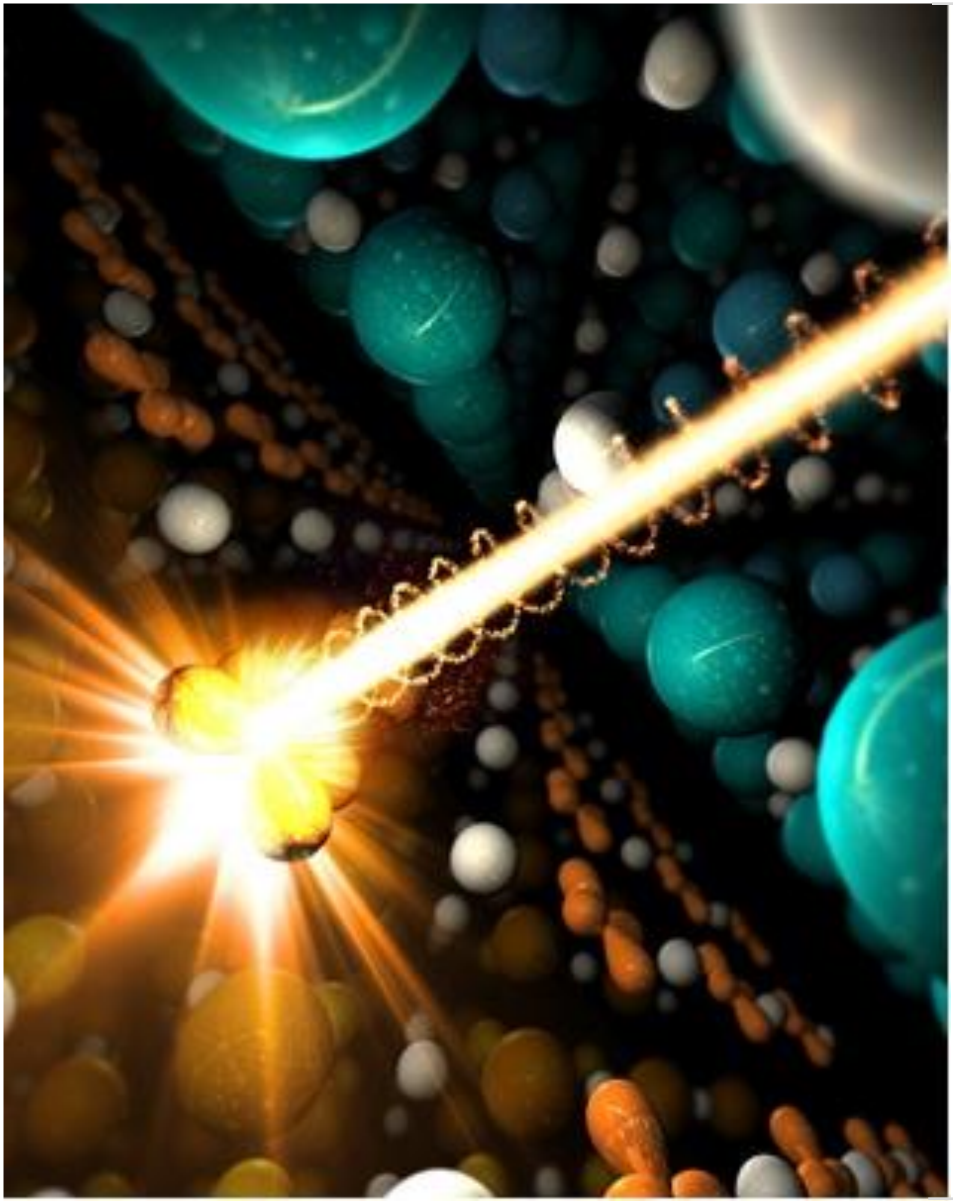
Condensed Matter Physics Forum, Peking U.
June 4, 2015

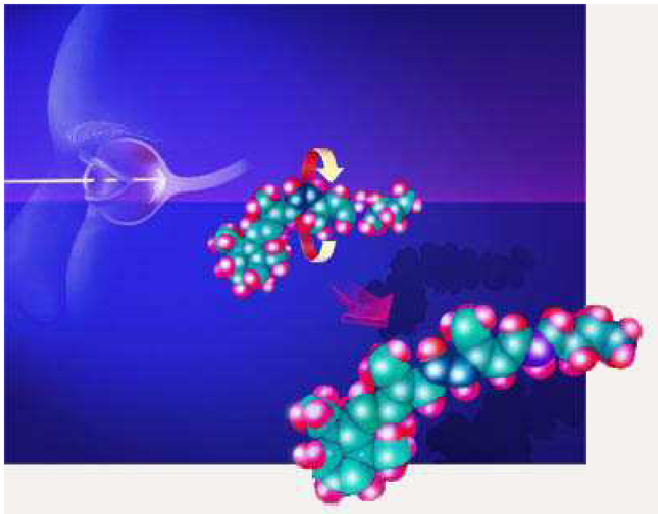


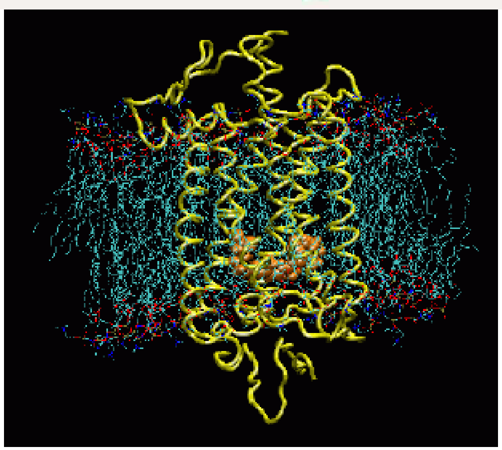
Excited state electron-ion dynamics at interface

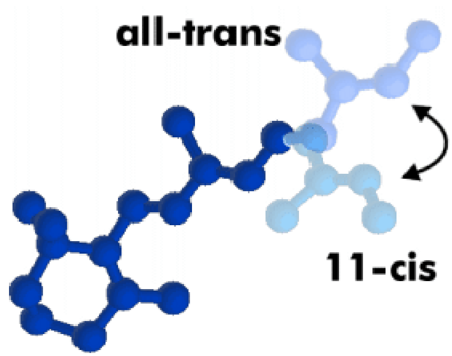
Sheng Meng (孟胜)
Institute of Physics,
Chinese Academy of Sciences
2015.6.4

Understanding vision

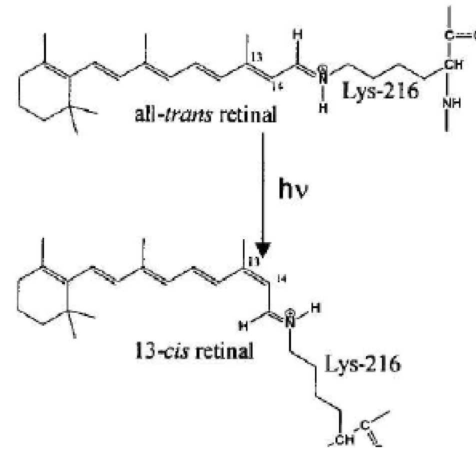
First-principles contribution to understanding the vision process.
Photoisomerization processes in retinal and other bio-photoreceptors

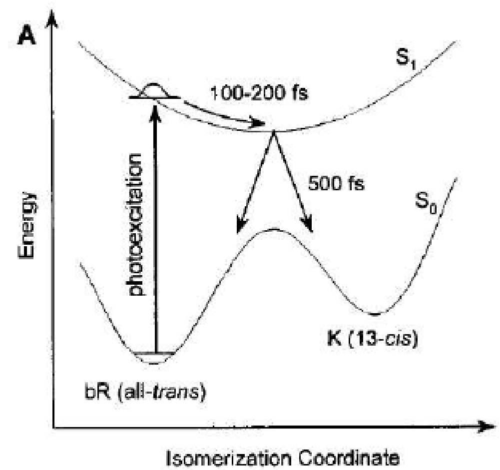






F. Gai et al. Science
<u>279</u>, 1886 (1998)

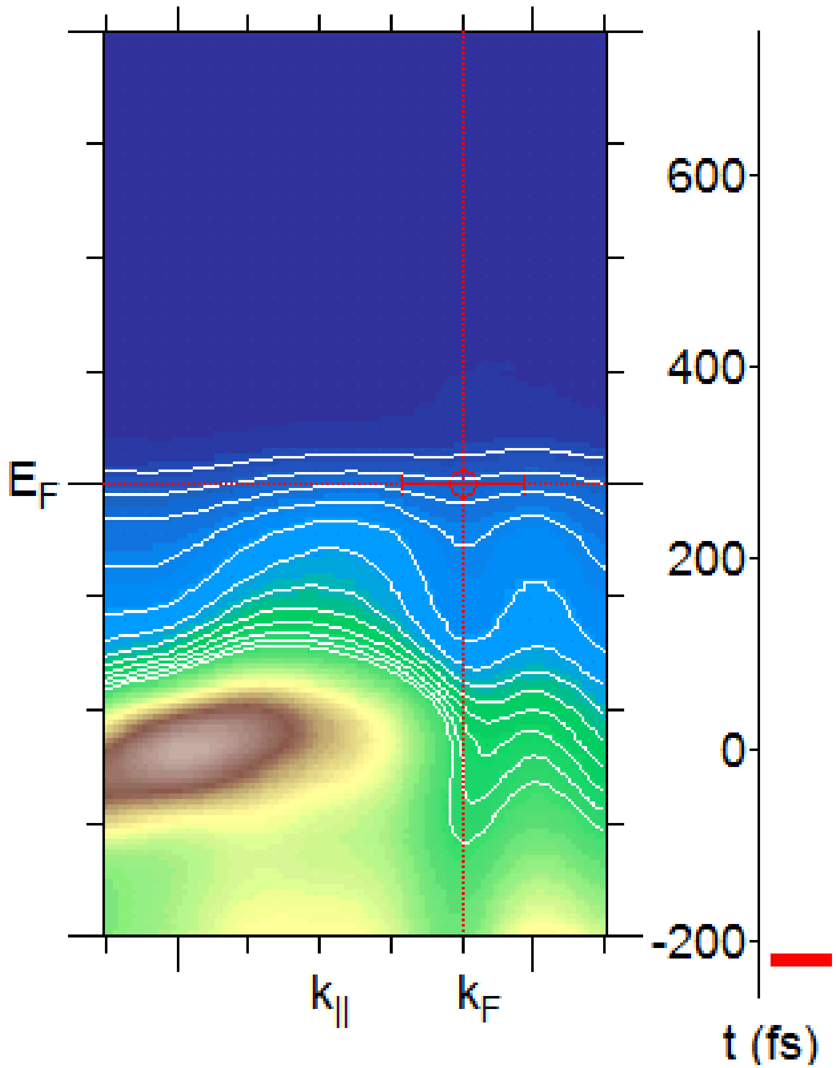




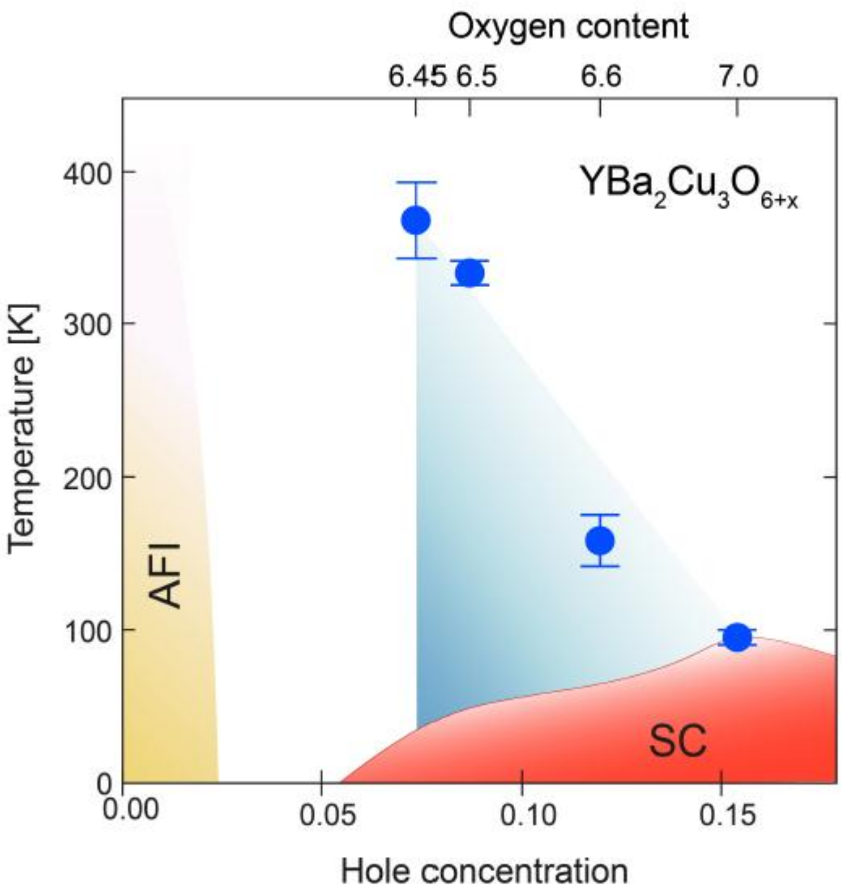
A. Rubio

Experimental Observations

TR-ARPES



Light-driven superconductor @RT



Schmitt *et al.* Science **321**, 1649 (2008)

Cavelleri *et al.* PRB 89, 184516(2014);Nature (2014)

Developing first-principle methods for e-ion dynamics

Time-dependent density functional theory (TDDFT) **Gross 1984'**

$$\Psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N;t) \rightleftarrows \rho(\vec{r},t)=\int\left|\Psi(\vec{r},\vec{r}_2,...,\vec{r}_N;t)\right|^2\prod_{j=2}^{N}d\vec{r}_j$$

$$\text{Given } \Psi(0),\quad i\hbar\frac{\partial\Psi(t)}{\partial t}=\hat{H}\left[\rho(\vec{r},t),t\right]\Psi(t)$$

Coupled electron-ion dynamics **Beyond Born-Oppenheimer**

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

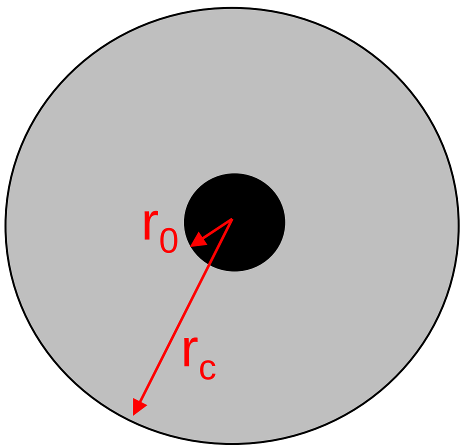
<u>Our implementation:</u>

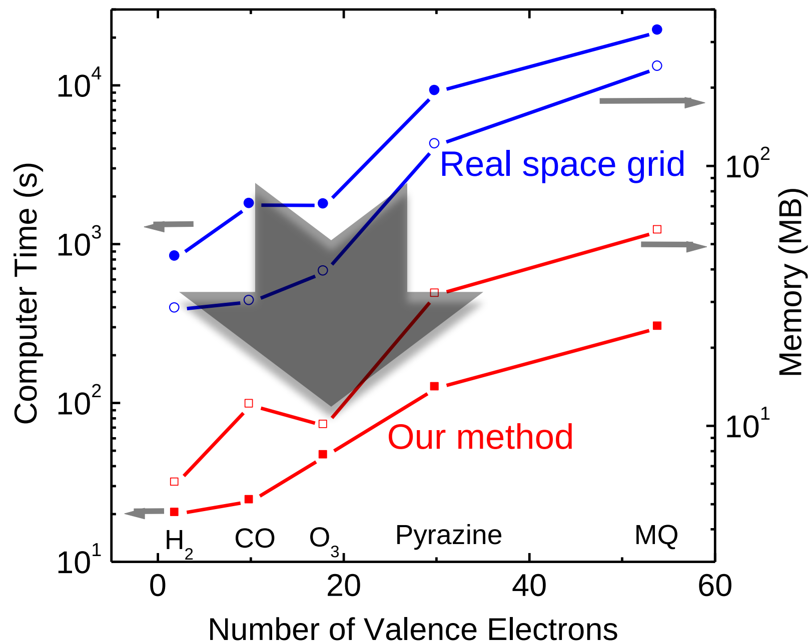
- Real time (nonlinear, dynamics)
- Local bases: numeric atomic orbitals
- Paralleling over Kohn-Sham orbitals

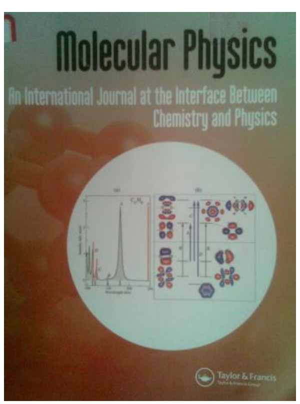
Time-Dependent Ab-initio Package
for excited state dynamics

Computational efficiency

Pseudopotential + Numerical atomic orbitals







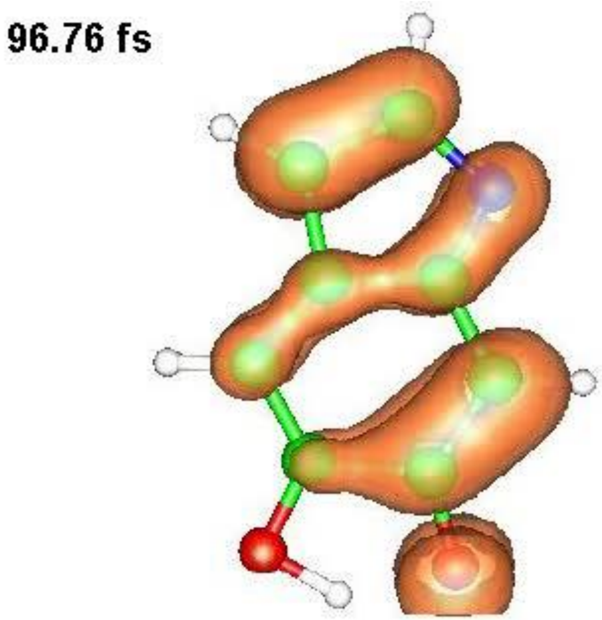
Optical properties of clusters and molecules from real-time time-dependent density functional theory using a self-consistent field

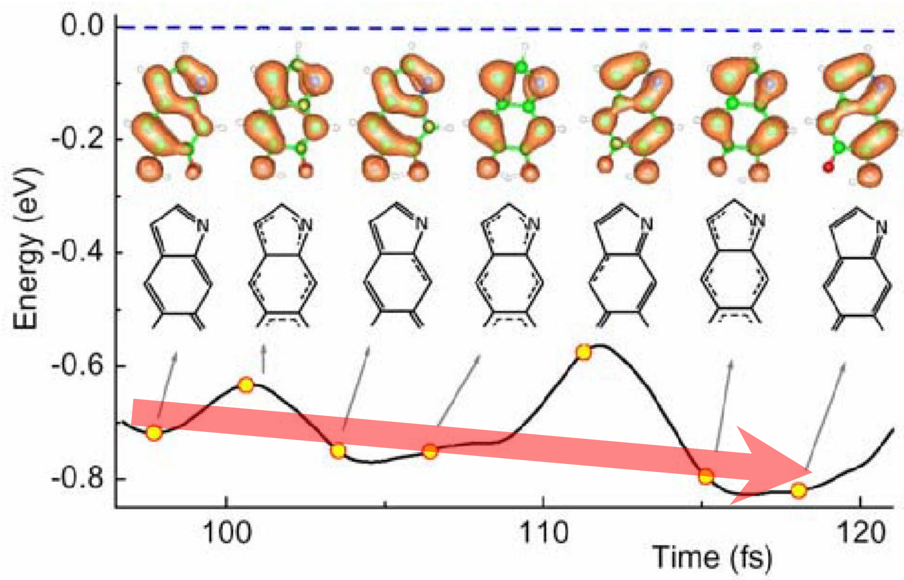
J. Ren, E. Kaxiras, <u>S. Meng</u>,

Mol. Phys. 108, 1829 (2010).

