First-Principles Investigations of Charge Carrier Dynamics in Nanostructured Hybrid Photovoltaics

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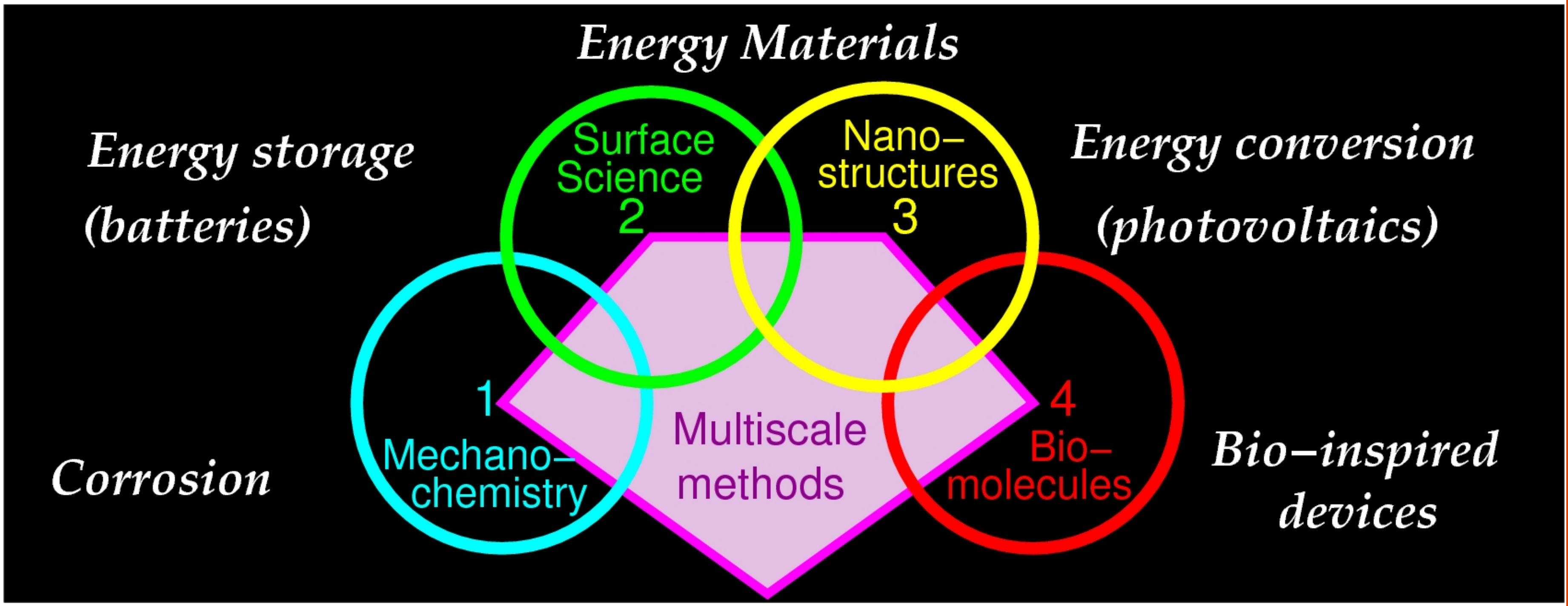
NNIN/C Conference ENCON:

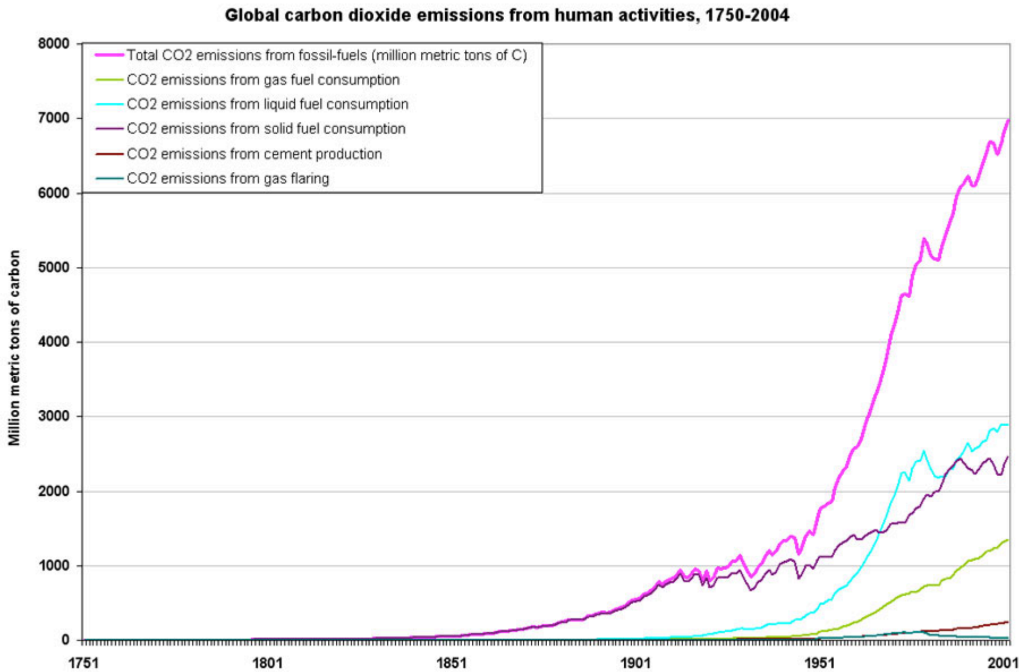
Synergy Between Experiment and Computation in Energy – Looking to 2030.

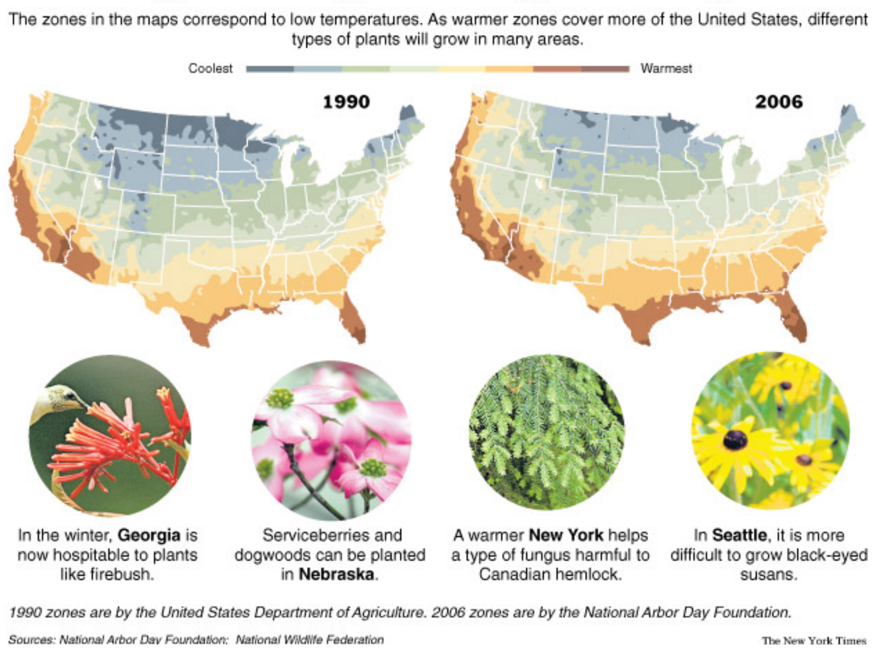
Materials for Energy through Computational Methods

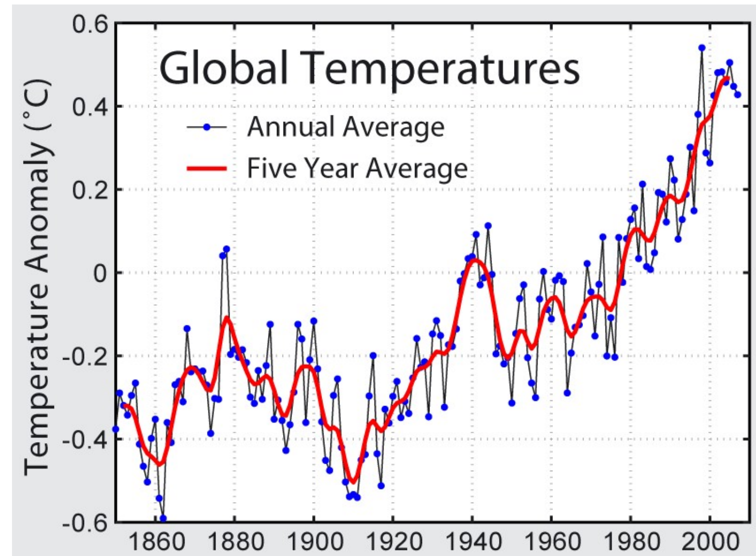


E. Kaxiras Research Group – Physics and SEAS

The need for alternative energy sources

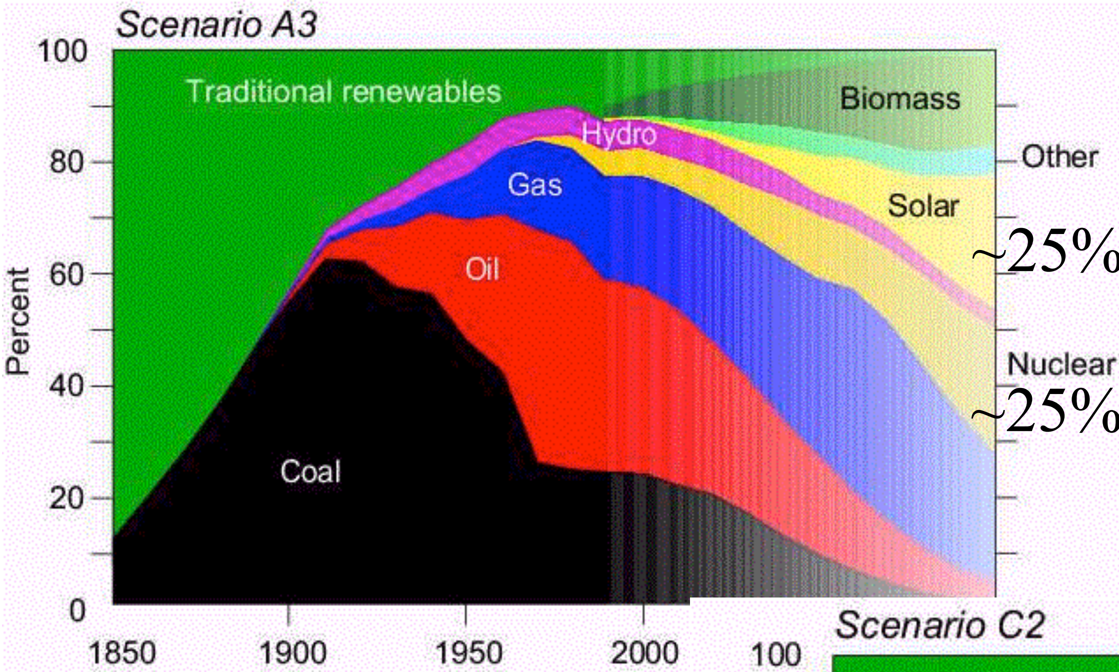


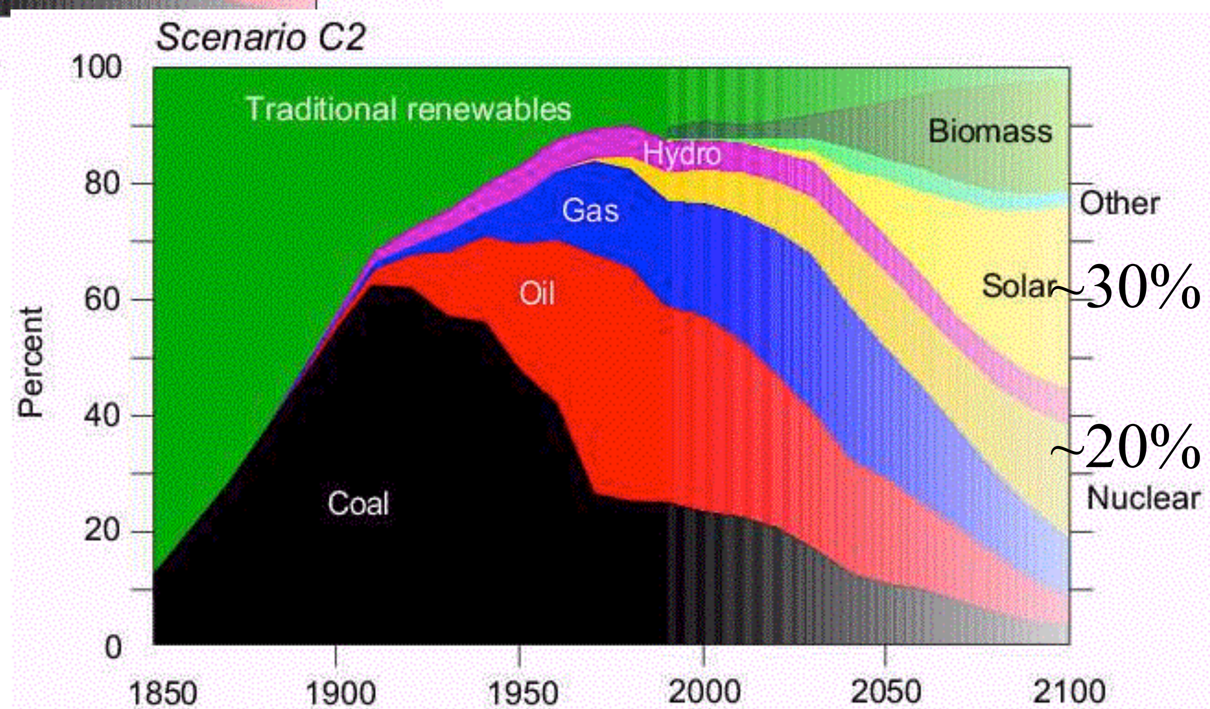




http://www.celsias.com/2007/03/20/channel-4-distances-itself-from-global-warming-documentary/

The relevance of Solar Energy

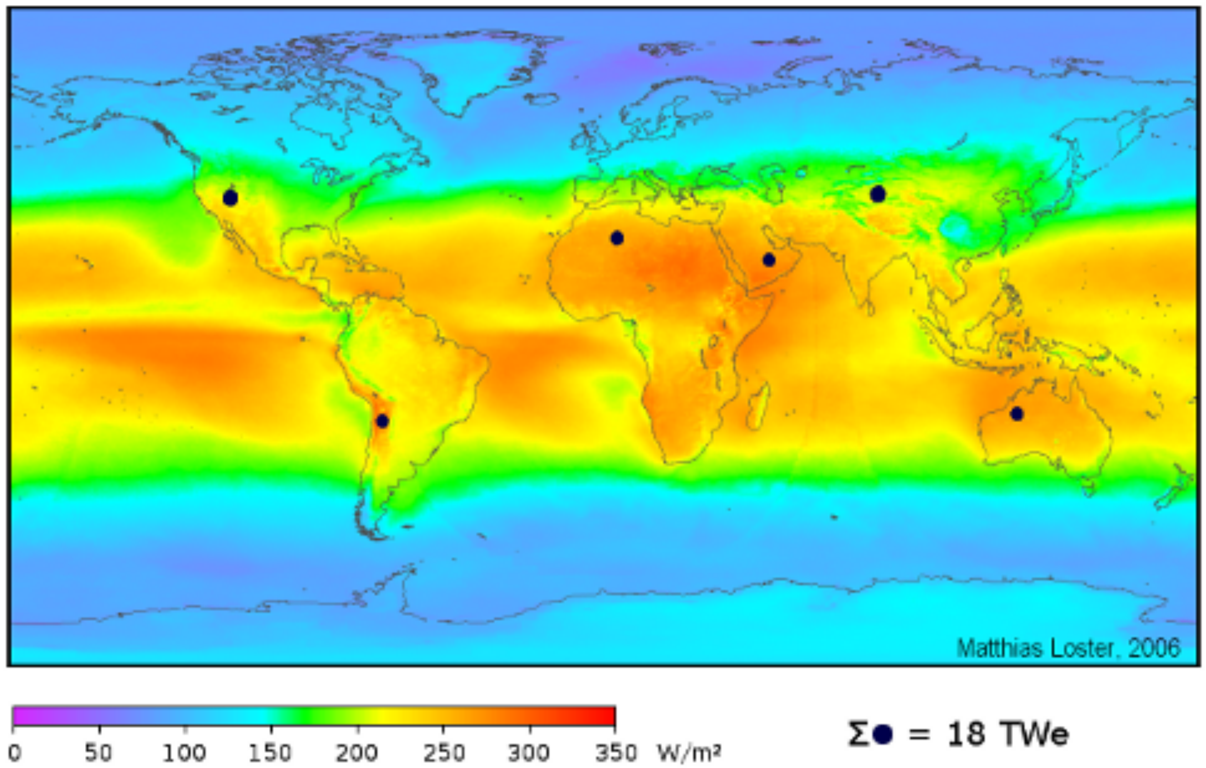




Report of Intergovernmental Panel on Climate Change

2007 Nobel Peace Prize (with A. Gore)

The abundance of Solar Energy

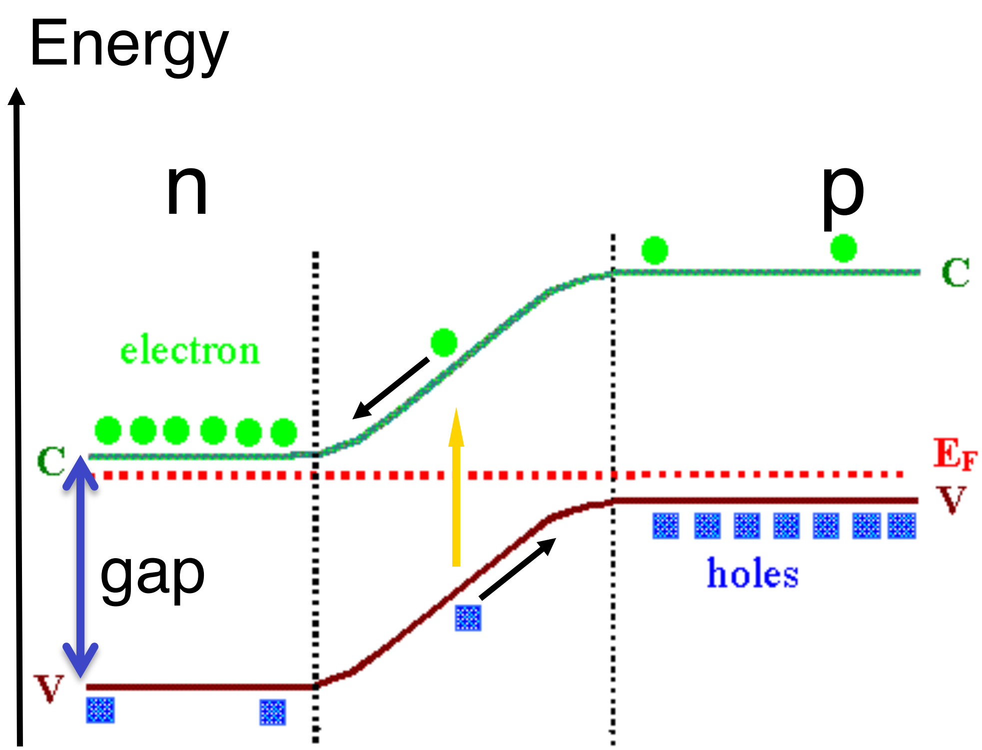


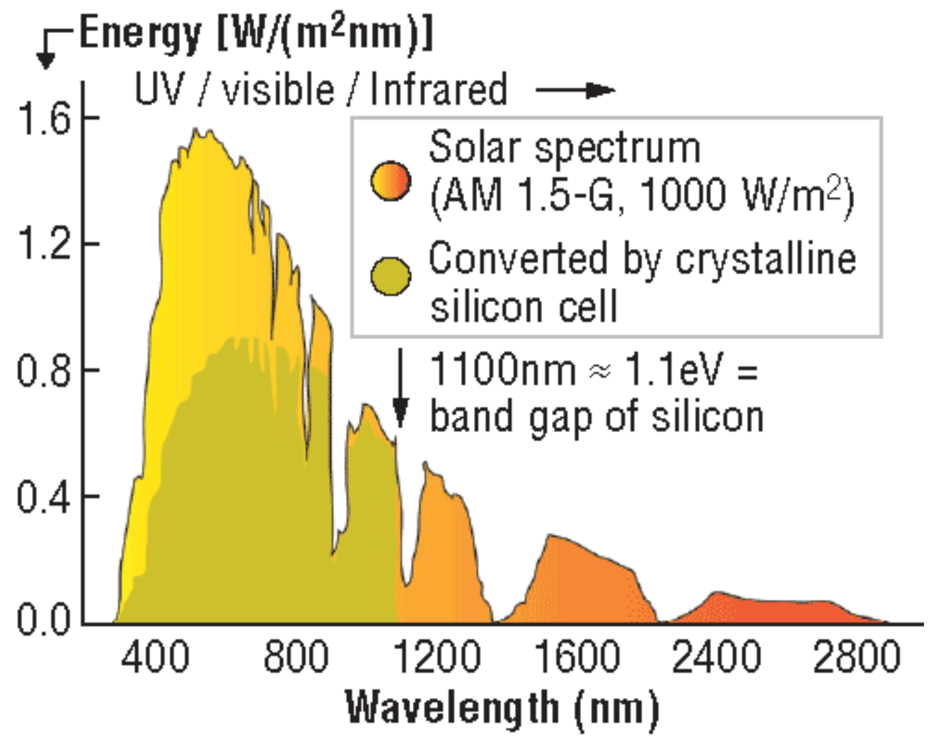
Sunlight hitting the dark discs could power the whole world:

at 8% efficiency, averaged solar irradiation over 1 year: **18 TW**

(more than the total power currently available from all our primary energy sources, including coal, oil, gas, nuclear, and hydro!)

