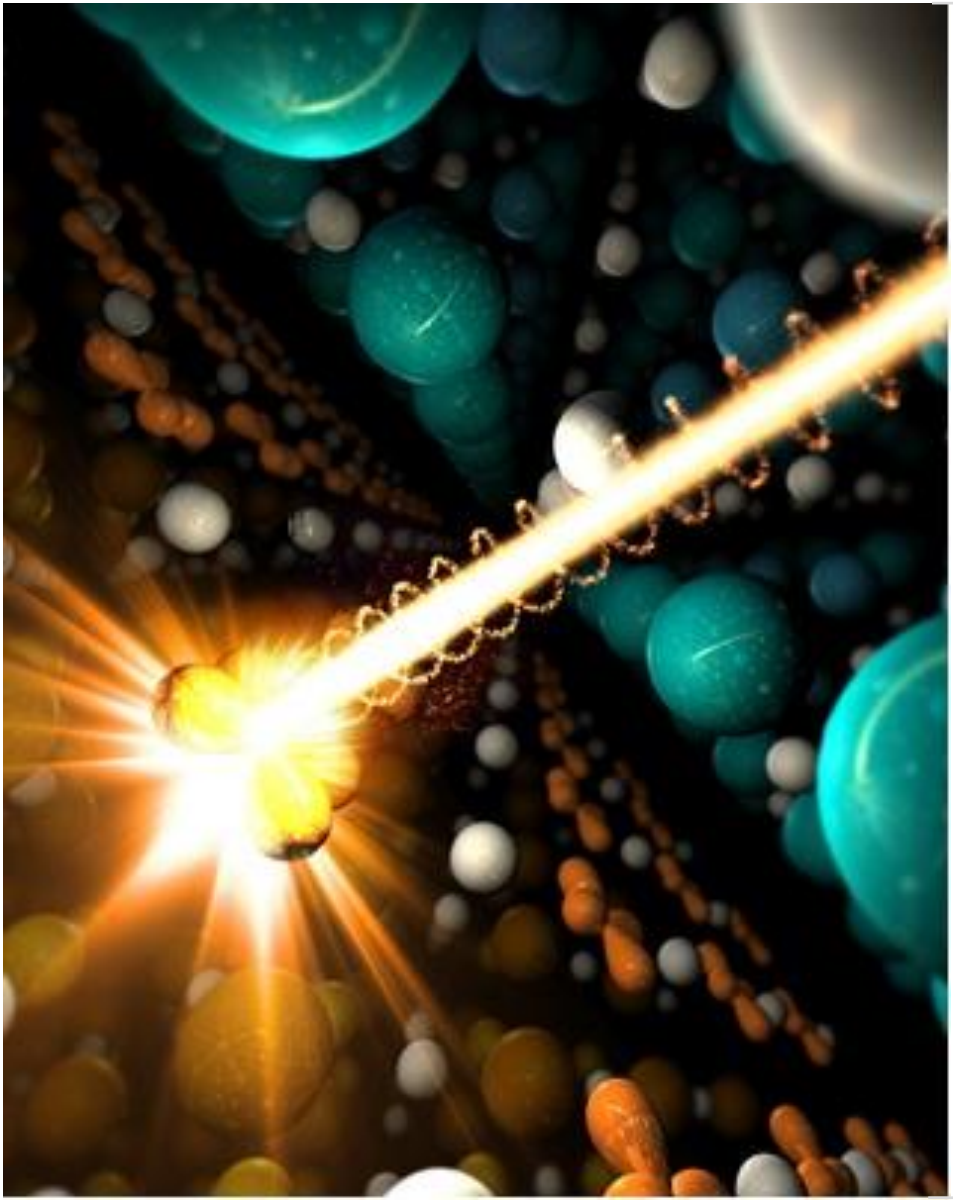
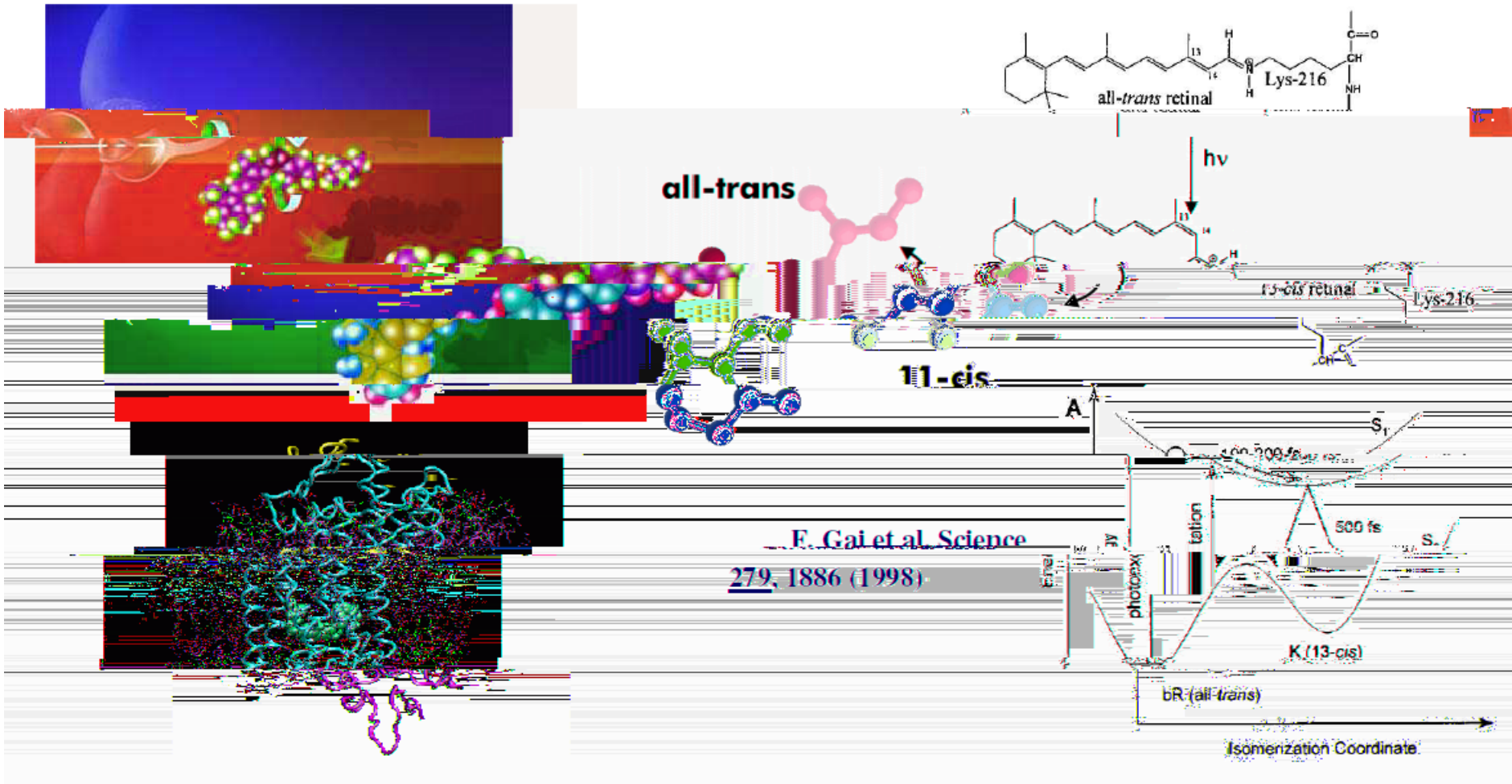