Photodynamics in a molecule

e-proton concerted dynamics





Clouds = e density in excited state

Natural and artificial photosynthesis

Real time TDDFT for electron-ion quantum dynamics

OUTLINE

I. Background: building computational tools for excited state dynamics

II. Photovoltaic applications

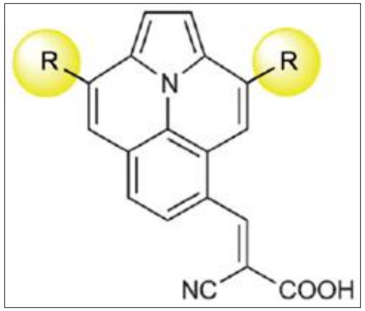
- ”virtual solar cells”
- interface control in perovskite solar cells
- electron-hole dynamics in 2D materials heterojunction

III. Photosplitting dynamics

- orbital dependent quantum interaction of water
- photolysis dynamics of H_2

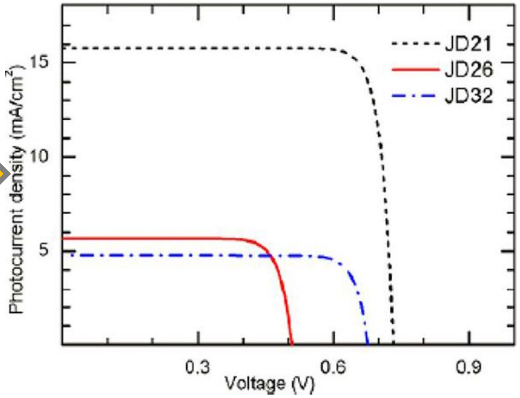
1. Build “virtual solar cells” for photovoltaics

INPUT

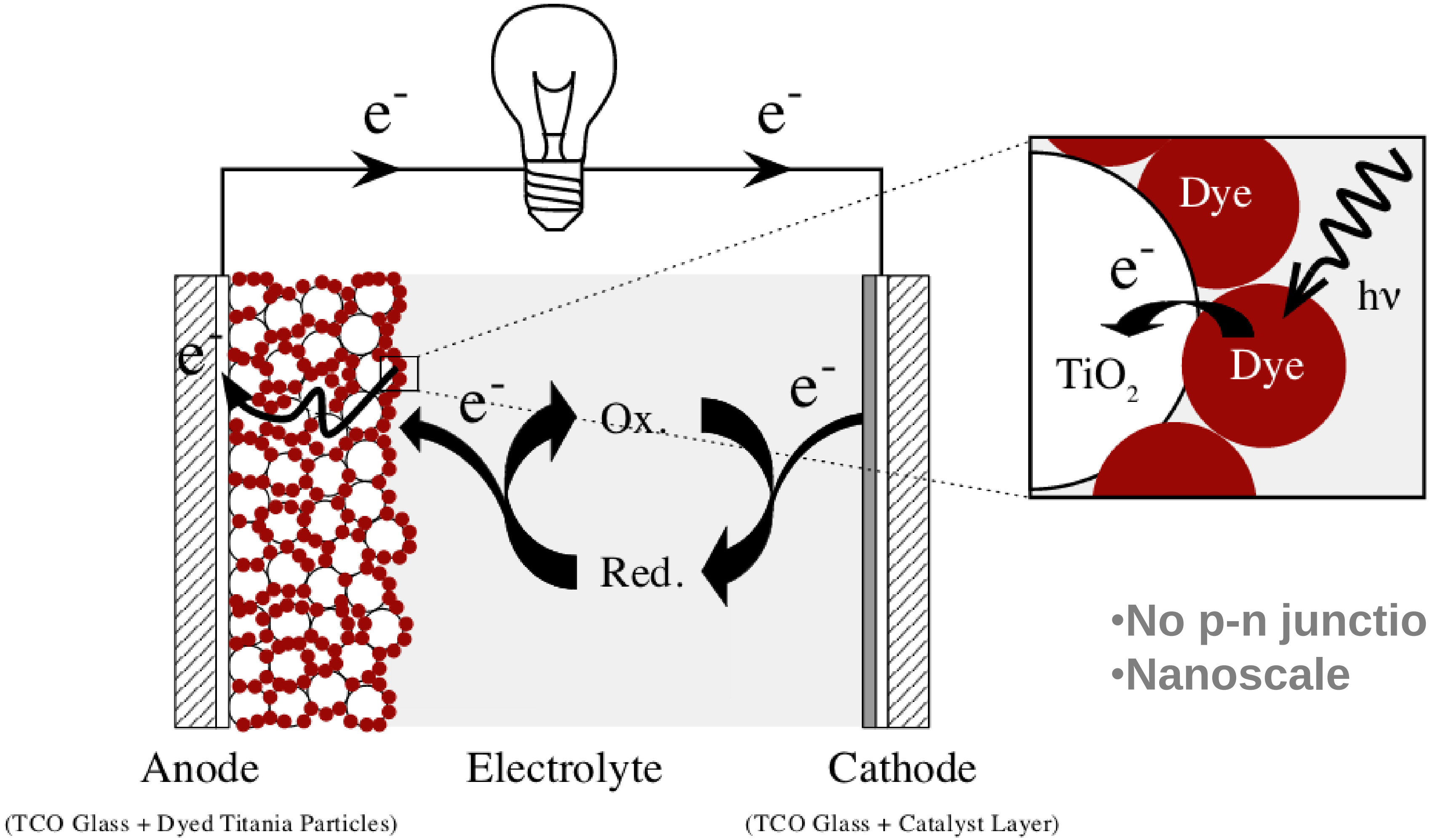


“Virtual solar cell”

OUTPUT



Dye solar cell: A 3rd Generation Solar Cell



- •No p-n junction
- •Nanoscale

• organic molecule | quantum dot | perovskite

O' Regan & Gratzel, Nature (1991).

From http://www.solaronix.com

- **Molecular Dyes**

  Metal-based:

  Ru, Pt, Os, Cu, Fe, …

  Porphyrin

  Phthalocyanine

  …

  All-organic:

  Coumarin

  Indoline

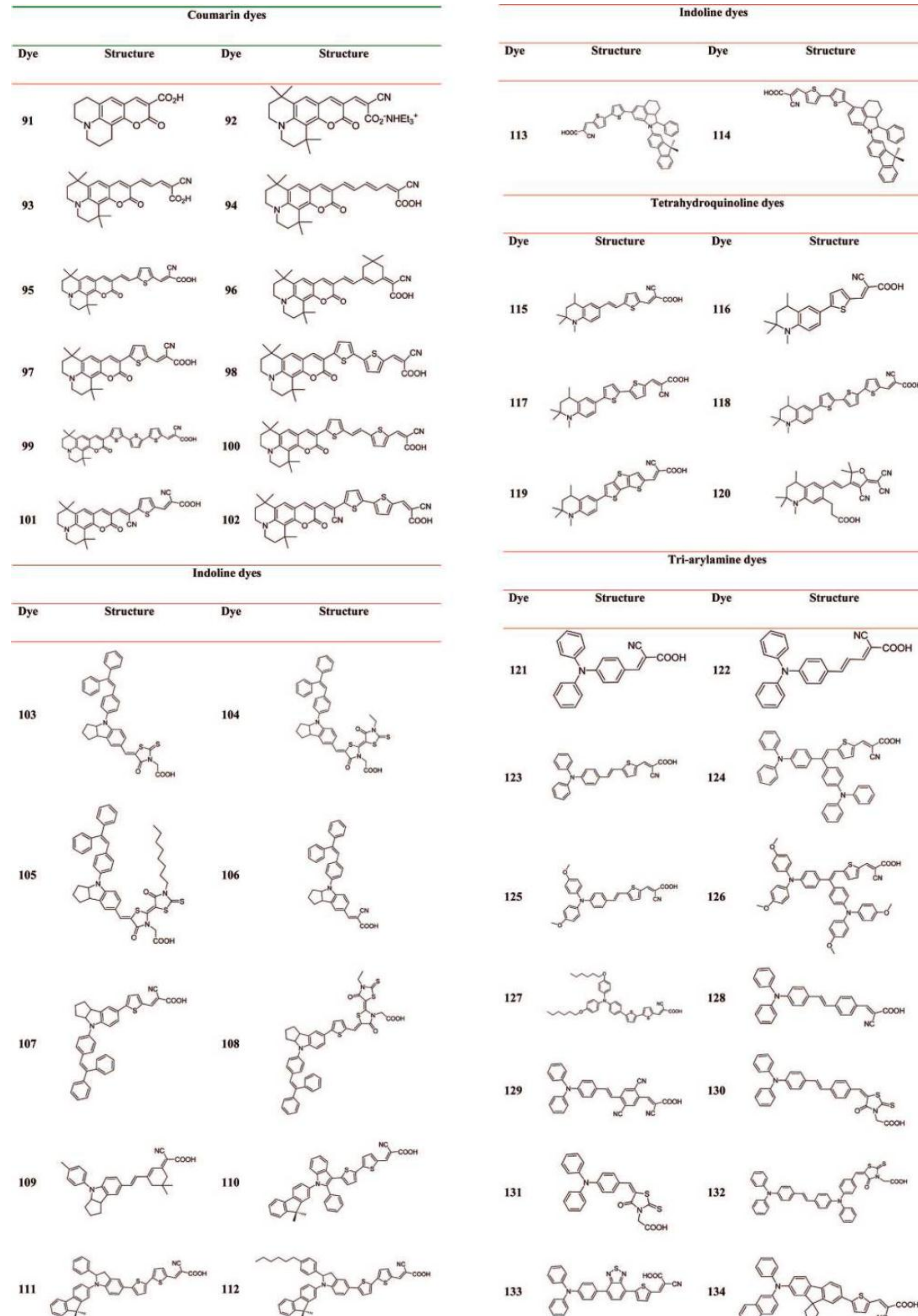
  Triarylamine

  Perylene

  Squarine

  …

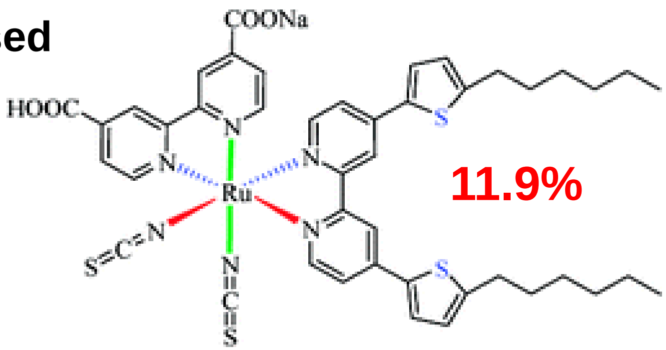
  >1000 species



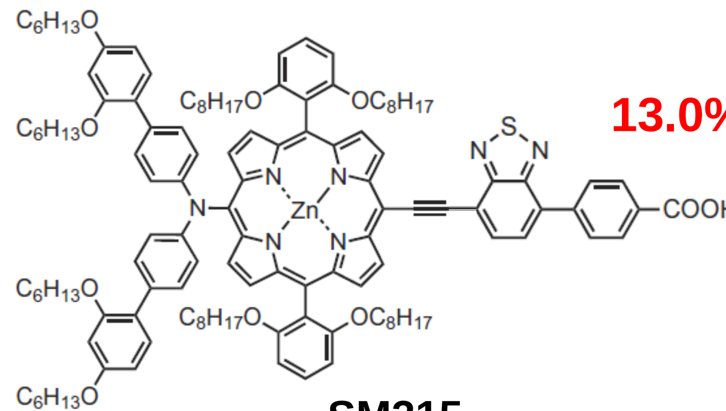
Hagfeldt et al., Chem. Rev. (2010).

State of the Art

Metal-based
C101



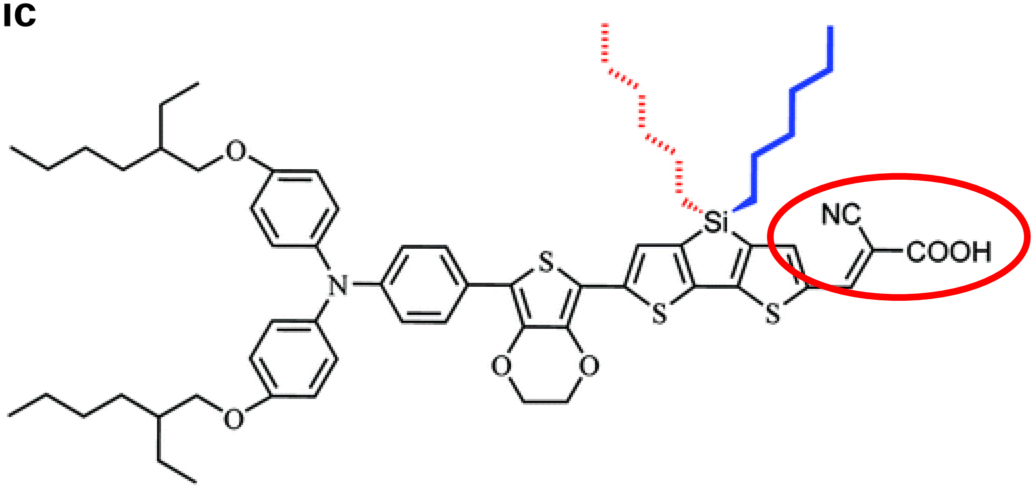
11.9%



13.0%

SM315

Organic
C219



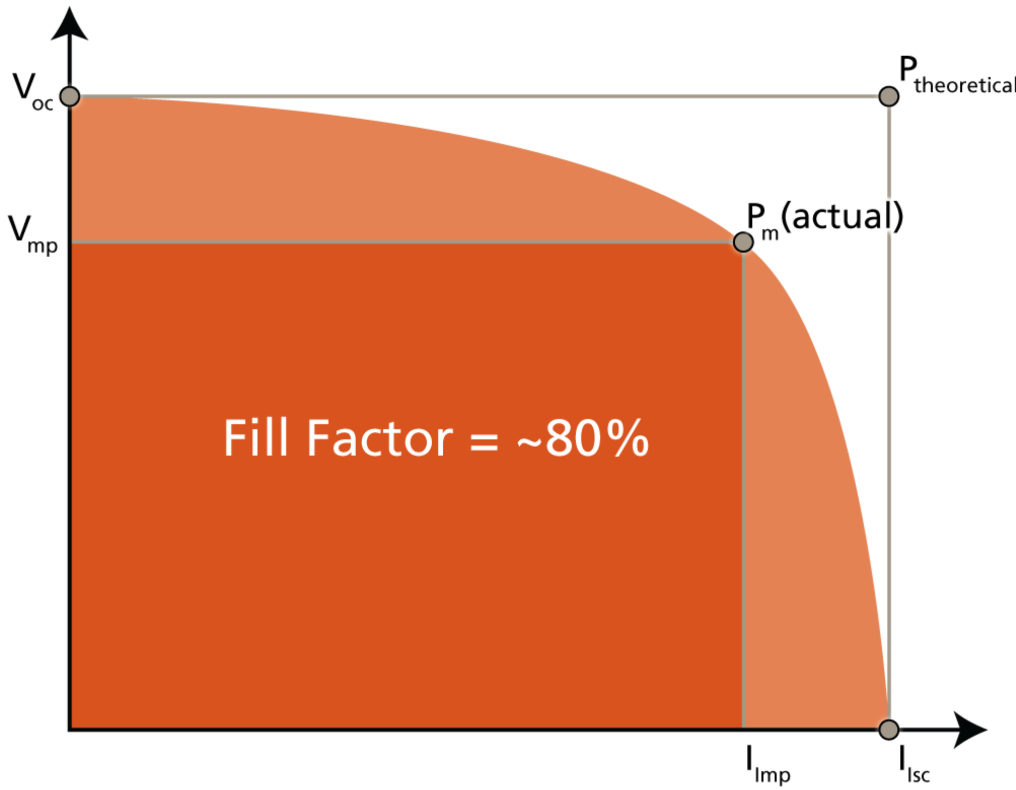
10.0-10.3%

M. Grätzel (2008).
W. Zeng, et al., Chem. Mater. (2010).
Yella et al., Science 334, 629 (2011).
Mathew et al., Nature Chem. 6, 242 (2014).

Can we predict DSC efficiency from first-principles?

$$\eta = \mathrm{FF}\frac{J_{SC}V_{OC}}{P_{inc}}$$

$$P_{inc} = 100\ \mathrm{mW/cm^2}$$



$$V = \frac{k_B T}{q}\ln\left(\frac{J_{sc} - I}{I_S} + 1\right), \quad I_S = \frac{J_{SC}}{\exp(qV_{OC}/k_B T) - 1}$$

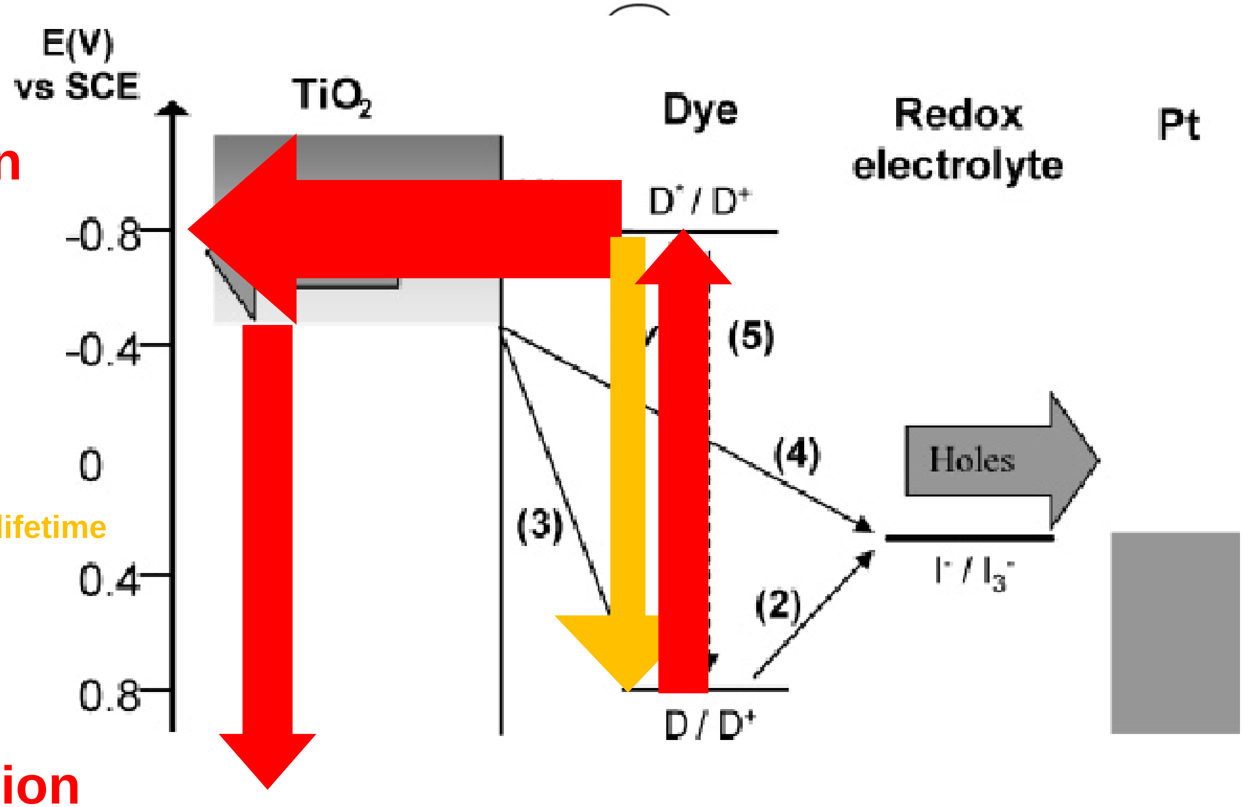
Interface electron dynamics plays a key role

1. Absorption

2. Injection

$\eta_{inj} = 1 - \tau_{inj} / T_{lifetime}$

3. Collection /Recombination



Injection: (1), 10^{-15} s~10^{-12} s
Relaxation: (5)10^{-12} s ~ 10^{-9} s
Collection→ TCO: 10^{-6} s ~ 10^{-3} s
Recombination: (3),(4), 10^{-12}~10^{-3} s
Reduction: (2),10^{-9} s

Difficulties in experiment:
1. Complexity
2. Precision

Ma, Zhang, Meng, Chin. Phys. B 23, 086801 (2014).

