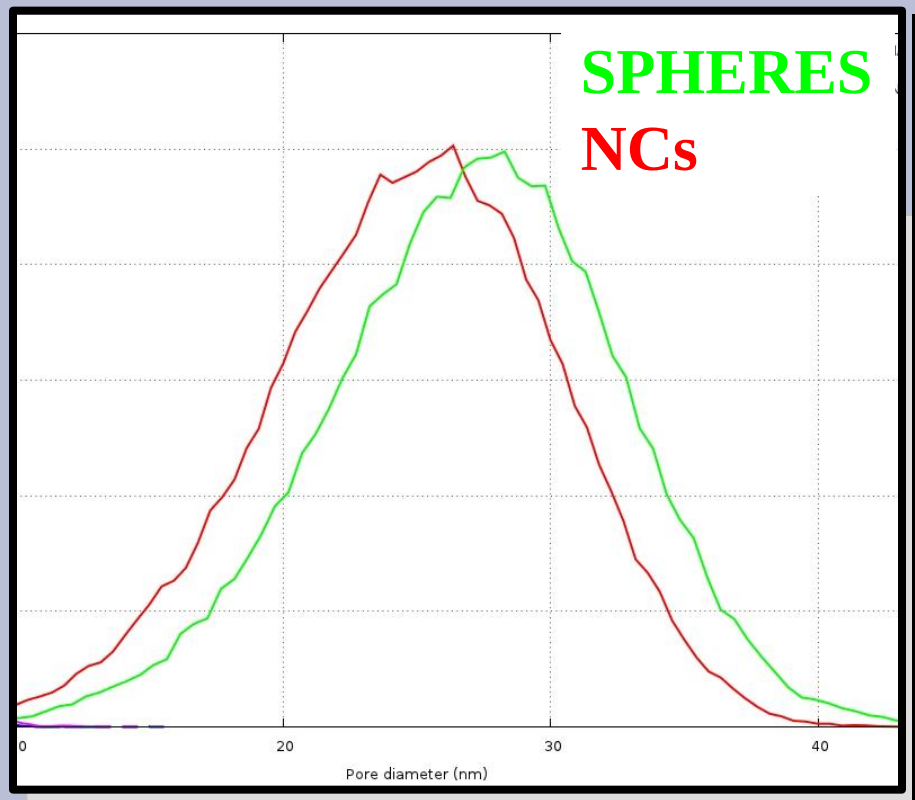
From individual TiO_2 NCs to the mesoporous film

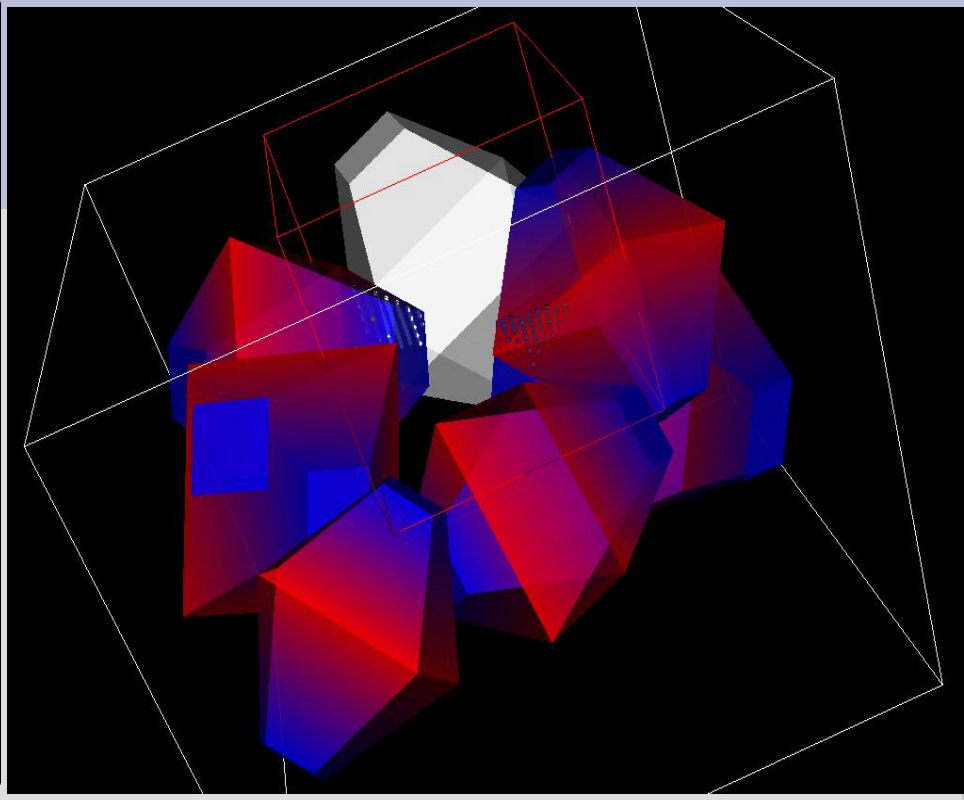




10 nm

PSD calculation for realistic NCs:





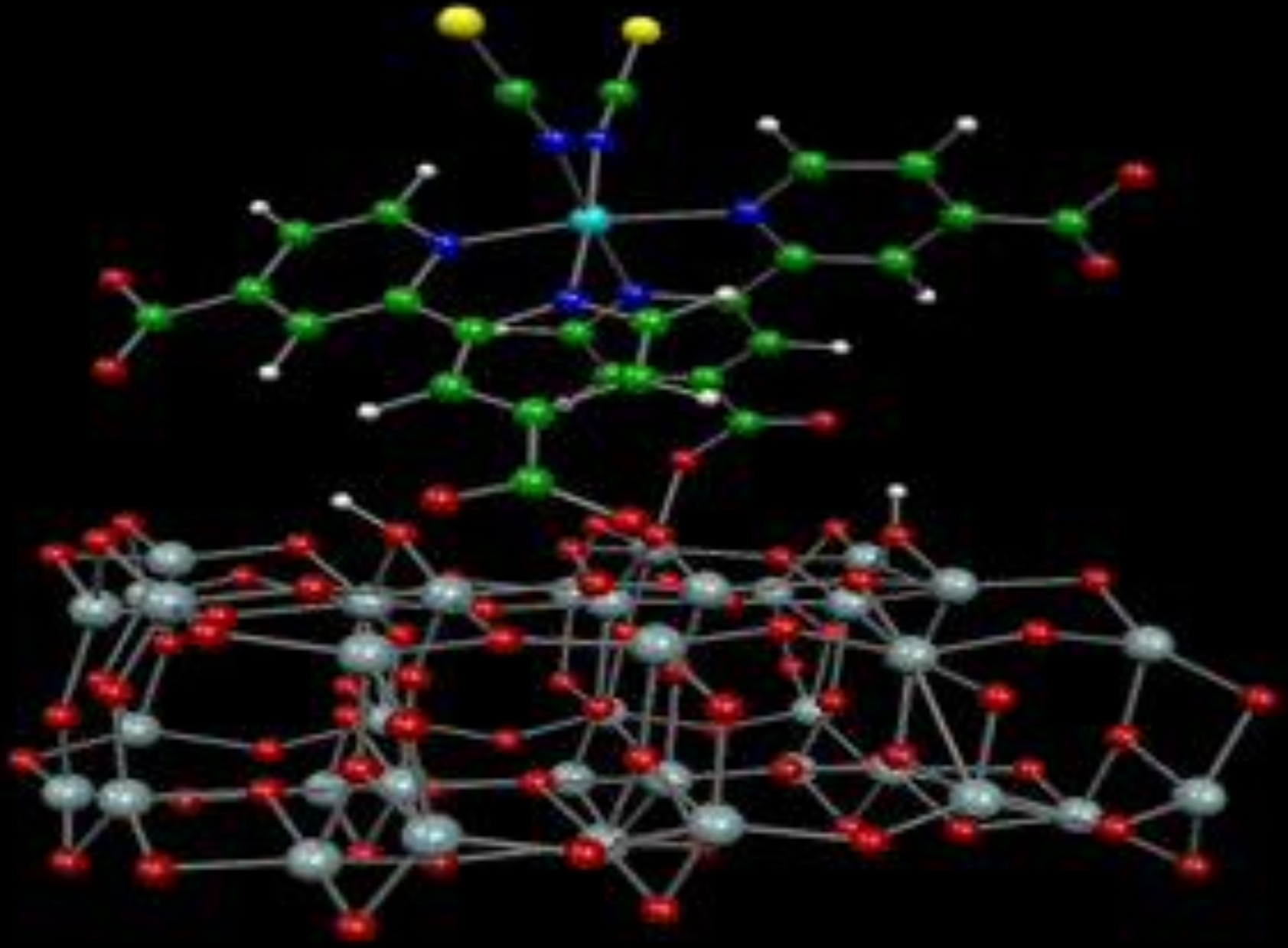
We calculated the intersection area of each NC with its neighbors, finding an average overlap of 1% of the total area.

Relation to transport?

Part III

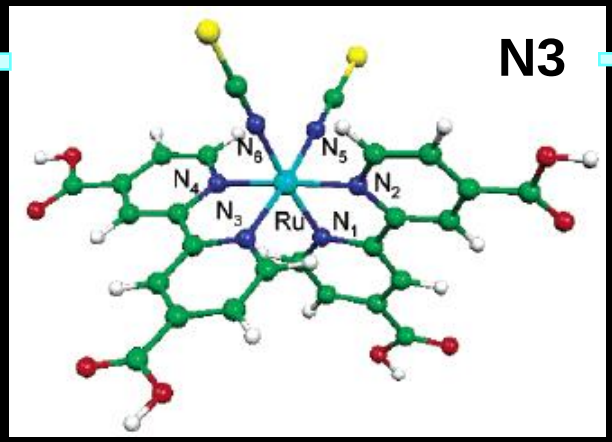
Dyes@TiO_2 Solvent/Electrolyte

N3 (N719) dye adsorption onto TiO_2: AIMD

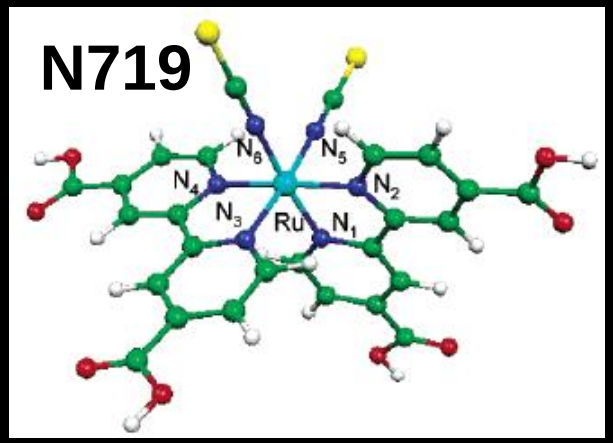


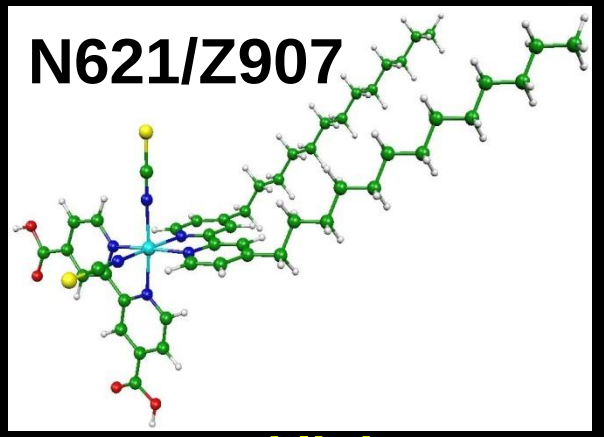
Tuning the properties of Ru(II) TiO_2 sensitizers