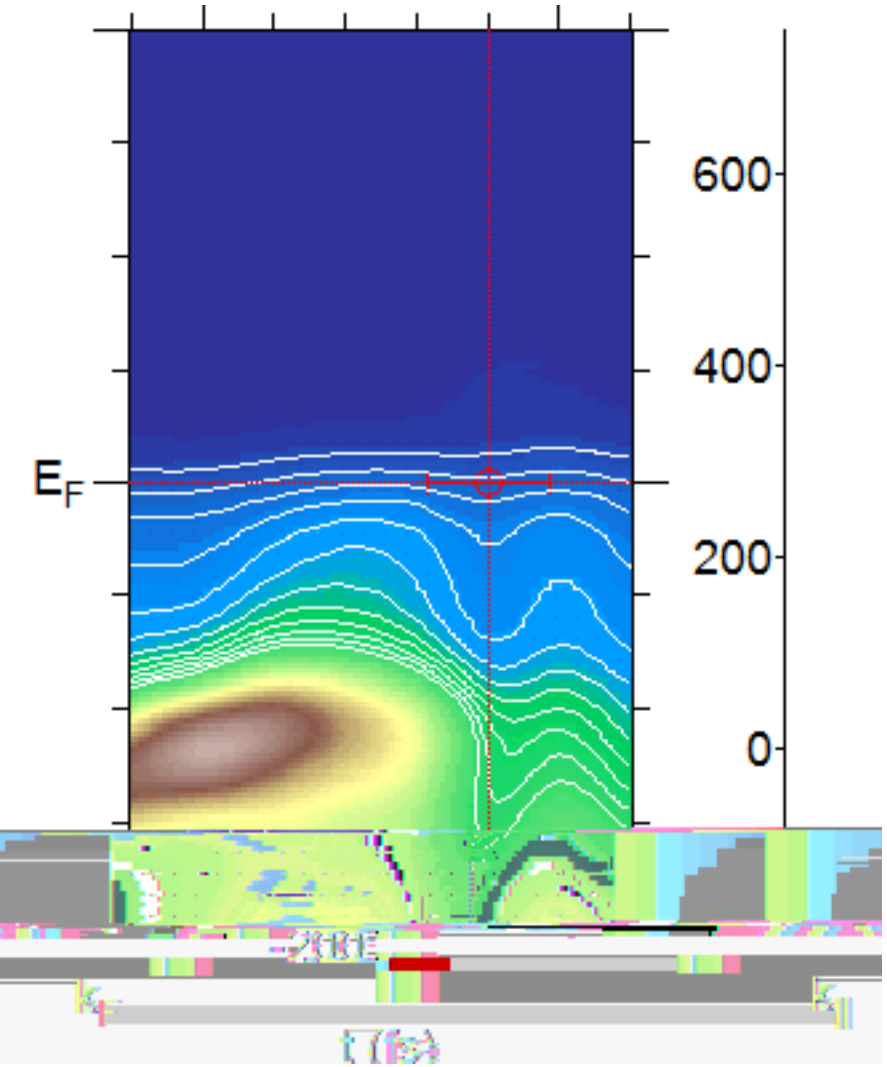
Sheng Meng（ ）
Institute of Physics,
Chinese Academy of Sciences
2015.6.4