Light absorption by solids: the pn-junction in semiconductors





Bulk semiconductor (inorganic)

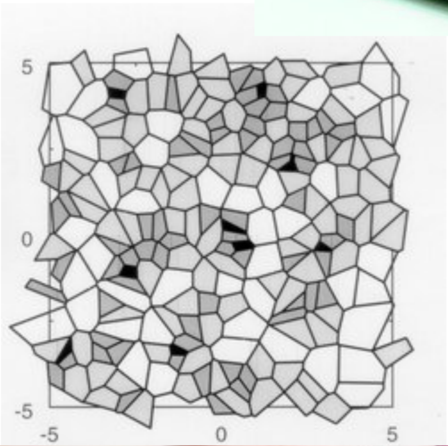
-delocalized states (band structure)

-nearly free electrons

-single band-gap

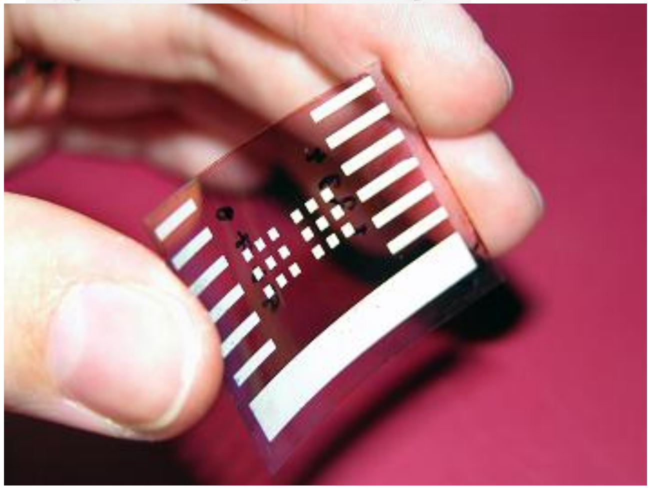
Three generations of solar cells

- 1st Gen.: monocrystal Si (86% in market)
  - expensive
- 2nd Gen.: thin-film
  - polycrystalline, amorphous Si
  - low efficiency, limited materials



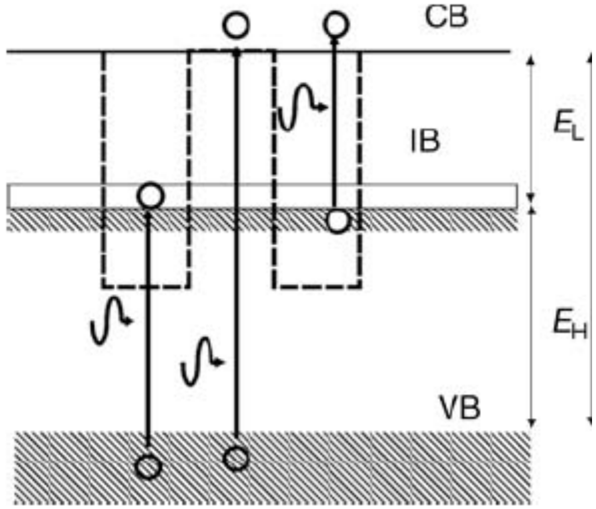
- 3rd Gen.: - intermediate band
  - quantum dots
  - multi-junction
  - dye-sensitized (Graetzel)

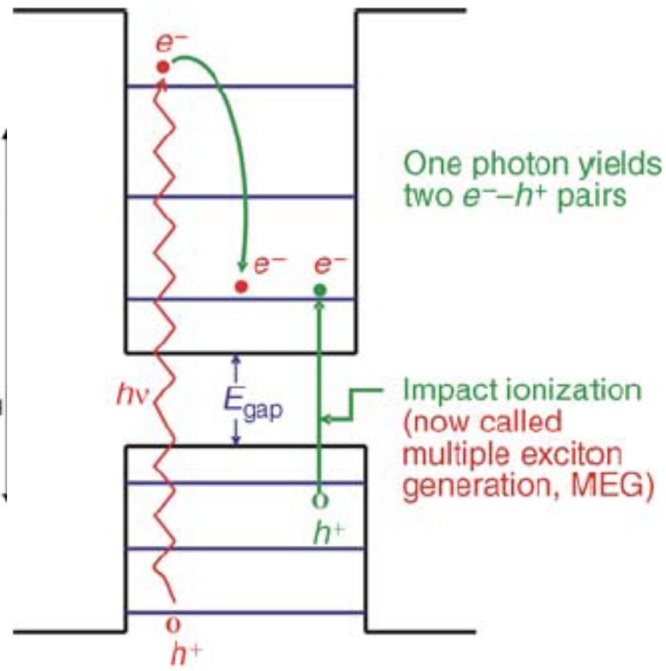
  low cost, flexible,
  transparent,
  natural/safe components

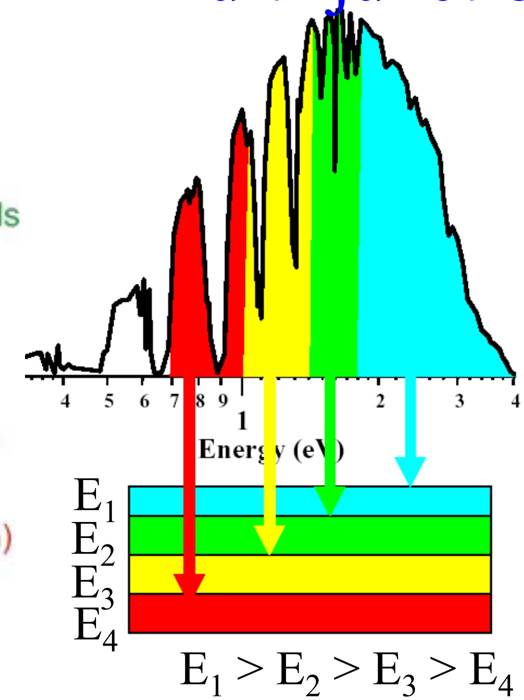


(may not solve all our problems …)

Intermediate band | Quantum dot | Multi-junction





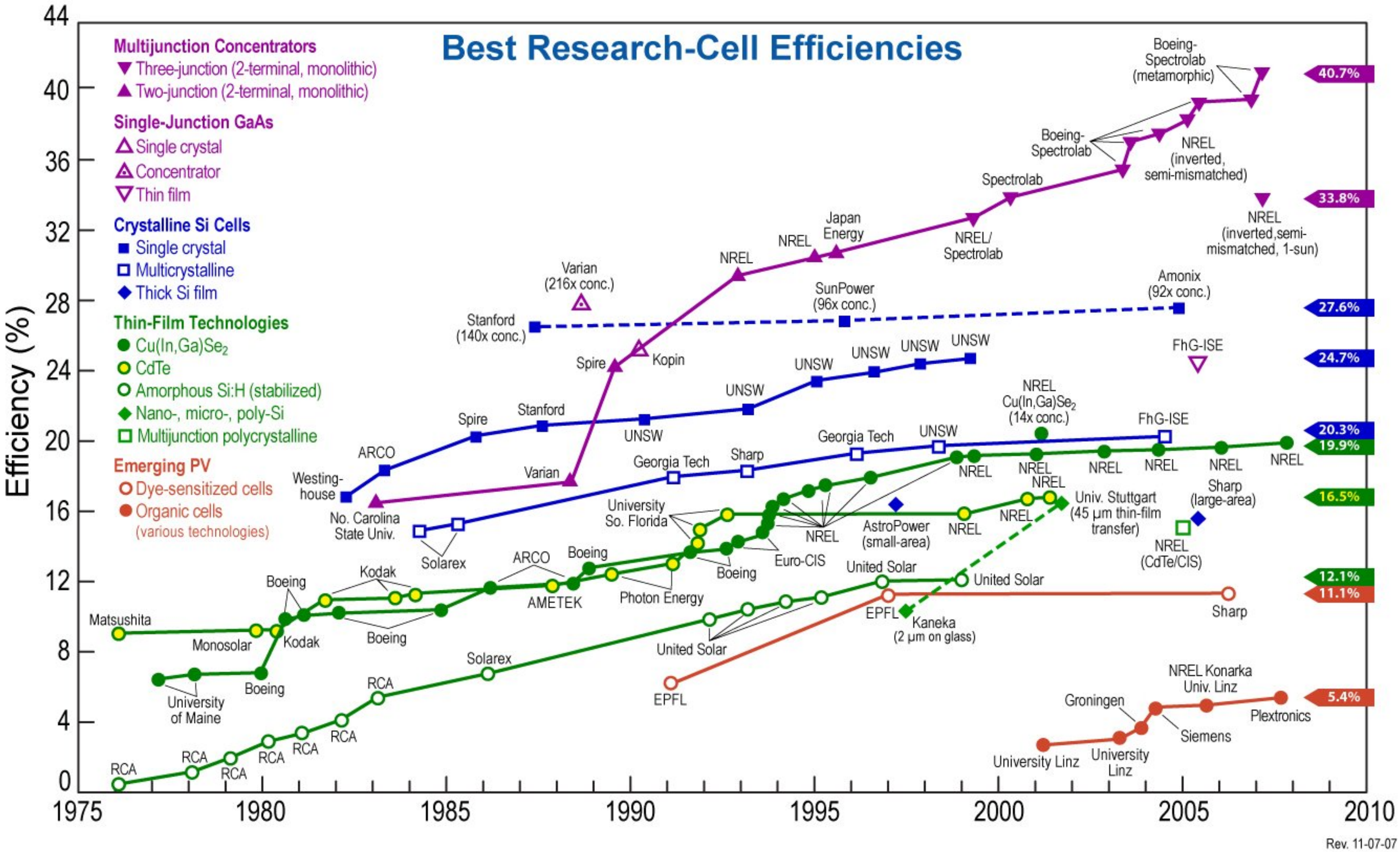


Theoretical limit: ~ 86 %

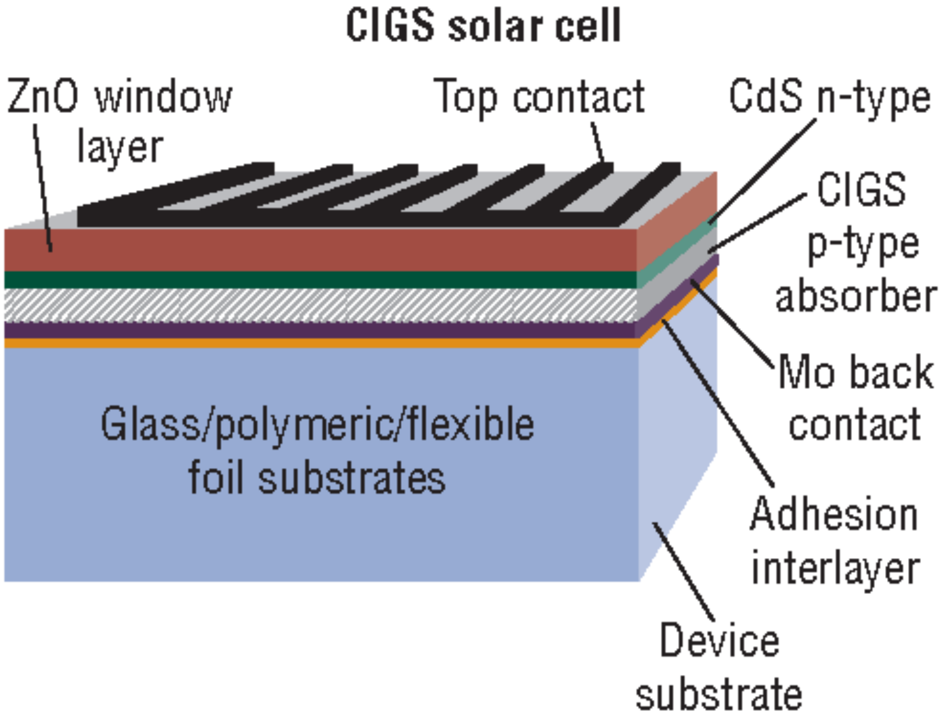
Experiment: 41%

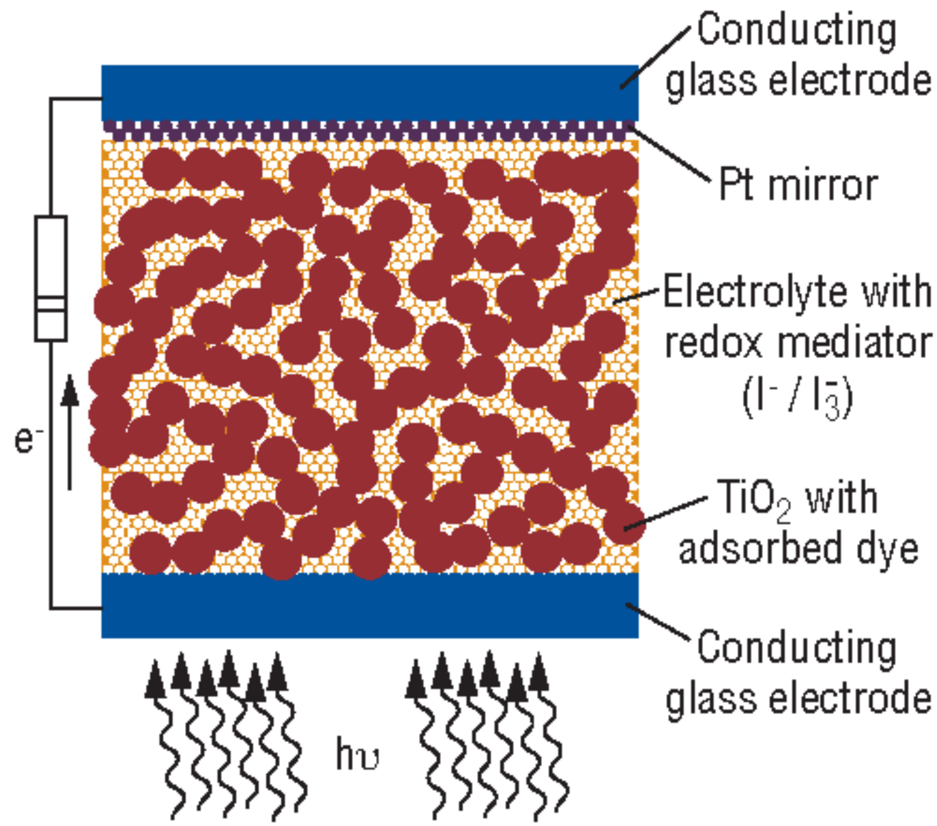
(NREL, Aug. 2008)

- **High cost**
- **Availability of materials**
- **Safety (toxic elements)**



Best Research-Cell Efficiencies
Multijunction Concentrators
Three-junction (2-terminal, monolithic)
Two-junction (2-terminal, monolithic)
Single-Junction GaAs
Single crystal
Concentrator
Thin film
Crystalline Si Cells
Single crystal
Multicrystalline
Thick Si film
Thin-Film Technologies
Cu(In,Ga)Se2
CdTe
Amorphous Si:H (stabilized)
Nano-, micro-, poly-Si
Multijunction polycrystalline
Emerging PV
Dye-sensitized cells
Organic cells (various technologies)
Efficiency (%)
40.7%
33.8%
27.6%
24.7%
20.3%
19.9%
16.5%
12.1%
11.1%
5.4%
Rev. 11-07-07

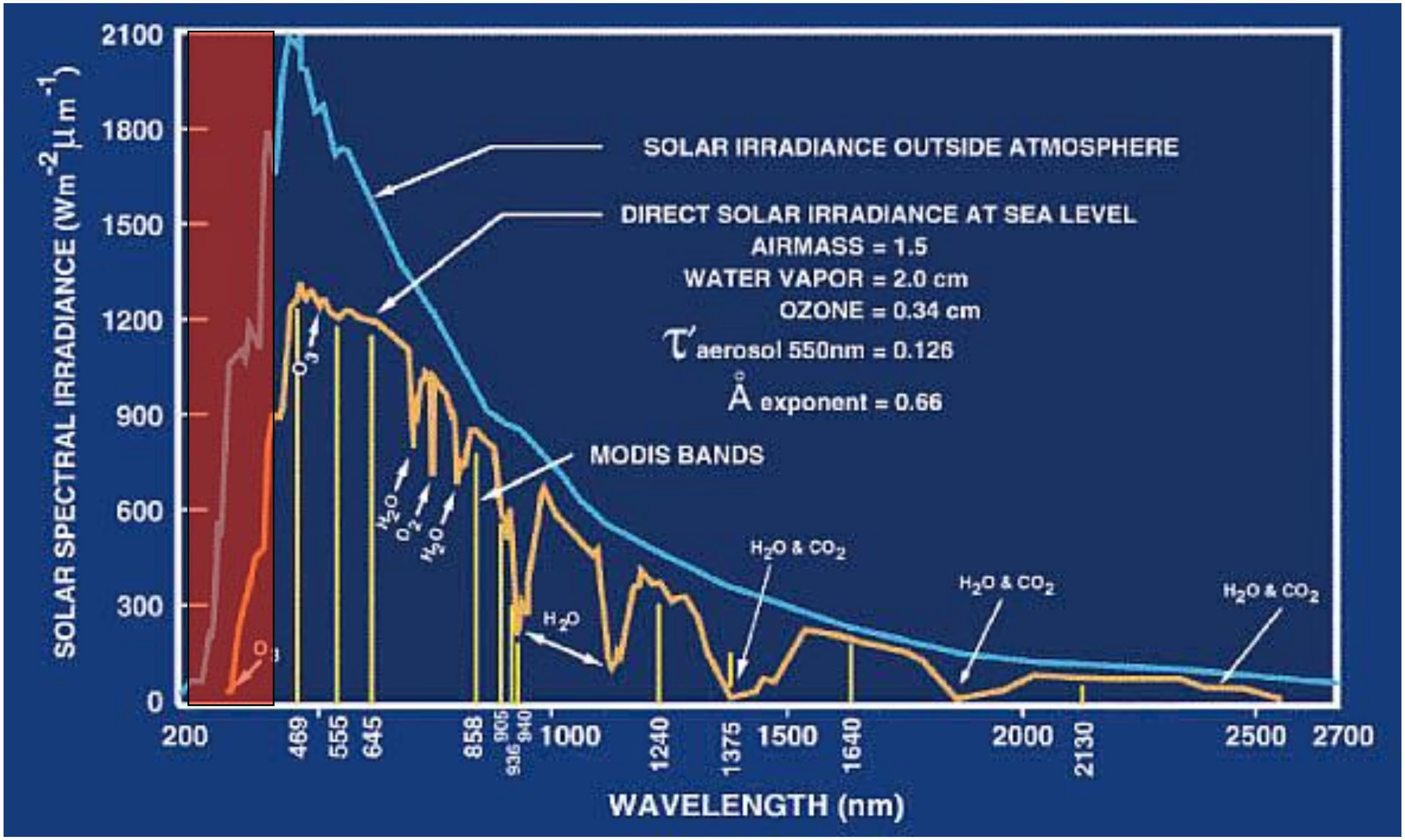

CIGS solar cell
ZnO window layer
Top contact
CdS n-type
CIGS p-type absorber
Mo back contact
Adhesion interlayer
Device substrate
Glass/polymeric/flexible foil substrates