Control of protonation/ conuterions



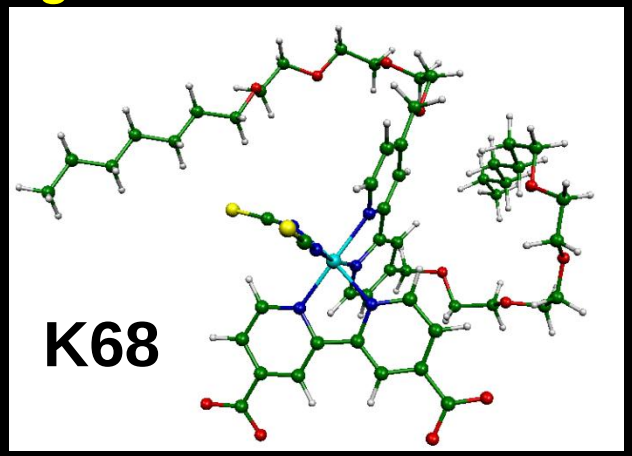
Stability/ Charge separation

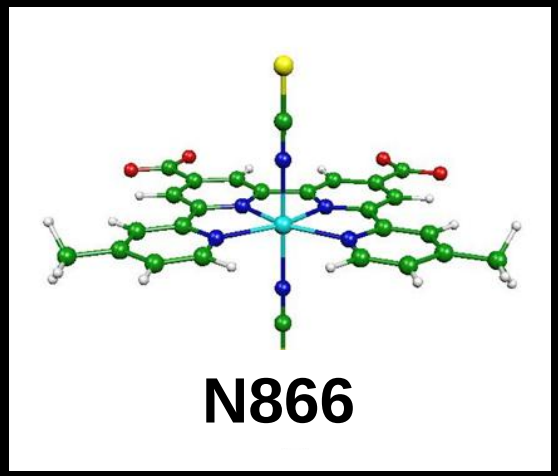




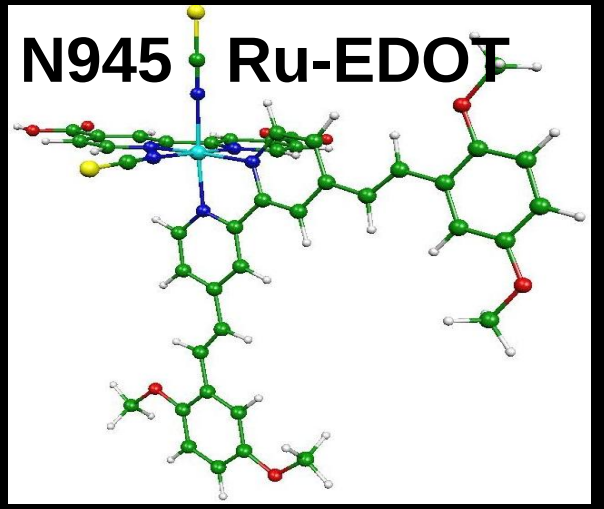
Improved light harvesting

Ion-coordinating ligands

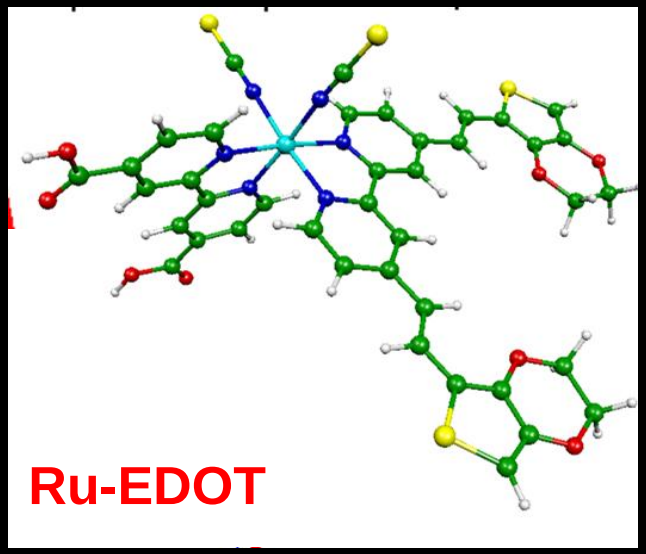


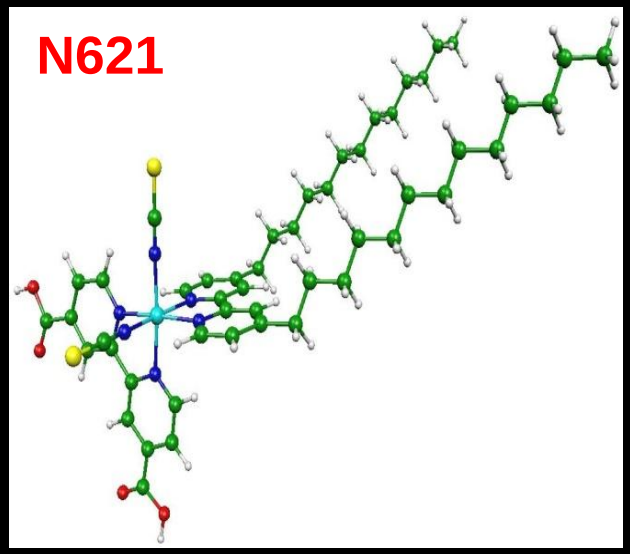


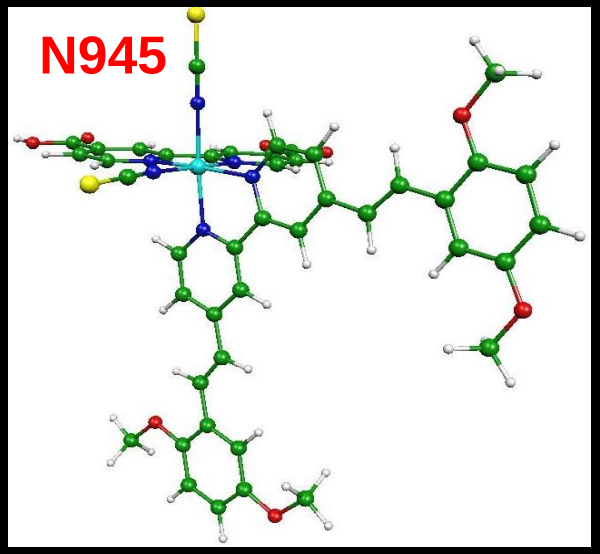
Quaterpyridil ligands
Trans isomers



Heteroleptic Ru(II) TiO_2 sensitizers







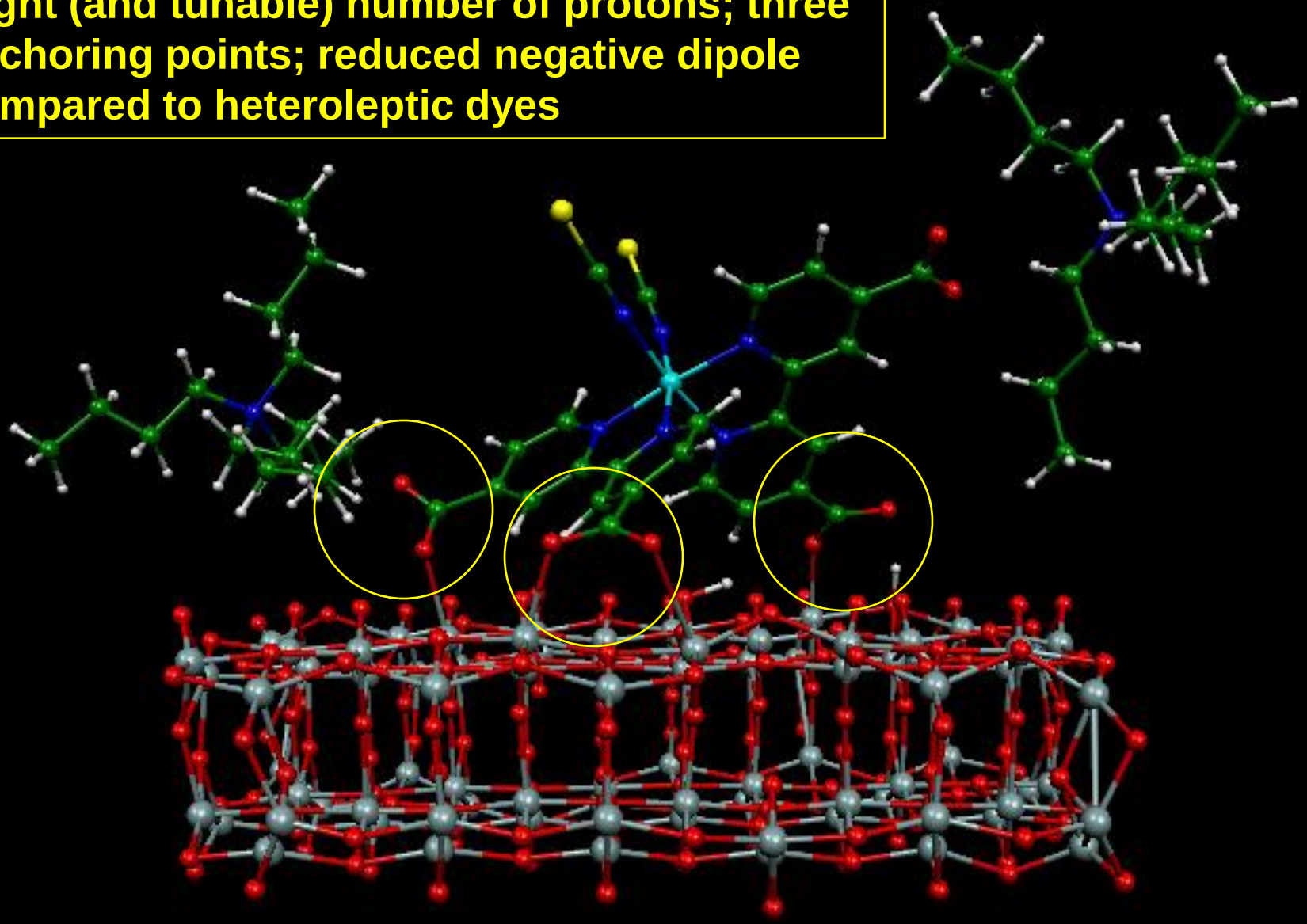
Sensitizer	Number of protons	Current mA/cm^2	Potential (mV)	Fill Factor	Efficiency at 1.5 AM
N719	2	16.66	846	0.73	10.28
N621	1	16.22	766	0.70	8.69
K19	1	16.40	768	0.73	9.19
N945	1	17.25	759	0.73	9.55
Ru-EDOT	2	**19.1**	**663**	0.72	**9.11**

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.**

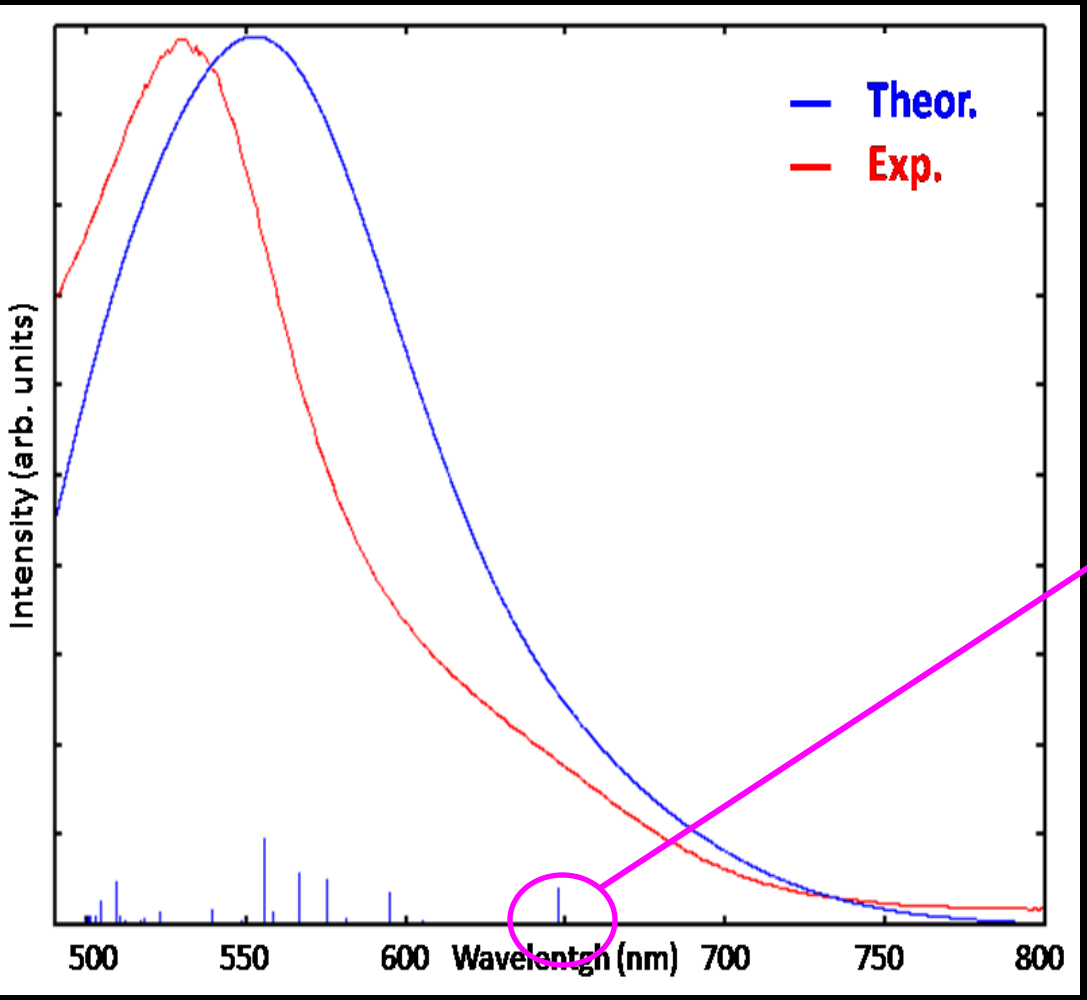
The success of N719: Adsorption geometry