PANDORA: Predictive algorithms for nano device operation rate assessment

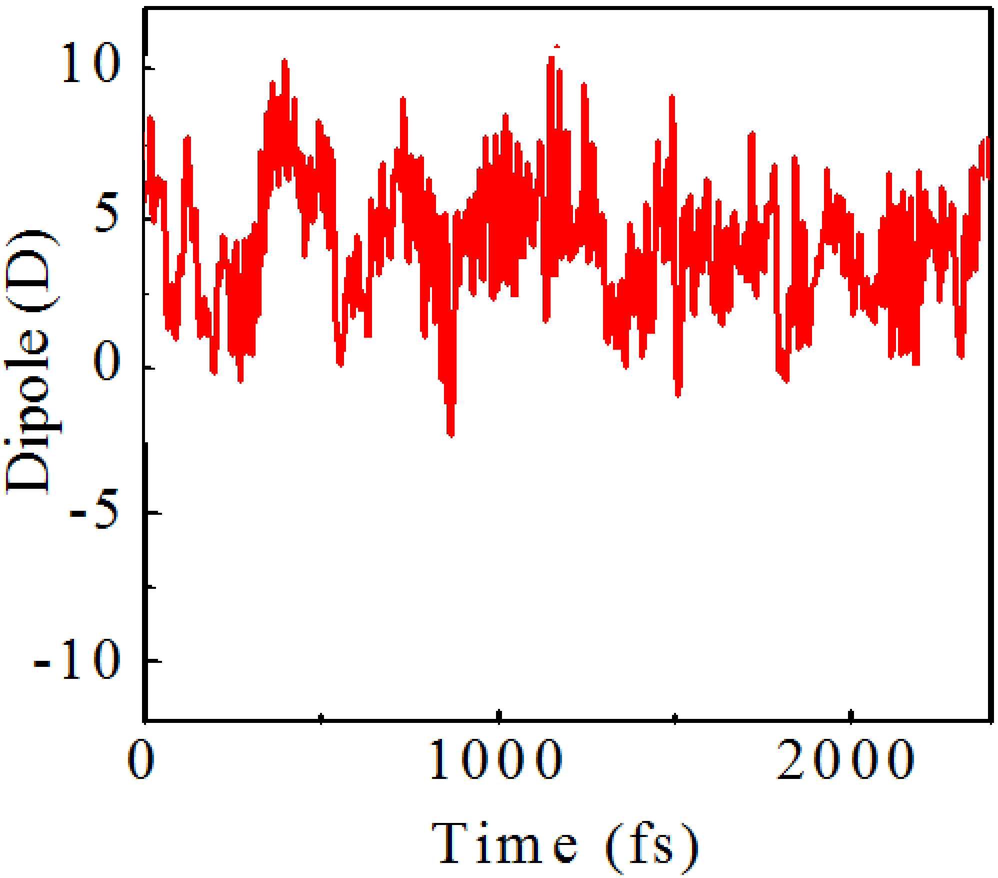
PANDORA

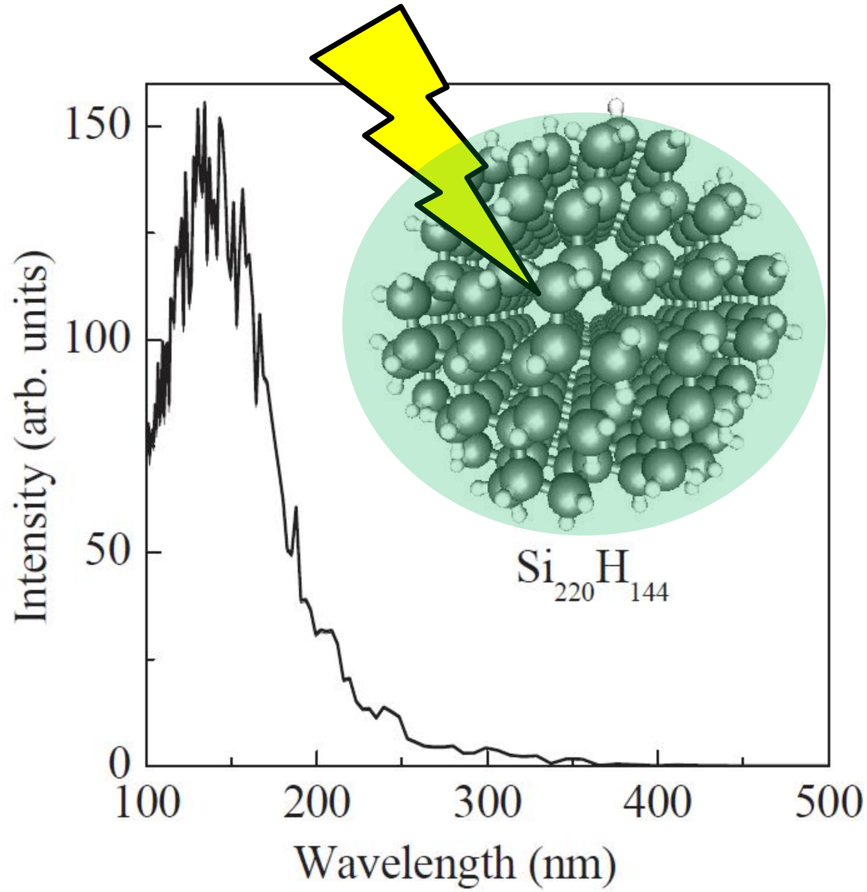
PCE η

- J_{SC}
  - $J_{SC} = \int [SI/(hc/e\lambda)] LHE \bullet \Phi_{inj} \bullet \eta_{coll} d\lambda$
  - LHE: $\mathrm{LHE}(\lambda) = \int \varepsilon\rho \exp(-\varepsilon\rho x) \mathrm{d}x$
  - Φ_{inj} : $\Phi_{inj} = 1 \Big/ \left(1 + \frac{\tau_{inj}}{\tau_{relax}}\right)$
  - η_{coll} : $\eta_{coll} = 1 \Big/ \left(1 + \frac{\tau_{trans}}{\tau_{rec}}\right)$
- V_{OC}
  - $V_{OC} = \frac{k_B T}{\beta' q} \ln \frac{\beta' q R_0 J_{SC}}{k_B T}$
  - $R_0 = \frac{\sqrt{\pi \lambda k_B T}}{q^2 d \gamma k_{rec} c_{ox} N_s} \exp\left(\gamma \frac{E_{CBM} - E_{redox}}{k_B T} + \frac{\lambda}{4 k_B T}\right)$
- FF → *I*-*V* curve

Ma, Jiao & Meng, J. Phys. Chem. C, *invited article* (2014).

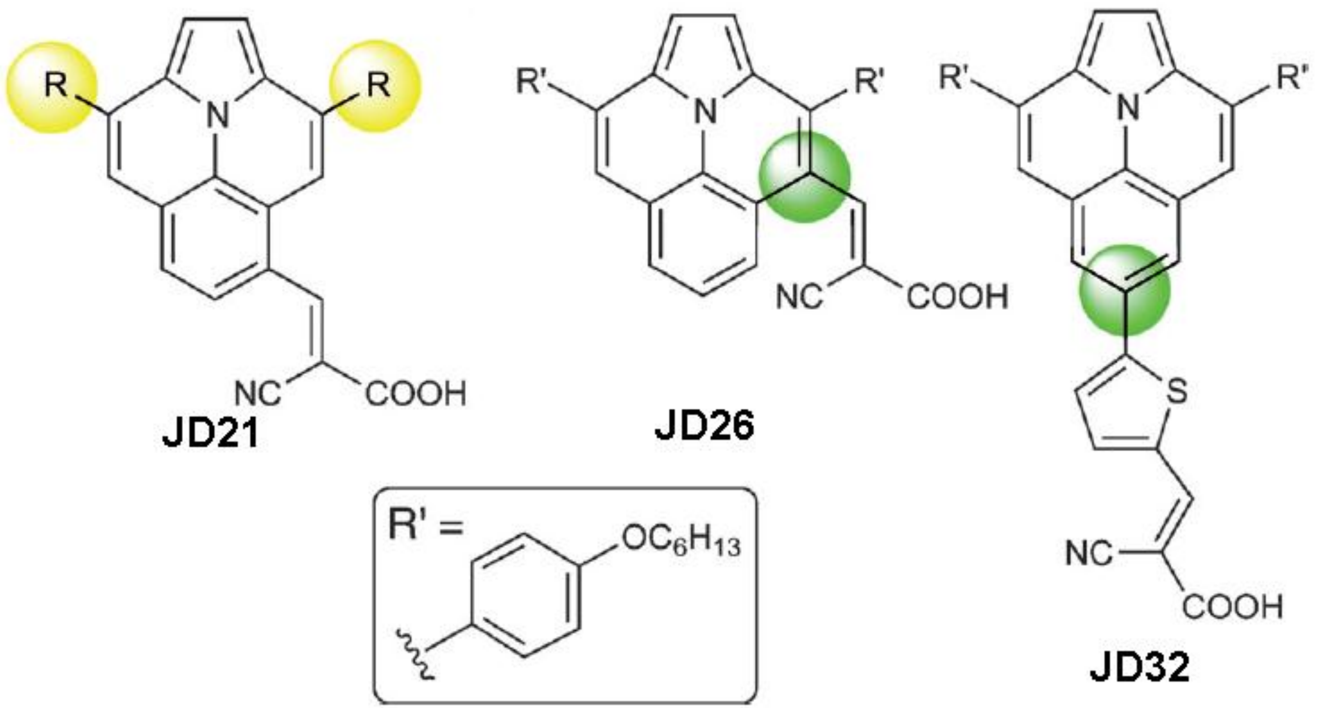
(1) Sunlight harvest : photoabsorption





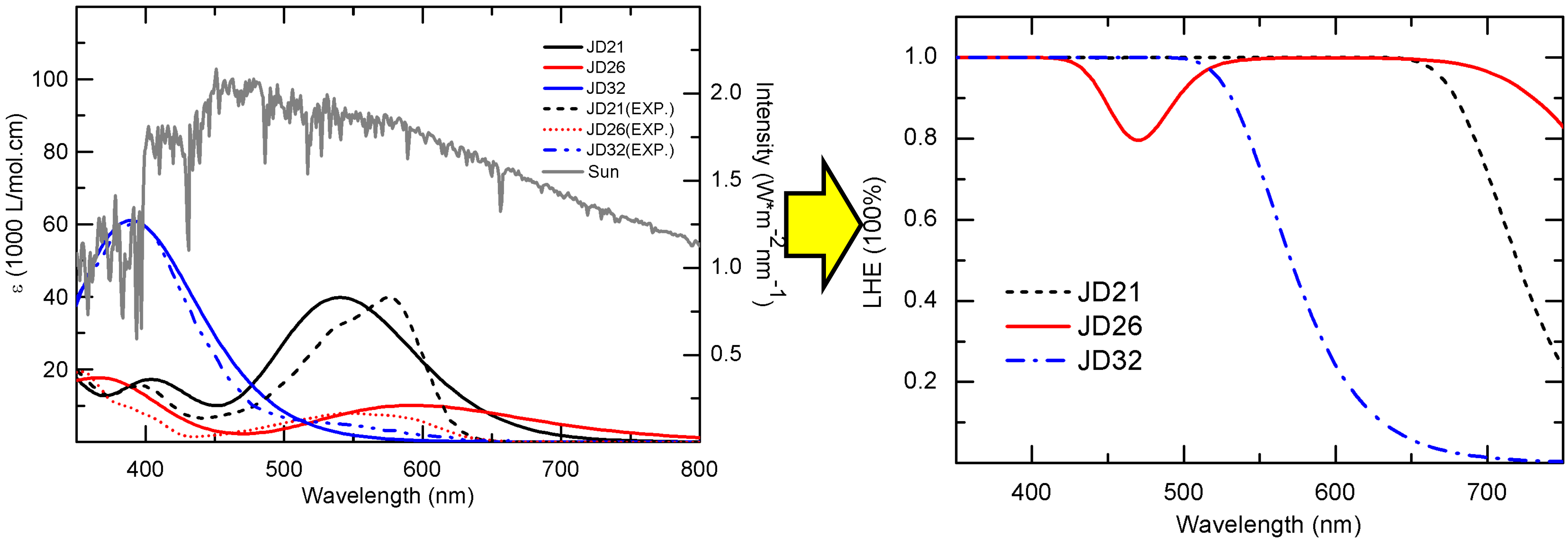
Gali, Kaxiras, Zimanyi, Meng, PRB 84, 035325 (2011).

Model dyes



Evaluation of Light Harvest Efficiency (LHE)

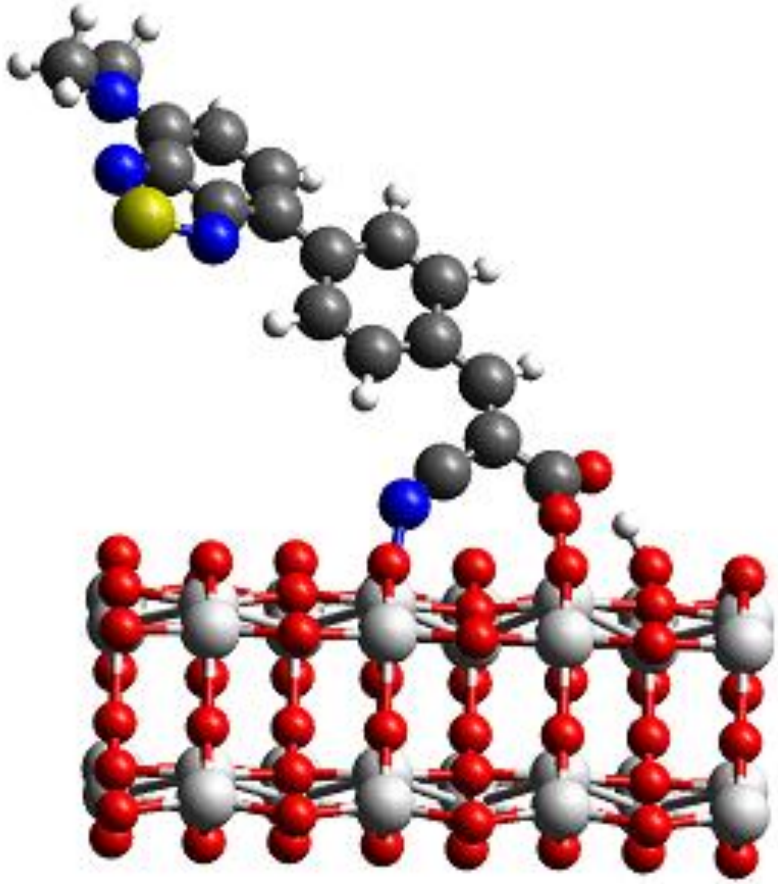
- $\mathrm{LHE}(\lambda) = \int \varepsilon\rho \exp(-\varepsilon\rho x)\, \mathrm{d}x$



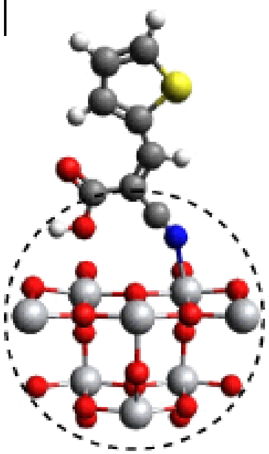
TiO_2 film thickness: d = 3 μm
dye loading: 300 mmol/L

(2) Electron Injection Efficiency

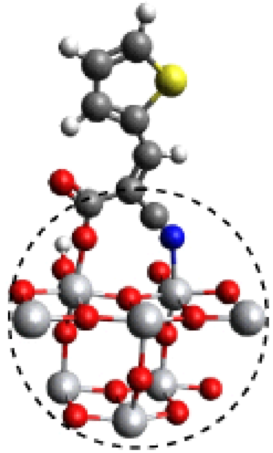
$$\Phi_{\text{inject}} = 1 \Big/ \left(1 + \frac{\tau_{\text{inj}}}{\tau_{\text{relax}}}\right)$$