Conducting glass electrode
Pt mirror
Electrolyte with redox mediator (I^- / I_3^-)
TiO_2 with adsorbed dye
Conducting glass electrode
e^-
hυ

- The Problem:

materials with large band gaps: TiO_2 gap = 3.2 eV (200 nm < λ < 400 nm)

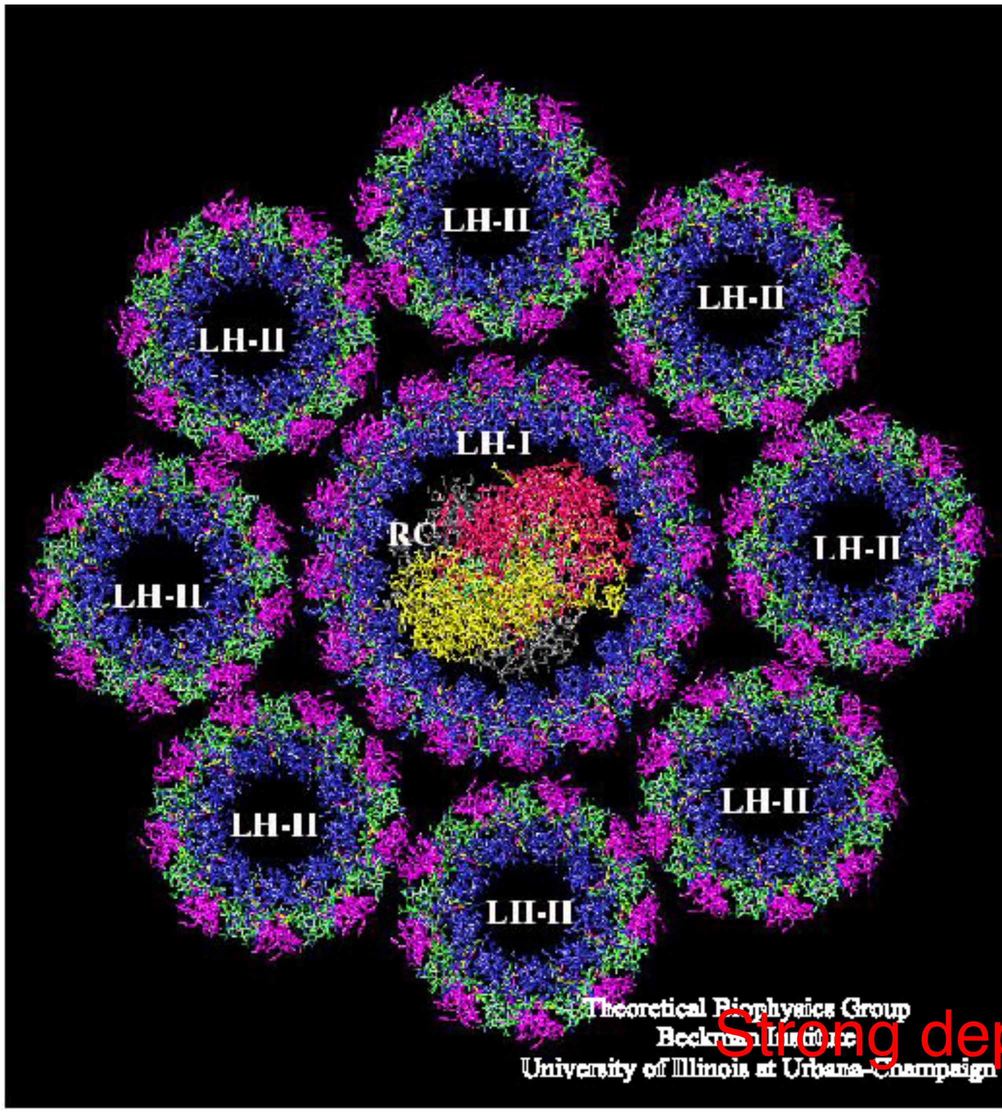
solar spectrum

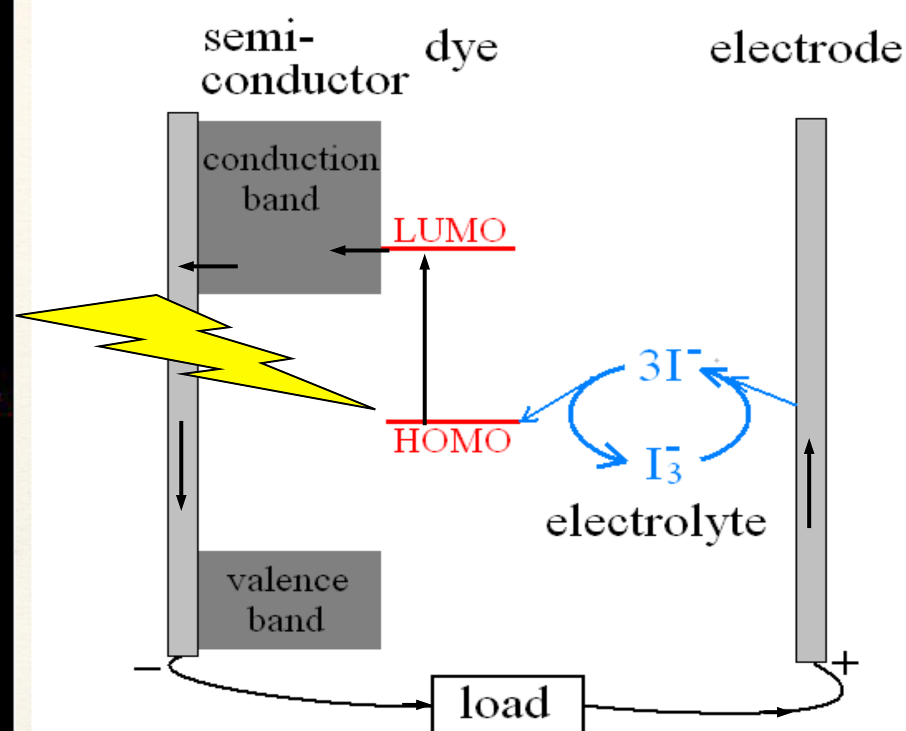


The dye-sensitized solar cell

The Principle: Separate light-absorption and charge collection processes

Typical plant: ~0.1%
Crop plants: ~1%
Sugarcane: ~8%





O'Regan & Graetzel, Nature (1991)

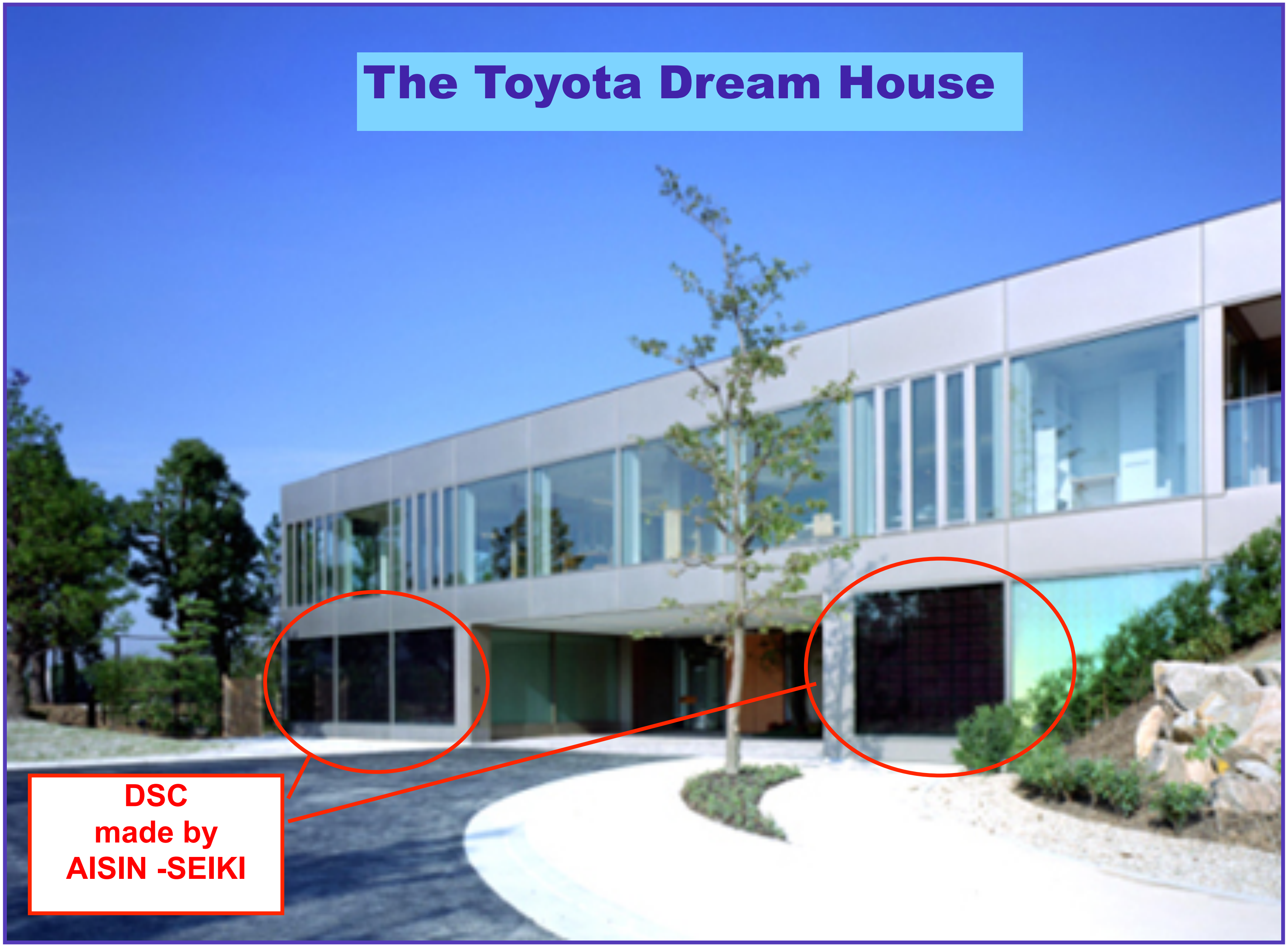
Strong dependence on detailed features

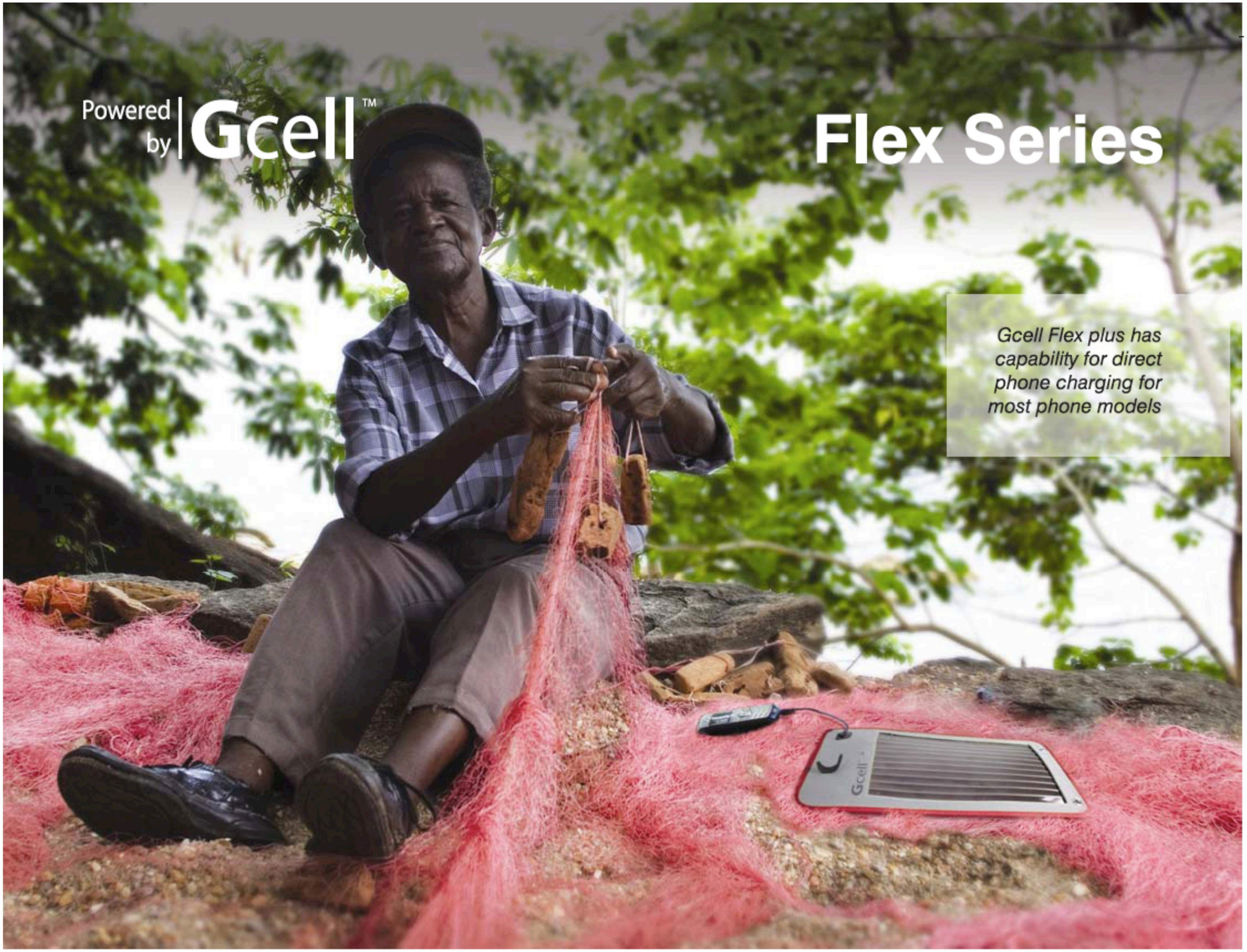
Real outdoor tests of Dye Sensitized Cell Modules

Series connected
64 DSC cells

Kariya City at lat. 35°10'N,
azimuthal angle: 0°
facing due South, tilted at 30°

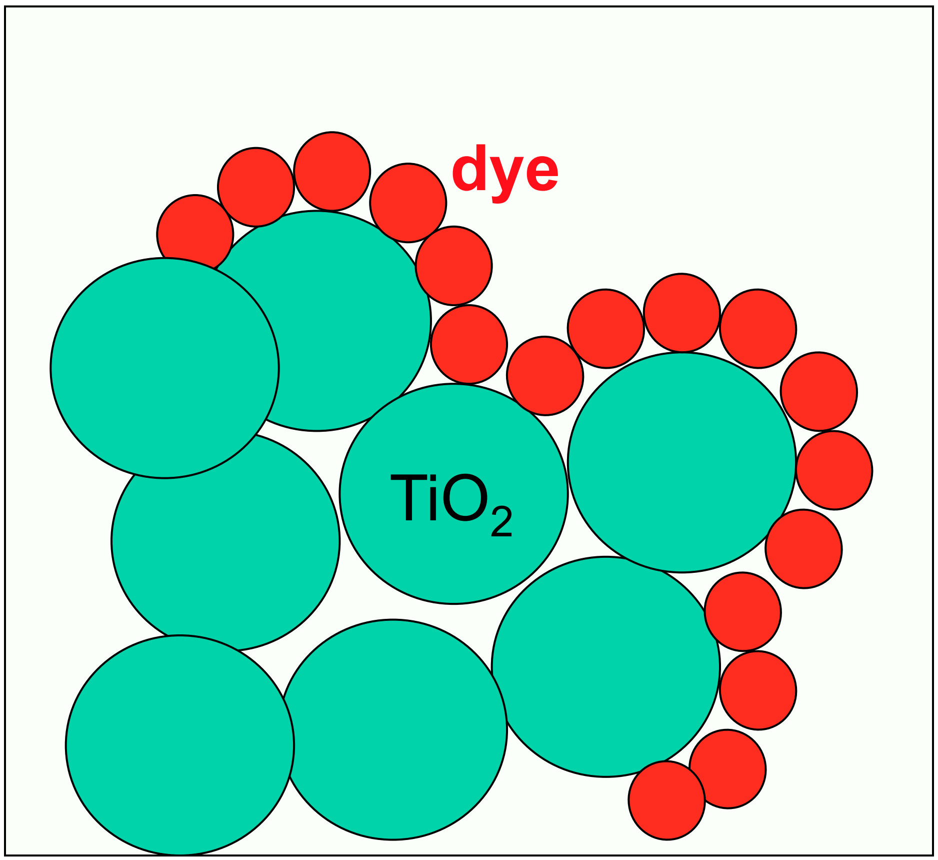

トイレ
トイレ

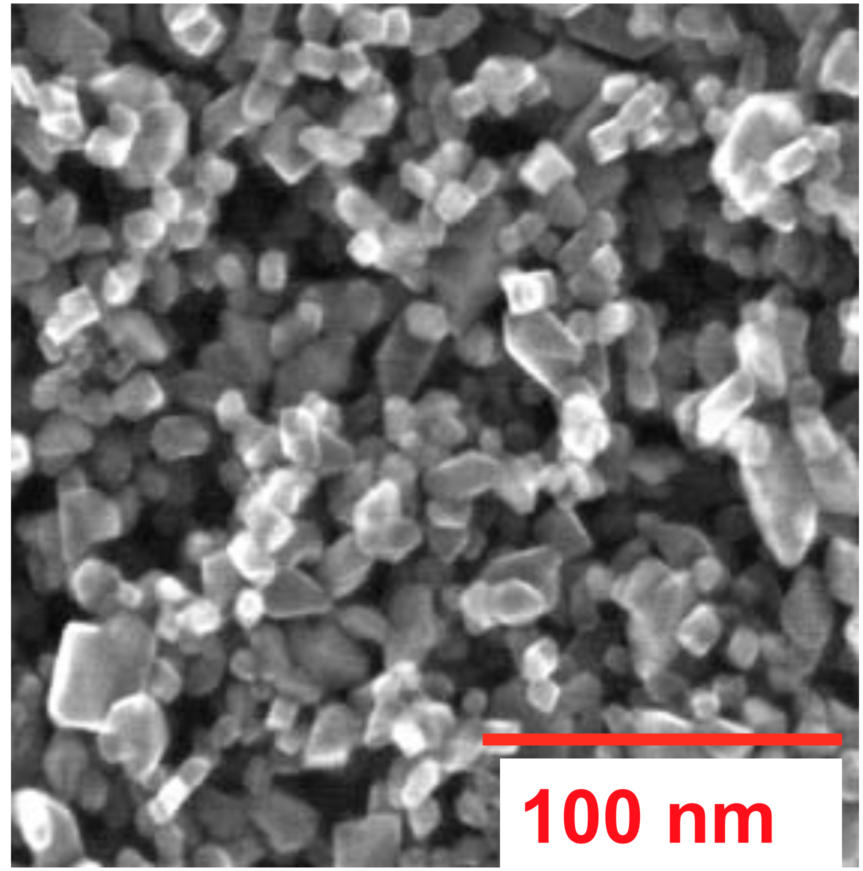

The Toyota Dream House
DSC
made by
AISIN -SEIKI



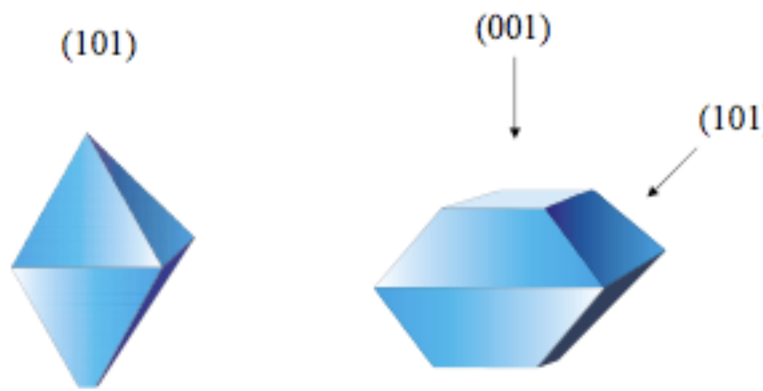
Efficient and light weight solar

Approximately complete surface coverage (i.e. densest possible packing of dye molecules)