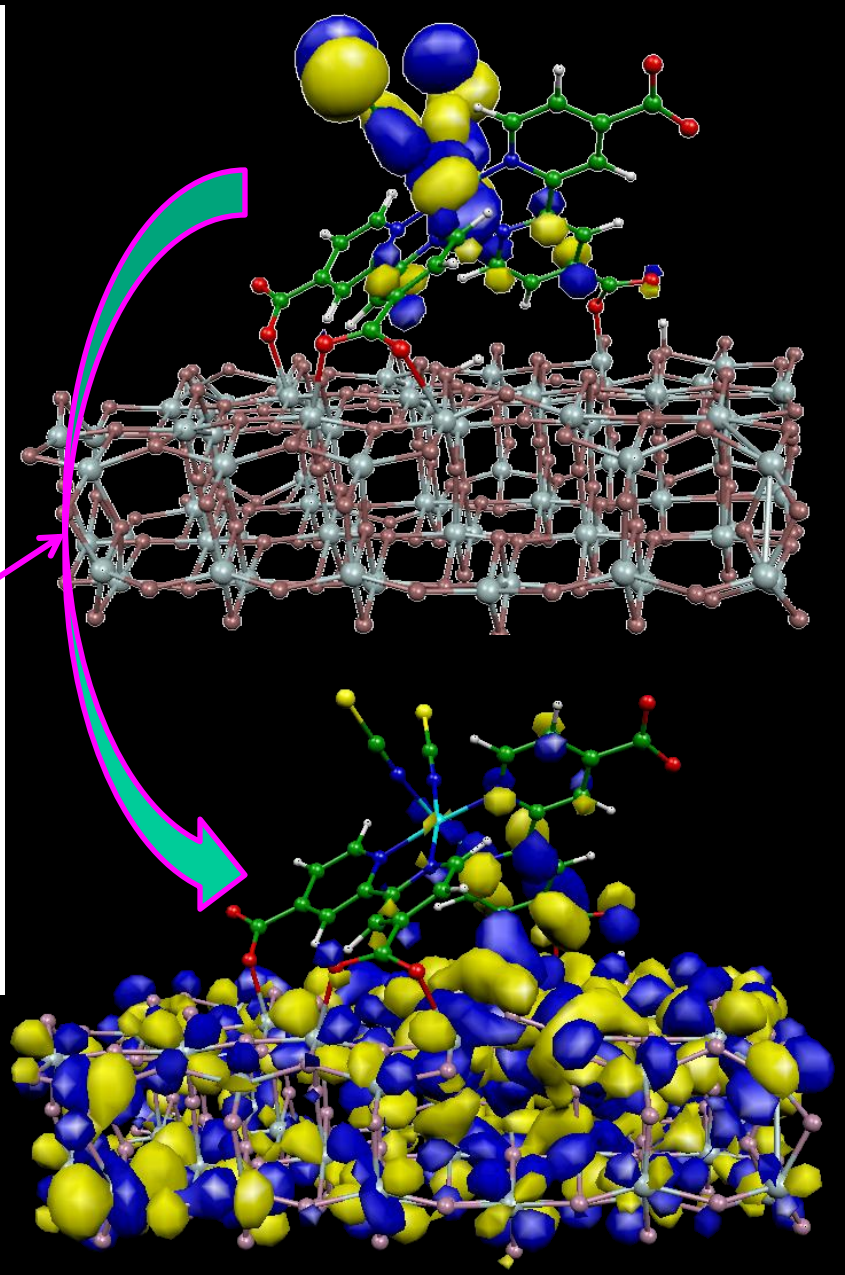
Right (and tunable) number of protons; three anchoring points; reduced negative dipole compared to heteroleptic dyes



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

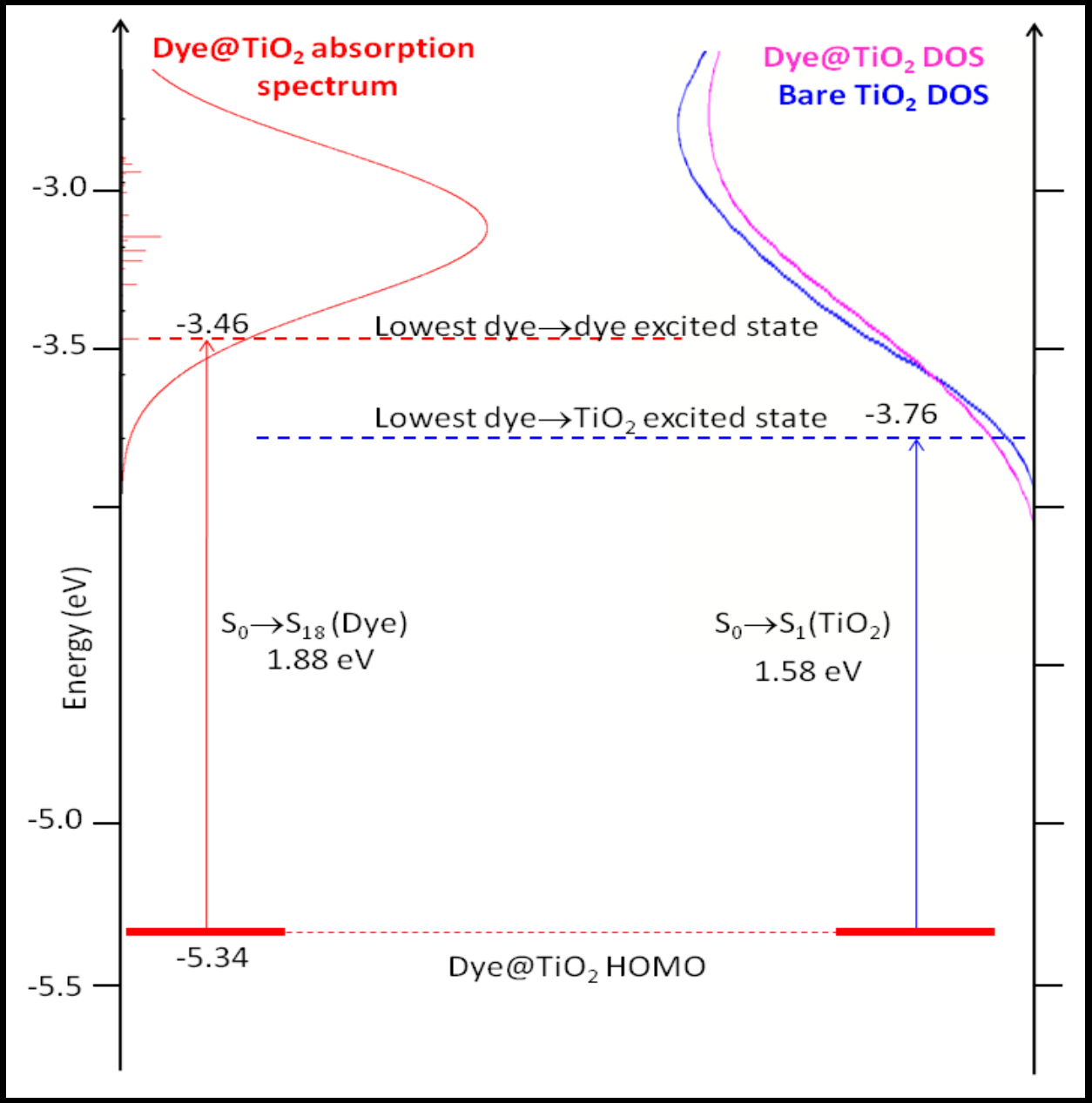
CALC. vs. EXP. ABSORPTION SPECTRA OF N719@TIO_2





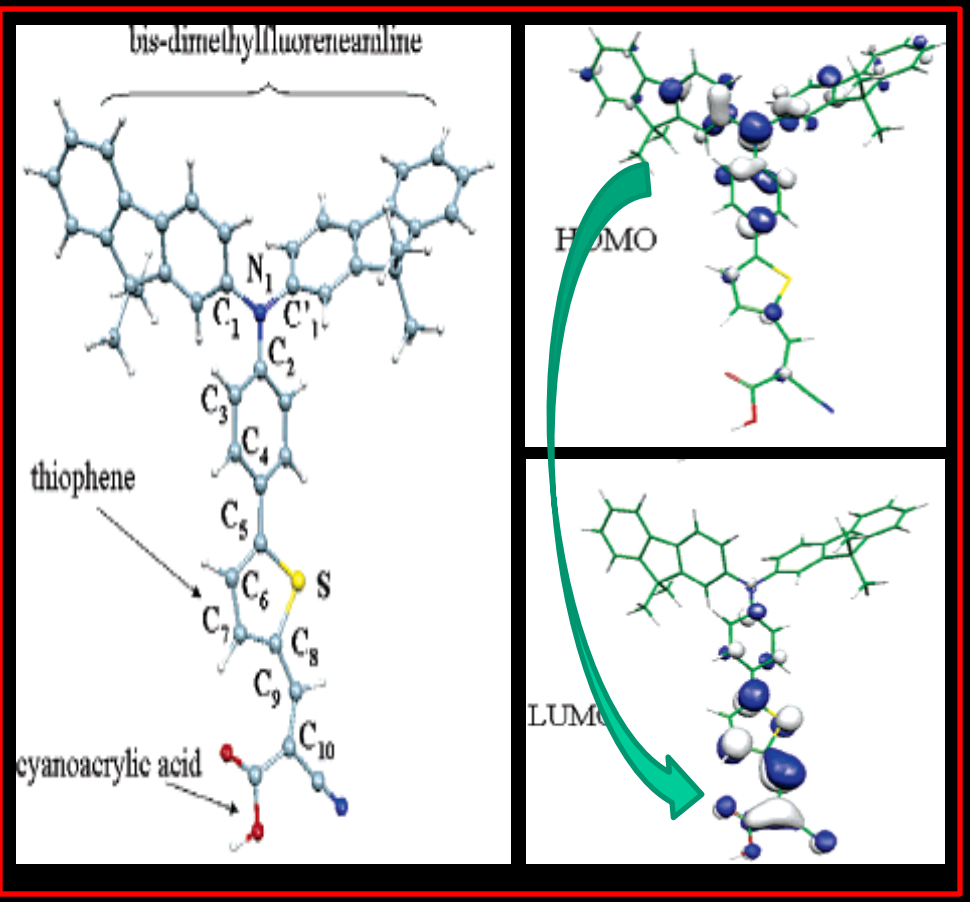
The lowest intense transition has a strong excited state delocalization into the TiO2, suggesting a strong coupling and an almost instantaneous electron transfer following light absorption.