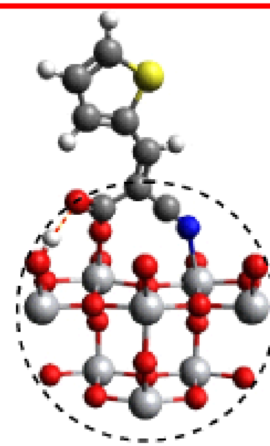
Binding geometry precisely determined



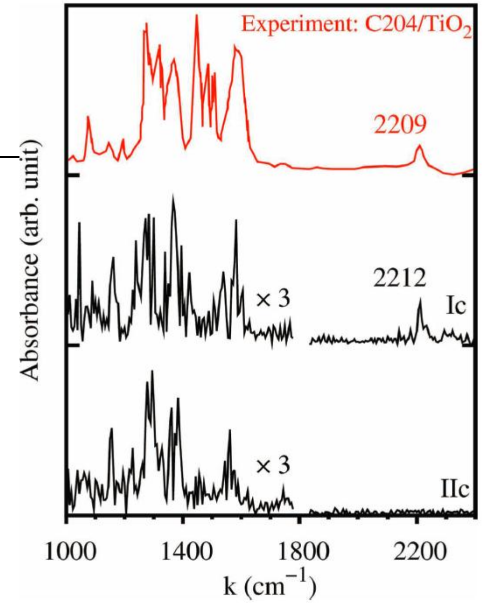
Ia: 0.731 eV

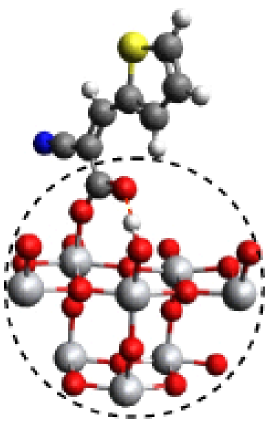


Ib: 1.121

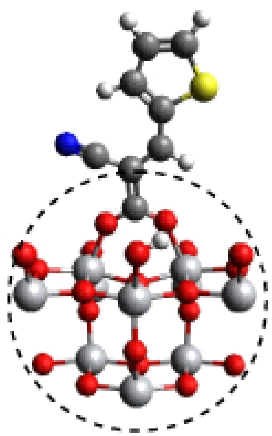


Ic: 1.426

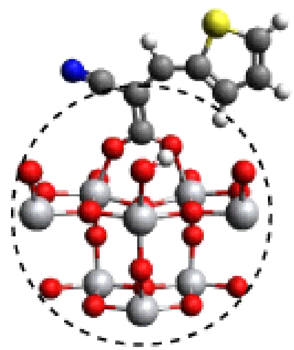




IIa: 0.932



IIb: 1.233



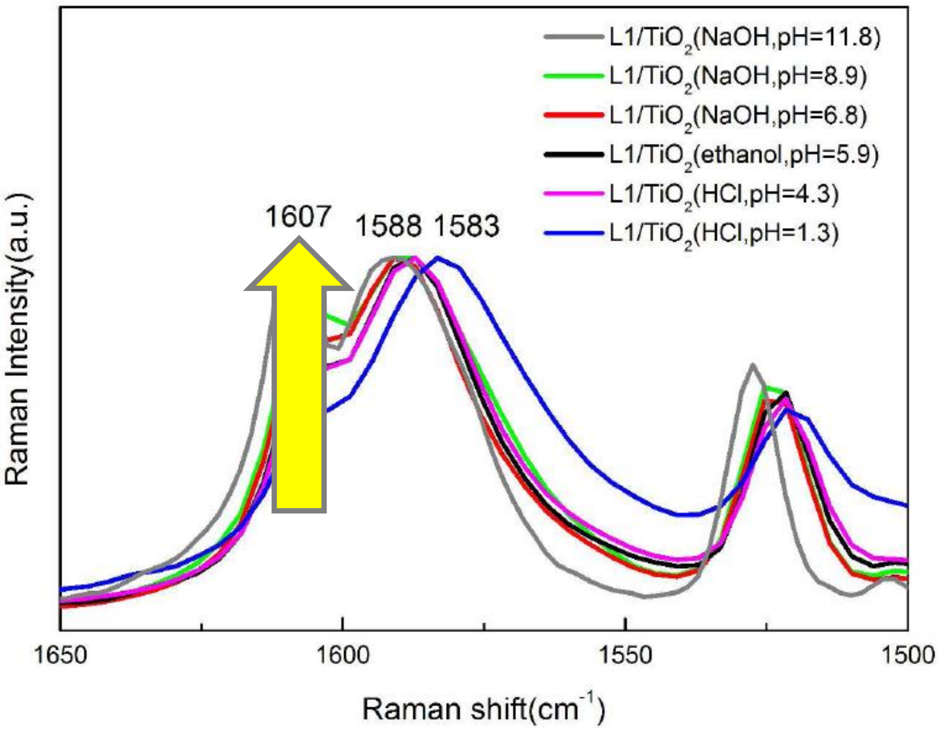
IIc: 1.010

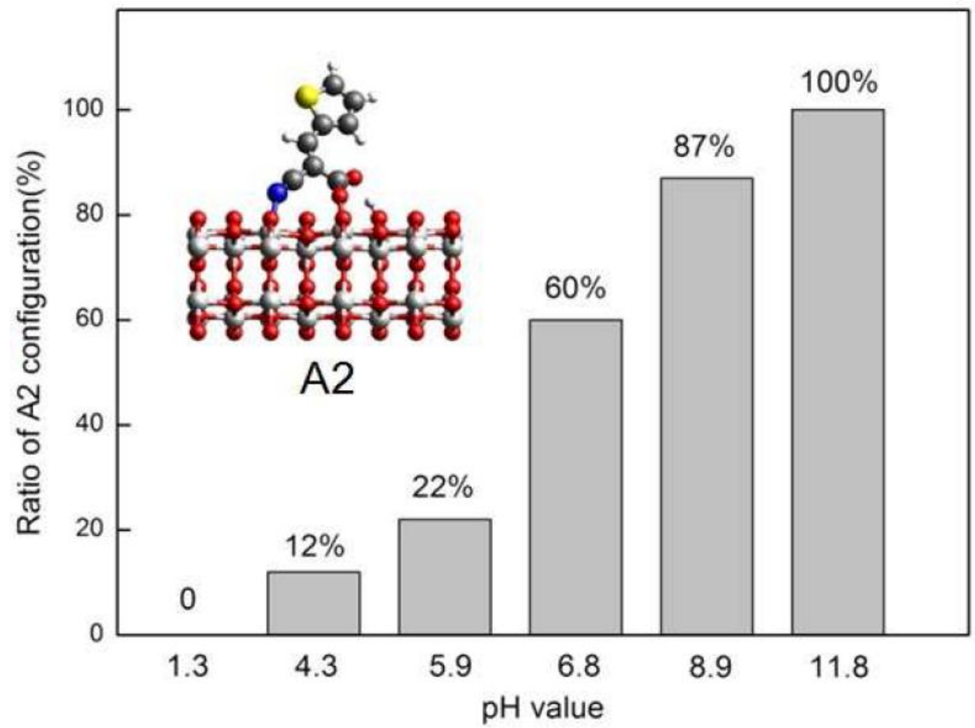
Ti-N: ~0.7 eV

Ti-O: ~0.5-0.6 eV

H-bond: ~0.3 eV

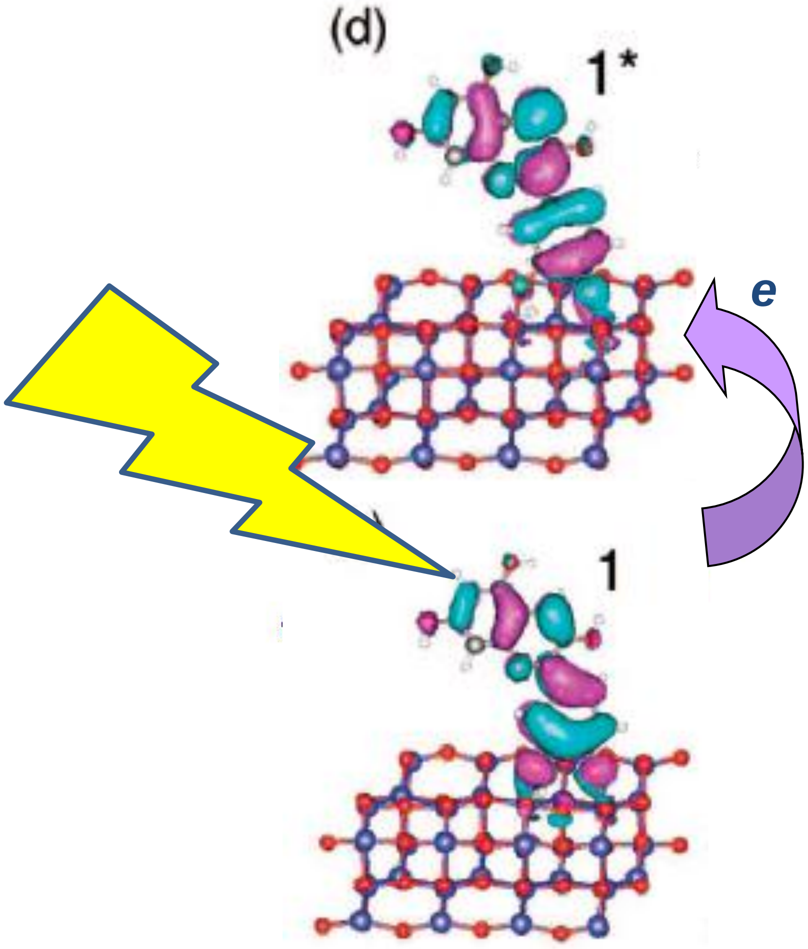
Quantitative proportion of a configuration



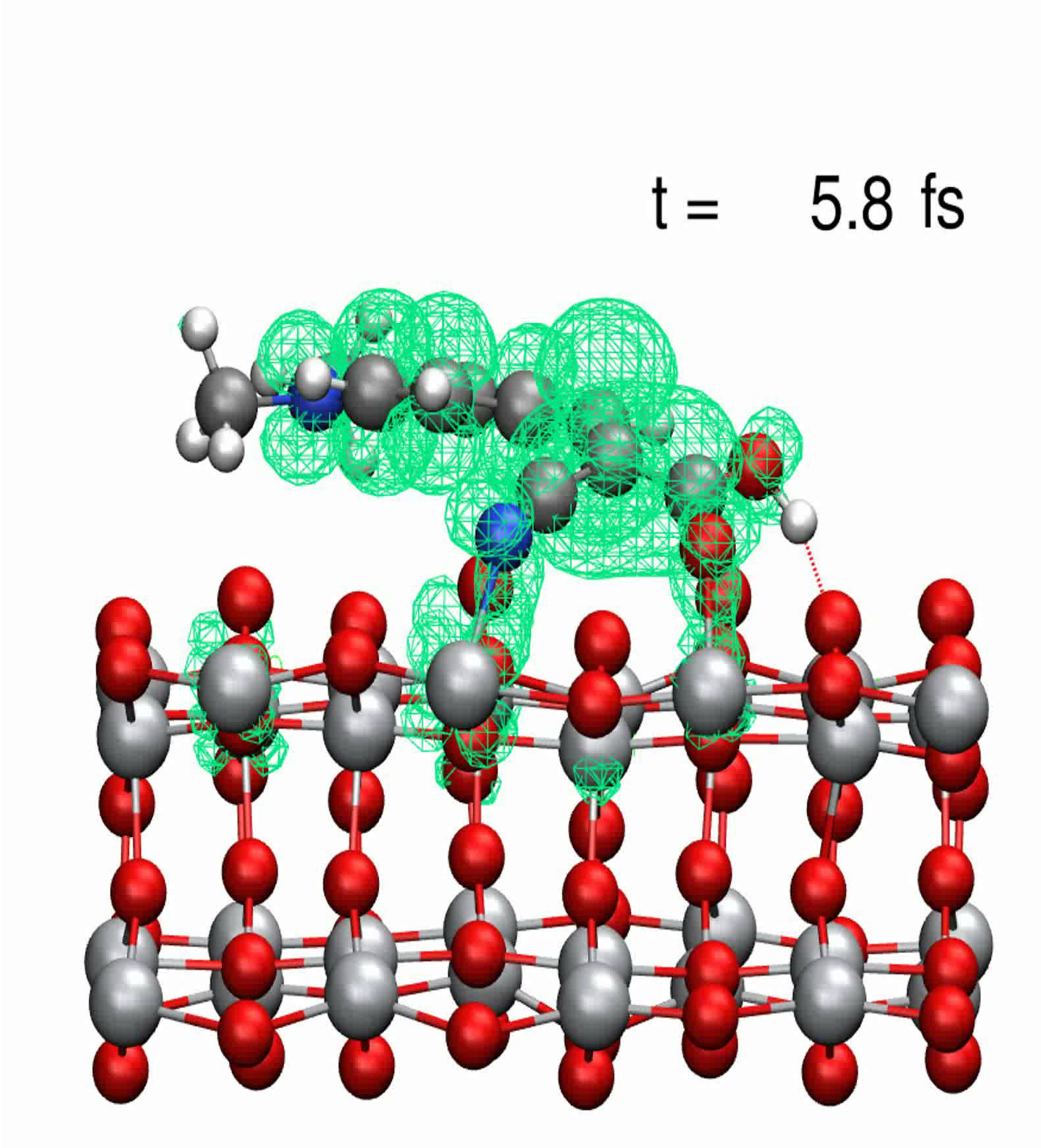


Zhang, Ma, Jiao, Wang, Shan, Li, Lu, Meng, ACS Appl. Mater. Interface (2014).

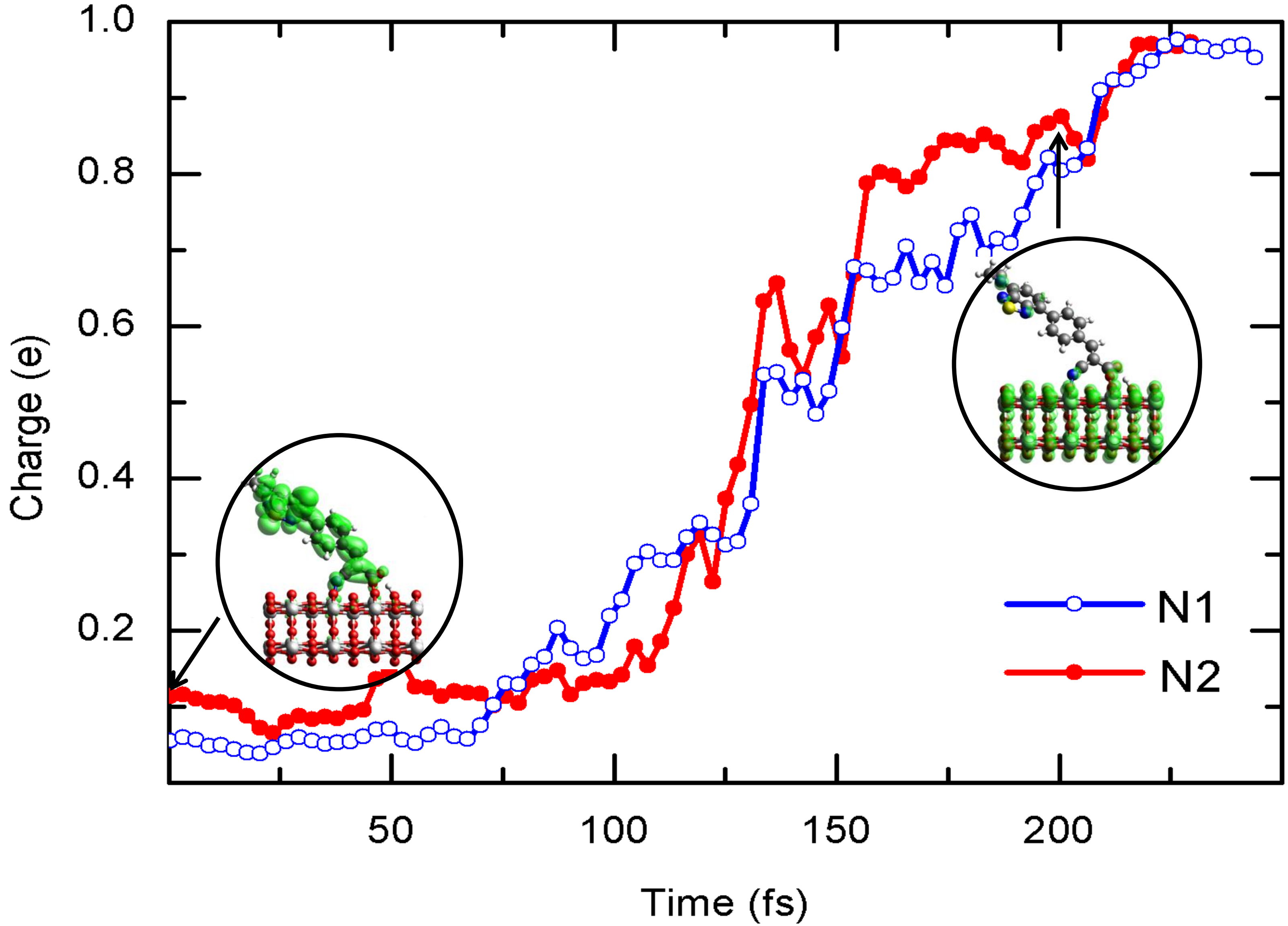
Electron Injection Dynamics



Electron Injection Dynamics

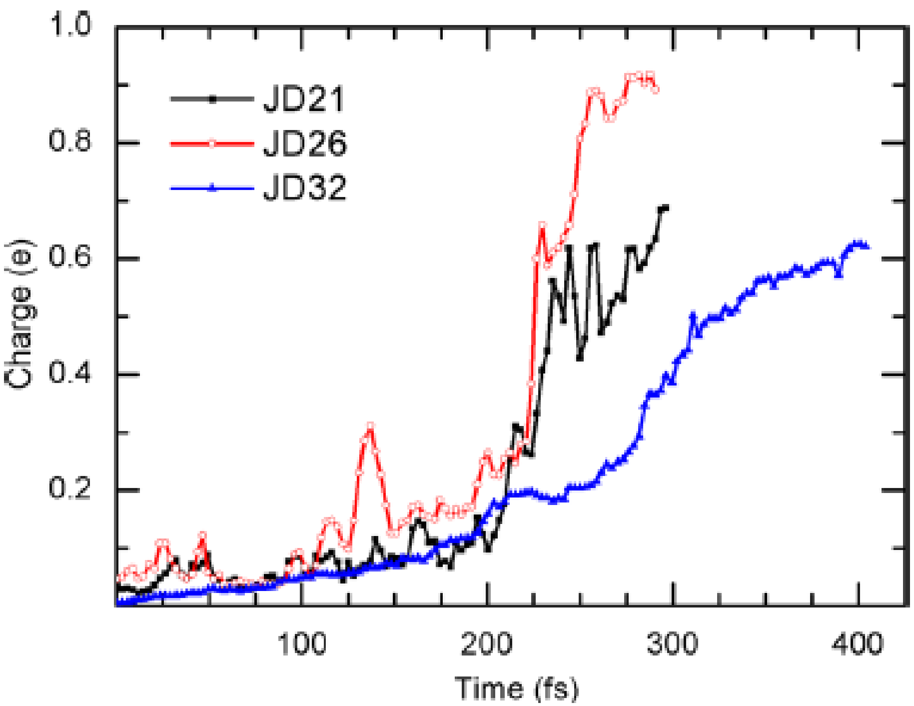


Electron injection dynamics



Electron Injection Efficiency

$$\Phi_{inject} = 1 \Big/ \left(1 + \frac{\tau_{inj}}{\tau_{relax}}\right) \quad , \quad \tau_{relax} = 10 \text{ ps (expt.)}$$



	JD21	JD26	JD32
τ_{inj} (fs)	290	240	400
Φ_{inj}	97.2%	97.7%	96.2%

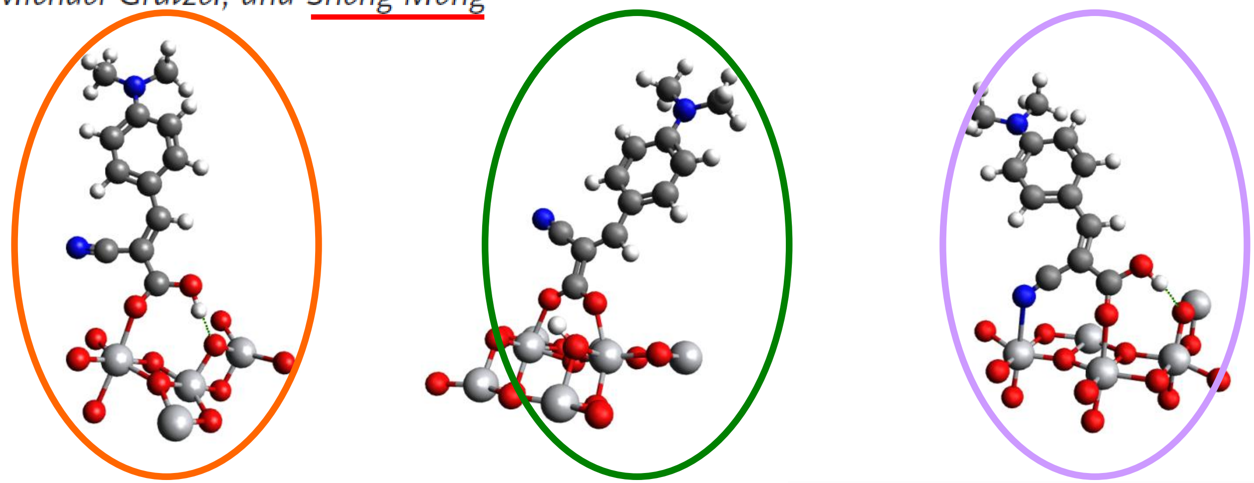
Jiao, Zhang, Gratzel, Meng, Adv. Funct. Mater. (2013).

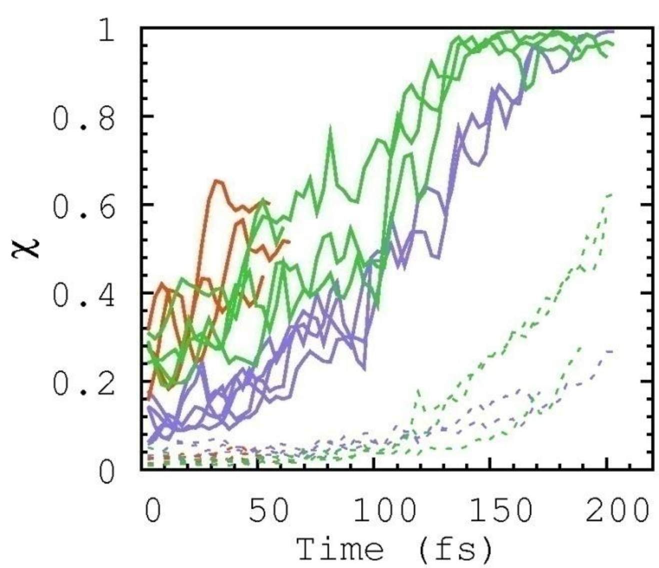
Ma, Jiao & Meng, J. Phys. Chem. C (2014).

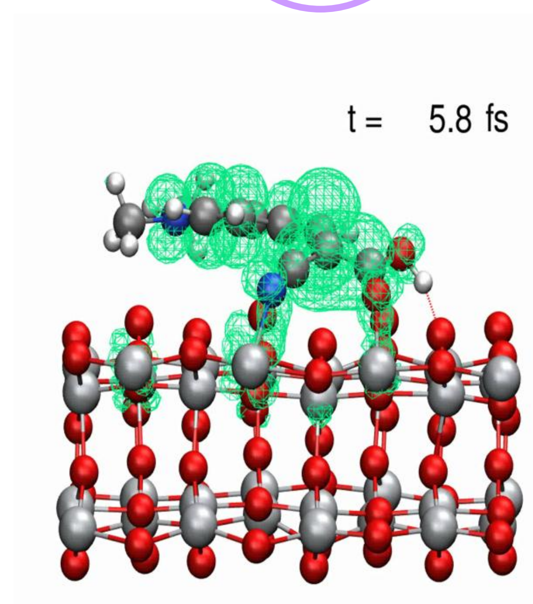
Materials Views
www.MaterialsViews.com
ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de