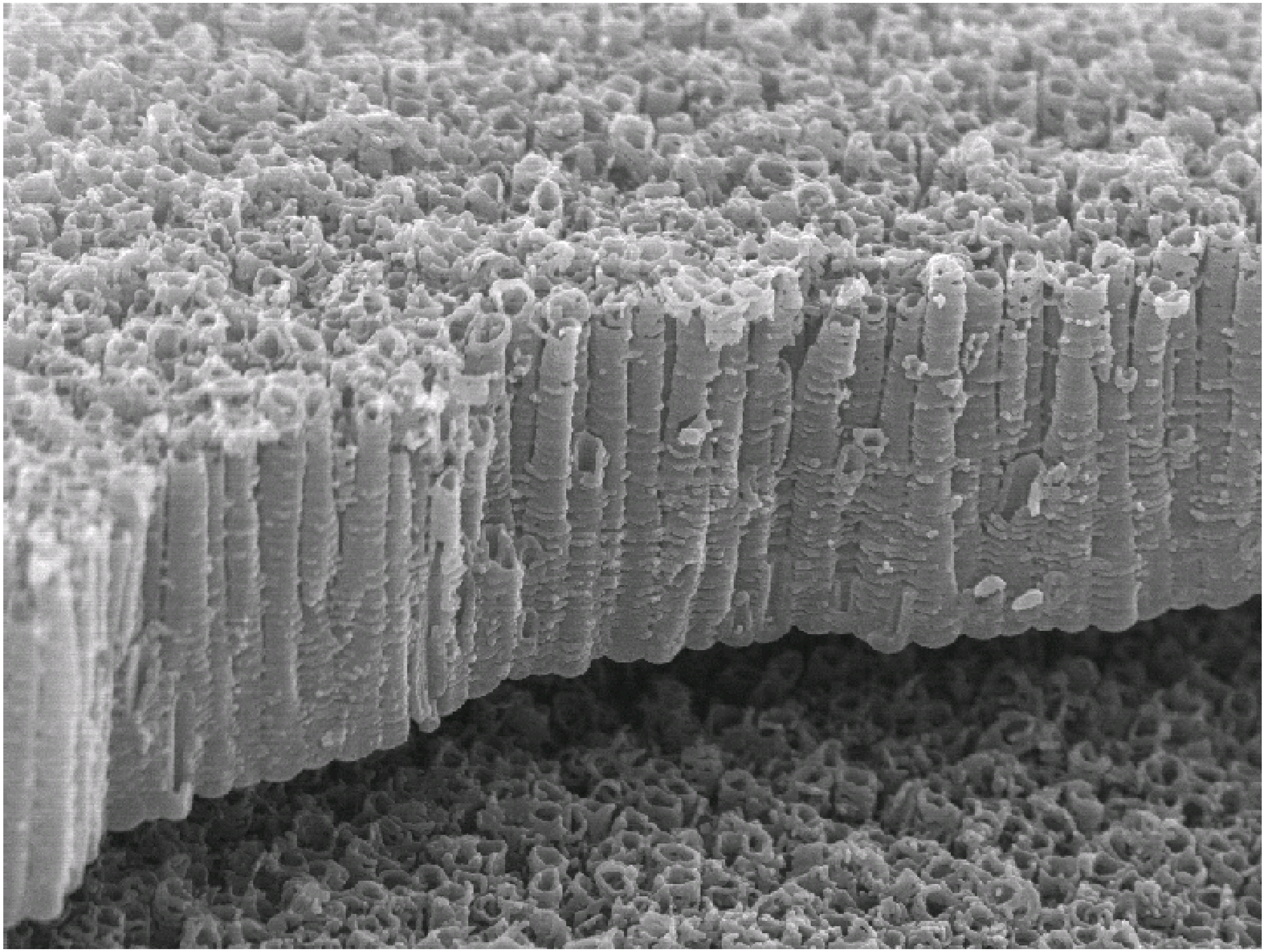


~20 nm sized faccetted anatase nanoparticles



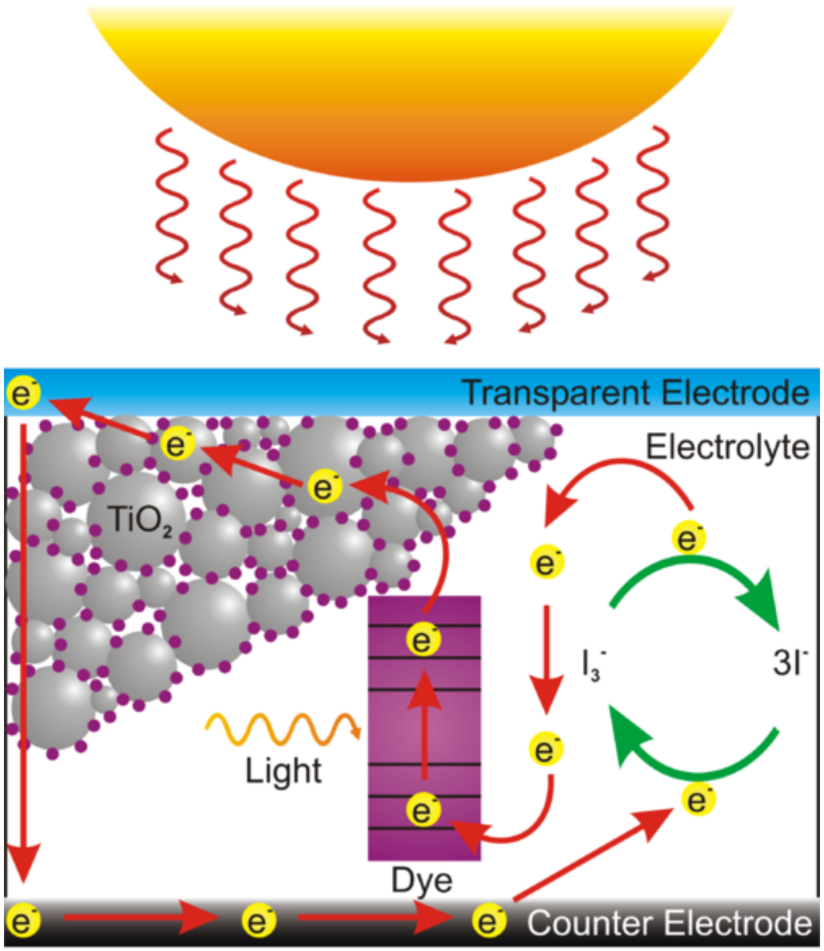
Nano-size: helps in many aspects (e.g. efficiency, transparency, transport, …)

TiO_2 Nanotubes



Q. Cai, M. Paulose, O. K. Varghese, C. A. Grimes, *J. Mater. Res.* 20 (2005) 230

The dye-sensitized solar cell



•stability

•efficiency

$$IPCE(\lambda) = LHE(\lambda) \times \Phi(inj) \times \eta(c)$$

IPCE = Incident Photon to Current Efficiency

LHE = Light Harvesting Efficiency

$\Phi(inj)$ = electron injection efficiency

$\eta(c)$ = charge collection efficiency

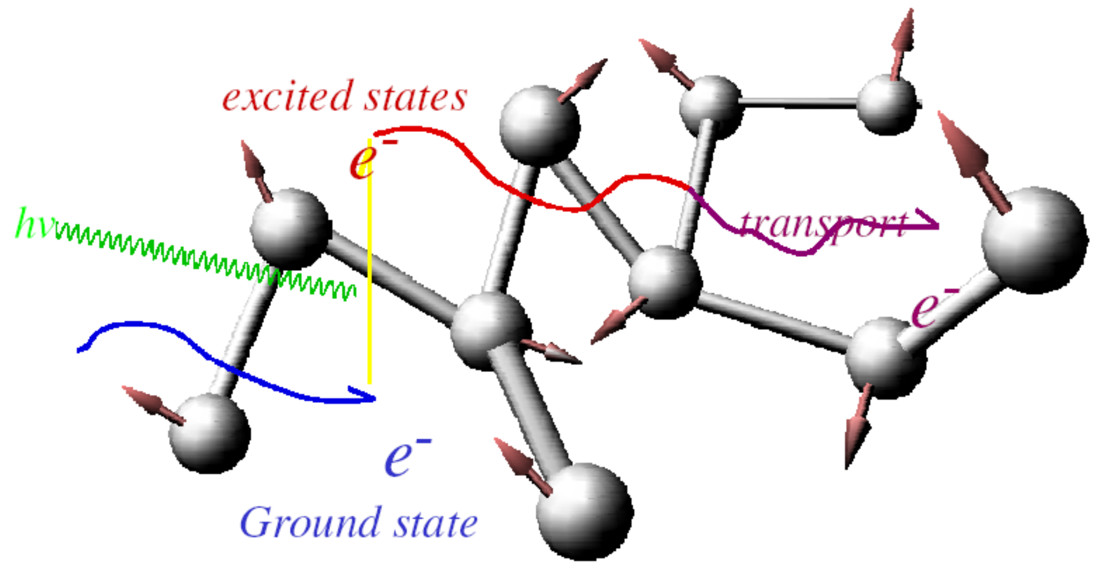
Main issue: coupled electron-ion dynamics

Previous work:

-Schroedinger eq. with model Hamiltonian
Thoss, Miller, Stock, JCP (2000);
Rego& Batista, JACS (2003);…

-semiempirical Hamiltonian (tight-binding)
Allen et al., JMO (2003);…

-ground state DFT + TDDFT
Prezhdo et al., PRL (2005); JACS (2007)…



Ours: self-consistent TDDFT with atomic motion

Coupled electron-ion dynamics

Similar to: Miyamoto *et al*.; Rubio *et al*.; Tavernelli *et al*..

$$\begin{cases} i\hbar\dfrac{\partial\phi_j(\mathbf{r},t)}{\partial t} = \left[-\dfrac{\hbar^2}{2m}\nabla^2_{\mathbf{r}} + v_{ext}(\mathbf{r},t) + \displaystyle\int \dfrac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' - \sum_I \dfrac{Z_I}{|\mathbf{r}-\mathbf{R}^{cl}_I|} + v_{xc}[\rho](\mathbf{r},t)\right]\phi_j(\mathbf{r},t) \\ M_J\dfrac{d^2\mathbf{R}^{cl}_J(t)}{dt^2} = -\nabla_{\mathbf{R}^{cl}_J}\left[V^J_{ext}(\mathbf{R}^{cl}_J,t) - \displaystyle\int \dfrac{Z_J\rho(\mathbf{r},t)}{|\mathbf{R}^{cl}_J-\mathbf{r}|}d\mathbf{r} + \sum_{I\neq J}\dfrac{Z_J Z_I}{|\mathbf{R}^{cl}_J-\mathbf{R}^{cl}_I|}\right] \end{cases}$$

Meng & Kaxiras, J. Chem. Phys. (2008).

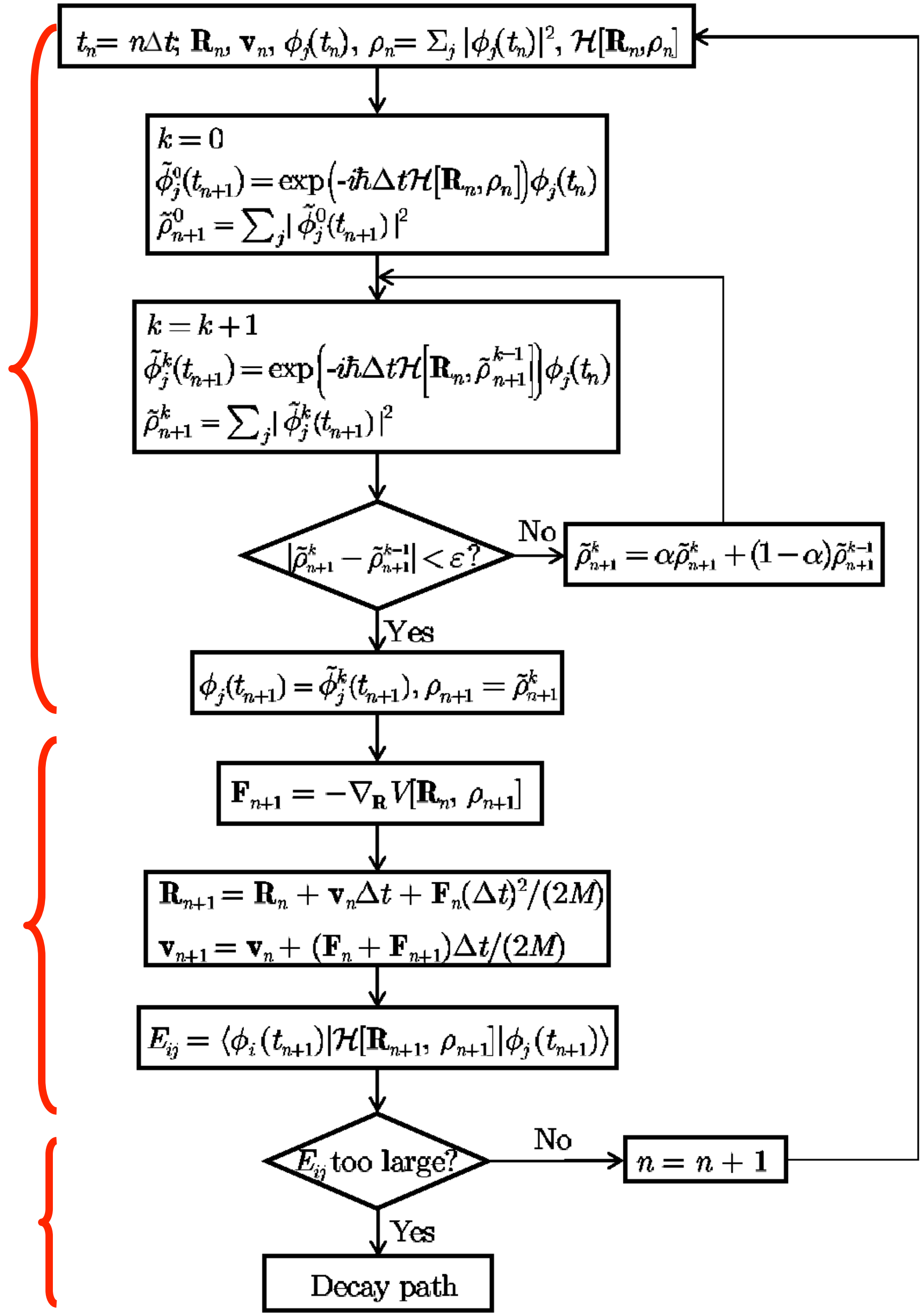
Computational flowchart

Self-consistent

e propagation

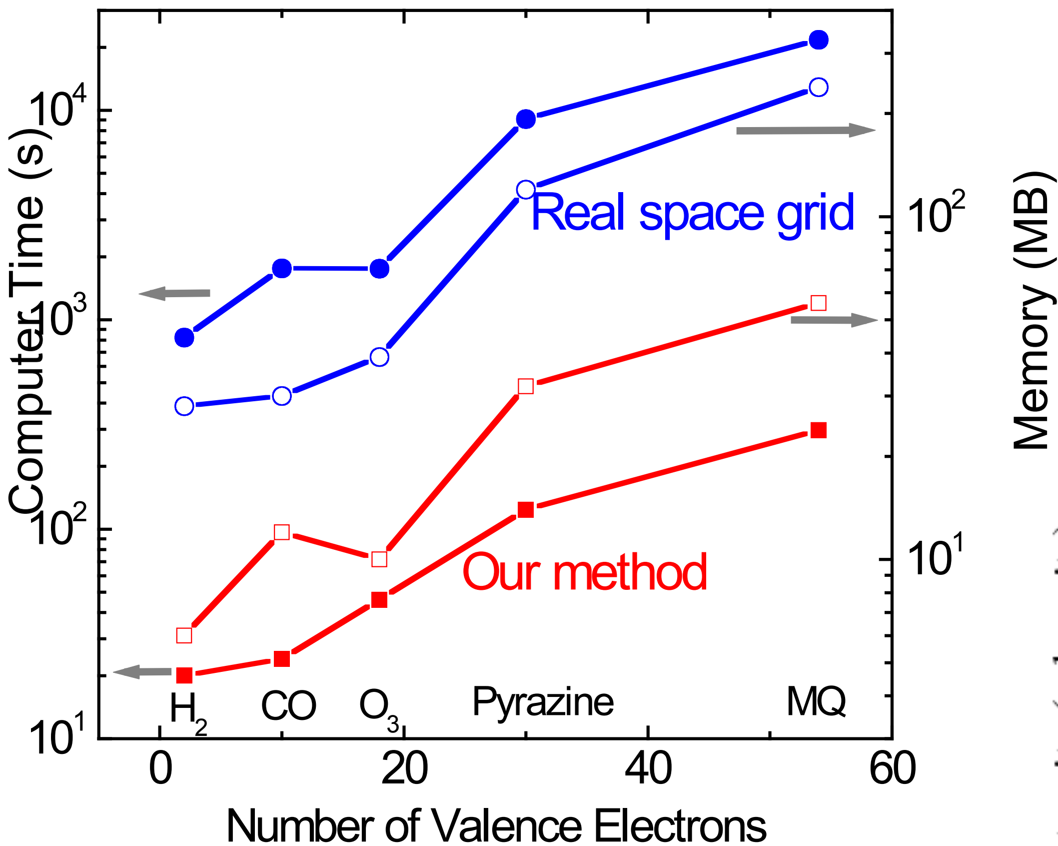
Ionic motion

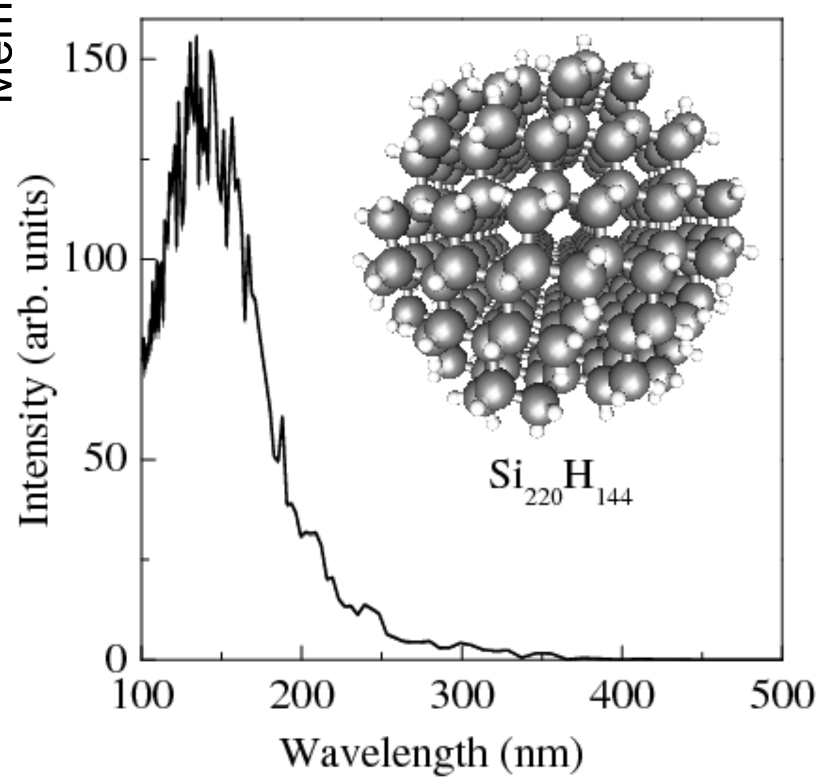
Break down



- Localized basis enhances performance
- Self-consistent cycle allows much larger time-step for e propagation