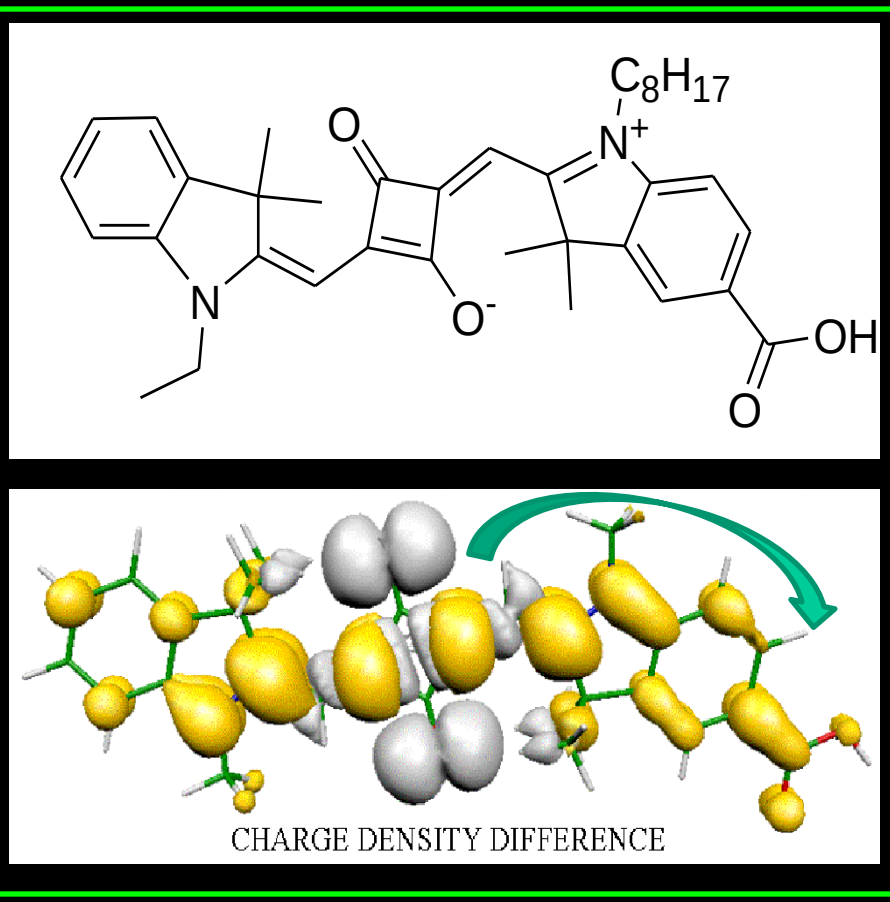
ALIGNMENT OF GROUND/EXCITED STATES ENERGY LEVELS



F. De Angelis, S. Fantacci, M.K. Nazeeruddin, M. Graeztel, *J. Phys. Chem. C.* **2011**.

DSSCs based on organic dye-sensitizers:





η=8.1 %

- S.Kim, F. De Angelis, S. Fantacci, M. Grätzel, et al.
- J.-H. Yum, F. De Angelis, M. Grätzel, et al.
- D.P. Hagberg, F. De Angelis, M. Grätzel, et al.
- M. Pastore, F. De Angelis, M. Grätzel, et al.

η= 4.5%

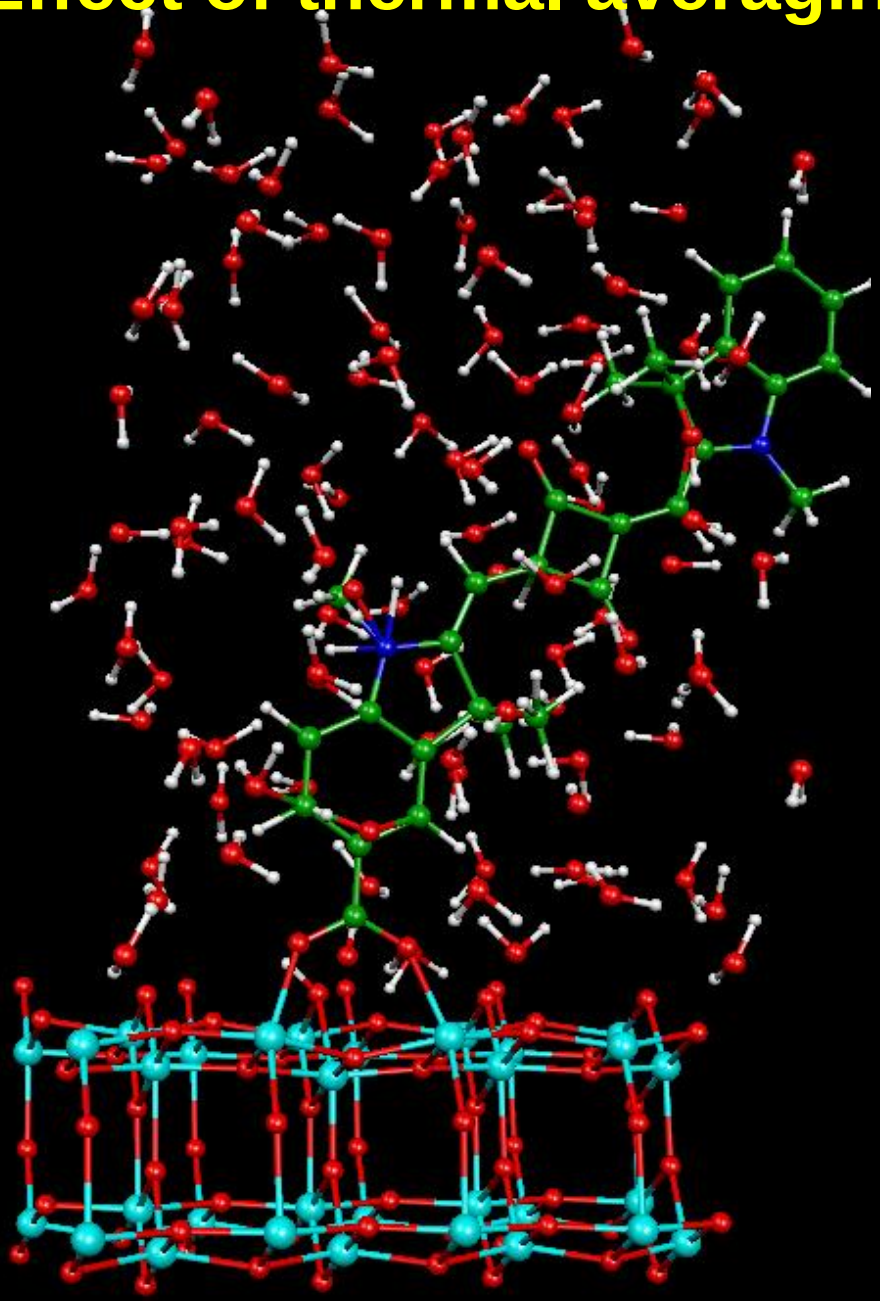
***J. Am. Chem. Soc.* 2006, 128, 16701.**

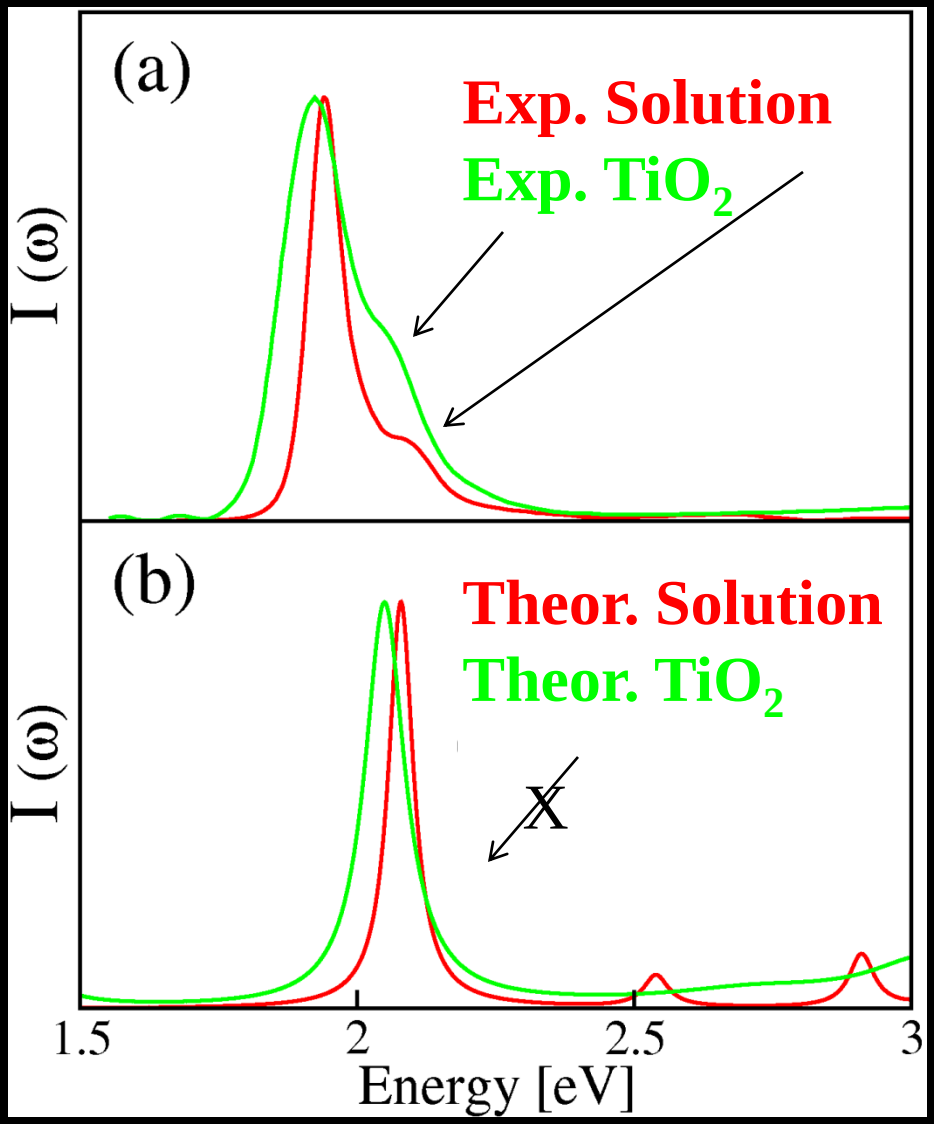
***J. Am. Chem. Soc.* 2007, 129, 10320.**

***J. Am. Chem. Soc.* 2008, 130, 6259.**

***J. Phys. Chem. C.* 2010, in press.**

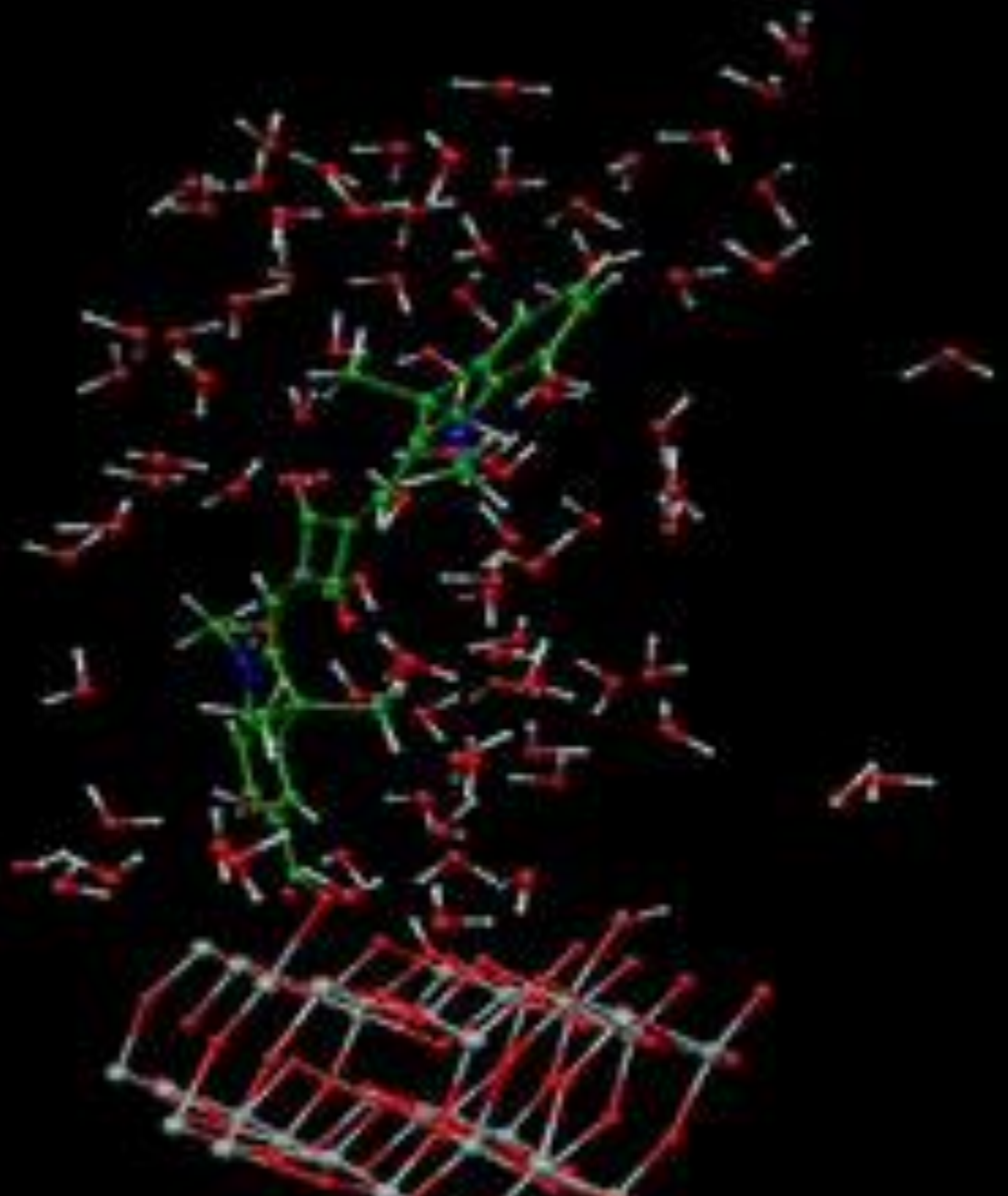
Effect of thermal averaging and of explicit solvation:



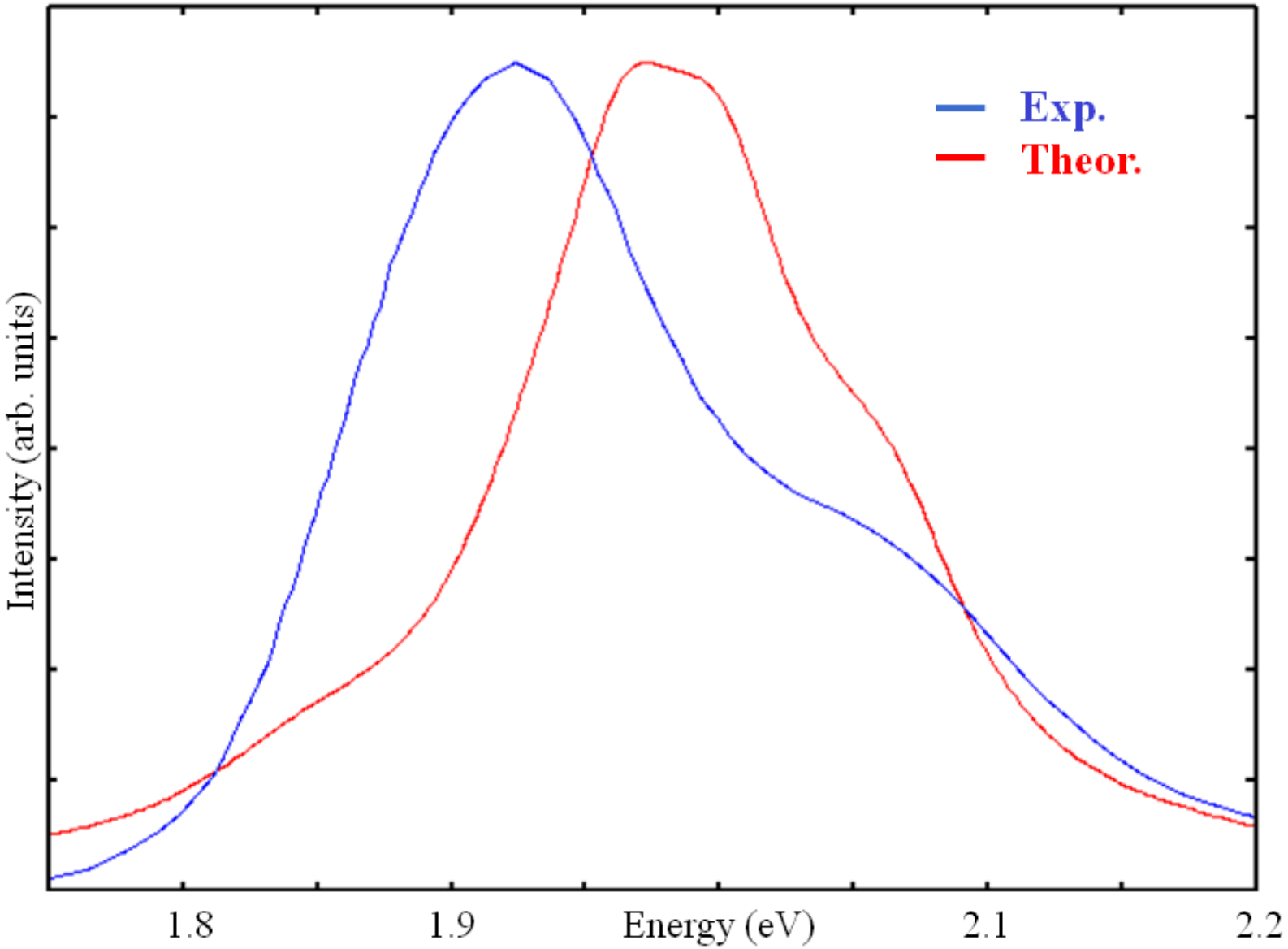


D. Rocca, F. De Angelis et al. *Chem. Phys. Lett.* **2009**, 475, 49.

Effect of thermal averaging and of explicit solvation:



Solution thermally averaged UV-vis spectrum:



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

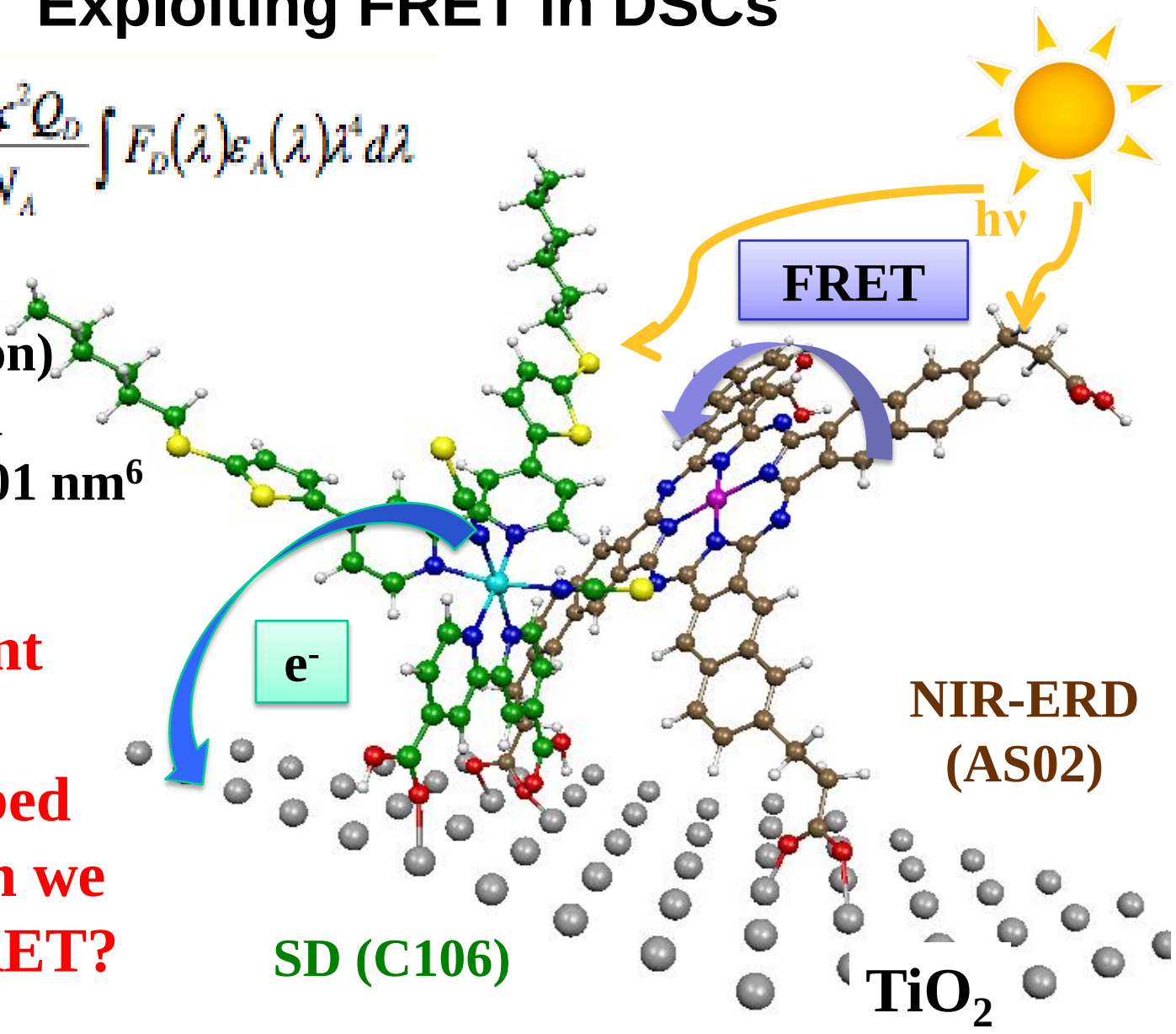
Exploiting FRET in DSCs

$$R_0^6 = \frac{9000 \cdot \ln(10)\kappa^2 Q_D}{128 \cdot \pi^5 n^4 N_A} \int F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda$$

k^2= 2/3 (solution)

R_0= 1.5-1.8 nm

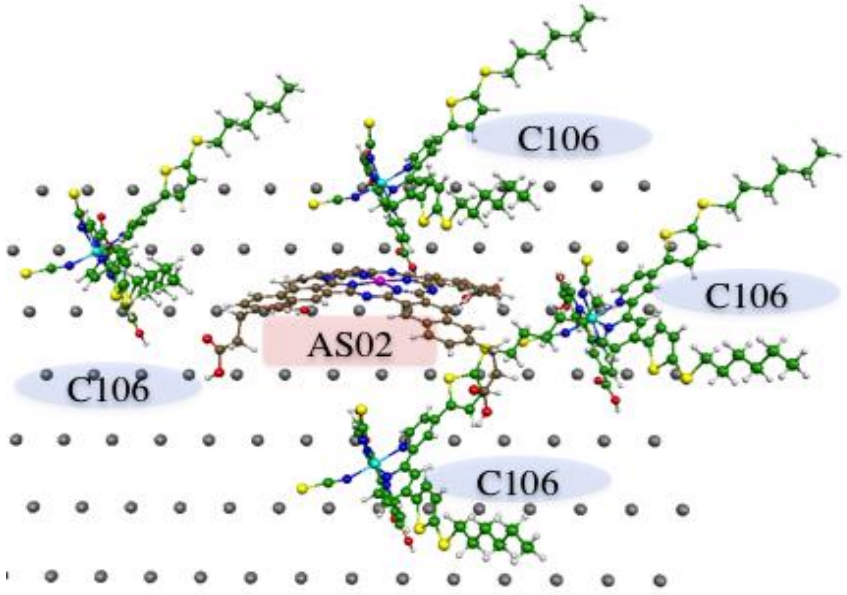
R_0^6= 11.39-34.01 nm^6



Is k^2 different from 2/3 for TiO_2-adsorbed species? Can we optimize FRET?

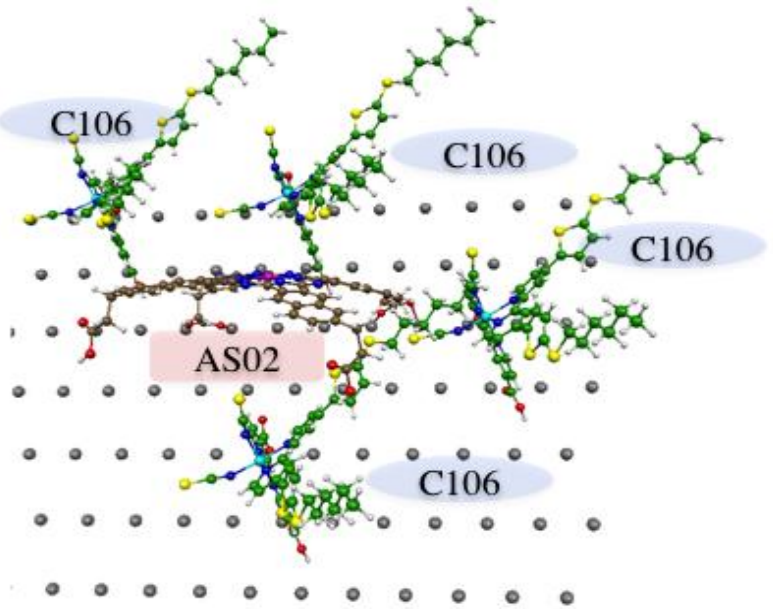
Hardin, B. E.; Sellinger, A.; Moehl, T.; Humphry-Baker, R.; Moser, J.-E.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M.; McGehee, M. D., *J. Am. Chem Soc.* **2011**, *133*, 10662.