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

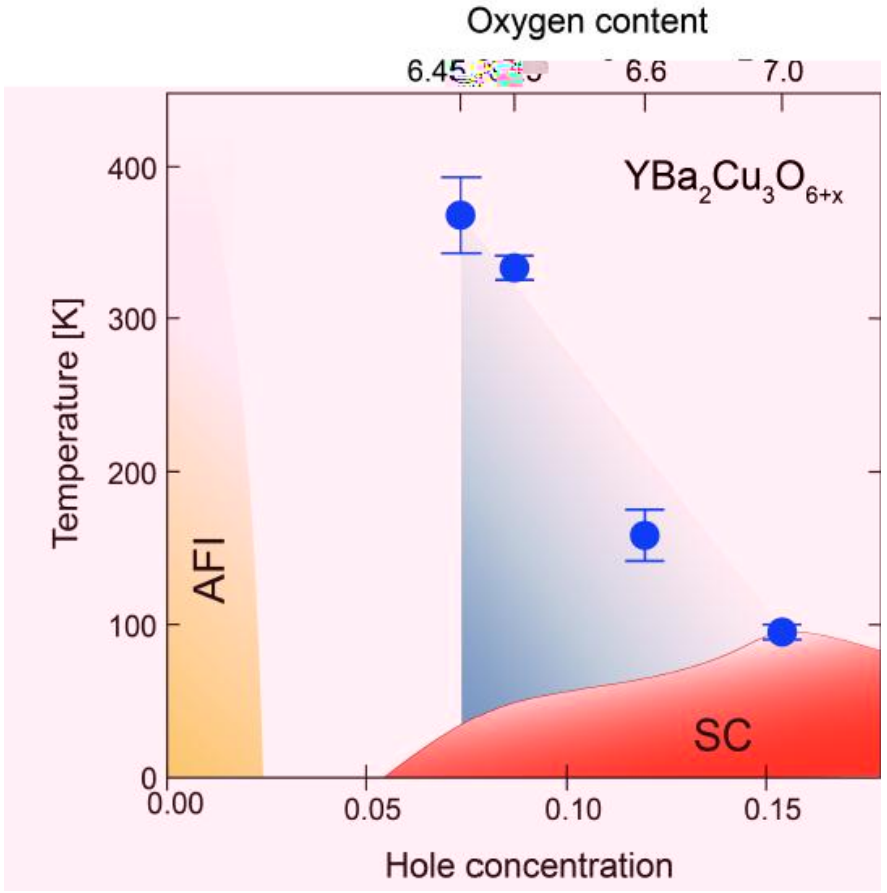


Experimental Observations

TR-ARPES



Light-driven superconductor @RT



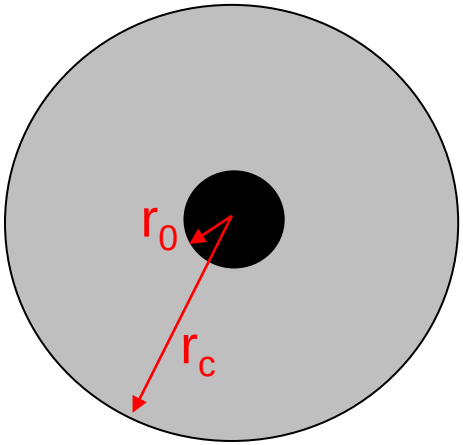
Schmitt *et al.* Science **321**, 1649 (2008)