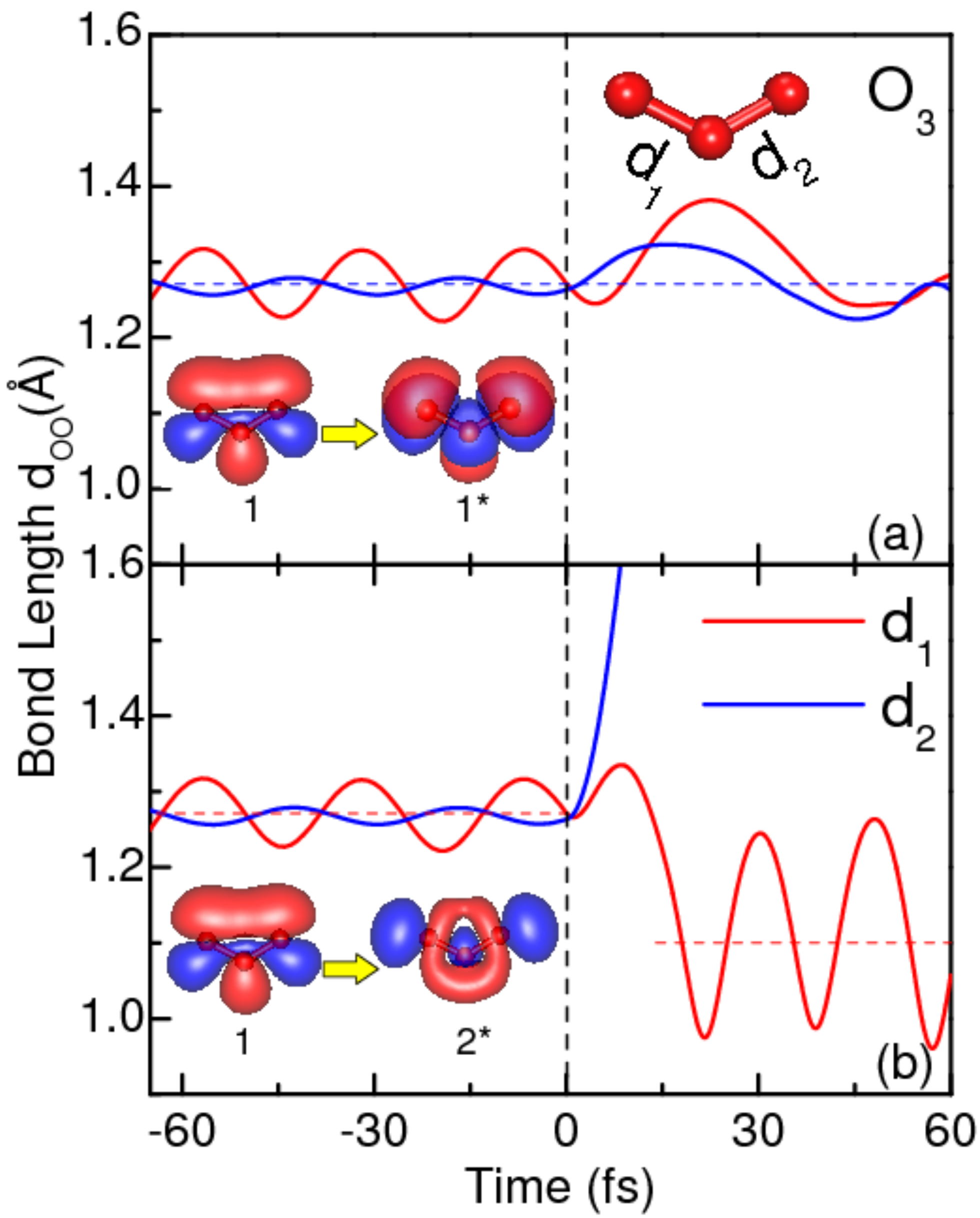
Code performance (compared to standard code - "octopus")



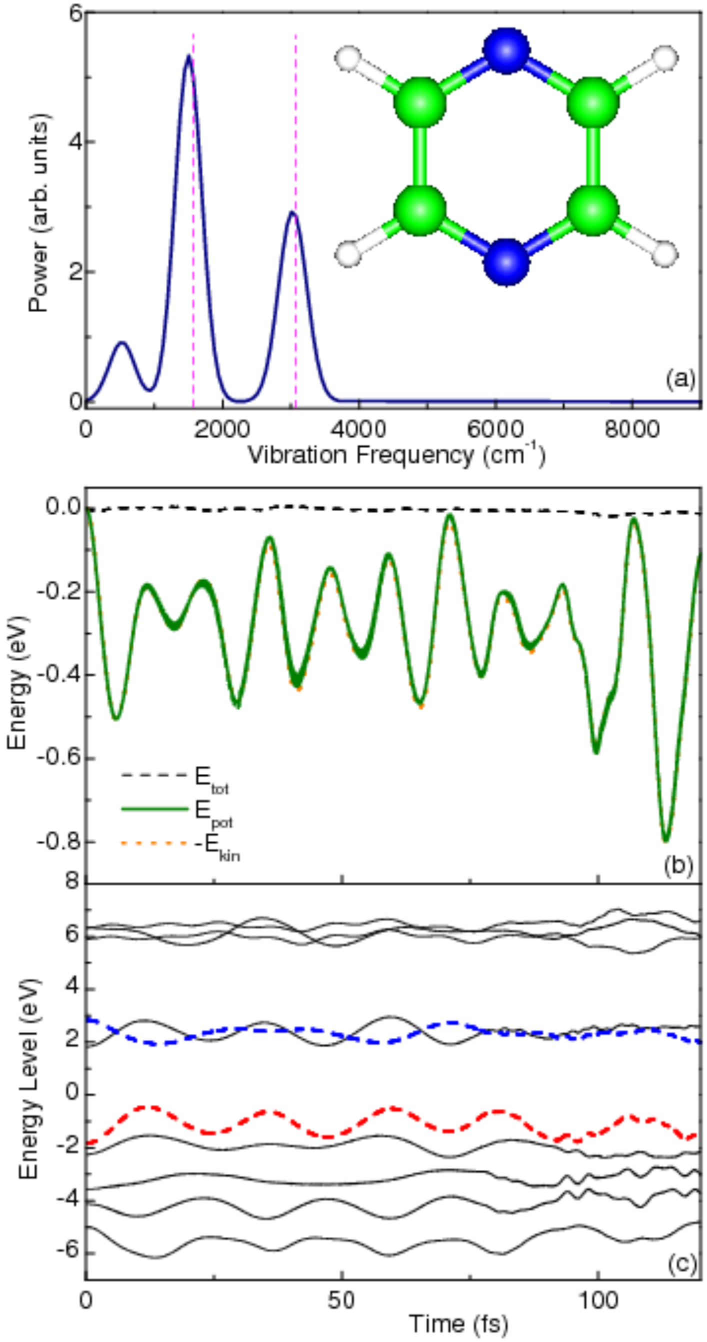


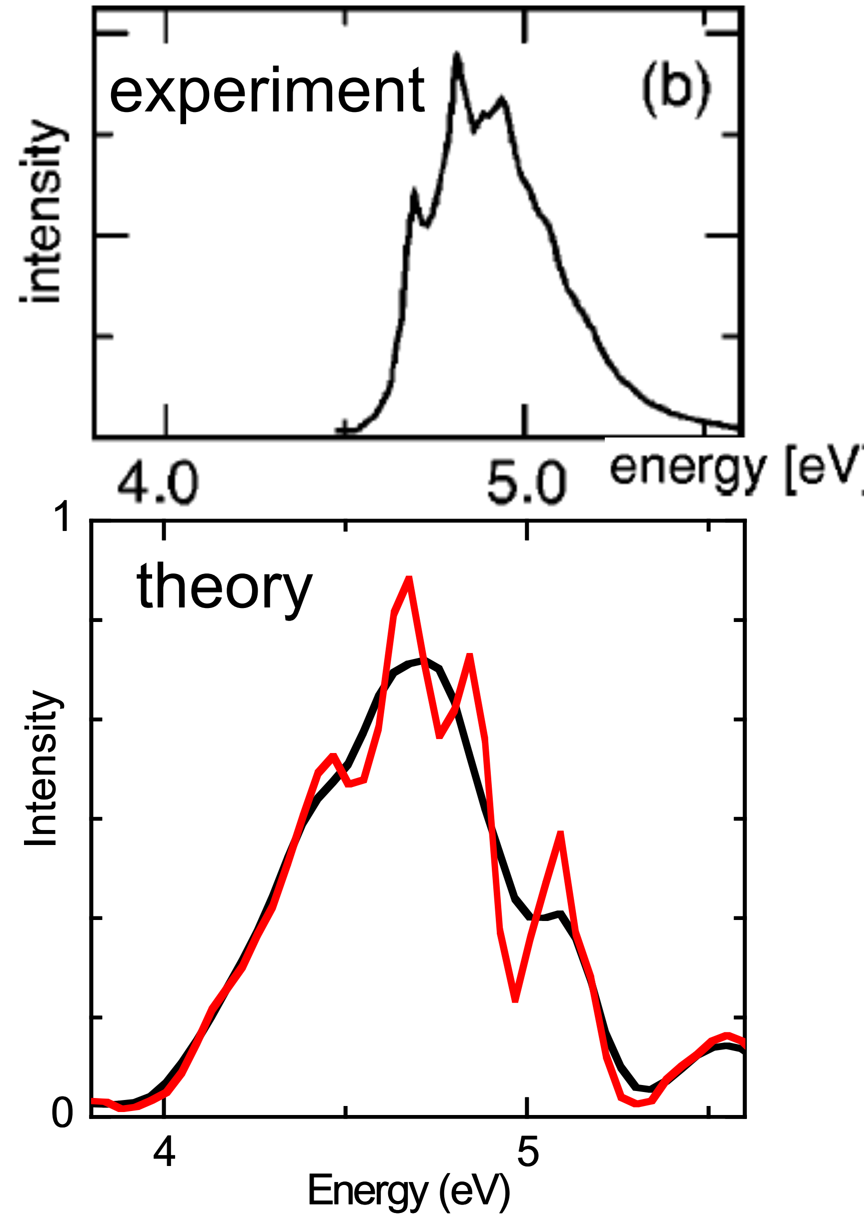
~ 500 atoms

Tests: ozone molecule - photo-dissociation



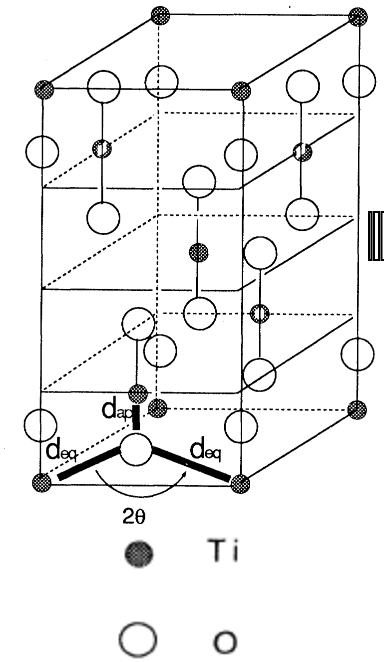
Test: spectrum of pyrazine



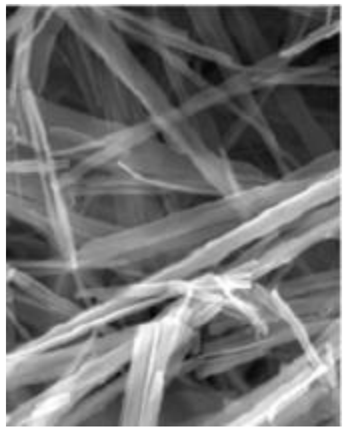


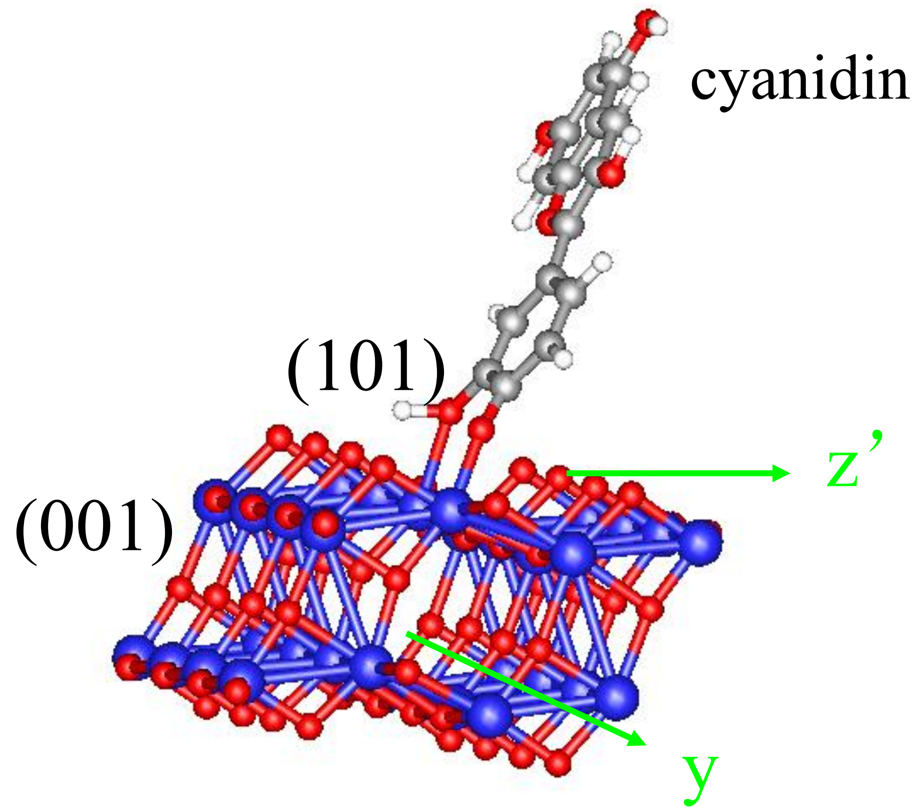
Model System: Cyanidin adsorption on TiO_2 nanowire

anatase



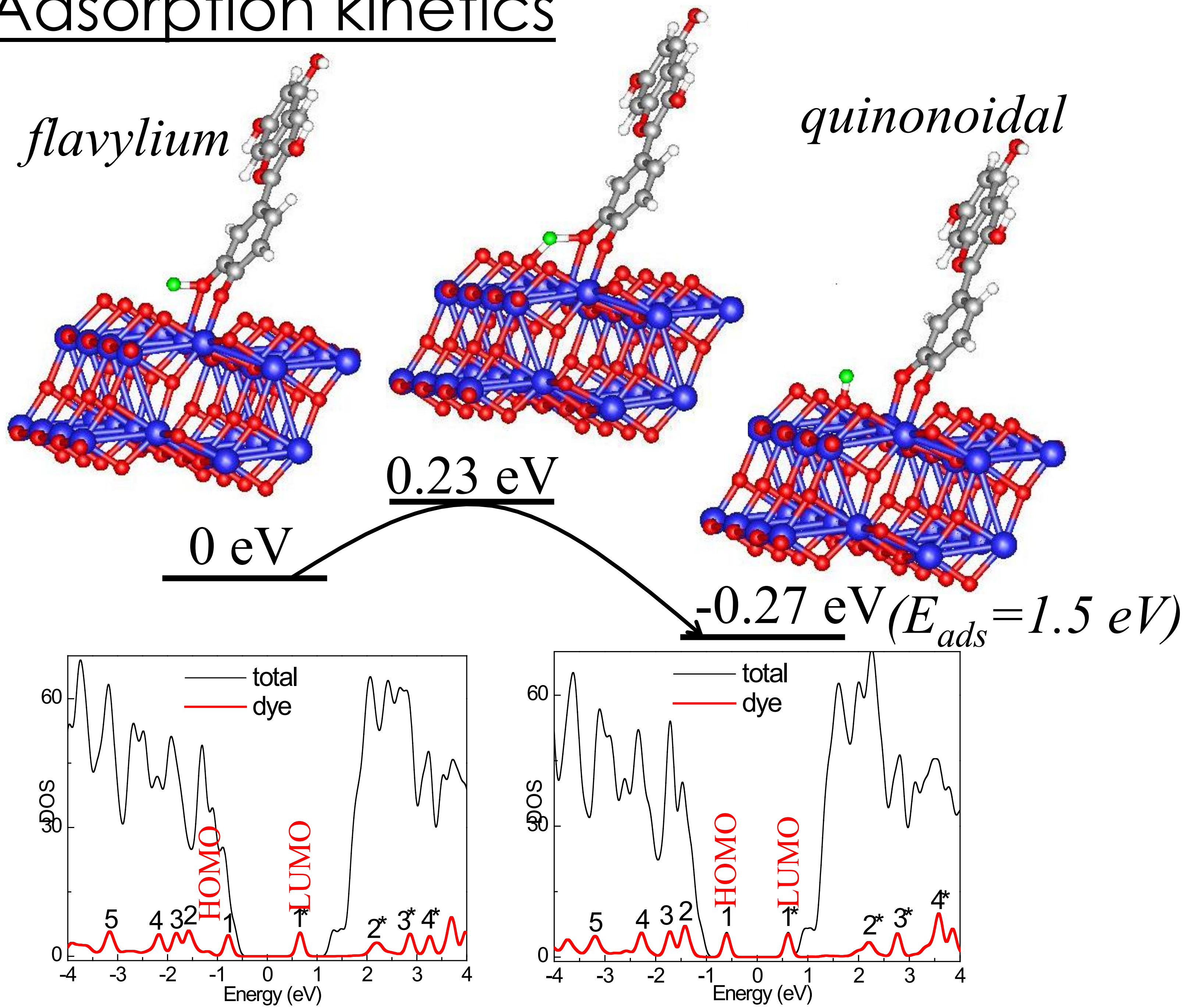
nanowire





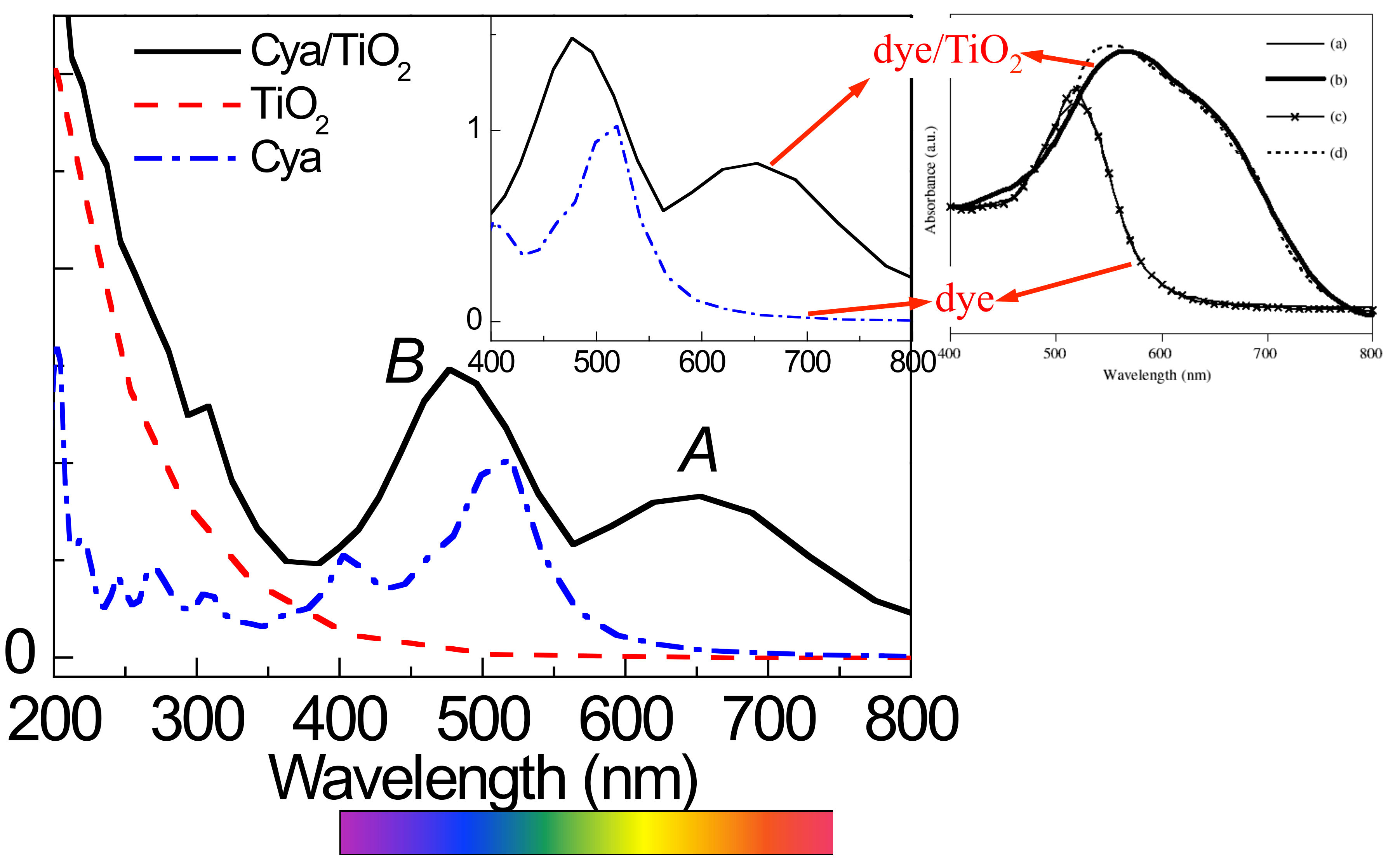
Meng, Ren, Kaxiras, Nano Lett. (2008).