Modeling FRET between TiO_2-adsorbed ERD/SD



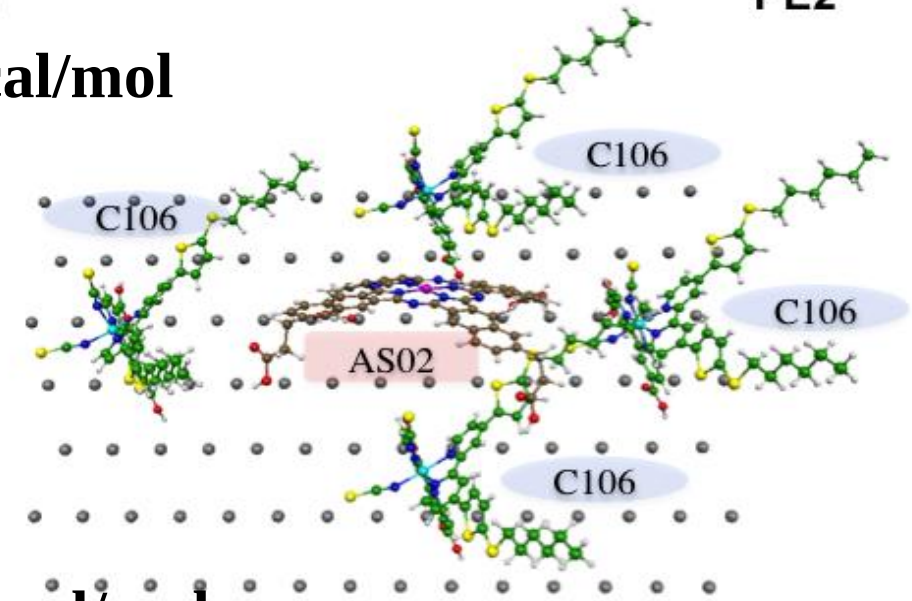
PE1

0.0 kcal/mol



PE2

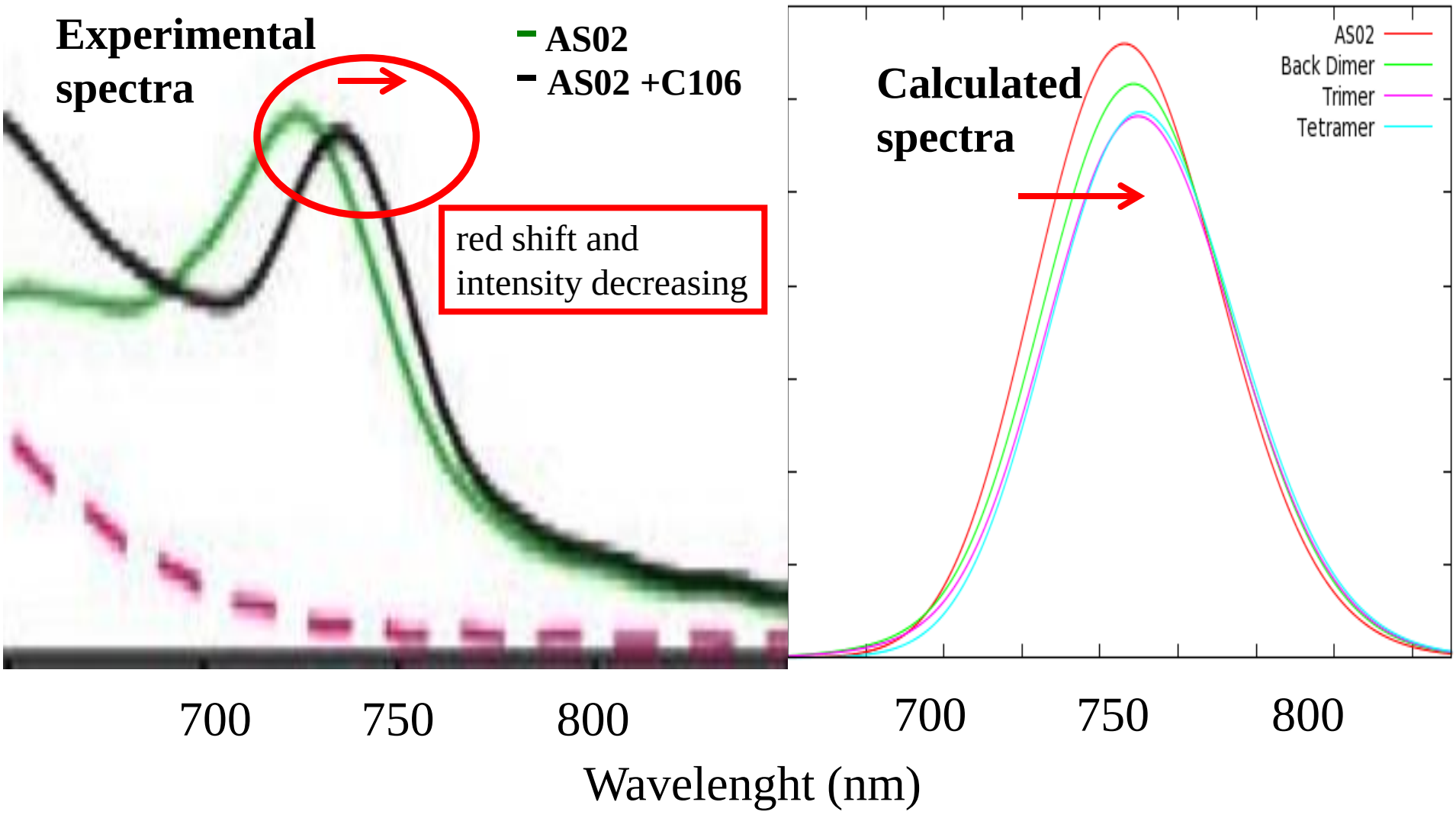
+3.8 kcal/mol



+5.8 kcal/mol

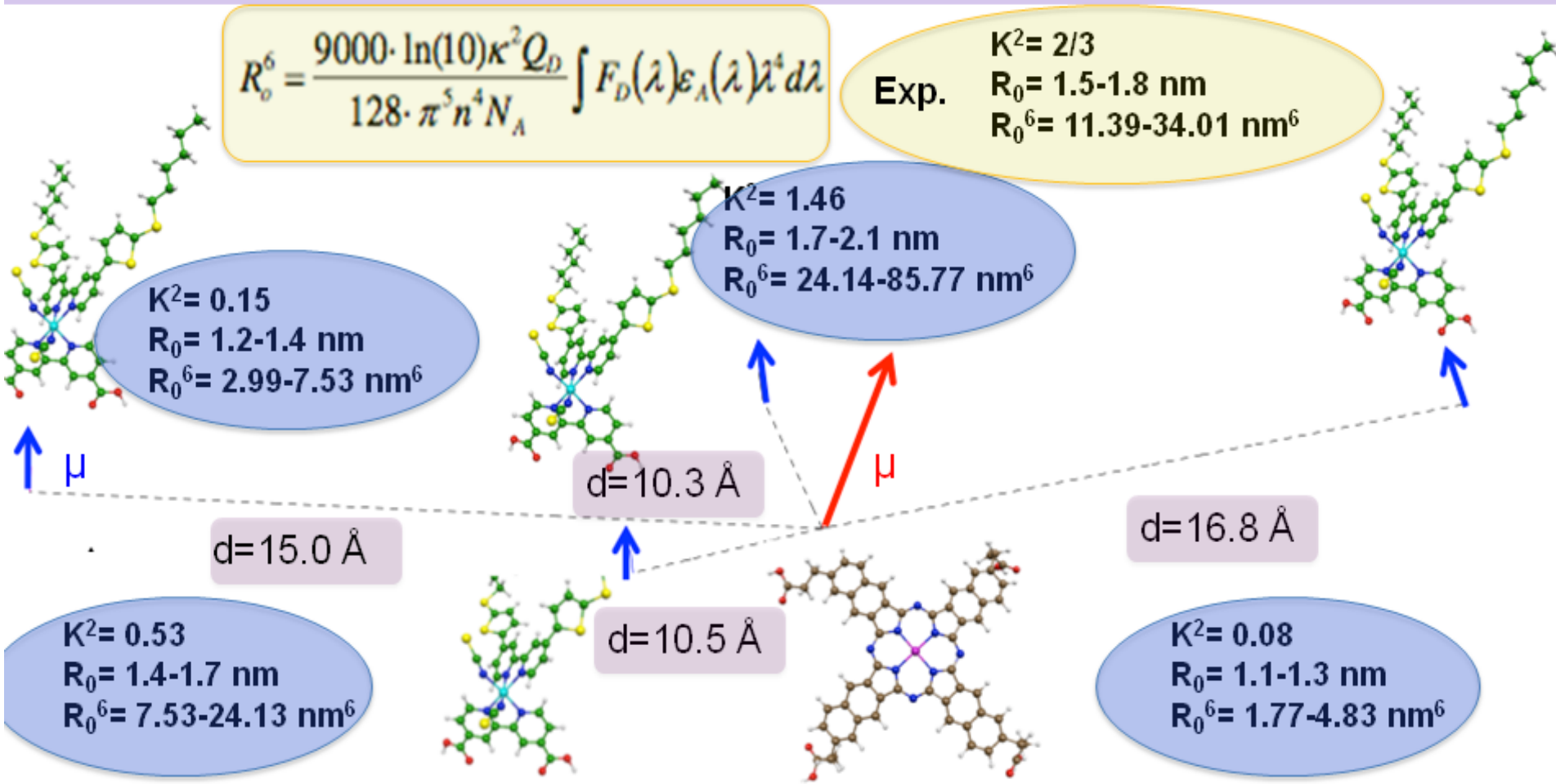
PE3

Optical properties TiO_2-adsorbed ERD/SD aggregates



The SD perturbs the electronic levels of the ERD

k^2 calculation for TiO_2-adsorbed ERD/SD aggregates



k^2 varies from 0.08 to 1.46!

R^6_0 varies from 2 to 86 !!