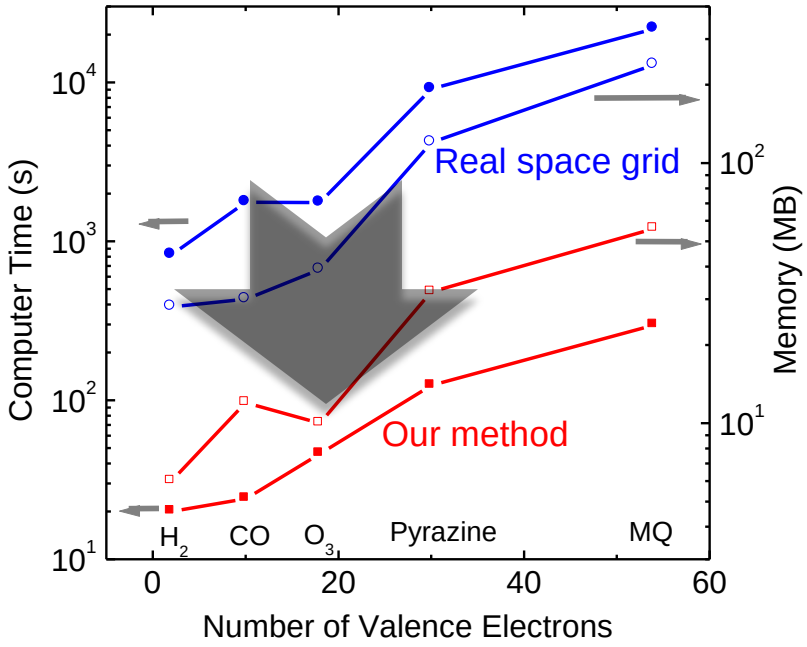
Cavelleri *et al.* PRB 89, 184516(2014);Nature (2014)

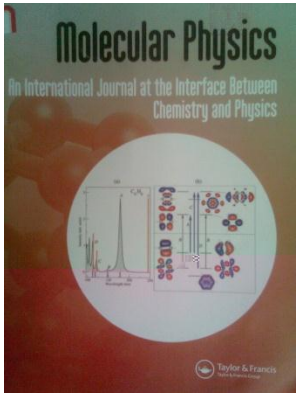
$$M_J \frac{d^2 \mathbf{R}_J^{cl}(t)}{dt^2} = -\nabla_{\mathbf{R}_J^{cl}} \left[V_{ext}^J(\mathbf{R}_J^{cl}, t) - \int \frac{Z_J \rho(\mathbf{r}, t)}{|\mathbf{R}_J^{cl} - \mathbf{r}|} d\mathbf{r} + \sum_{I \neq J} \frac{Z_J Z_I}{|\mathbf{R}_J^{cl} - \mathbf{R}_I^{cl}|} \right]$$