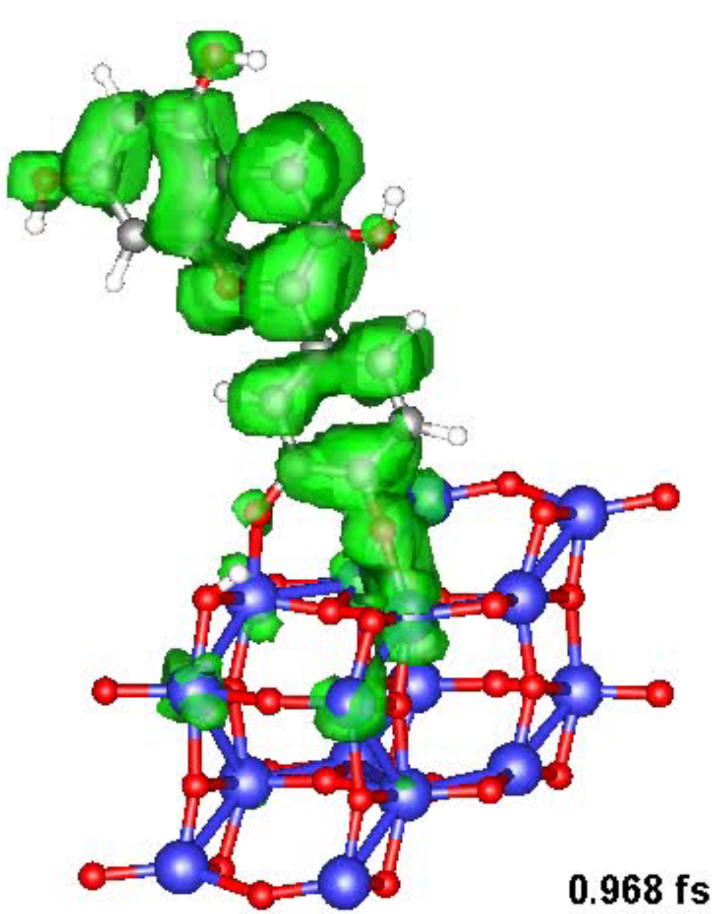
Adsorption kinetics

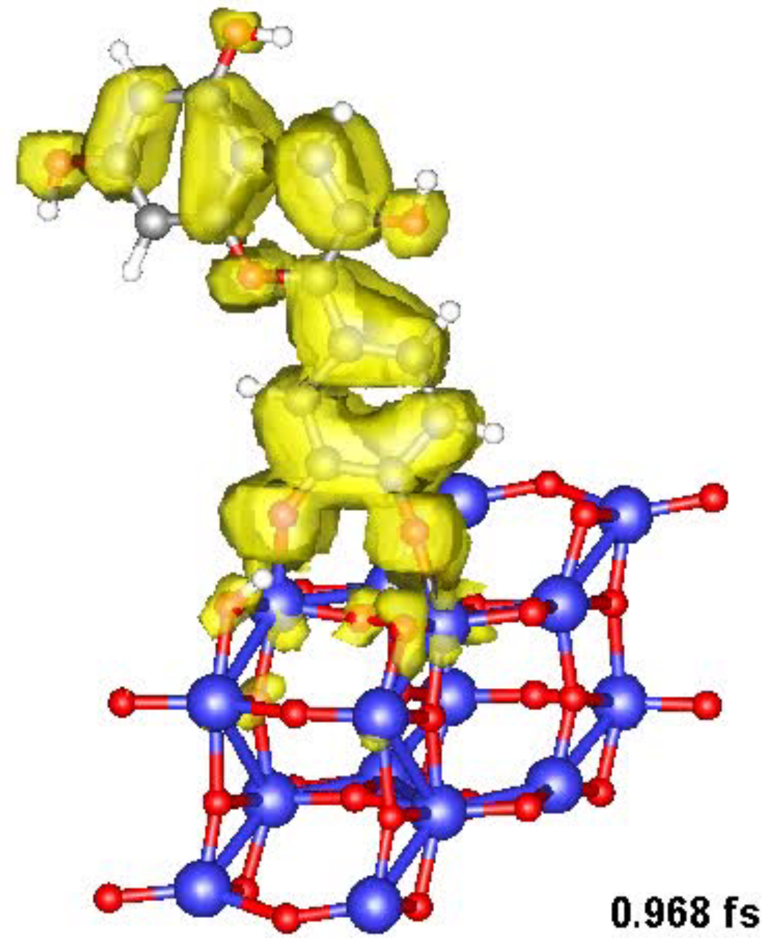


Optical absorption (TDDFT)

Calculated Experiment (Wongcharee et al., 2007)

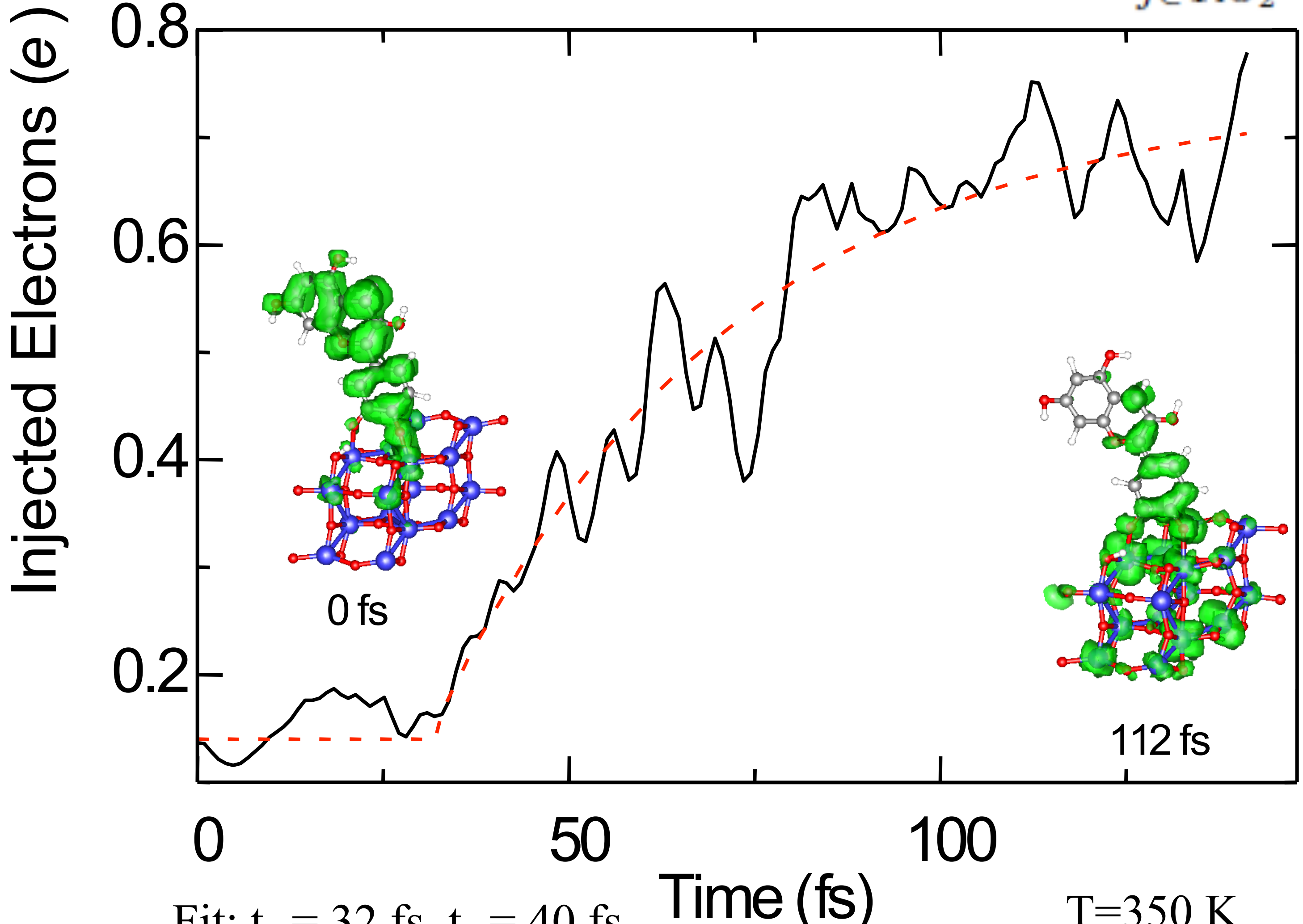



0.968 fs


0.968 fs

Charge injection dynamics:

$$\chi = \int d\mathbf{r} |\tilde{\psi}(\mathbf{r})|^2, \qquad \tilde{\psi}(\mathbf{r}) = \sum_{j \in TiO_2} c_j \phi_j(\mathbf{r}),$$



Fit: t_0 = 32 fs, t_1 = 40 fs

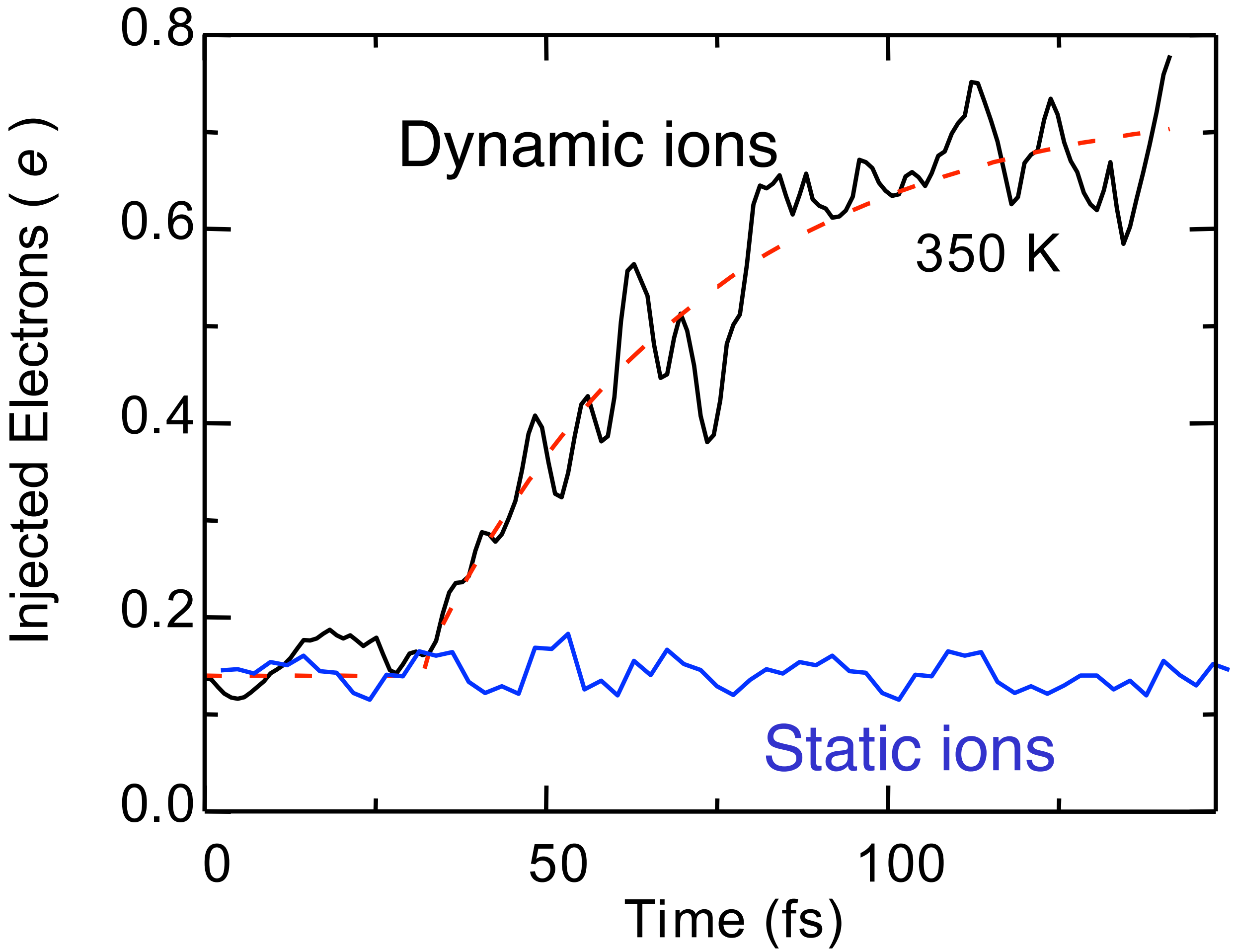
Expt.[a] : <100 fs

[a] Cherepy et al., JPCB (1997).