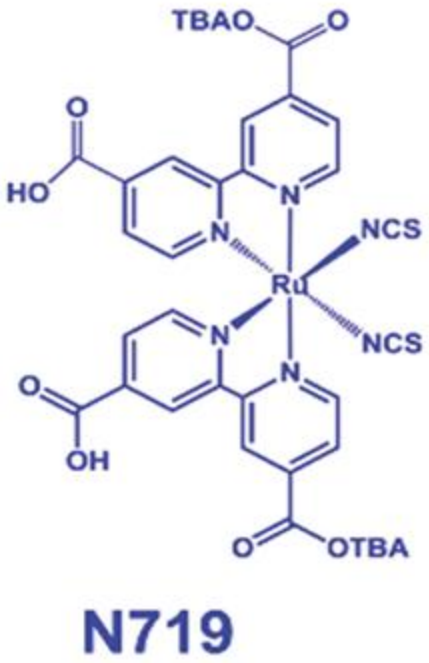
THE JOURNAL OF PHYSICAL CHEMISTRY C

ARTICLE

pubs.acs.org/JPCC

Cobalt Redox Mediators for Ruthenium-Based Dye-Sensitized Solar Cells: A Combined Impedance Spectroscopy and Near-IR Transmittance Study

Yeru Liu,[†] James R. Jennings,[†] Yao Huang,[†] Qing Wang,[*,†] Shaik M. Zakeeruddin,[*,‡] and Michael Grätzel[*,‡]



N719

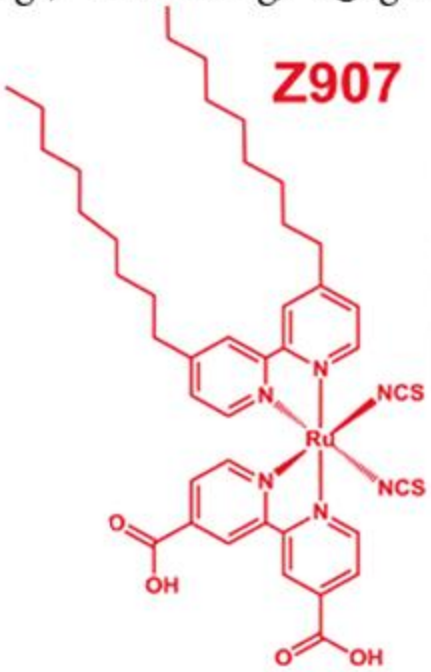


Table 1. Photovoltaic Parameters for DSCs Employing Different Electrolytes and Sensitizing Dyes, Measured under Simulated AM1.5 1 Sun Illumination[a]

cell	j_{sc} (mA cm^{-2})	V_{oc} (mV)	fill factor	η (%)
Z907-I	15.9	790	0.61	7.7
N719-I	16.8	758	0.63	8.0
Z907-Co	14.0	744	0.62	6.5
N719-Co	3.8	620	0.76	1.8

$\eta = 1.8\%$ $\eta = 6.5\%$

An Alternative Efficient Redox Couple for the Dye-Sensitized Solar Cell System

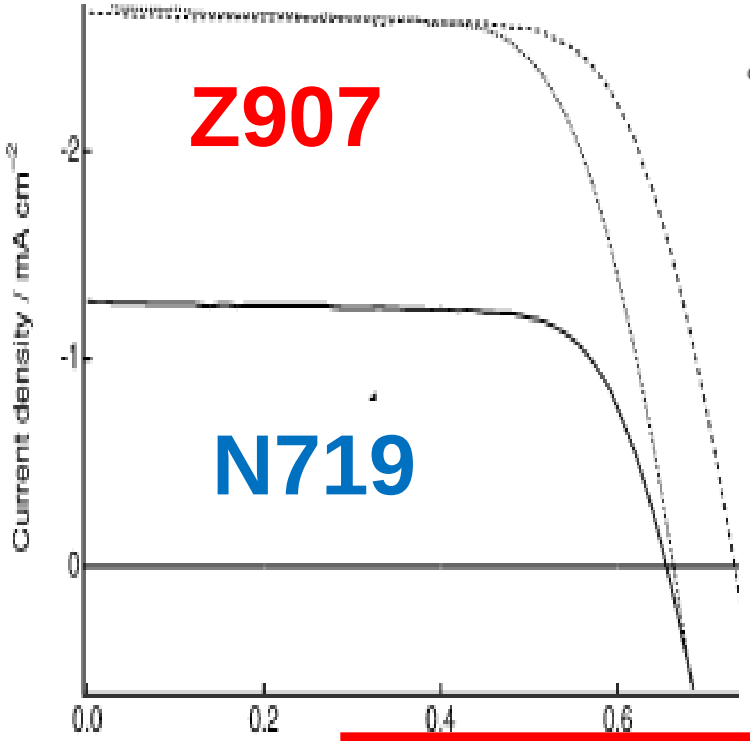
Hervé Nusbaumer,* Shaik M. Zakeeruddin, Jacques-E. Moser, and Michael Grätzel[a]

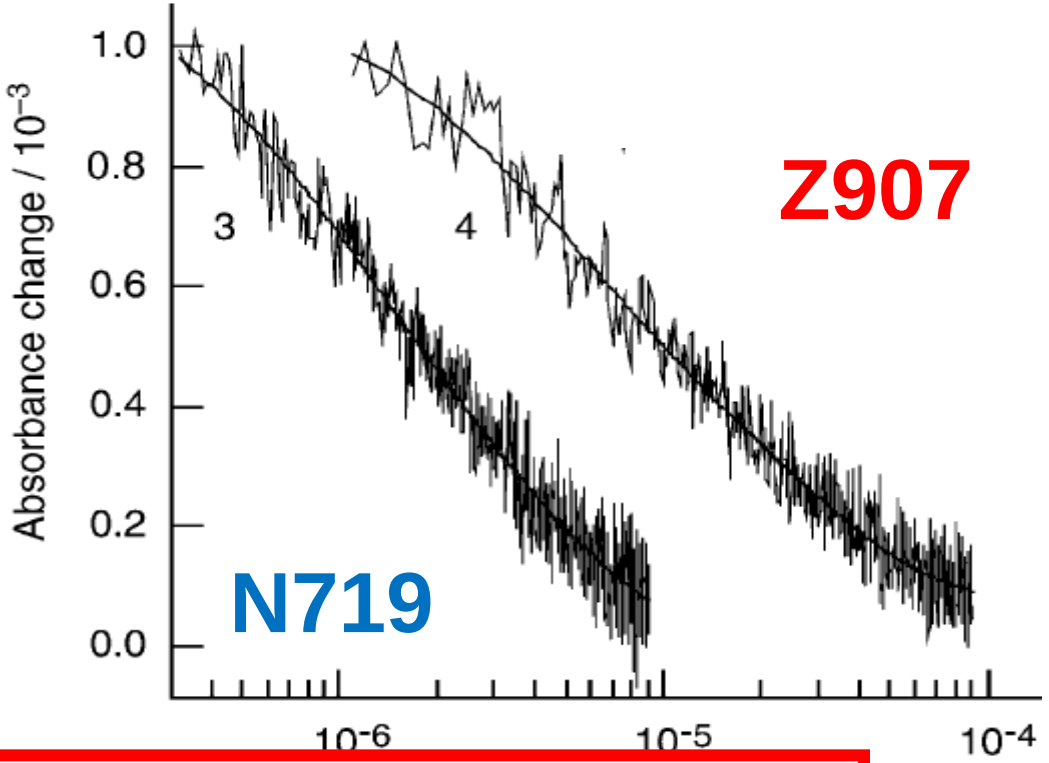
3756

DOI: 10.1002/chem.200204577 *Chem. Eur. J.* 2003, 9, 3756–3763

Z907: HIGHER PERFORMANCES **SLOWER REGENERATION**

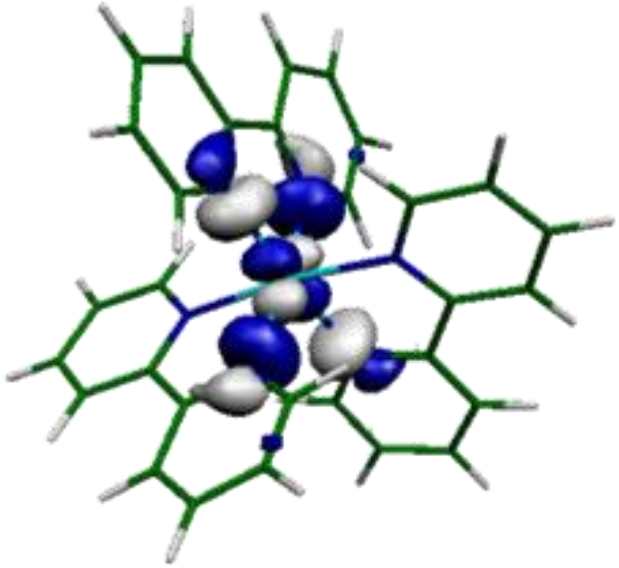
N719: LOWER PERFORMANCES **FASTER REGENARATION**

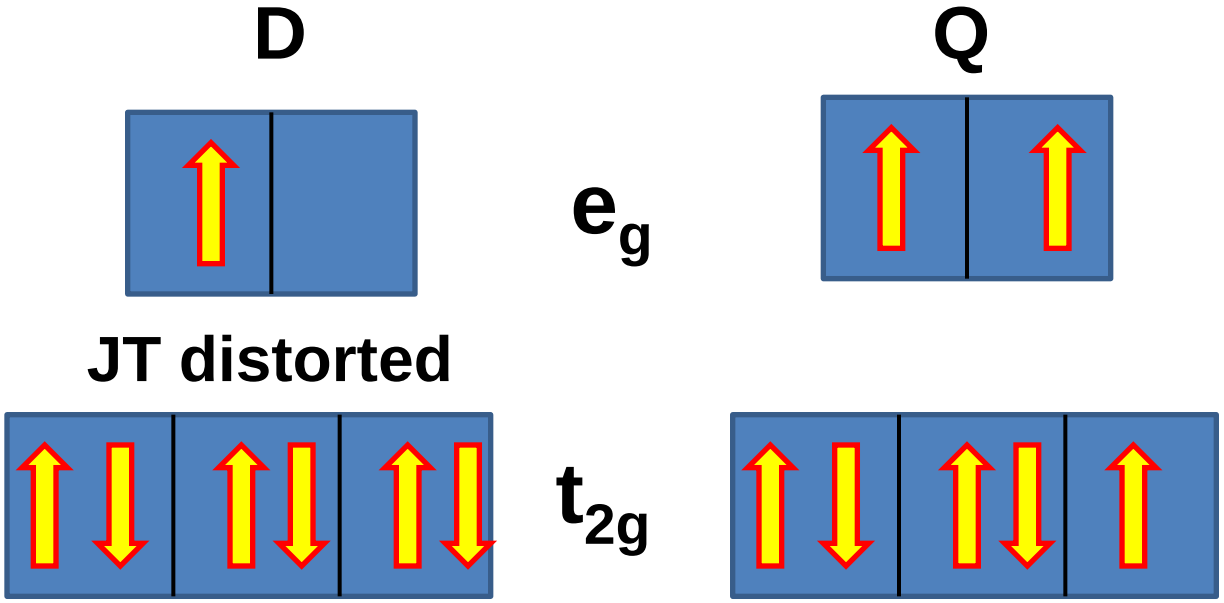




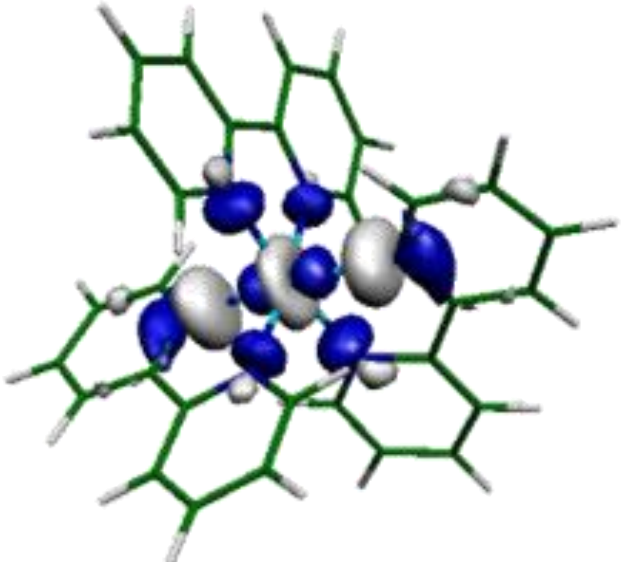
ROLE OF ION-PAIRING ?