Structure–Property Relations in All-Organic Dye-Sensitized Solar Cells

*Yang Jiao, Fan Zhang, Michael Grätzel, and Sheng Meng**

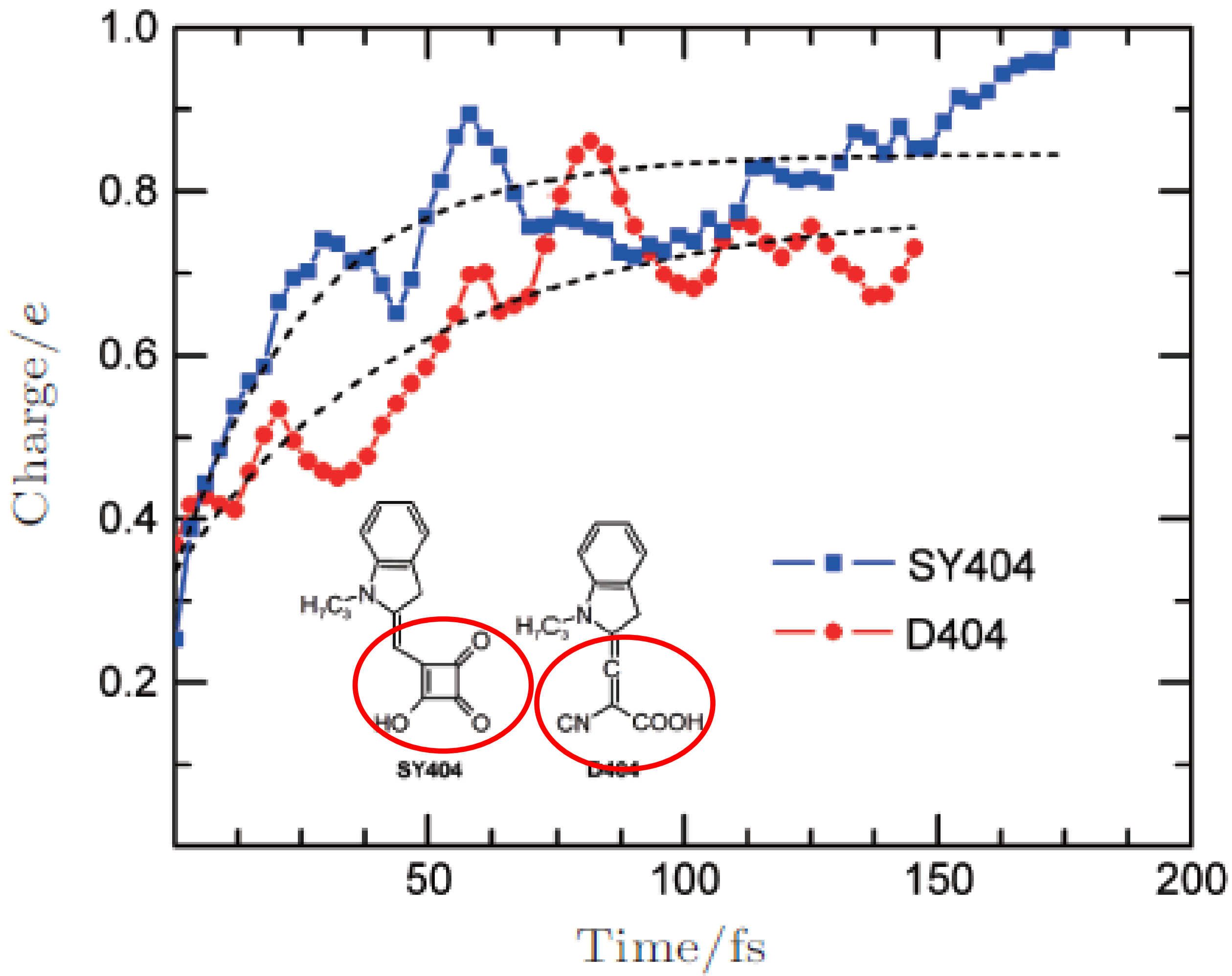






χ : injected electron

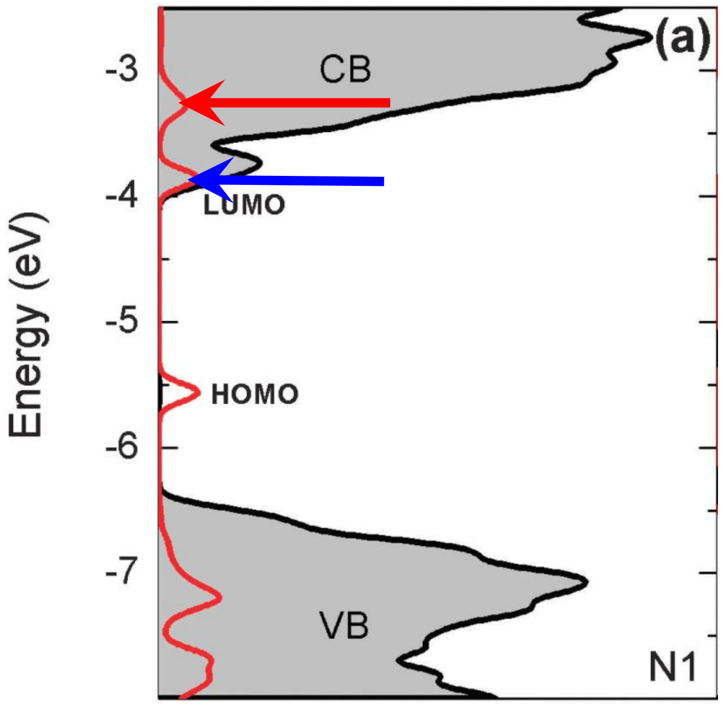
Different anchors

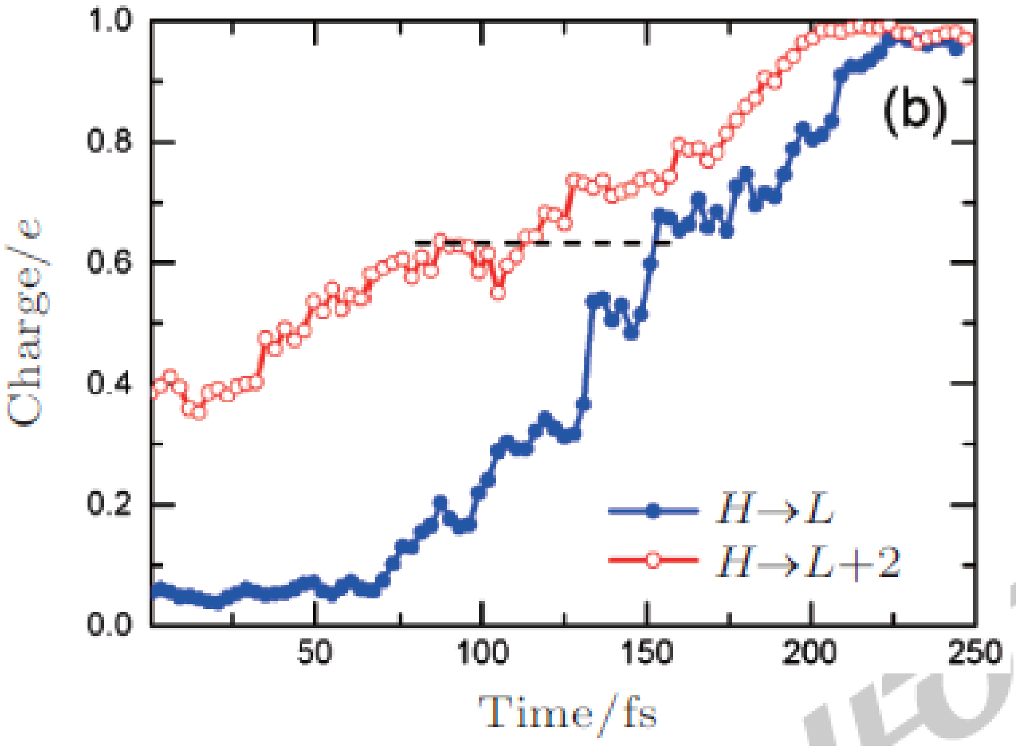


	SY404	D404
Theory	**33 fs**	**60 fs**
Expt. [a)]	**50±13 fs**	

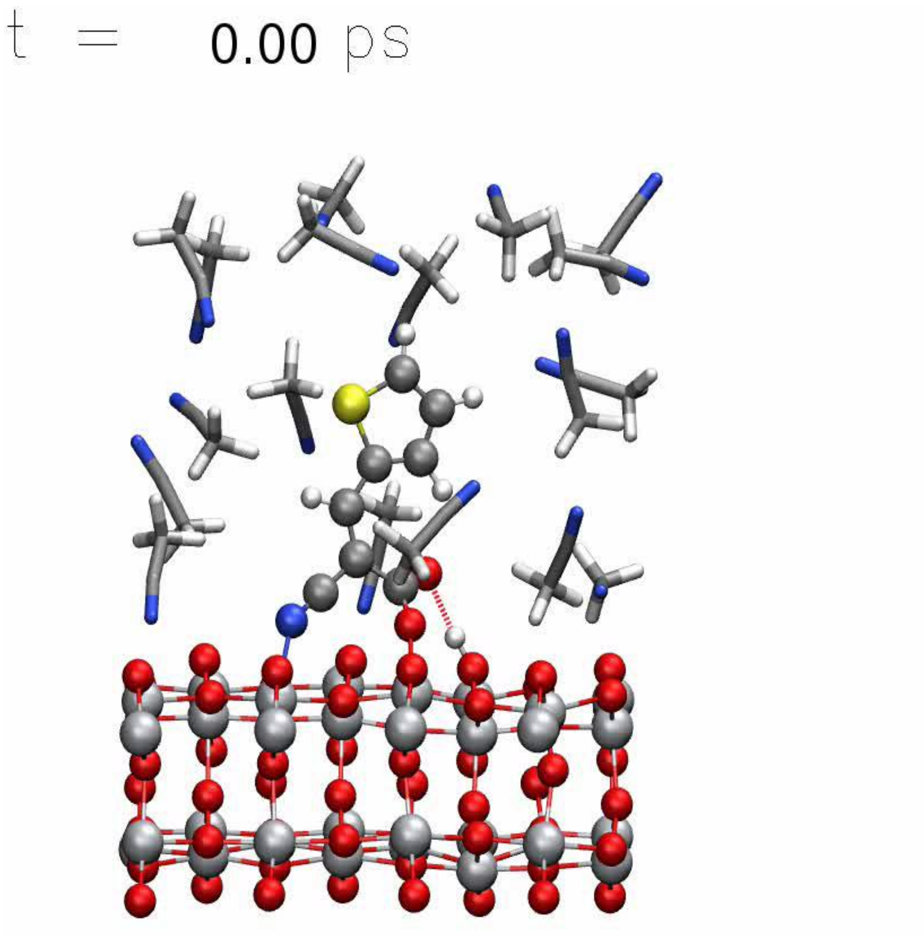
a) Bartelt et al. JPCC (2014).

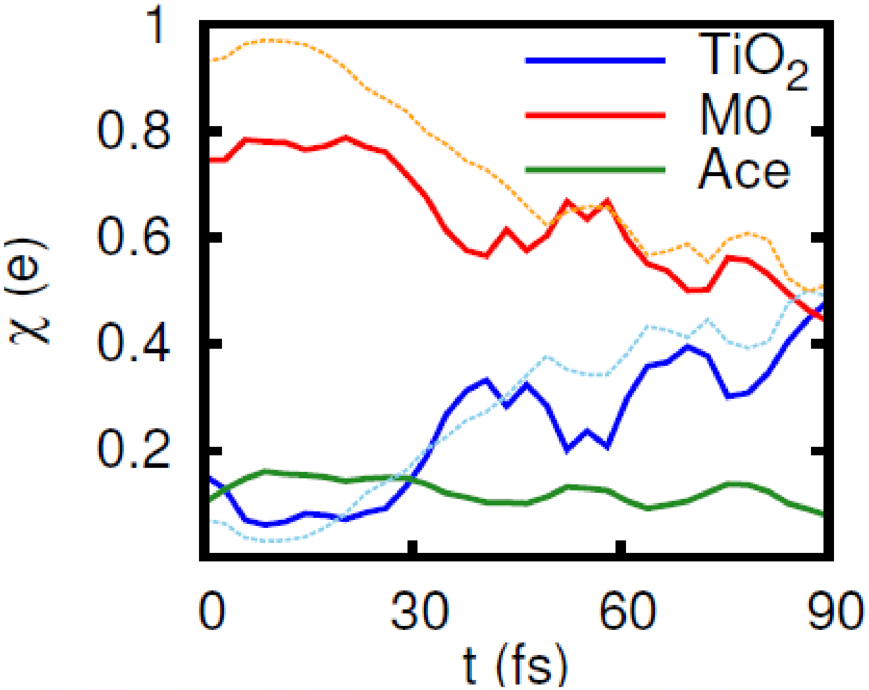
Hot electron effect

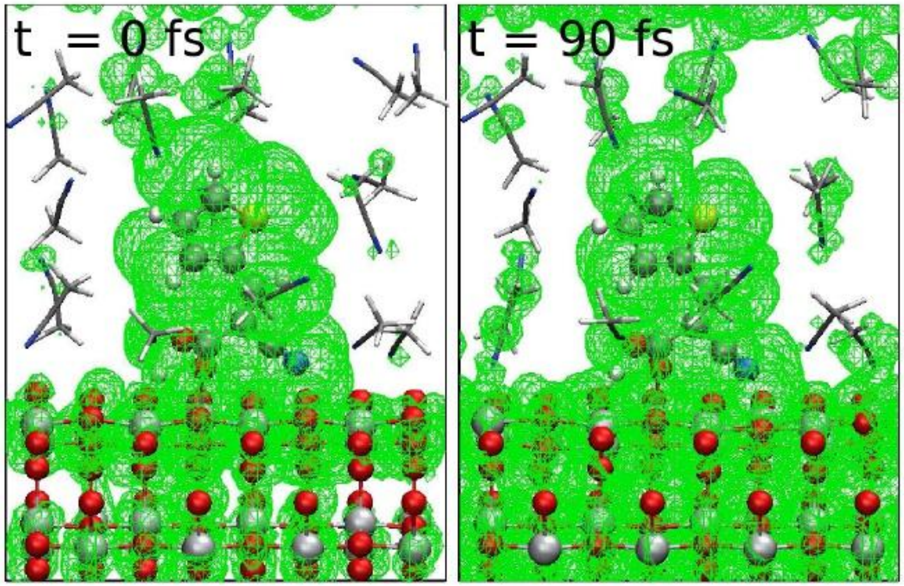




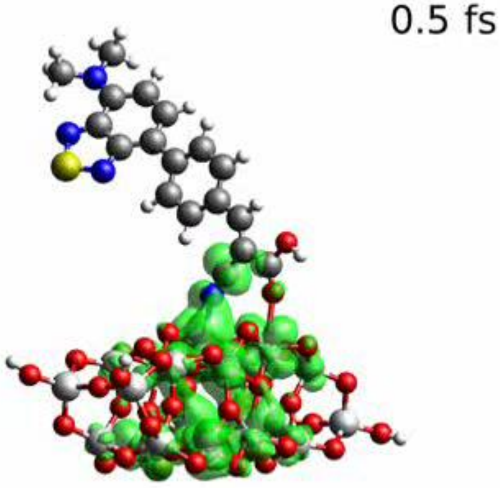
Solvent effect

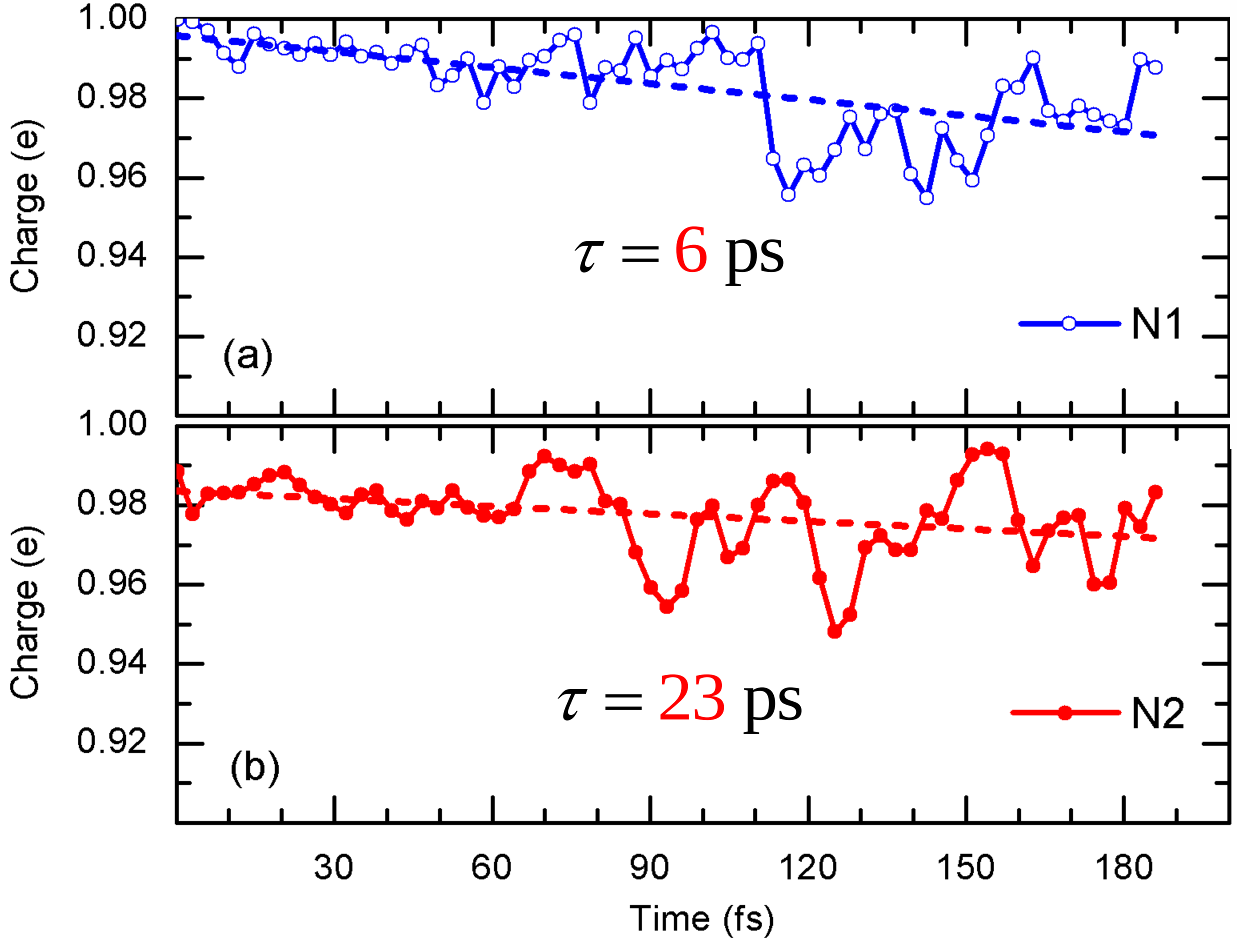






(3) Electron-hole recombination (back-transfer)

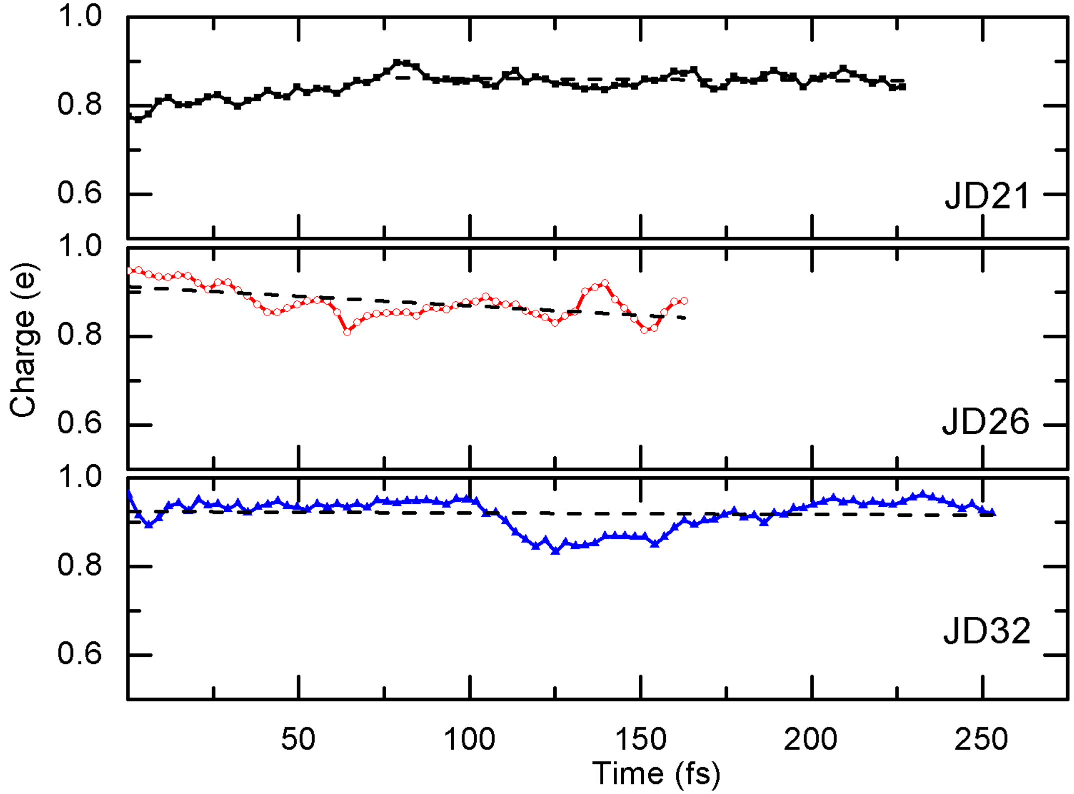


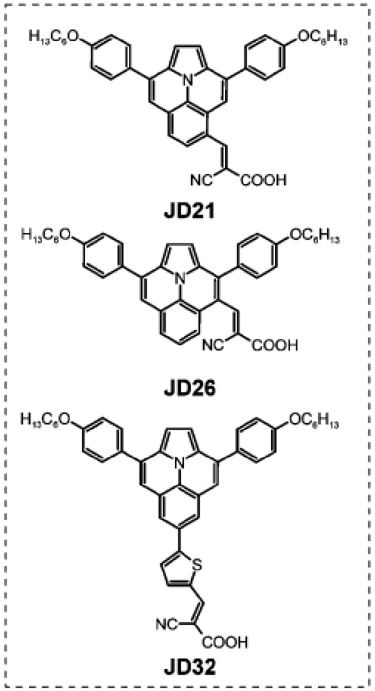


Experiment: 5 times difference using ultrafast laser photolysis.

Ma, Jiao, <u>Meng</u>, PCCP (2013).

Electron Collection Efficiency





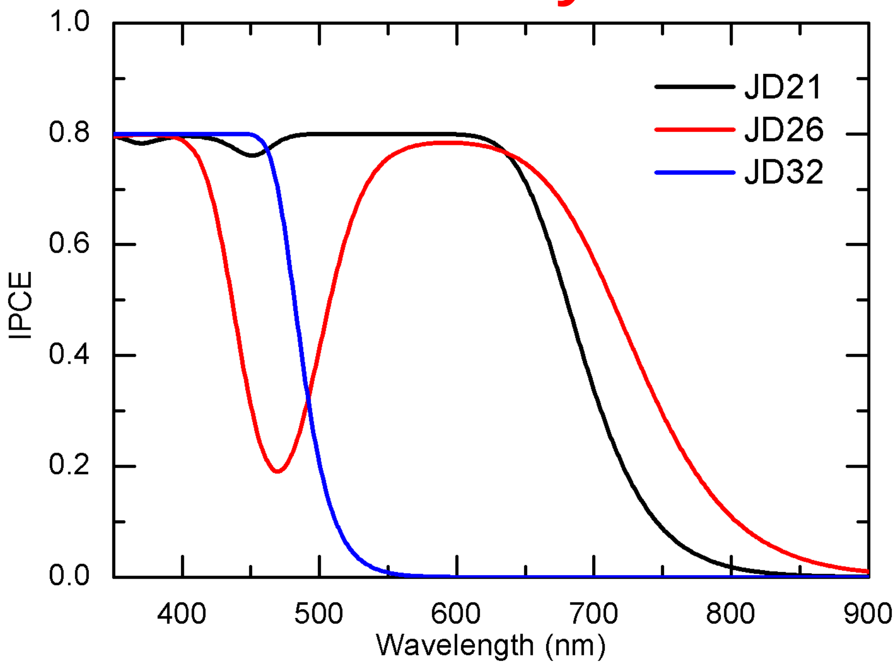
$$\eta_{\text{collect}} = 1 \Big/ \left(1 + \frac{\tau_{\text{trans}}}{\tau_{\text{rec}}}\right)$$

$\tau_{\text{trans}} = 5$ ps (exp.)