Computational efficiency

Pseudopotential + Numerical atomic orbitals

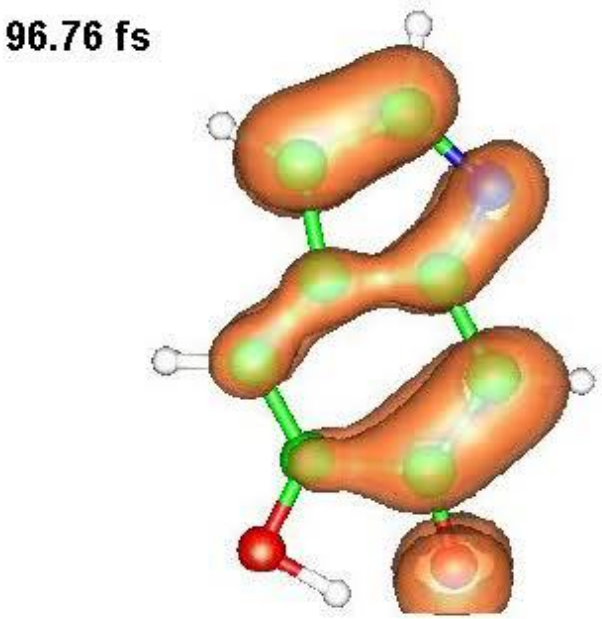


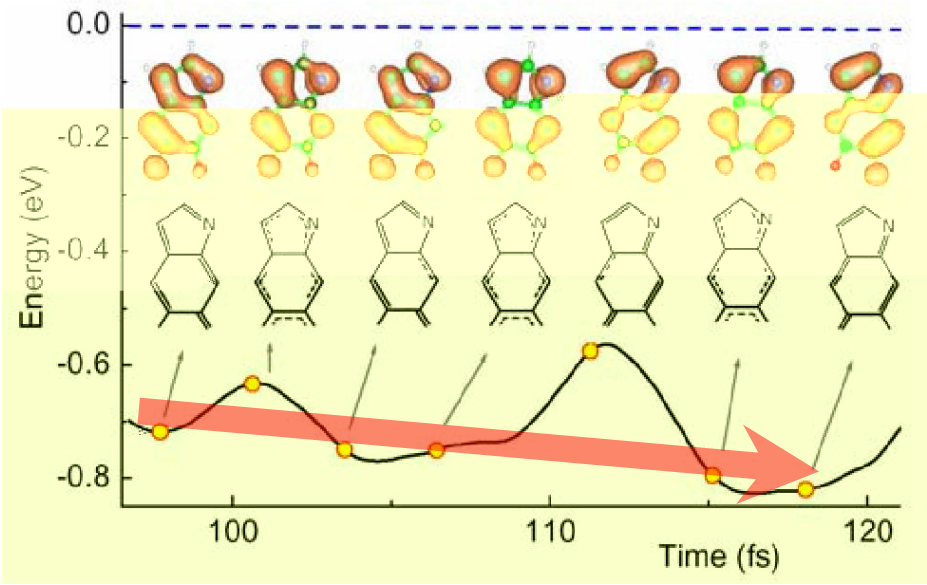




Optical properties of clusters and molecules from real-time time-dependent density functional theory using a self-consistent field

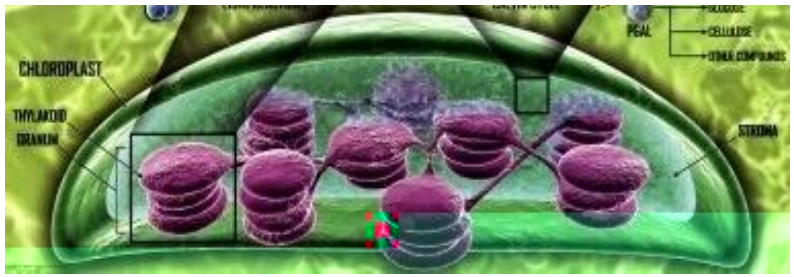
J. Ren, E. Kaxiras, S. Meng,
Mol. Phys. 108, 1829 (2010).





Clouds = e density in excited state

I.



Real time TDDFT for electron-ion quantum dynamics

OUTLINE

I. Background: building computational tools for excited state dynamics

II. Photovoltaic applications

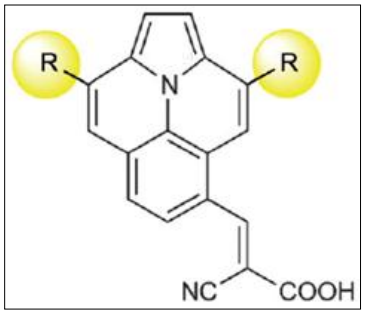
-
- interface control in perovskite solar cells
- electron-hole dynamics in 2D materials heterojunction

III. Photosplitting dynamics

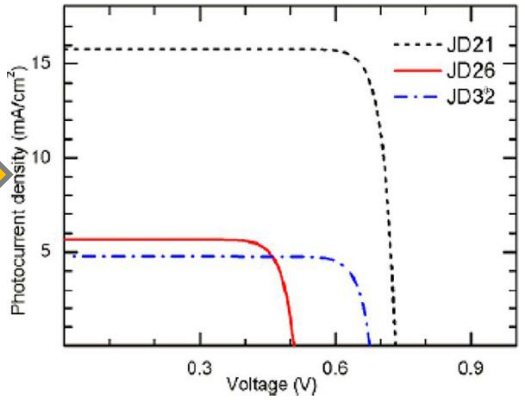
- orbital dependent quantum interaction of water
- photolysis dynamics of H_2