$[Co(bpy)_3]^{+2}$ QUARTET / DOUBLET STATES





e_g states



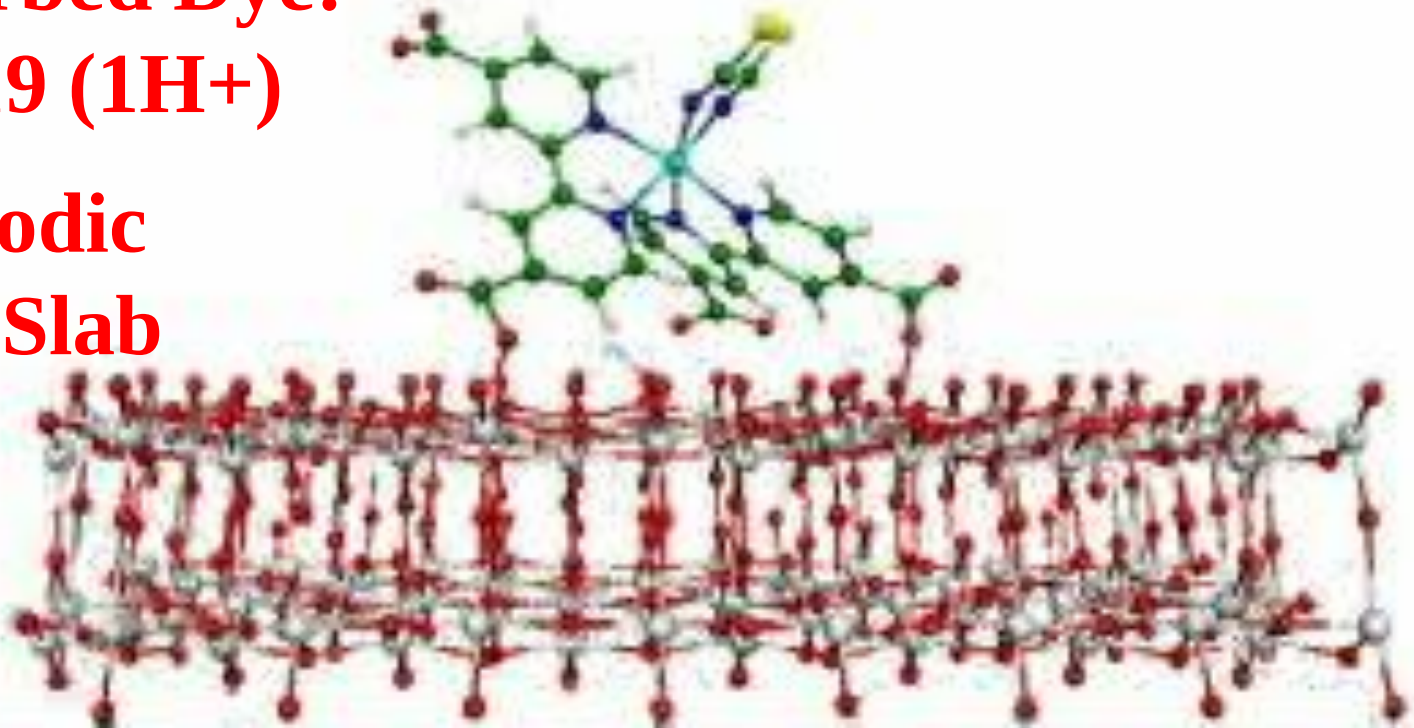
	Theor. (eV)	Exp (eV)
Co(II) Q-D	0.02	0.02
Co(III) S-T	1.43	??
	ΔG_{ox}(V)	
$Co(II)^Q$	+0.62 vs. NHE	+0.56
$Co(II)^D$	+0.60 vs. NHE	

N719@TiO_2 and $Co(bpy)_3^{+3}$ Redox Mediator

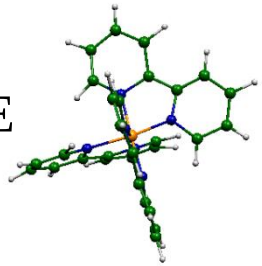
Electrolyte:
$[Co(bpy)_3]^{+3}$

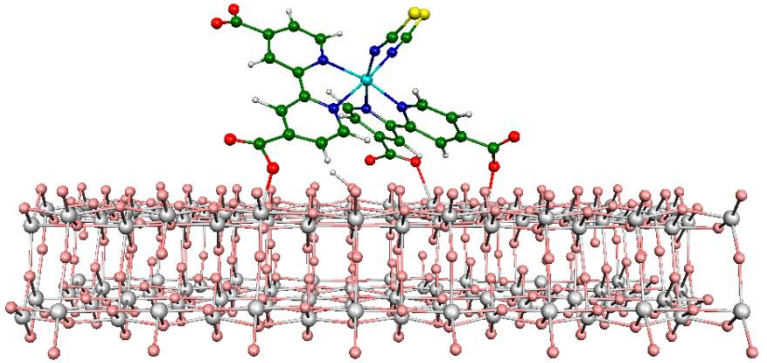
Adsorbed Dye:
N719 (1H+)

Periodic
TiO_2Slab

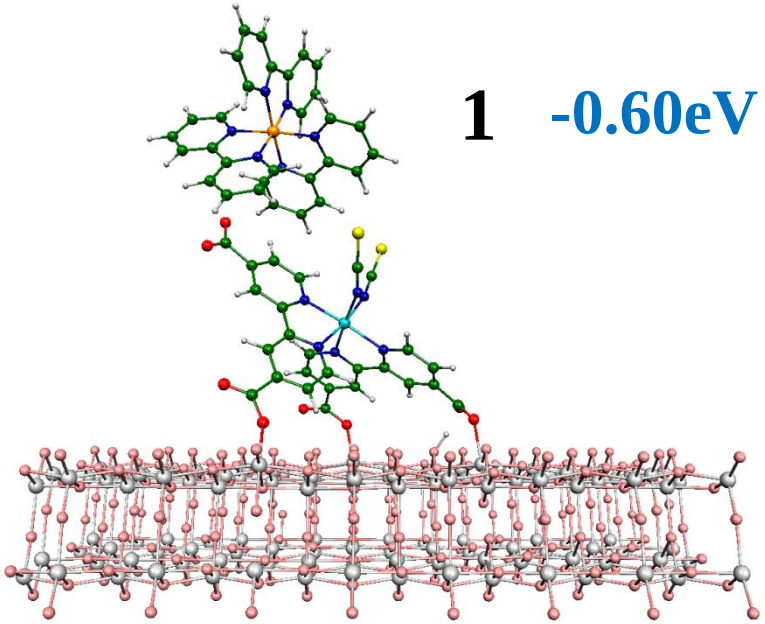


STARTING STRUCTURE

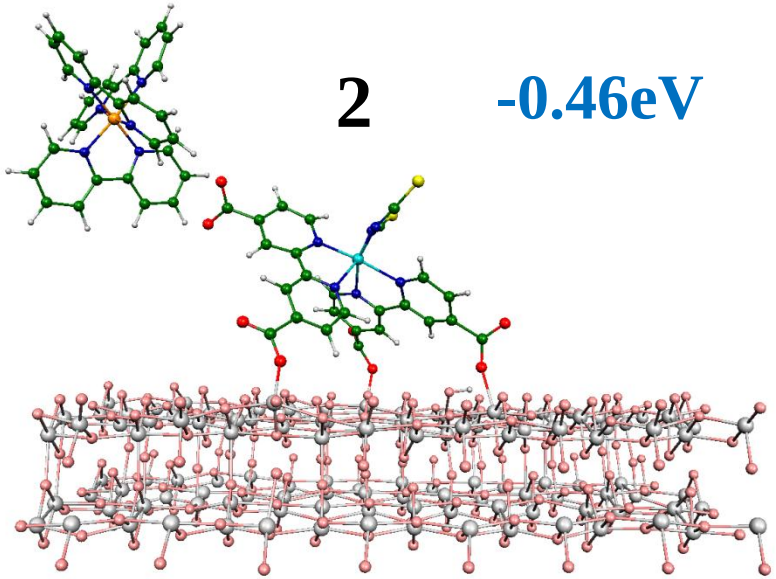




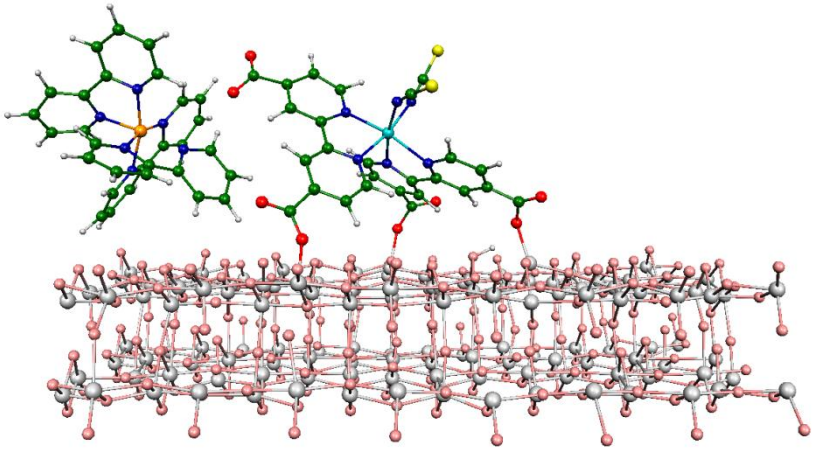
1 **-0.60eV**



2 **-0.46eV**



3 **-0.71eV**



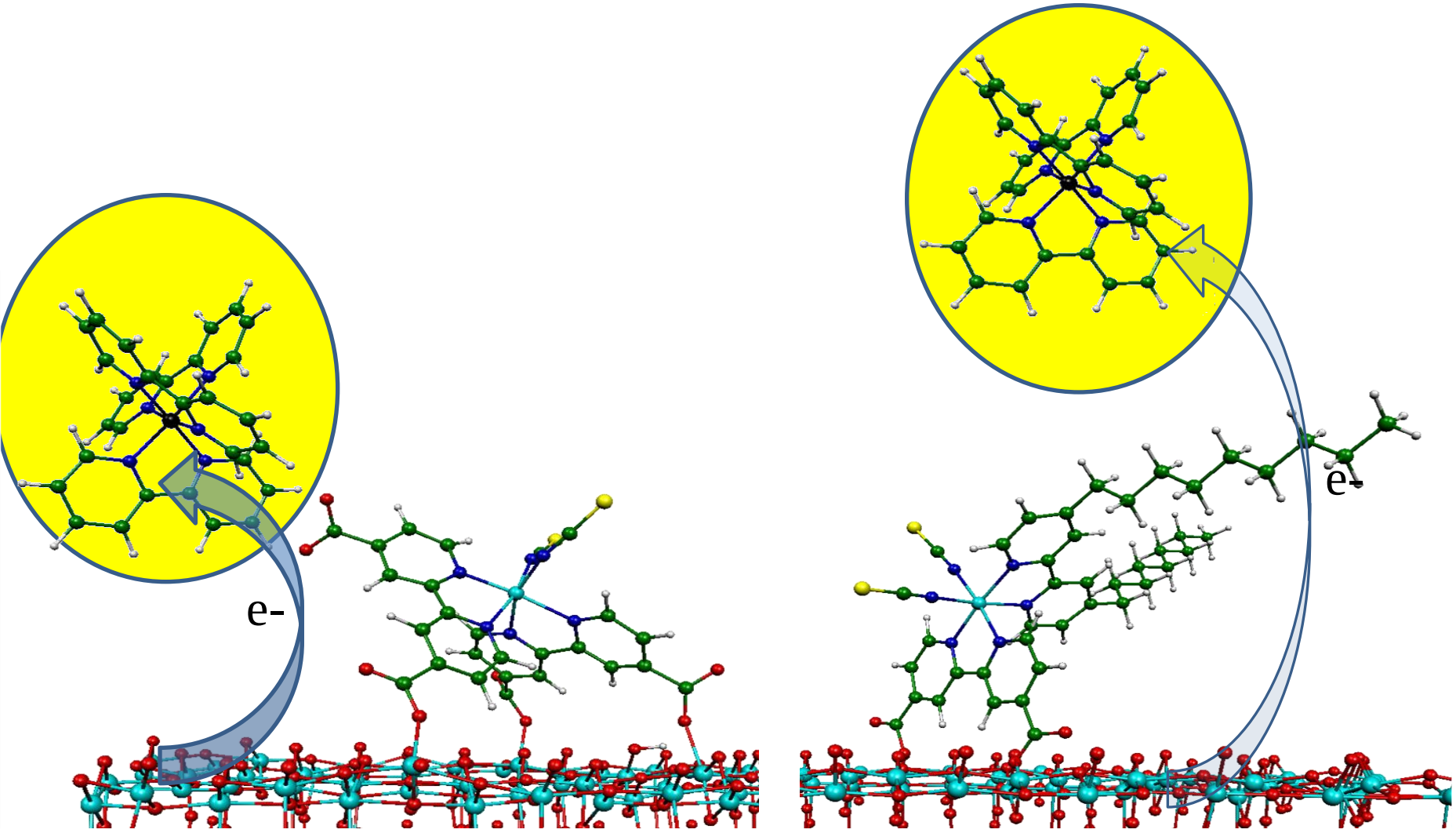
N719

Z907

-0.60 eV

ION PAIR BINDING ENERGY

-0.18 eV



N719: HIGHER RECOMBINATION

Z907: LOWER RECOMBINATION

Computational Laboratory for Hybrid/Organic Photovoltaics

Collaborations:

•Md. K. Nazeeruddin, M. Grätzel , A. Selloni

Financial support:

EU-FP7: NMP-2009 "SANS" ENERGY-2010 "ESCORT"