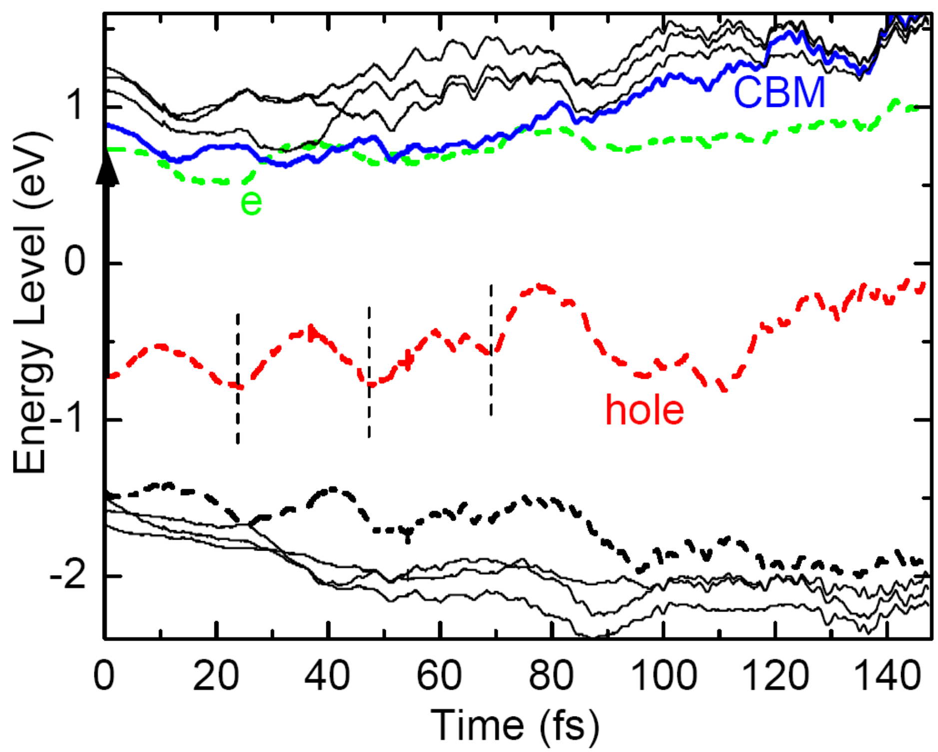
T=350 K

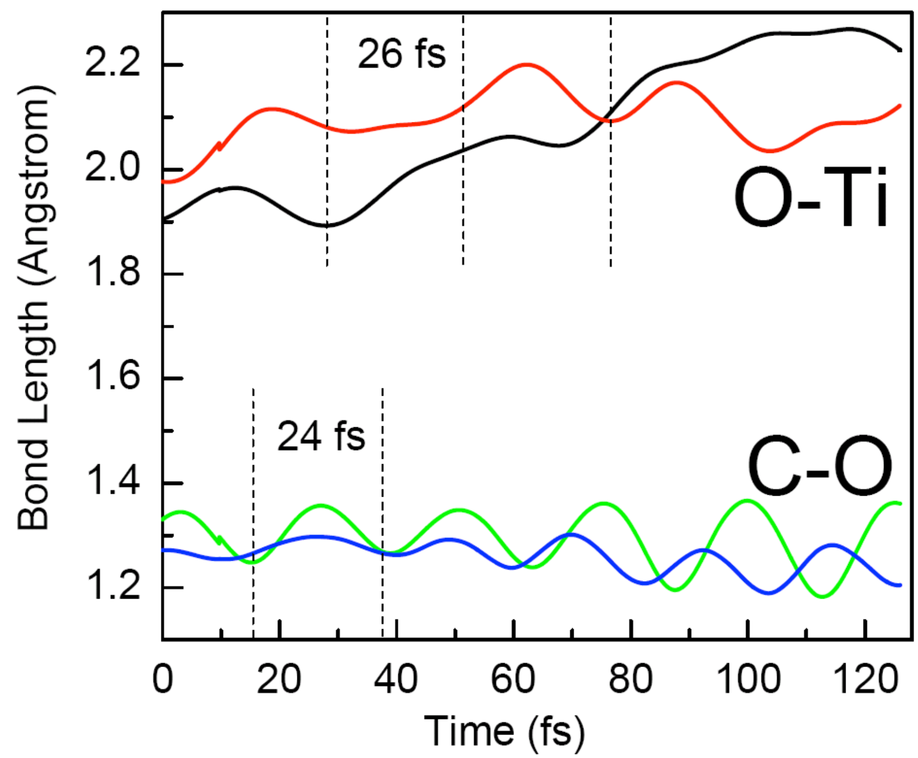
δt=0.02419 fs

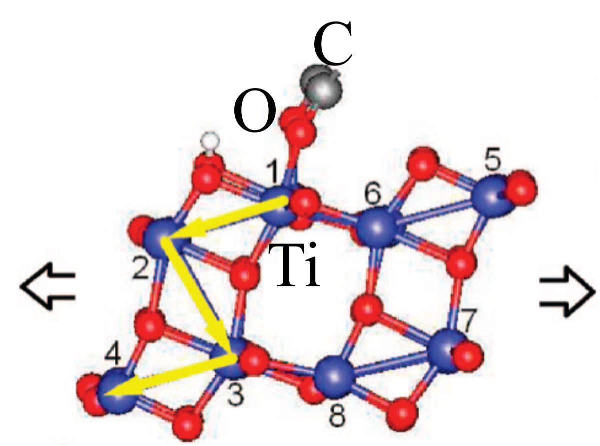
Importance of ion dynamics



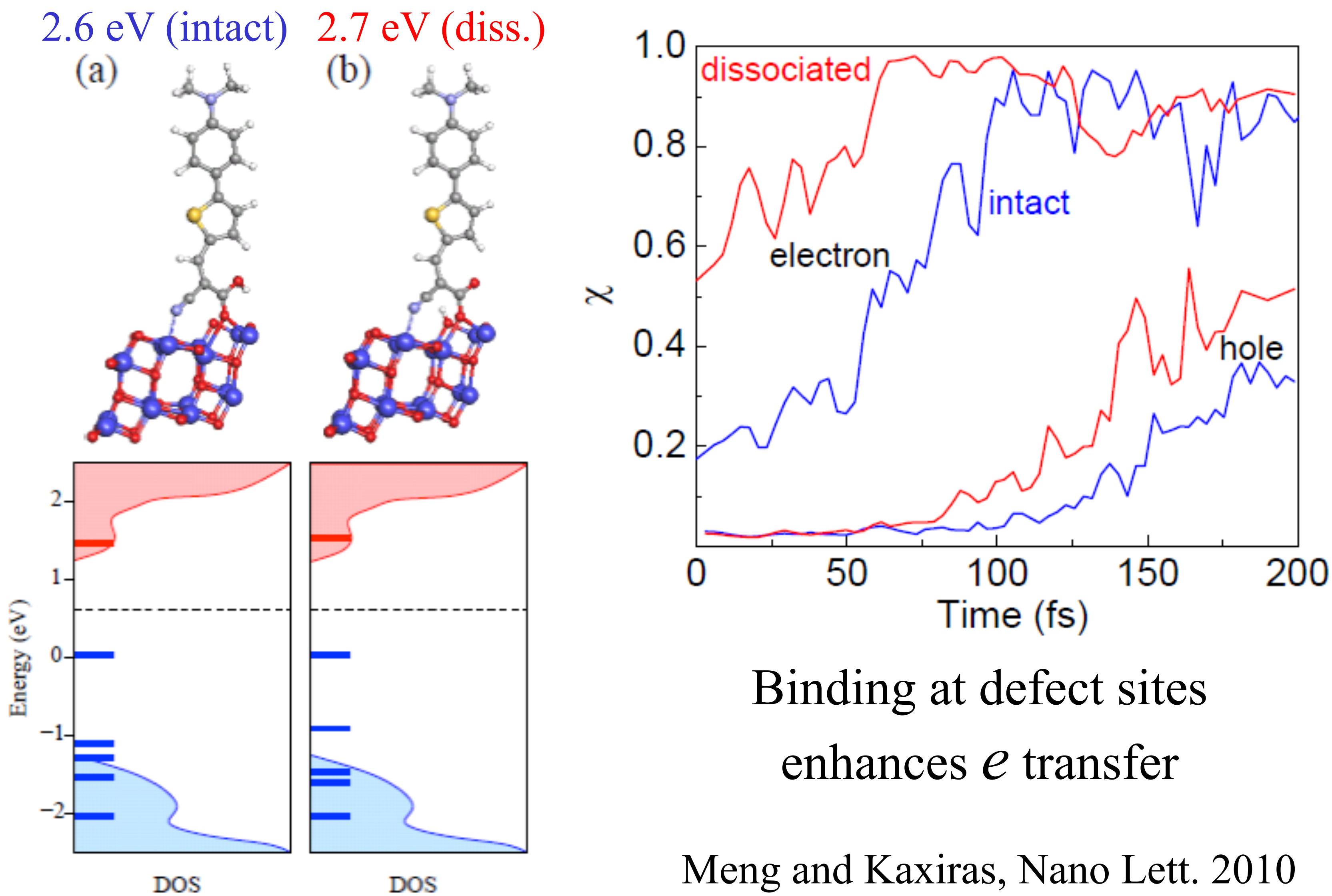
Relation between electron-phonon motion







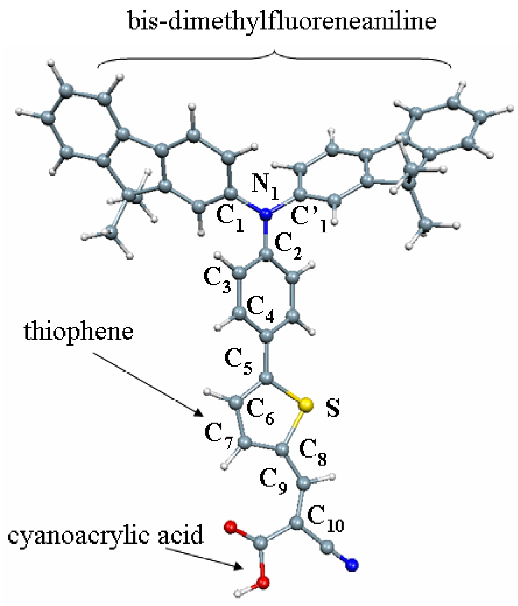
Oxygen vacancy defects



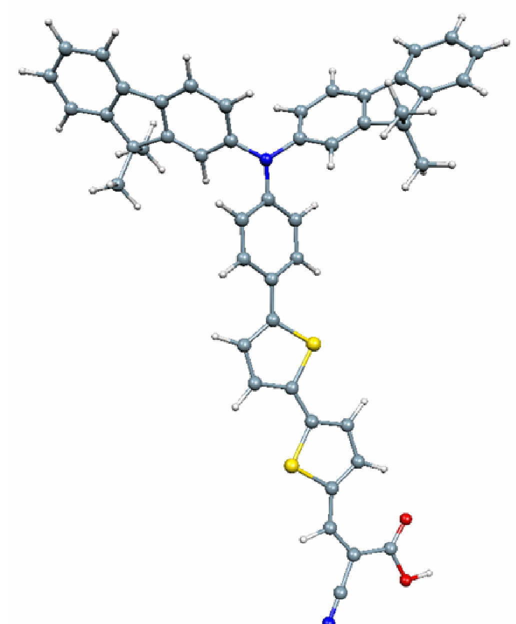
Binding at defect sites enhances *e* transfer

Meng and Kaxiras, Nano Lett. 2010

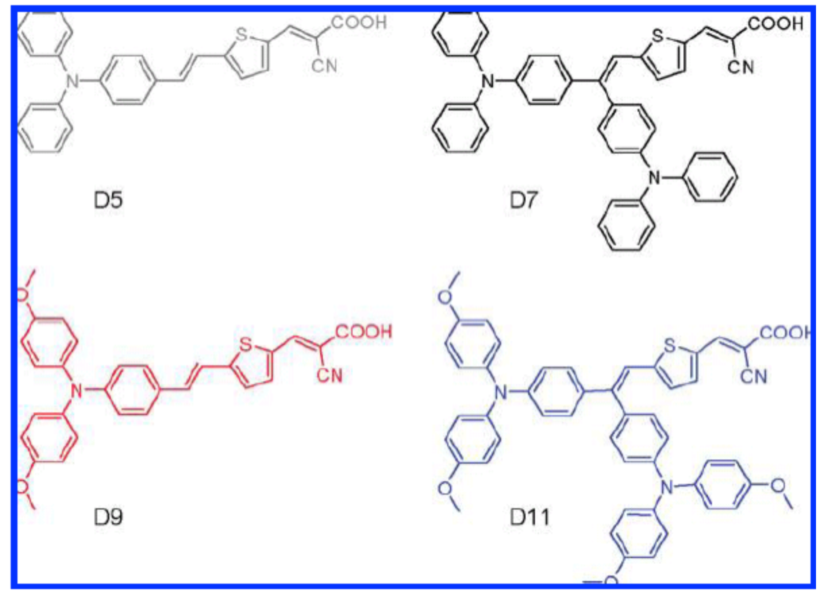
Realistic organic dyes



JK-1

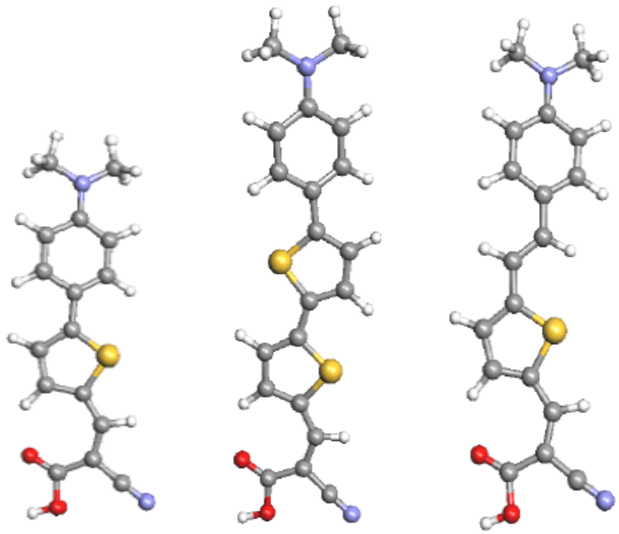


JK-2

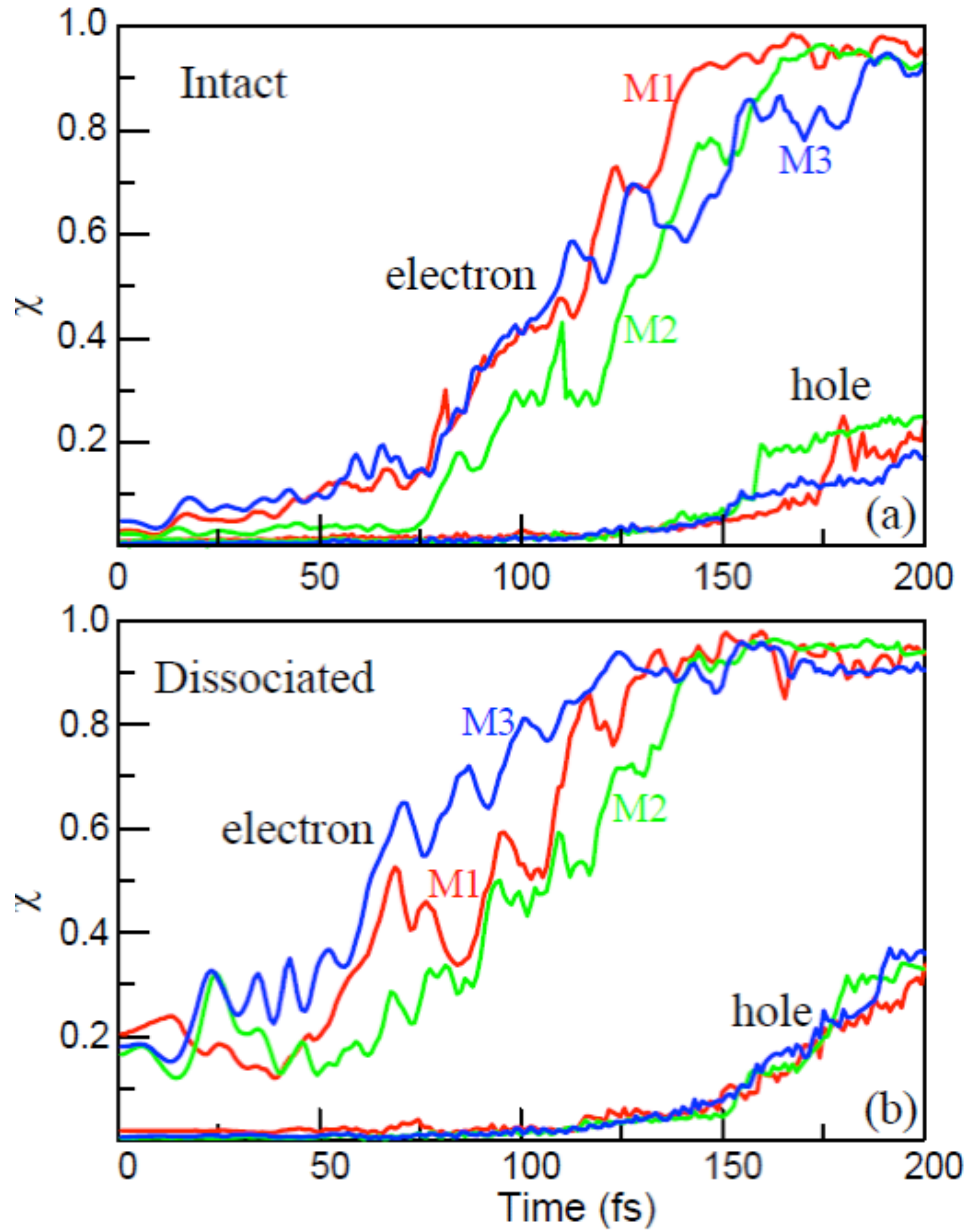


Hagberg et al., JACS(2008).

Kim et al., JACS (2006).