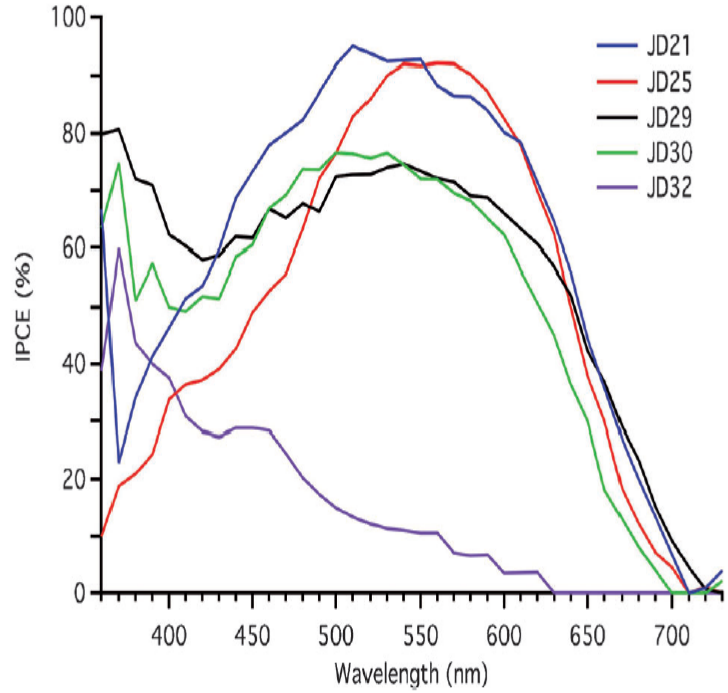
	JD21	JD26	JD32
τ_{rec} (ps)	21.25	2.12	28.11
η_{collect}	81.0%	29.8%	84.9%

$$\mathrm{IPCE}(\lambda) = \mathrm{LHE}(\lambda)\Phi_{\mathrm{inj}}\eta_{\mathrm{coll}}$$

Theory



Experiment



$$J_{\mathrm{SC}} = \int J(\lambda)\mathrm{d}\lambda = \int \frac{\mathrm{SI}}{hc/e\lambda}\mathrm{IPCE}(\lambda)\mathrm{d}\lambda$$

	JD21	JD26	JD32
J_{SC}/ mA.cm^{-2}	15.81	5.66	4.77

Estimating the V_{OC}

$$V_{OC} = \frac{k_B T}{\beta' q} \ln \frac{\beta' q R_0 J_{SC}}{k_B T}$$

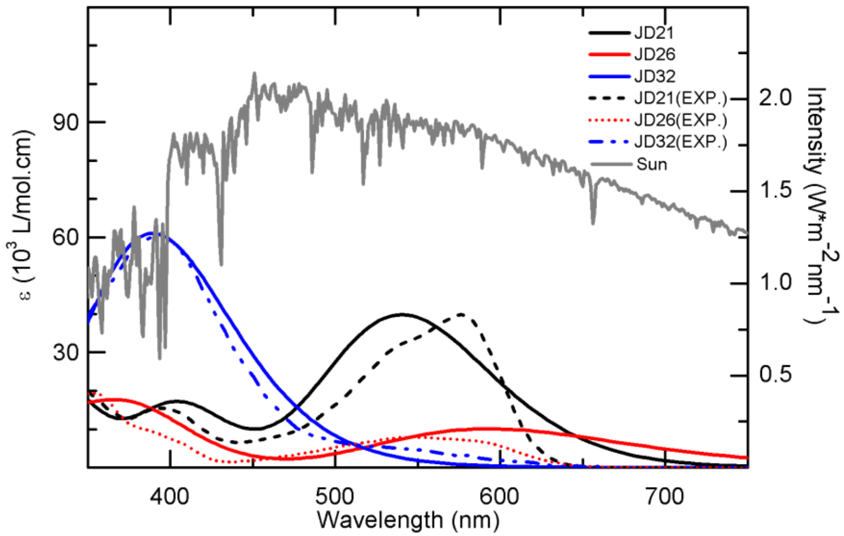
$$R_0 = \frac{\sqrt{\pi \lambda k_B T}}{q^2 d \gamma k_{rec} c_{ox} N_s} \exp\left(\gamma \frac{E_{CBM} - E_{redox}}{k_B T} + \frac{\lambda}{4 k_B T} \right)$$

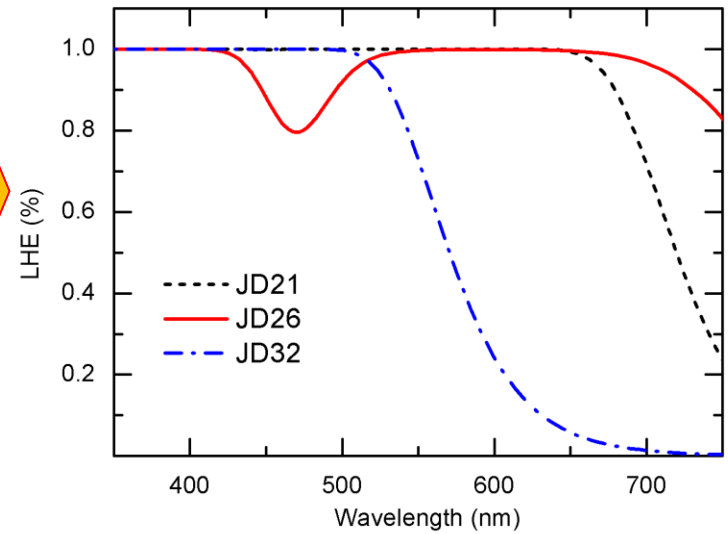
$$k_{rec} = 1/\tau_{rec}$$

Dye	k^{-1}_{inj} (fs)	k^{-1}_{rec} (ps)	J_{sc}/ (mA.cm^{-2})	V_{OC} (mV)	FF	J_{sc}(exp.) (mA.cm^{2})	V_{OC}(exp.) (mV)	FF(exp.)	η	η(exp.)
JD21	290	21.25	15.81	732	0.85	15.4	730	0.75	9.84%	8.4%
JD26	400	2.12	5.66	509	0.81	–	–	–	2.33%	–
JD32	240	28.11	4.77	676	0.84	3.7	553	0.78	2.71%	1.7%

Red: Theory   Blue: Experiment

Solar cell efficiency from first principles

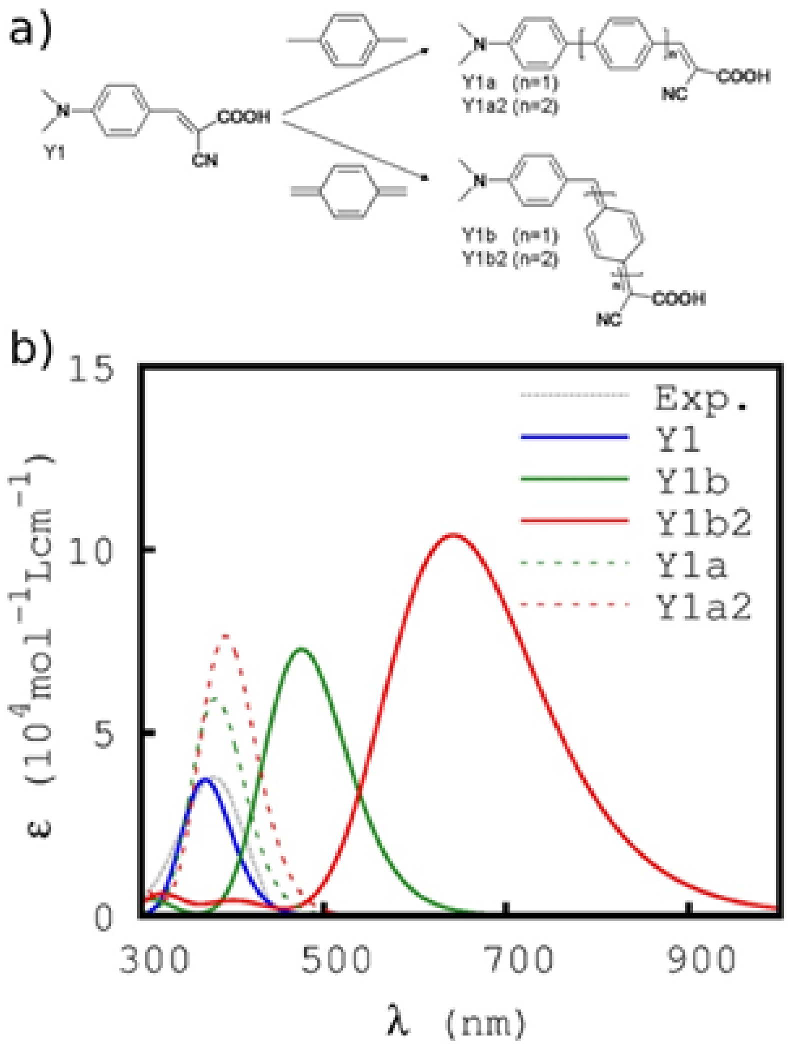


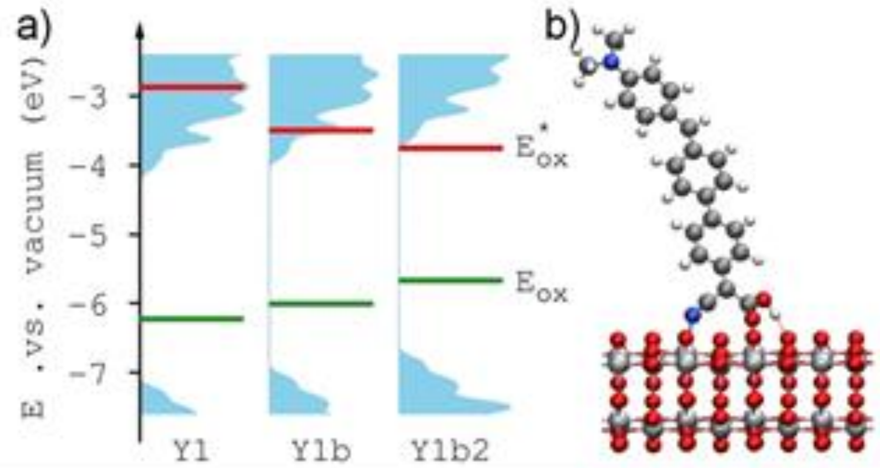


•Quantum mechanics based, parameter free

•Close to experiment values:1-2%

#1 Designing new dyes for enhanced efficiency

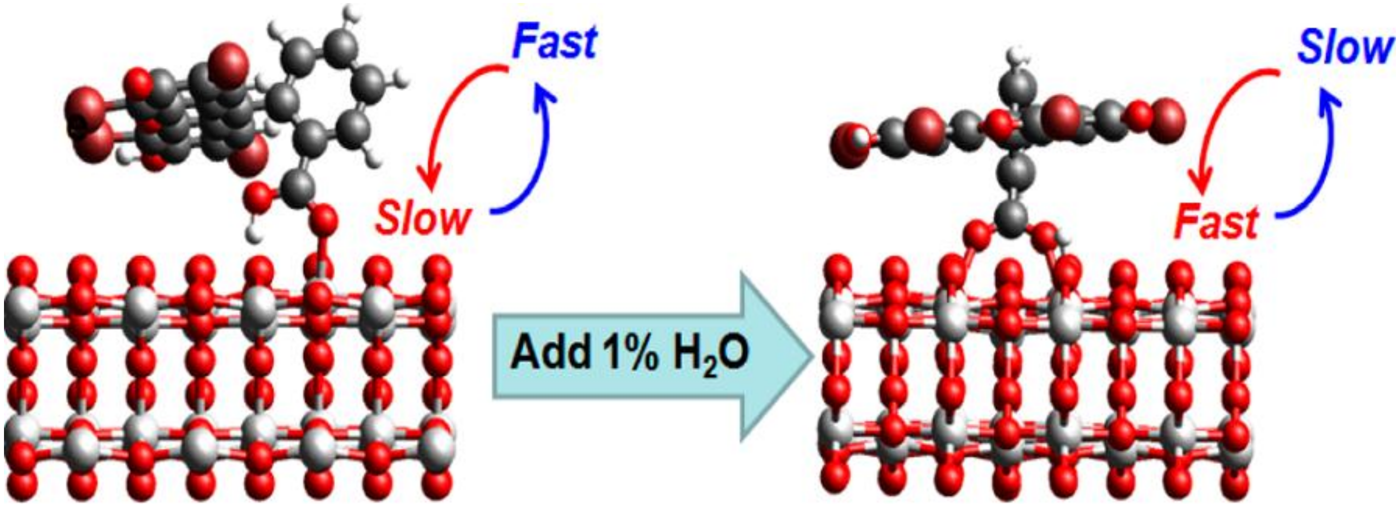


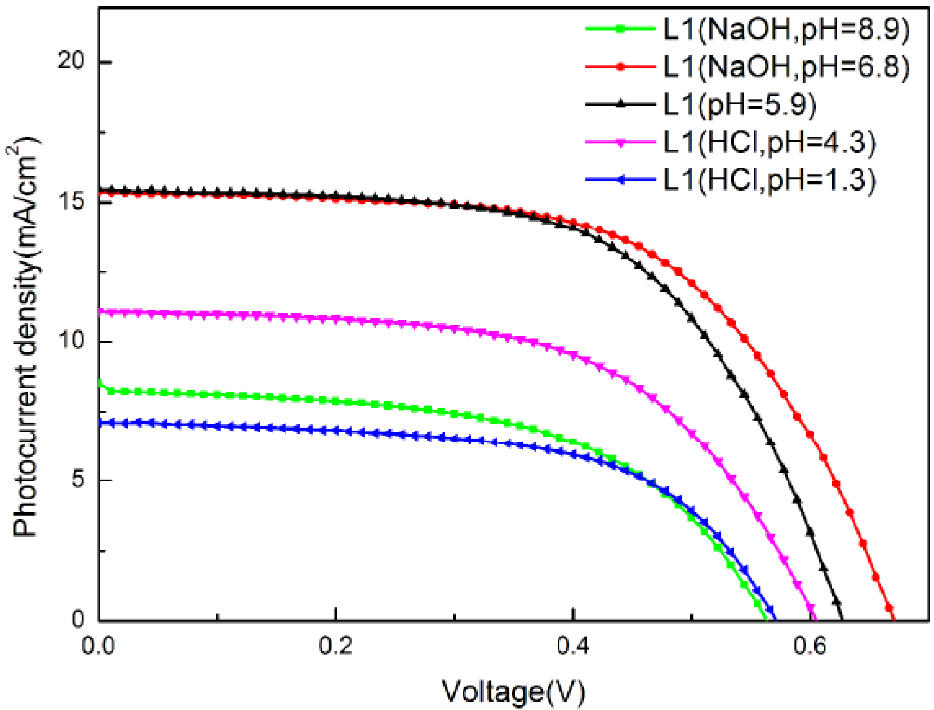


Dye	Y1	Y1b	Y1b2
Theory (%)	3.6	11.6	21.9
Expt. (%)	2.4	?	?

Jiao, Ma, <u>Meng</u> , Chem. Phys. Lett. (2013).

#2Tuning interface geometry: Experimental confirmation

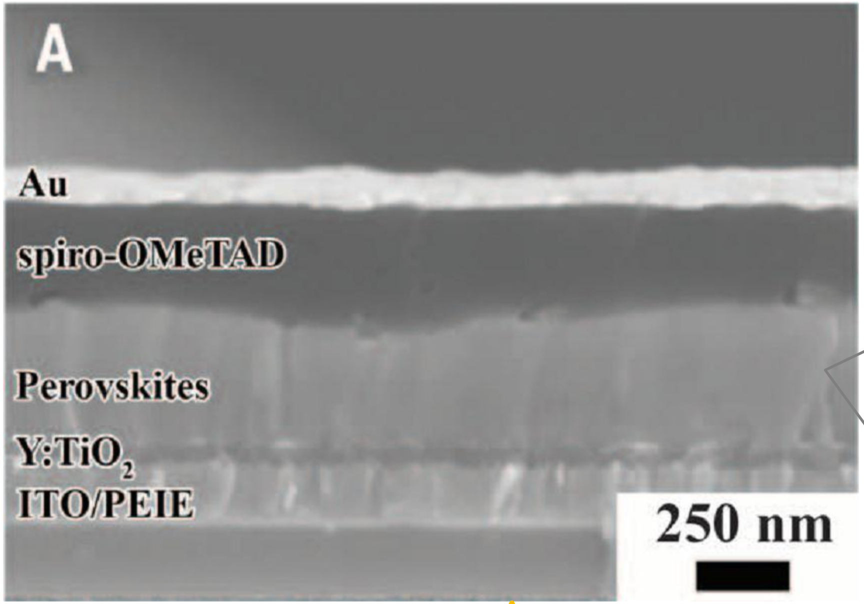


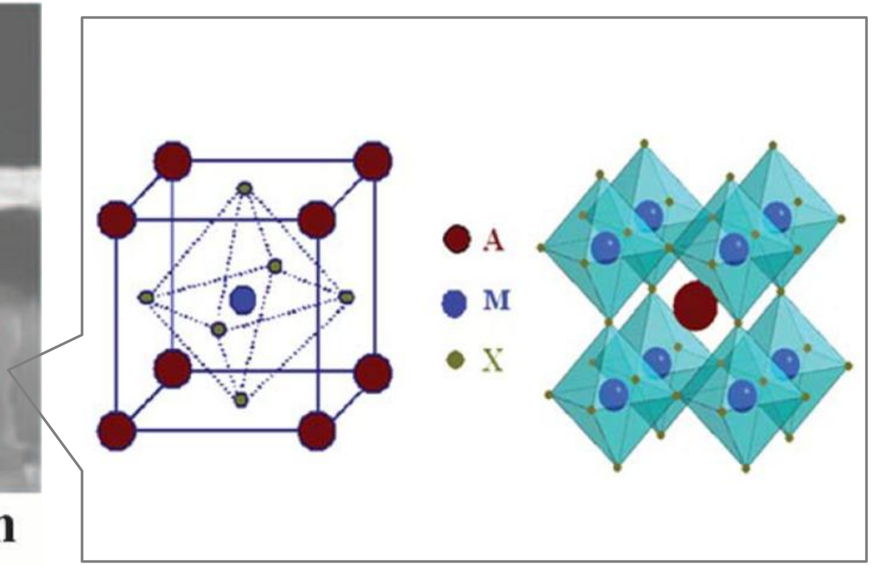


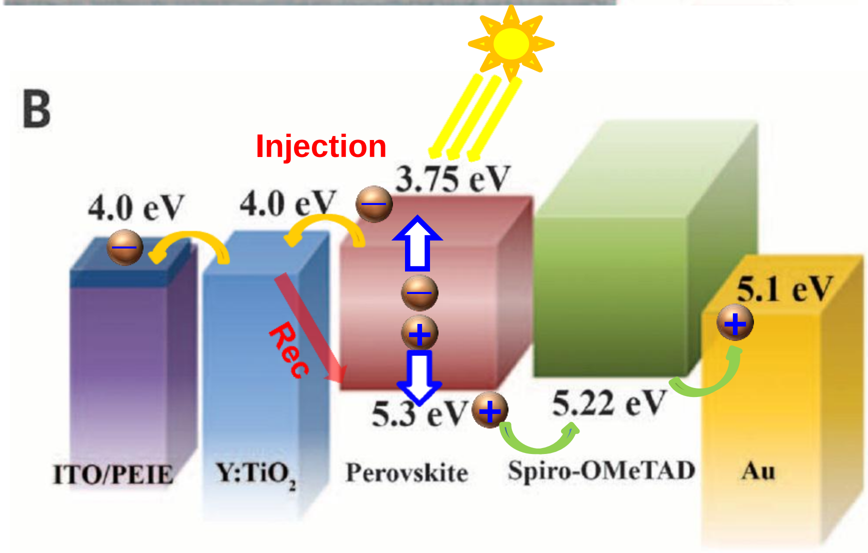
η: **2.4% → 6.1%**

F. Zhang et al., JPCC (2013).
F. Zhang et al., ACS Appl. Mater. Inter (2014).

2. Interface Control for Perovskite Solar Cell







Problems:

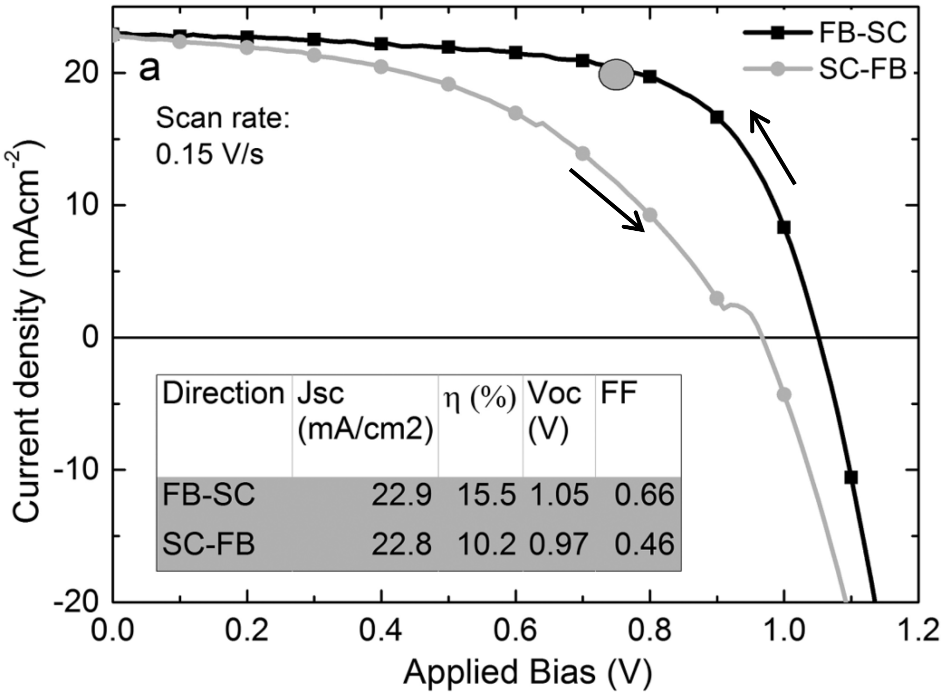
1.Pb

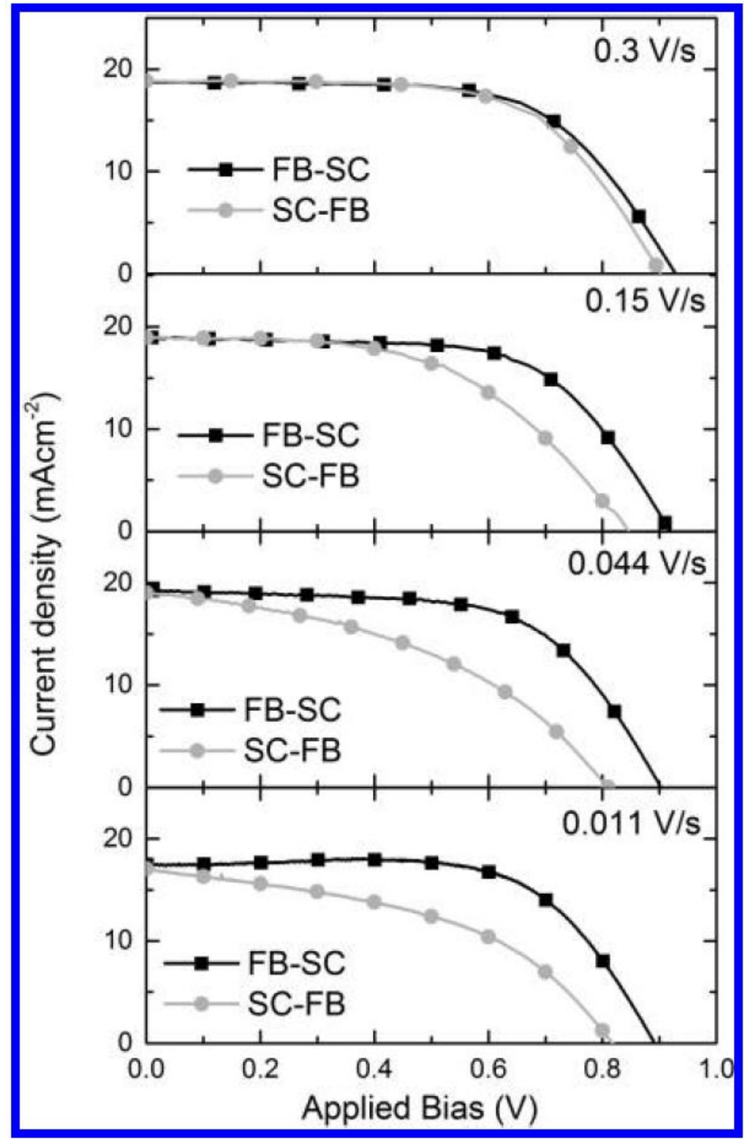
2. Unstability

3. Hysteresis

Perovskite solar cell η **= 20.1%**

Anomalous hysteresis

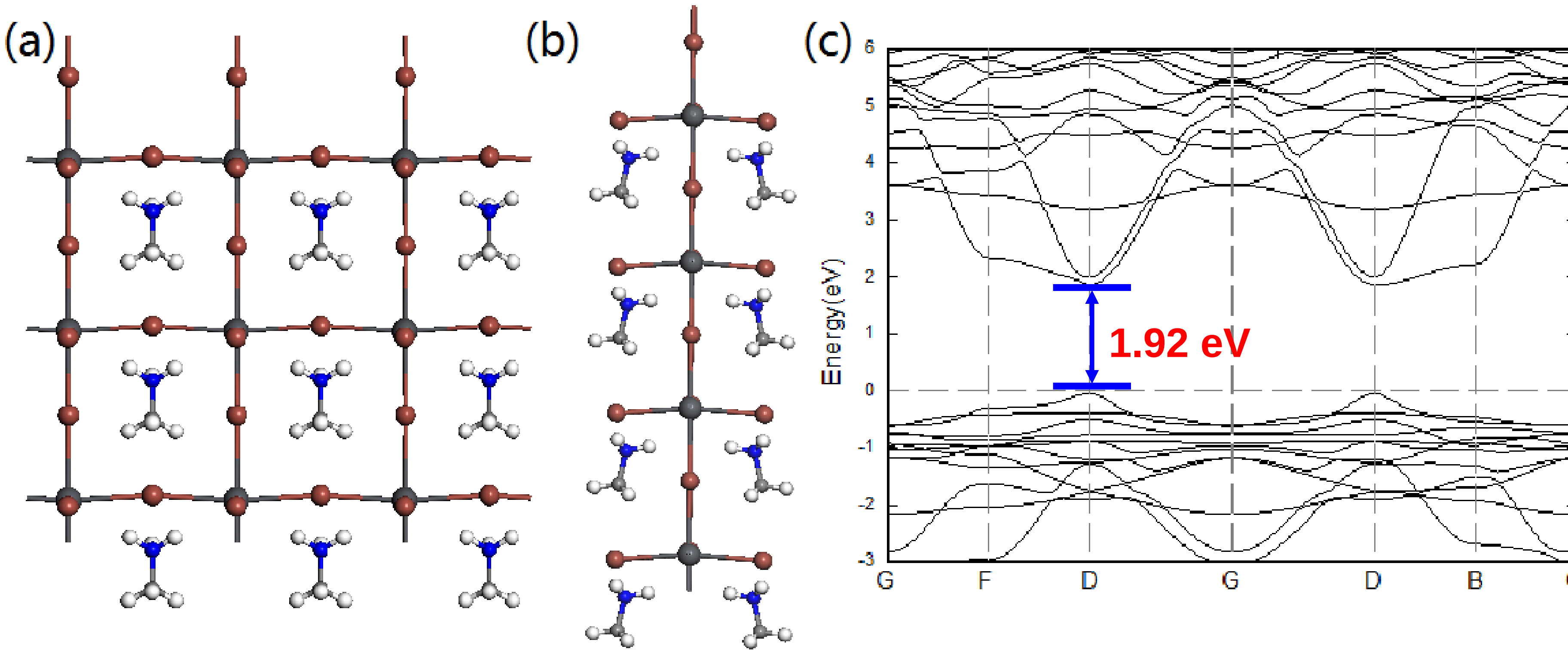




- **Different J-V/efficiency forward vs. backward**
- **More severe for slower scanning**

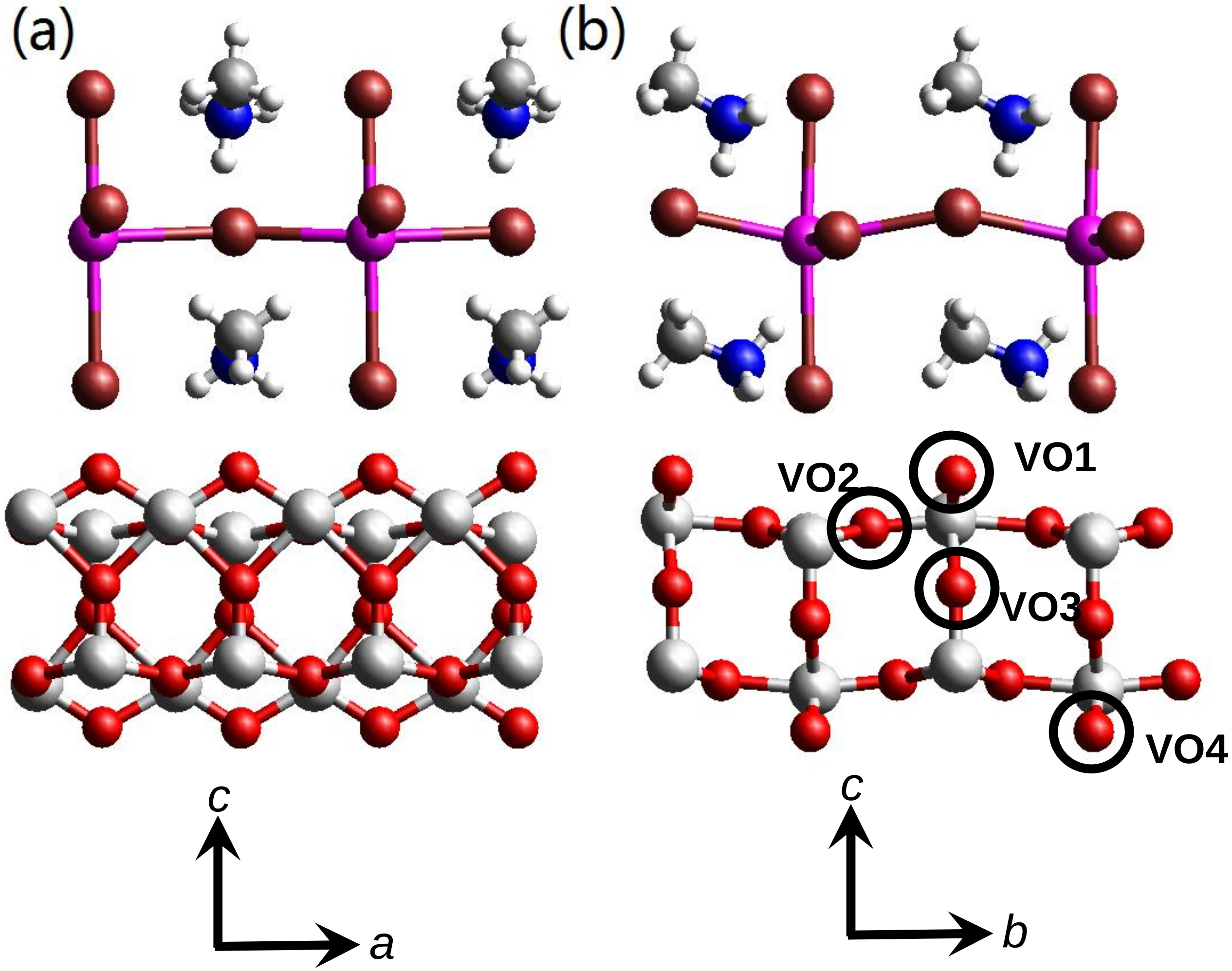
Snaith et al. JPCL (2014).

Band Structure

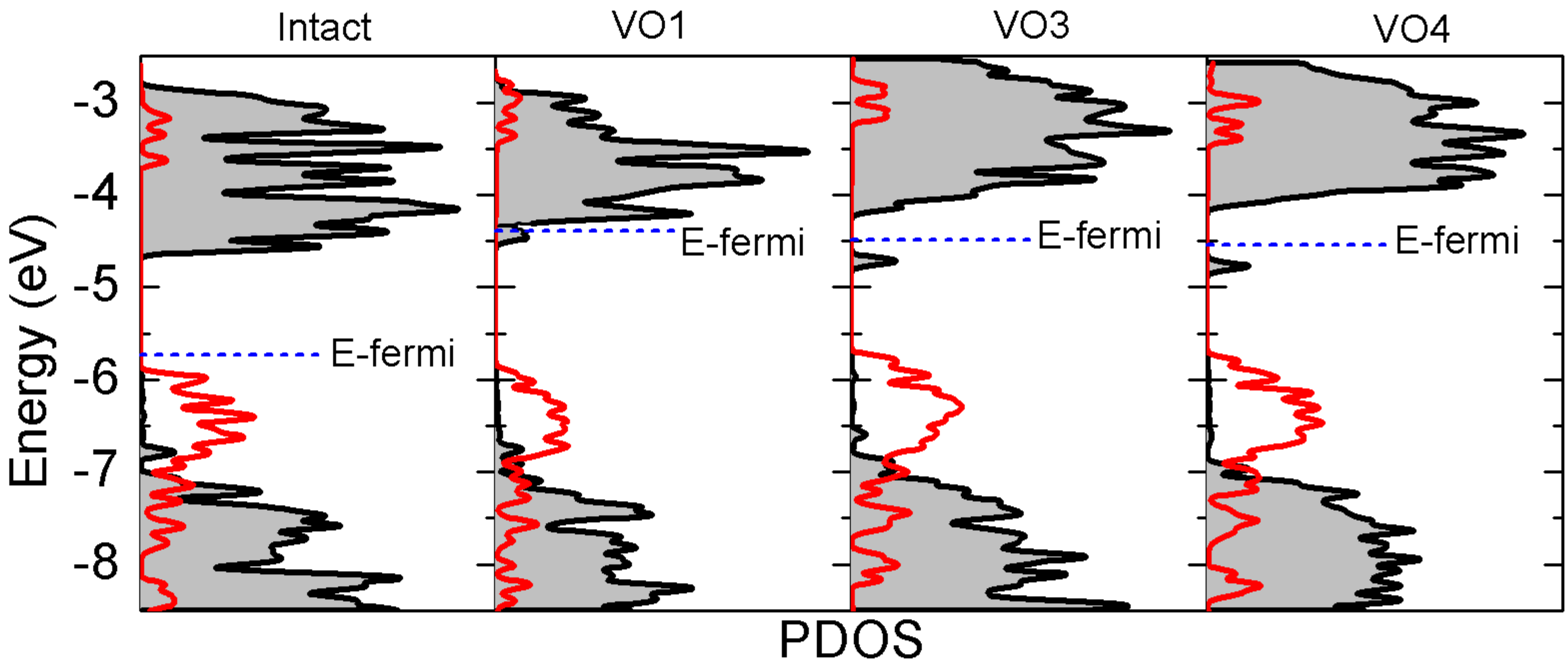


$MAPbI_3$
MA=methyl-ammonium

Perovskite/TiO_2 Interface



Electronic Structure of VO

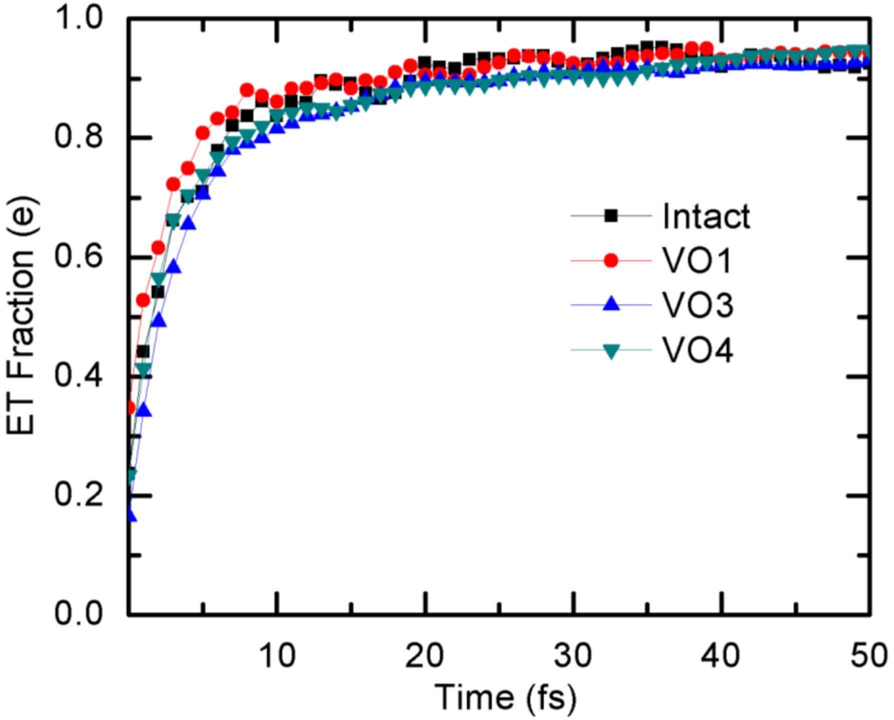


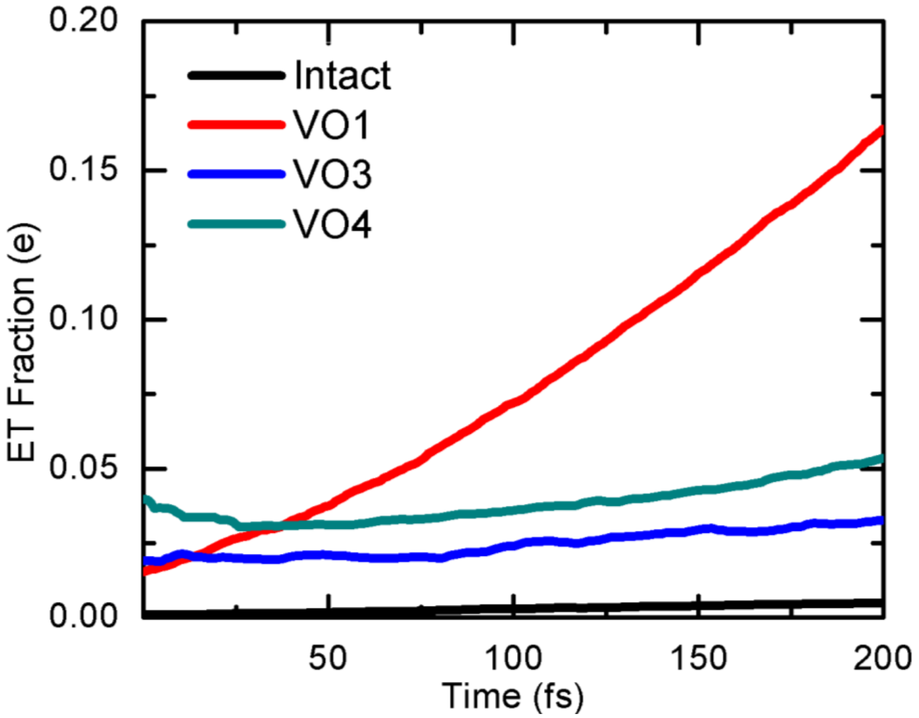
DFT+U (U=4.2 eV)