photovoltaics

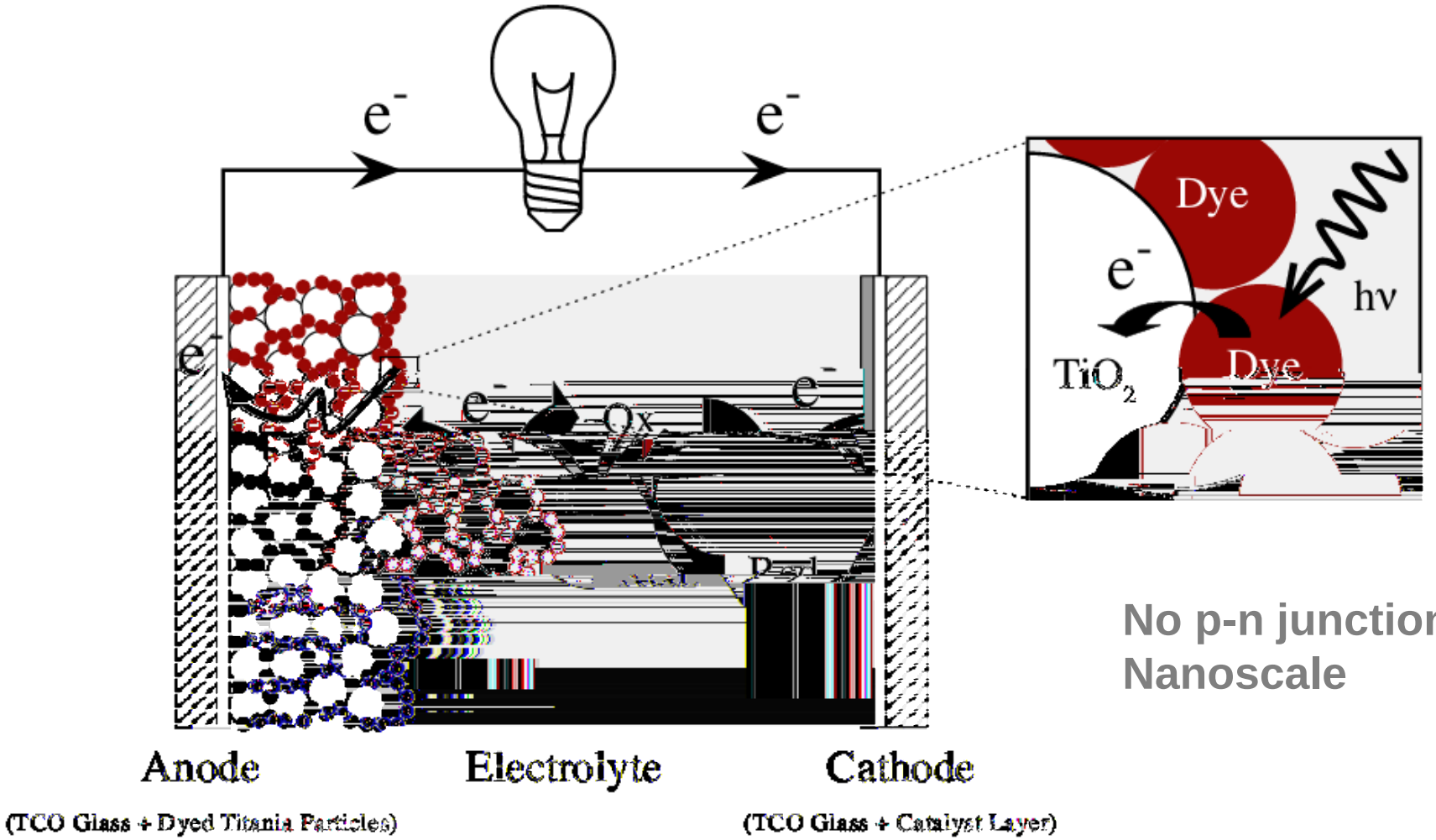
INPUT



OUTPUT



Dye solar cell: A 3rd Generation Solar Cell



No p-n junction
Nanoscale

organic molecule | quantum dot | perovskite

A 9 @ ++

From http://www.solaronix.com

Molecular Dyes

Metal-based:

Ru B A 5 8

Porphyrin

Phthalocyanine

All-organic:

Coumarin

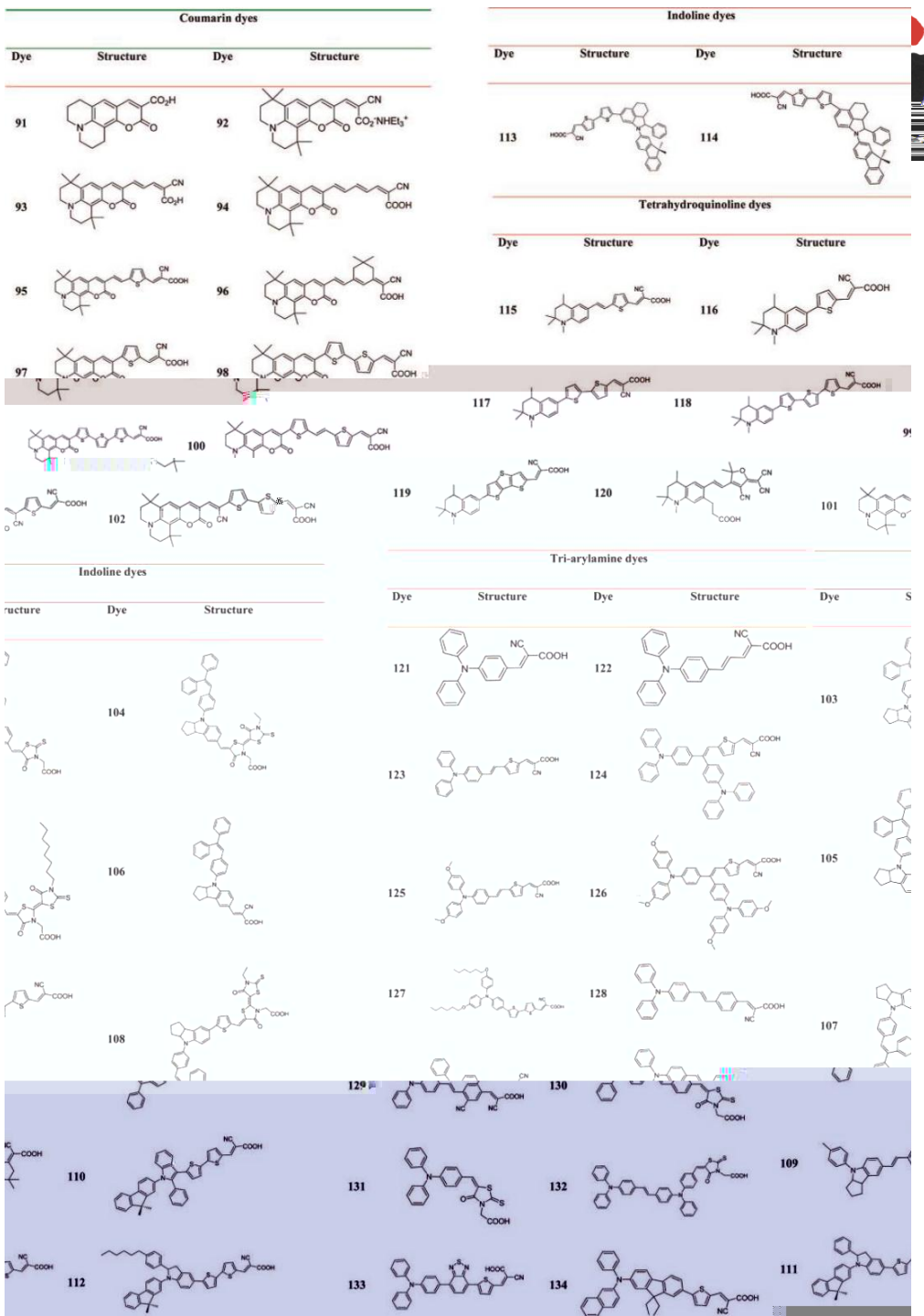
Indoline

Triarylamine

Perylene

Squarine

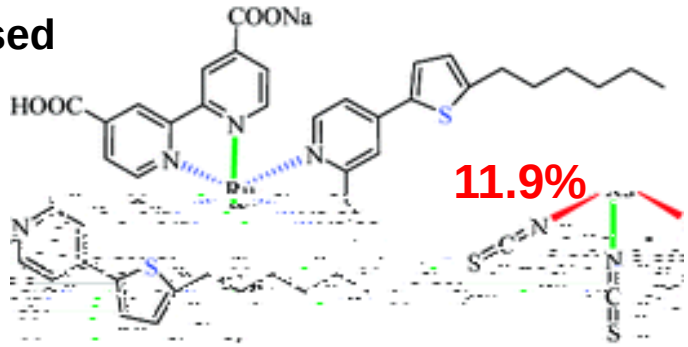
>1000 species



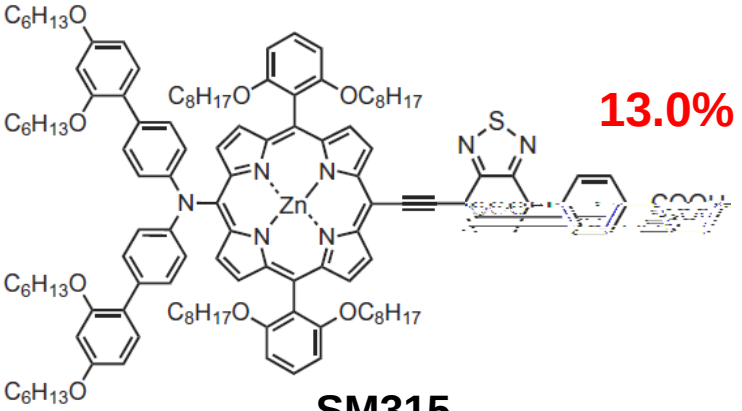
Hagfeldt et al., Chem. Rev. (2010).