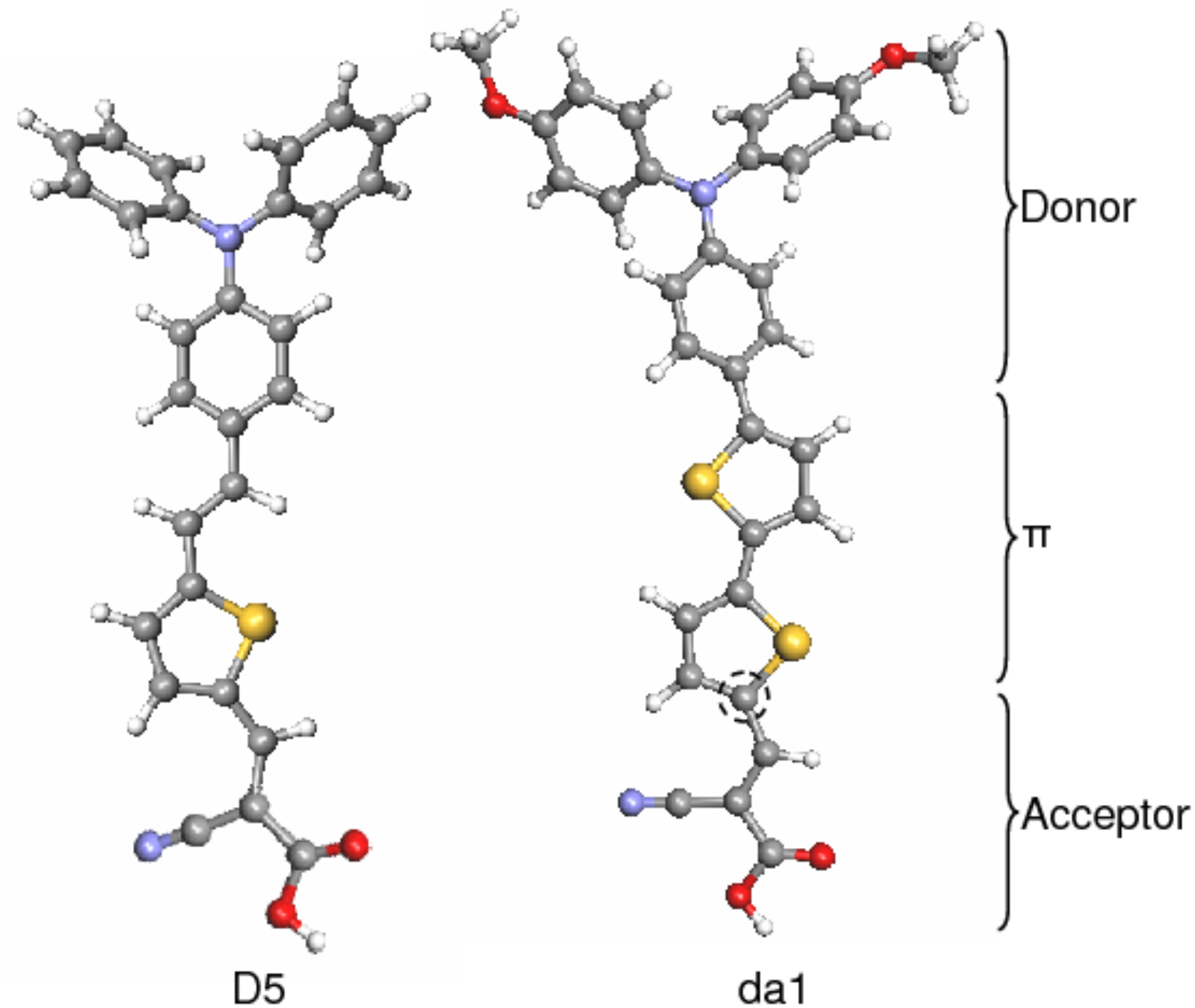


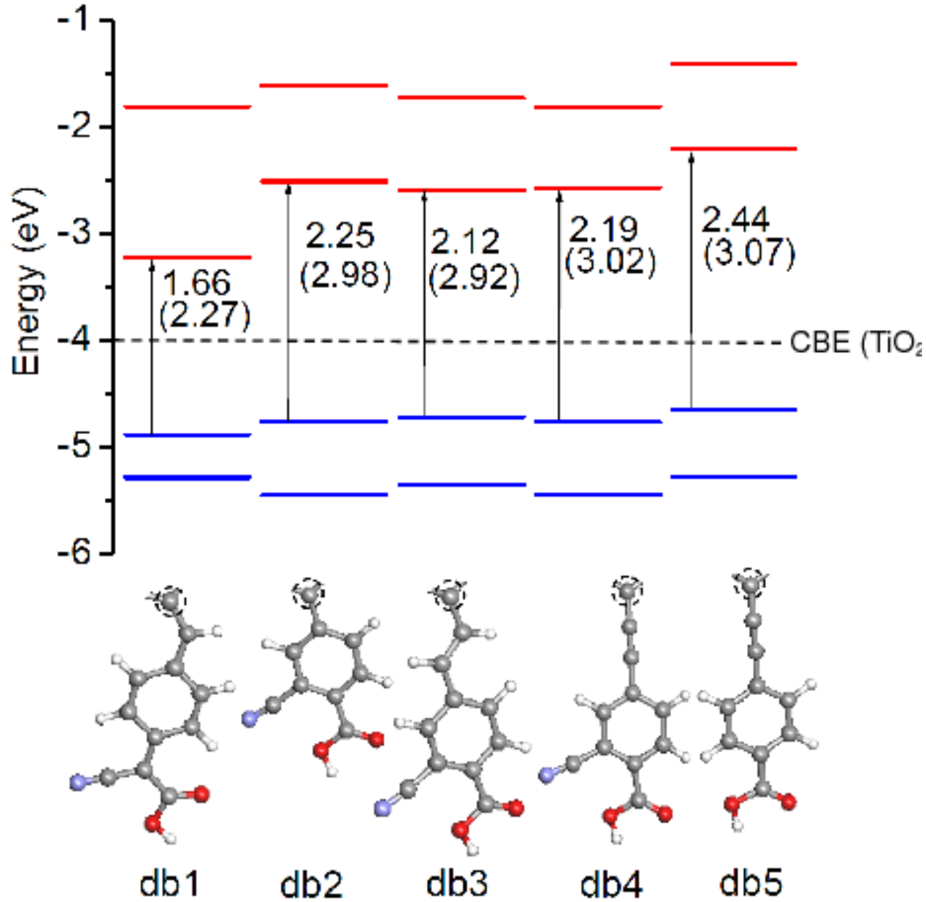
M1 M2 M3

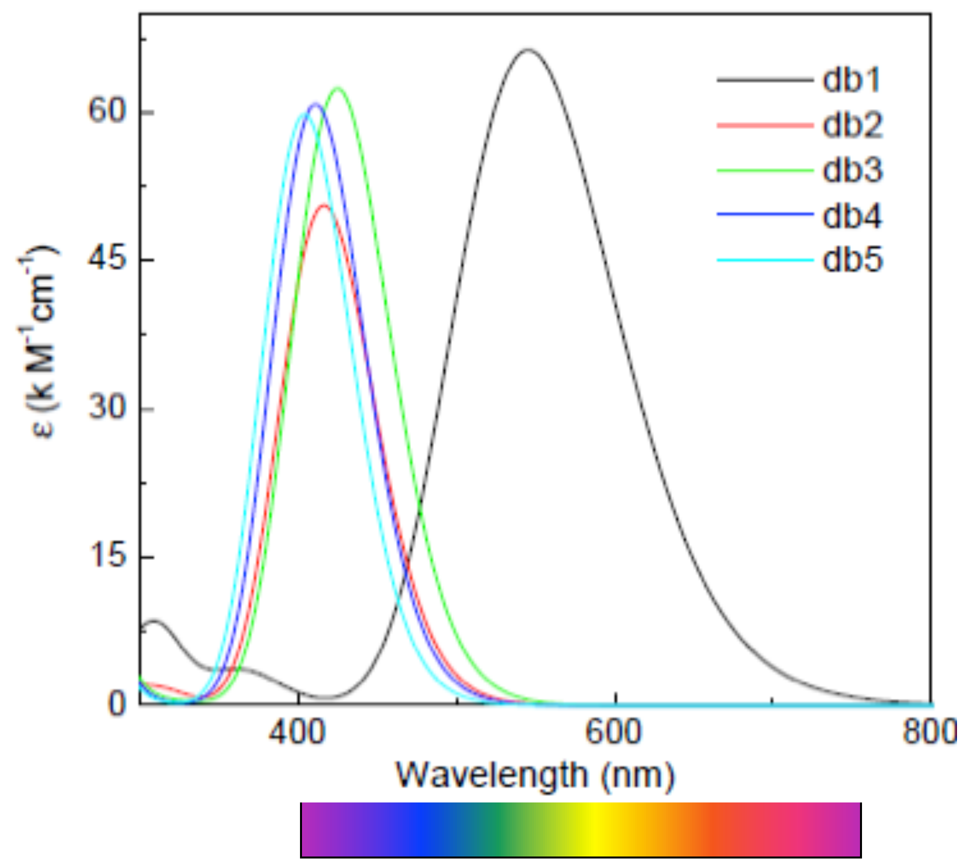


- $t_{M1} < t_{M2} < t_{M3}$
- $t_{disso.} < t_{intact}$

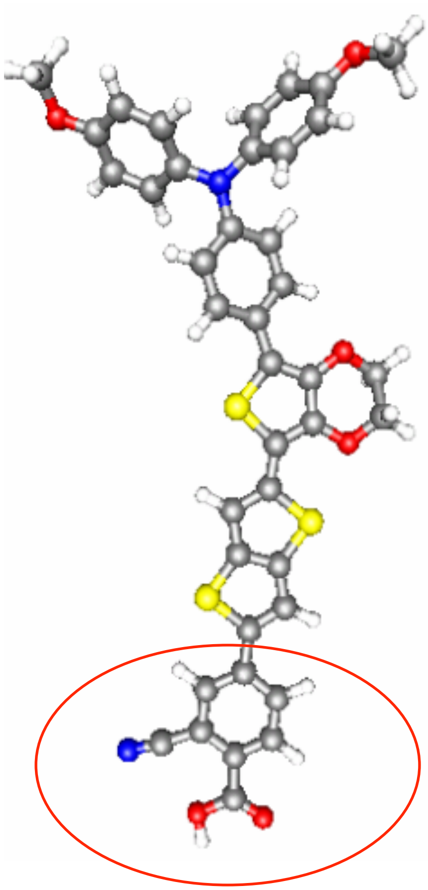
New dyes (not yet tried in experiments)

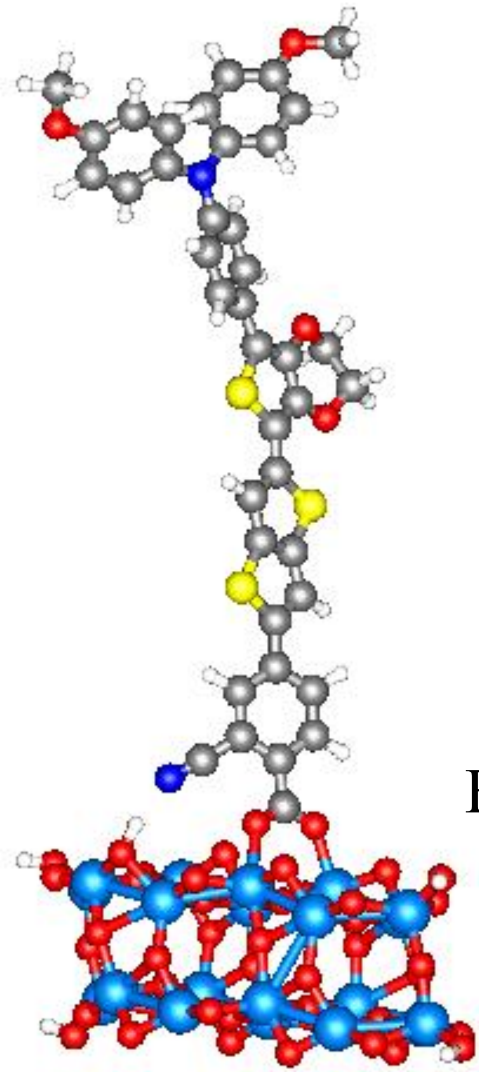



-1
-2
-3
-4
-5
-6
Energy (eV)
1.66
(2.27)
2.25
(2.98)
2.12
(2.92)
2.19
(3.02)
2.44
(3.07)
CBE (TiO₂
db1
db2
db3
db4
db5


ε (k M⁻¹cm⁻¹)
0
15
30
45
60
400
600
800
Wavelength (nm)
db1
db2
db3
db4
db5

Enhanced dye binding to TiO_2

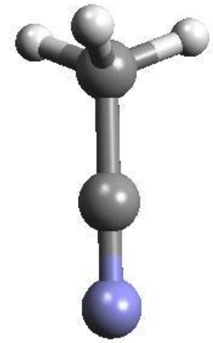


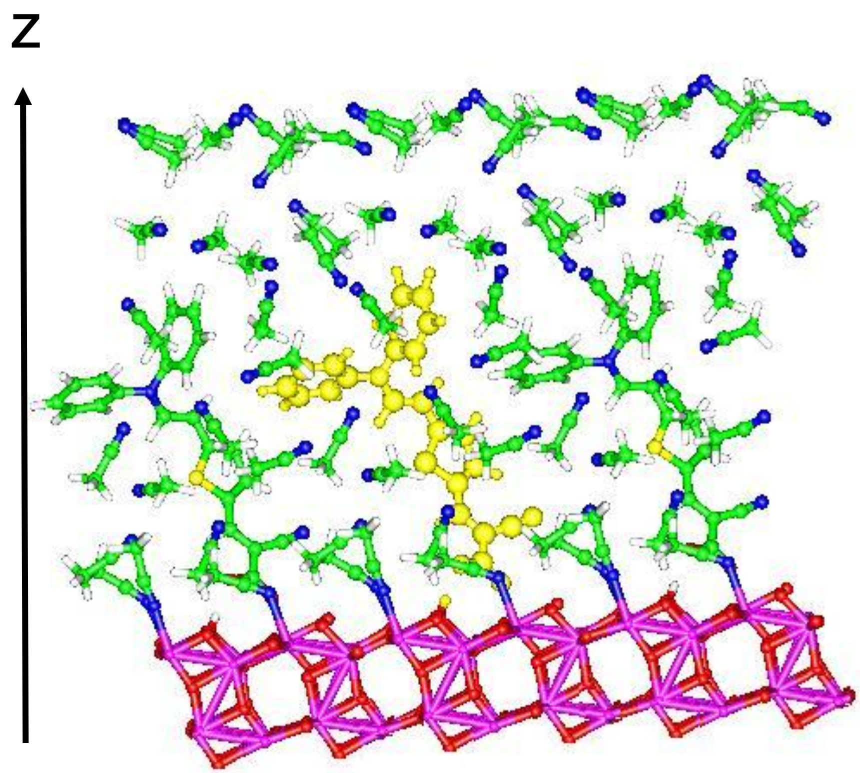


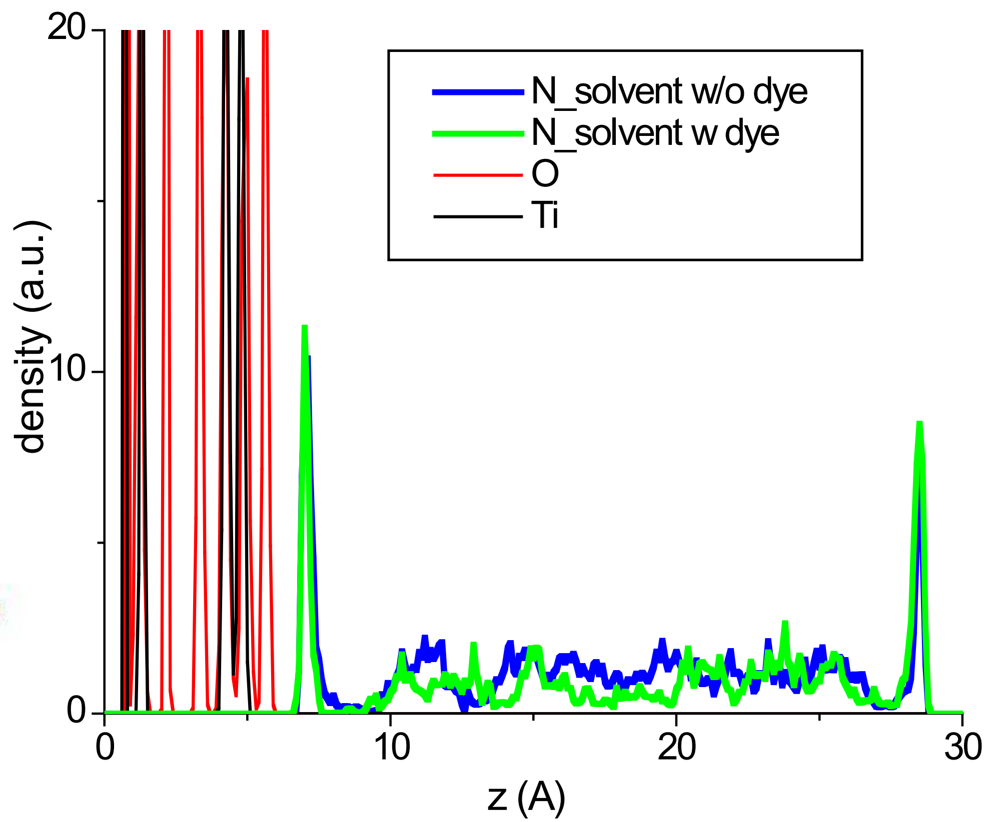
E_b=1.52 eV

Solvent effects

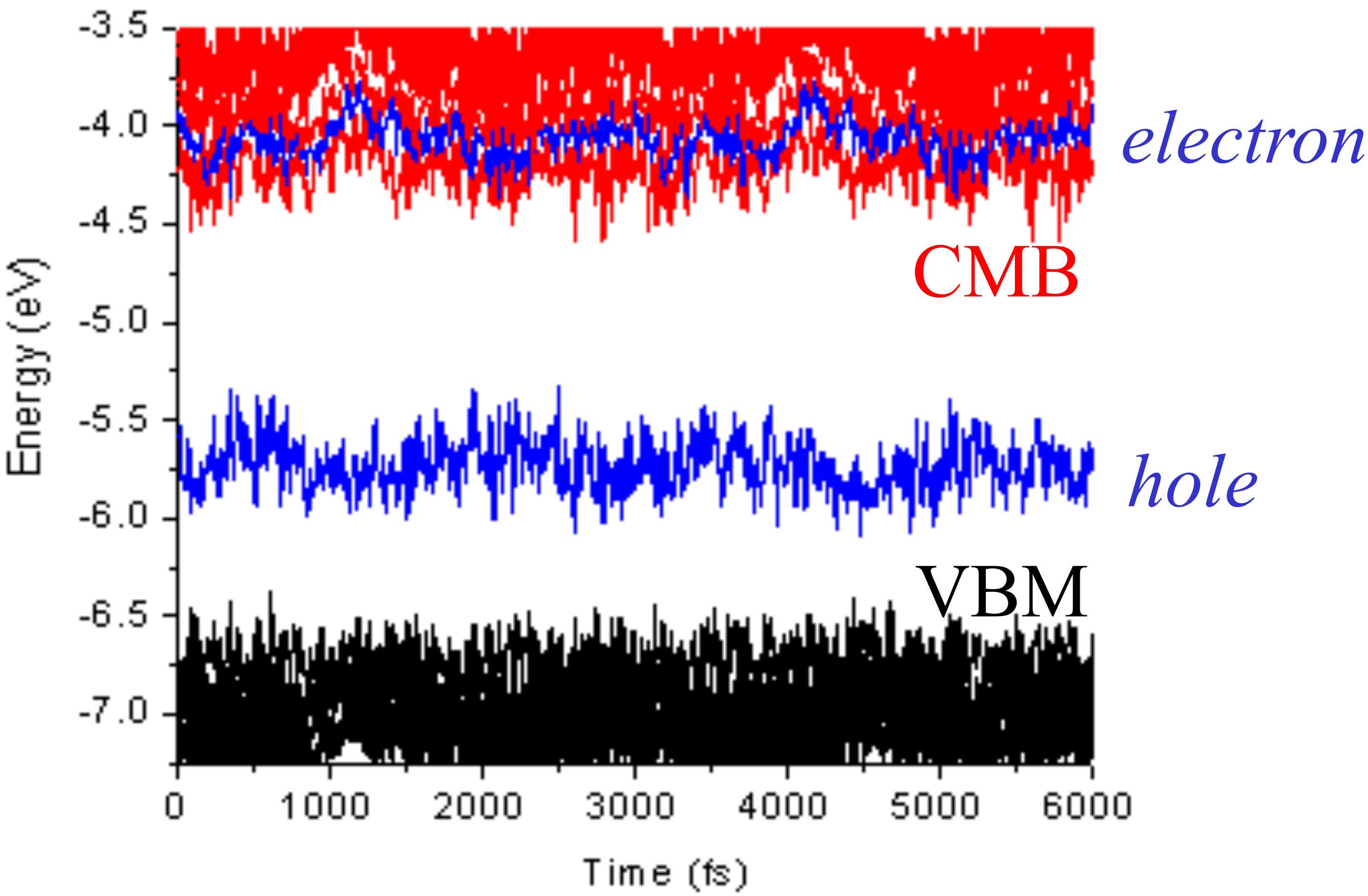
300 K







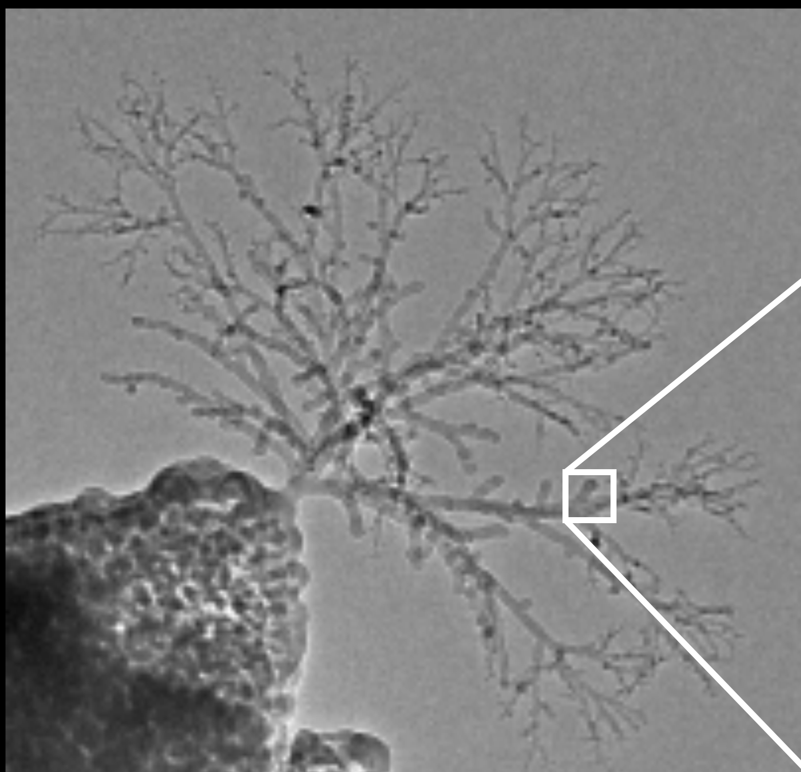
Effect of solvent on electronic states

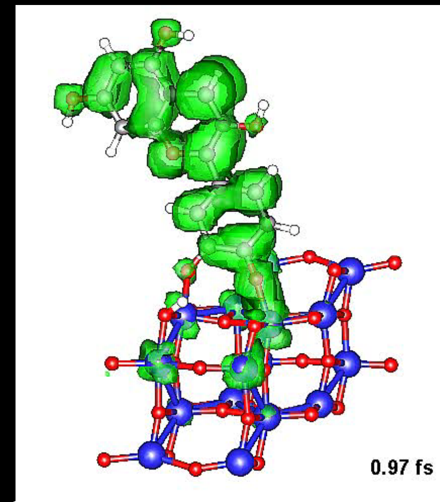


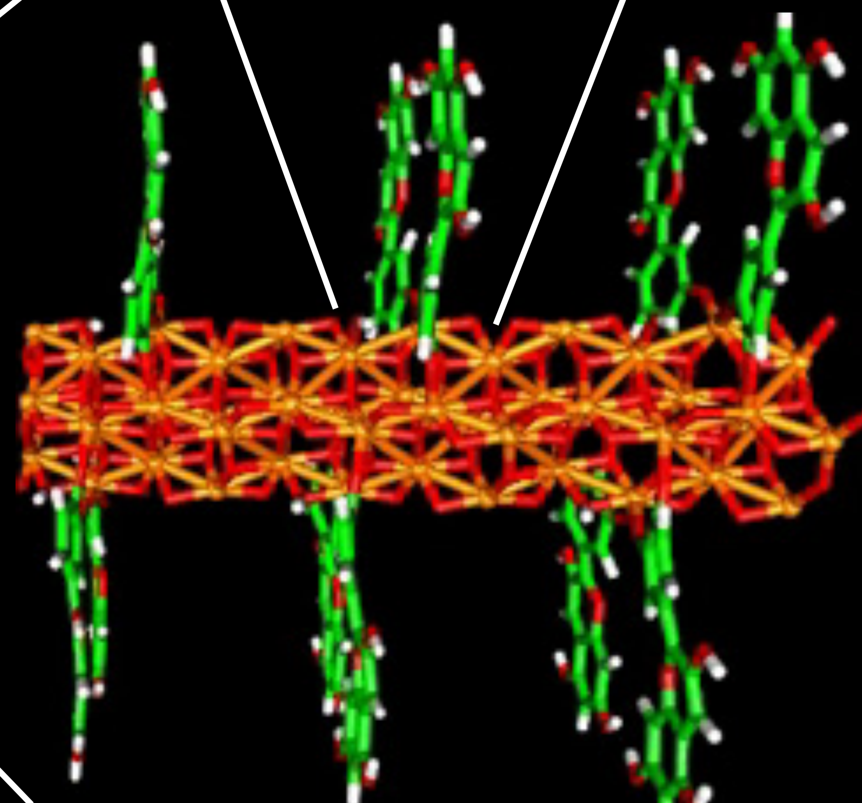
Artificial Nano Tree

electron injection

Fractal tree







Experiment:
Cheng et al., JPCC (2008).