VO induced **occupied trap state under TiO_2 CB.**

	VO1	VO3	VO4
ΔE/ eV	0.17	0.58	0.69

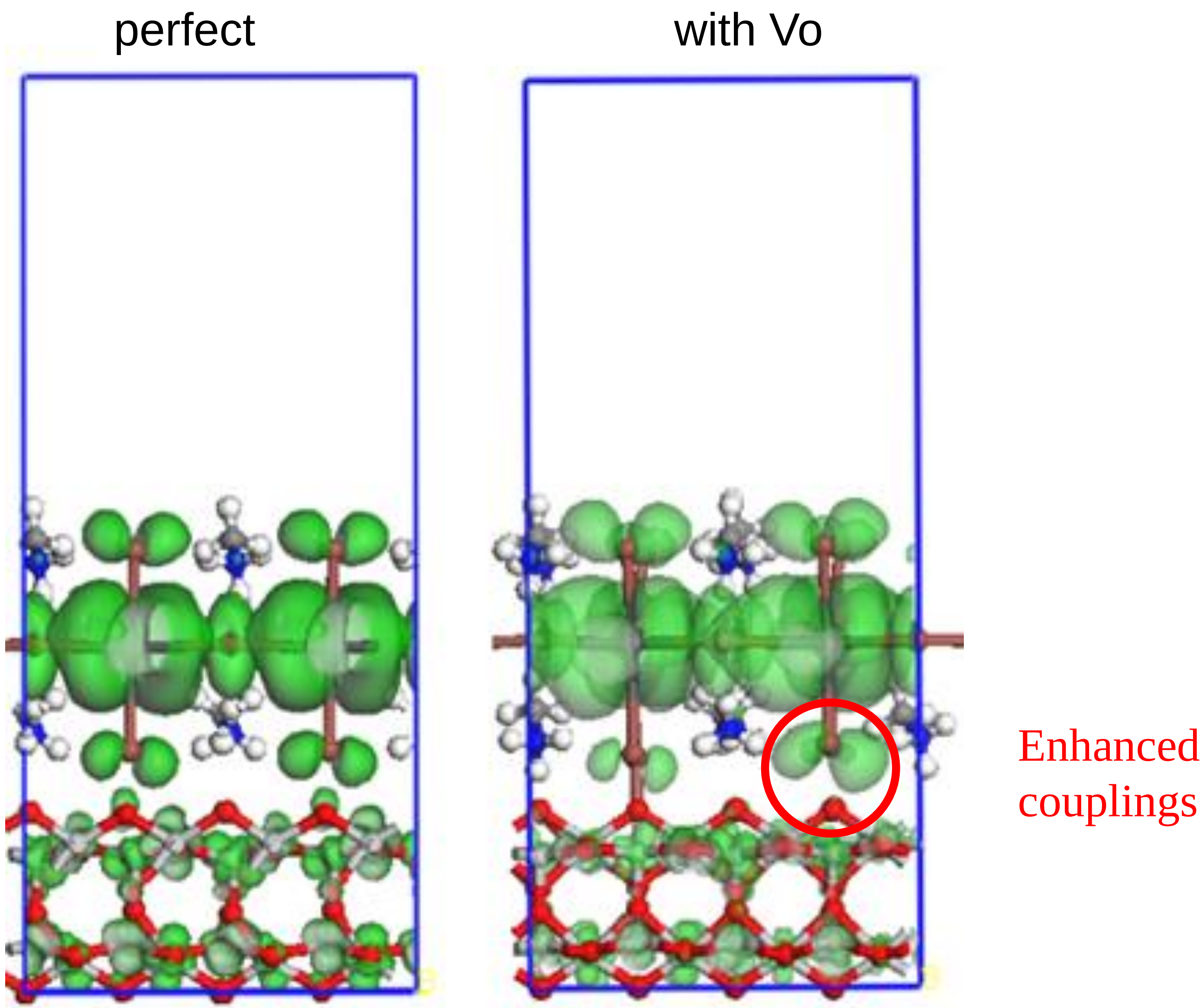
ET Dynamics of VO



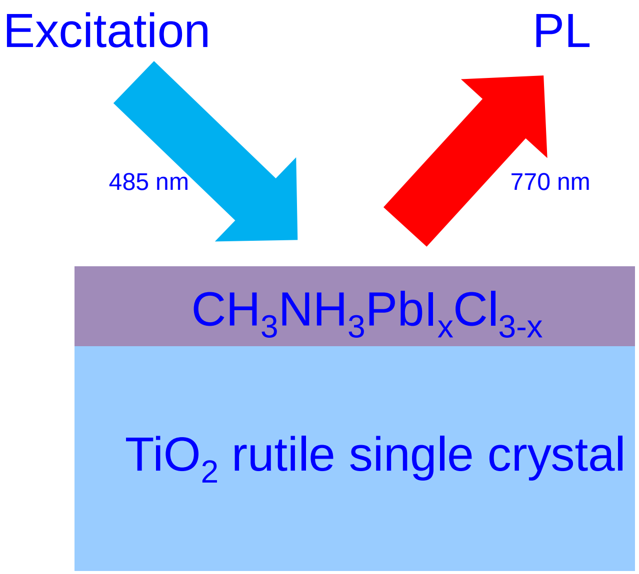


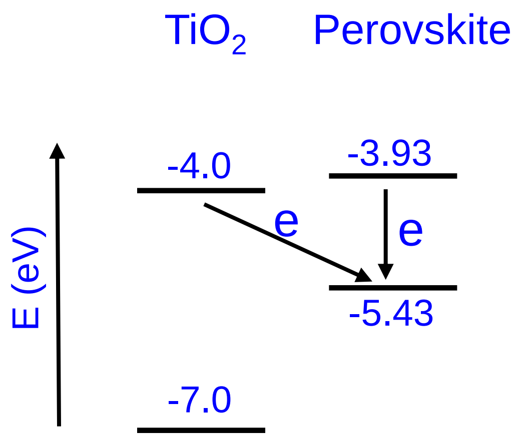
	Intact	VO1	VO3	VO4
τ_{inj}/ fs	**4.68**	**3.97**	5.35	5.71
τ_{rec}/ ps	**46.59**	**1.32**	13.65	9.87

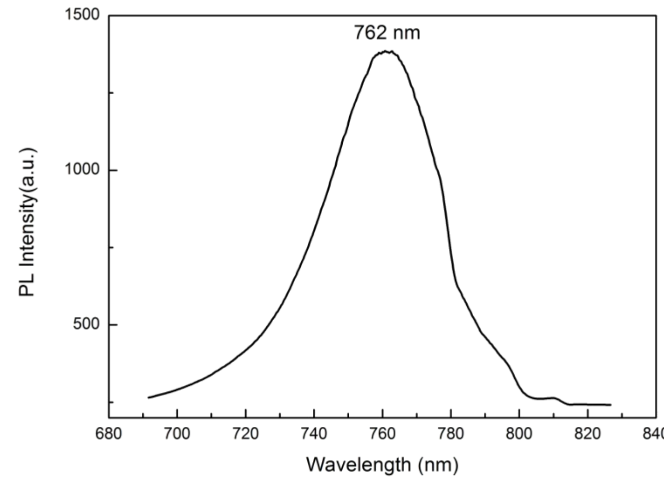
VO induced trap states **rarely influence injection,**
but facilitates recombination dynamics by several times.


perfect
with Vo
Enhanced
couplings

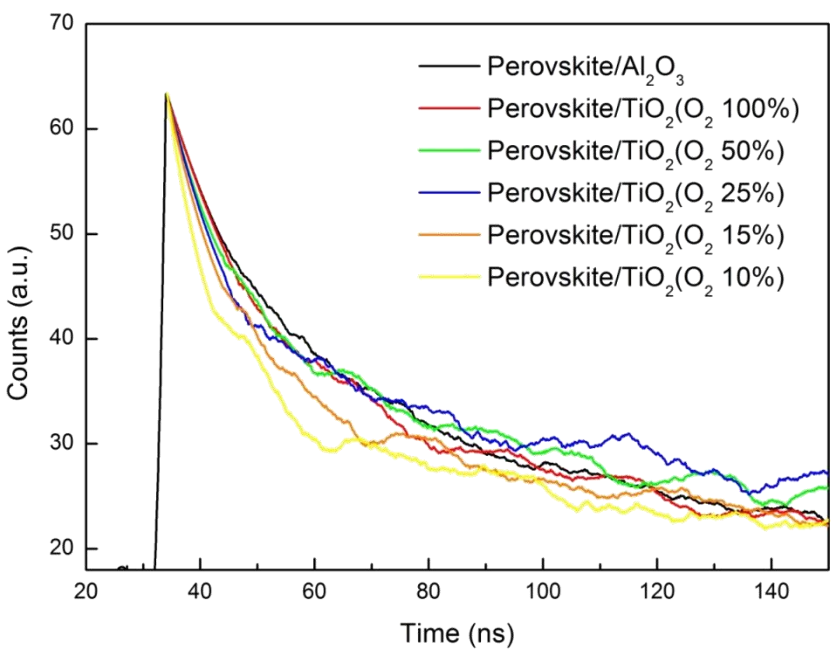
Experiment: Photoluminescence Spectra

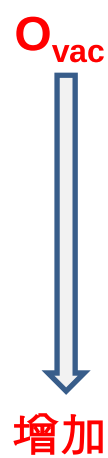






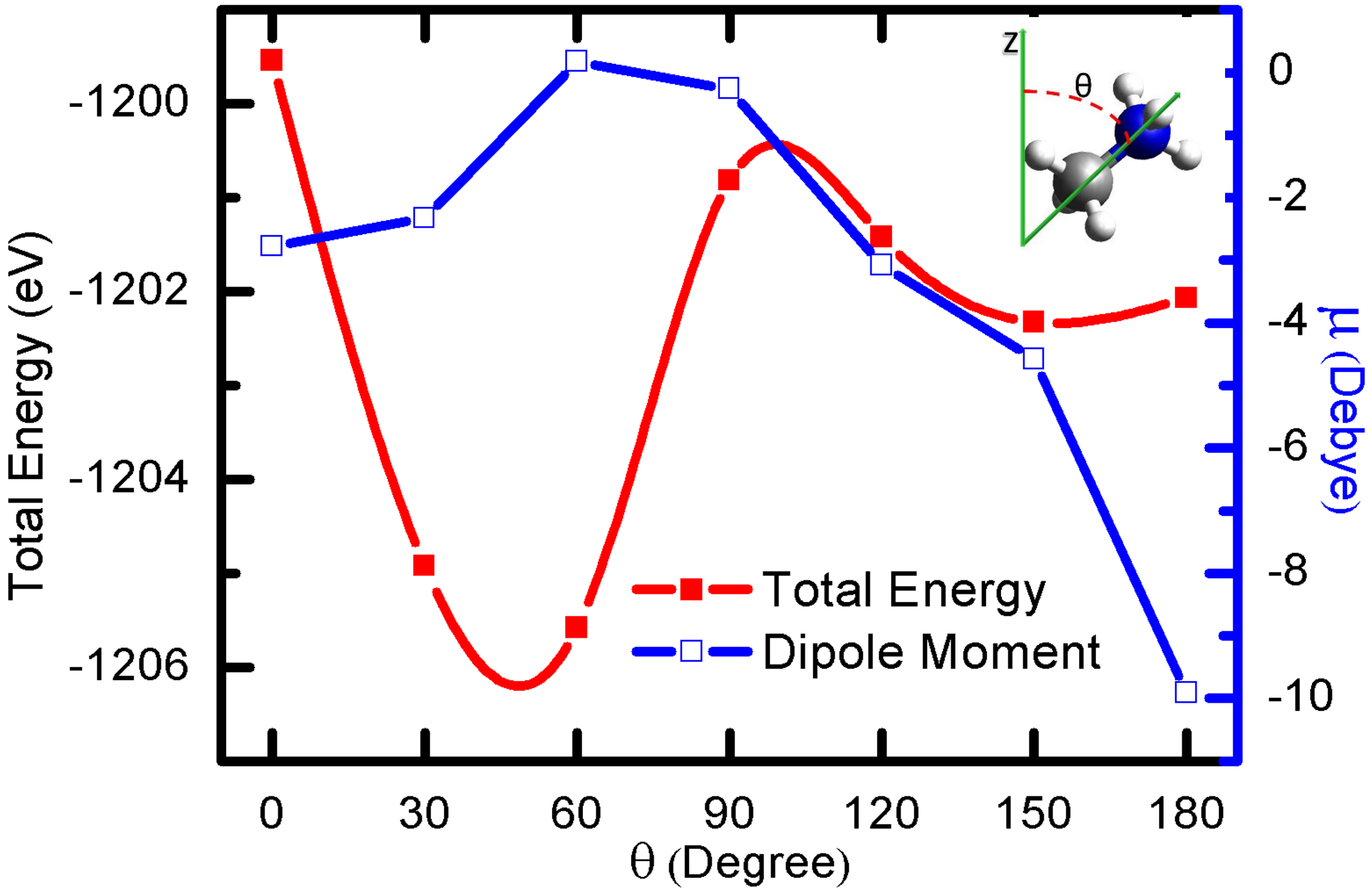
PL spectra (532 nm excitation)



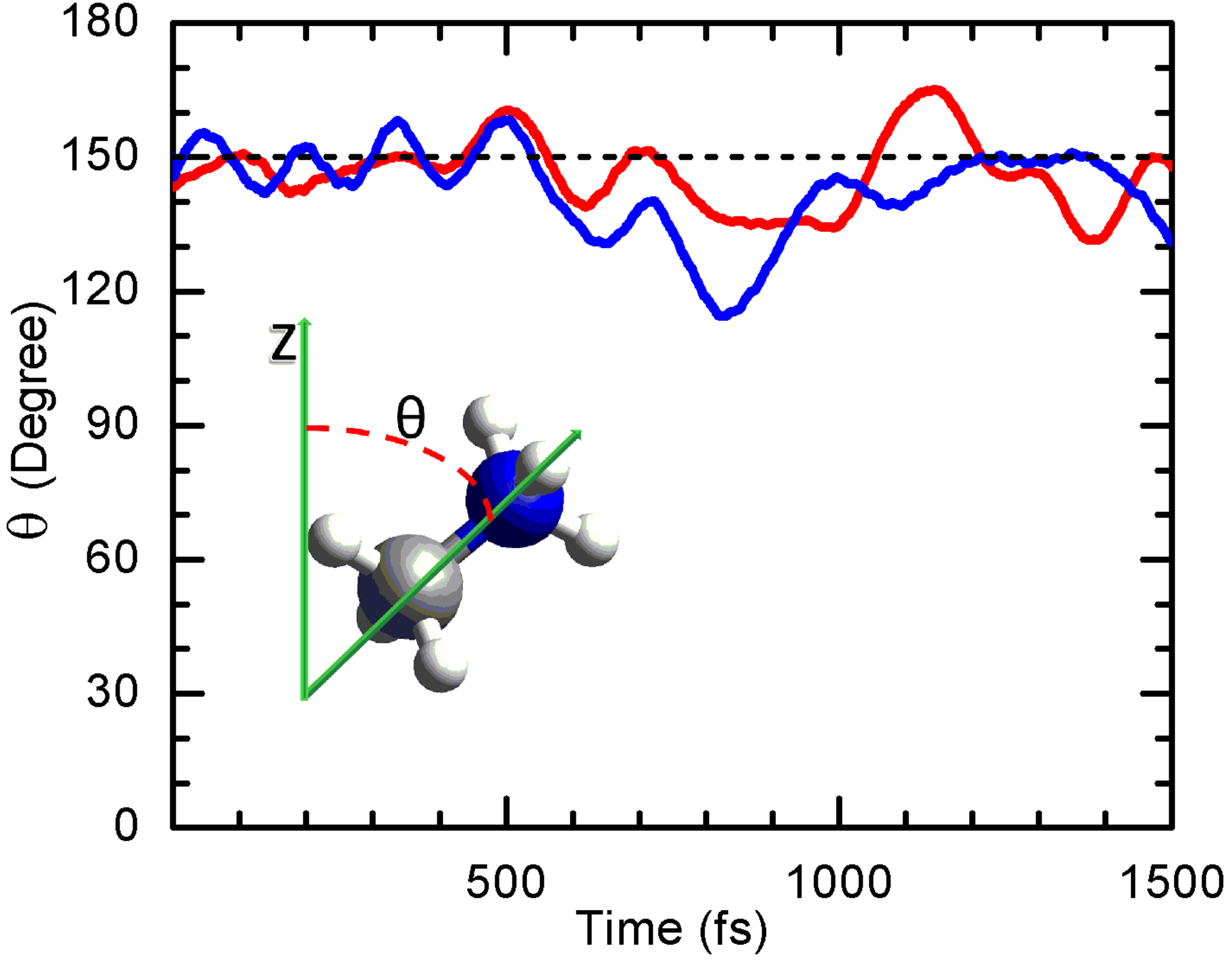


Type of substrate	PL lifetime(ns)
Al_2O_3	36.6±1.2
$TiO_2(O_2$ 100%)	32.7±1.1
$TiO_2(O_2$ 50%)	32.0±1.4
$TiO_2(O_2$ 25%)	28.6±1.6
$TiO_2(O_2$ 15%)	27.2±1.1
$TiO_2(O_2$ 10%)	24.6±1.2

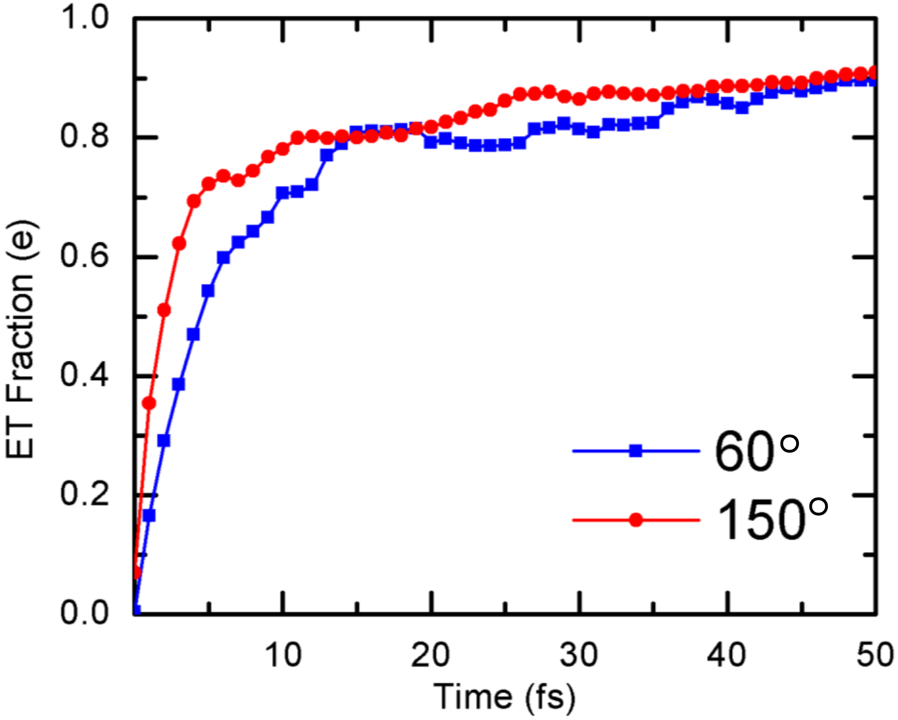
MA Orientation

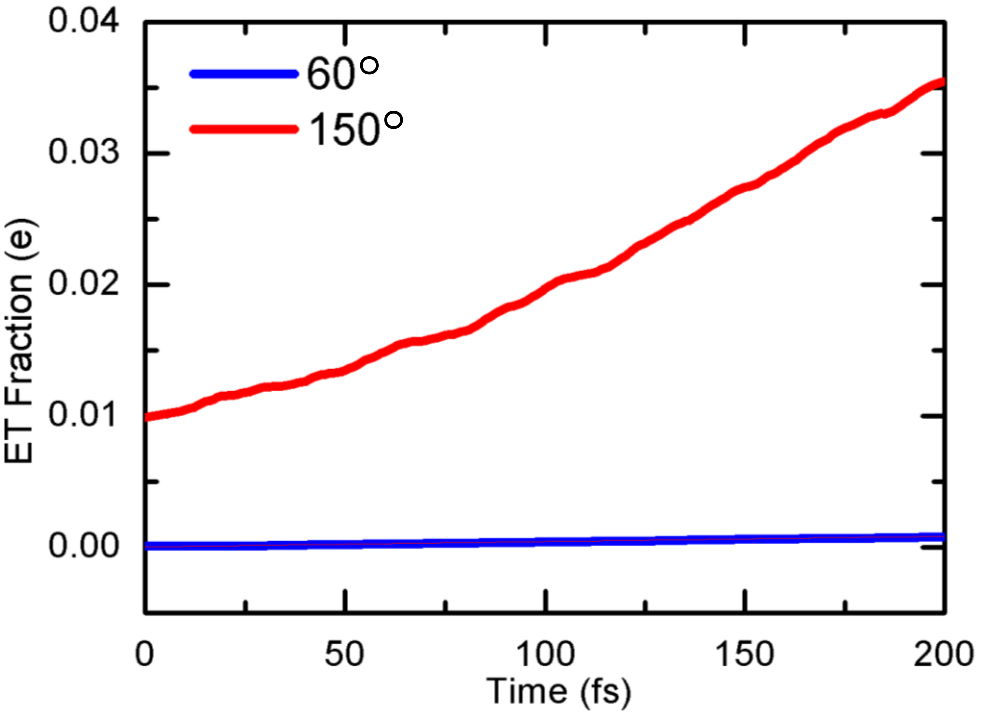


Molecular Dynamics Simulation at 350 K



Injection and Recombination Dynamics





	μ (Debye)	τ_{inj} (fs)	τ_{rec} (ps)
θ=60°	0.17	8.17	266.16
θ=150°	-4.58	5.55	7.48

Dramatic difference in recombination rates

Real time TDDFT for electron-ion quantum dynamics

OUTLINE

I. Background: building computational tools for excited state dynamics

II. Photovoltaic applications
- ”virtual solar cells”
- interface control in perovskite solar cells
- electron-hole dynamics in 2D materials heterojunction

III. Photosplitting dynamics
- orbital dependent quantum interaction of water
- photolysis dynamics of H_2
- NV center dynamics

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