State of the Art

Metal-based
C101



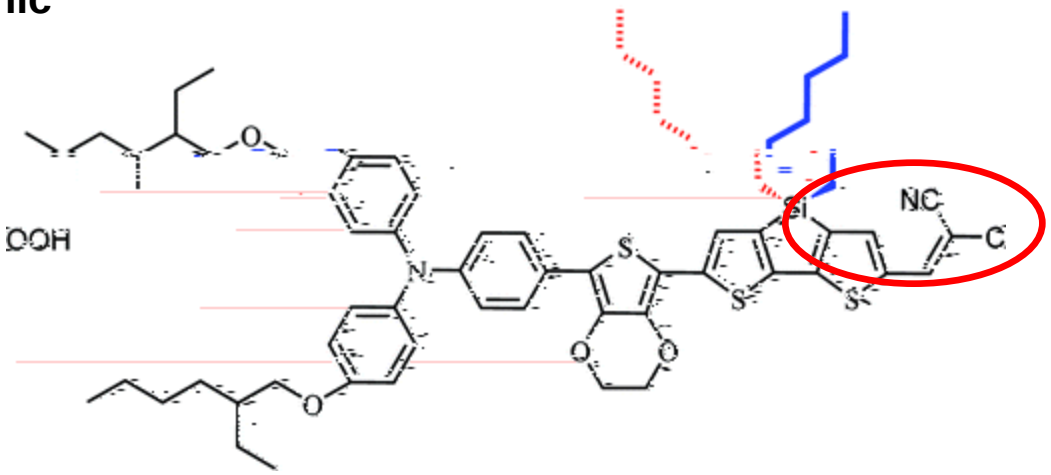
11.9%



13.0%

SM315

Organic
C219

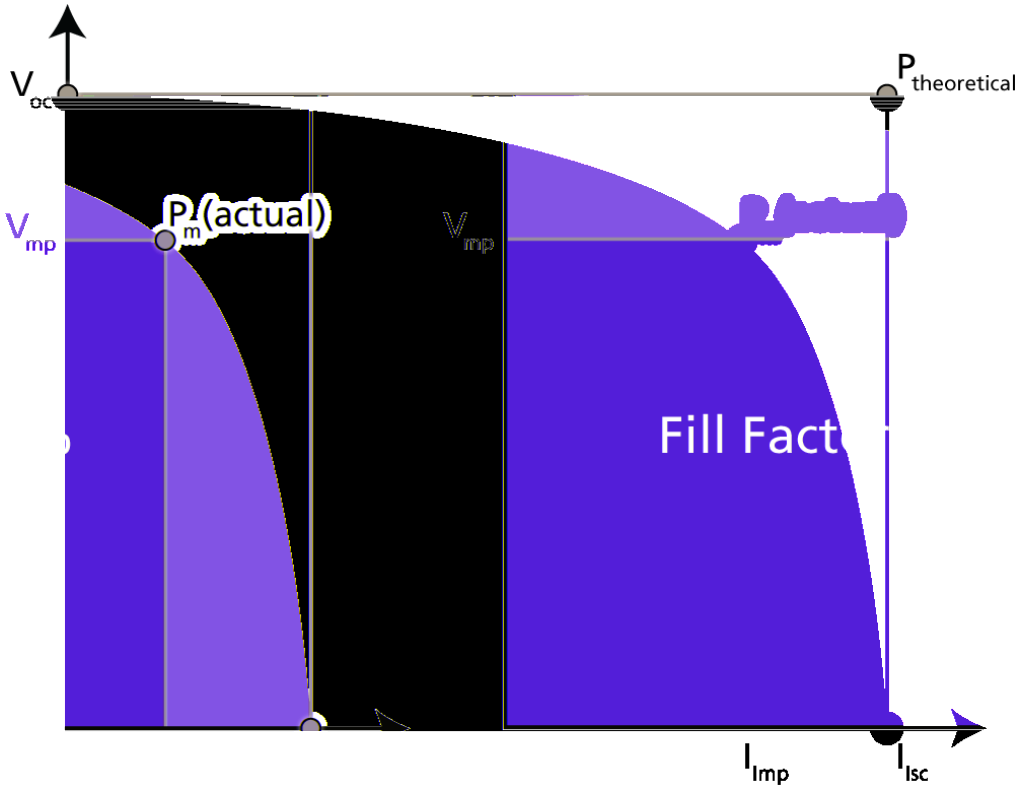


10.0-10.3%

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?

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



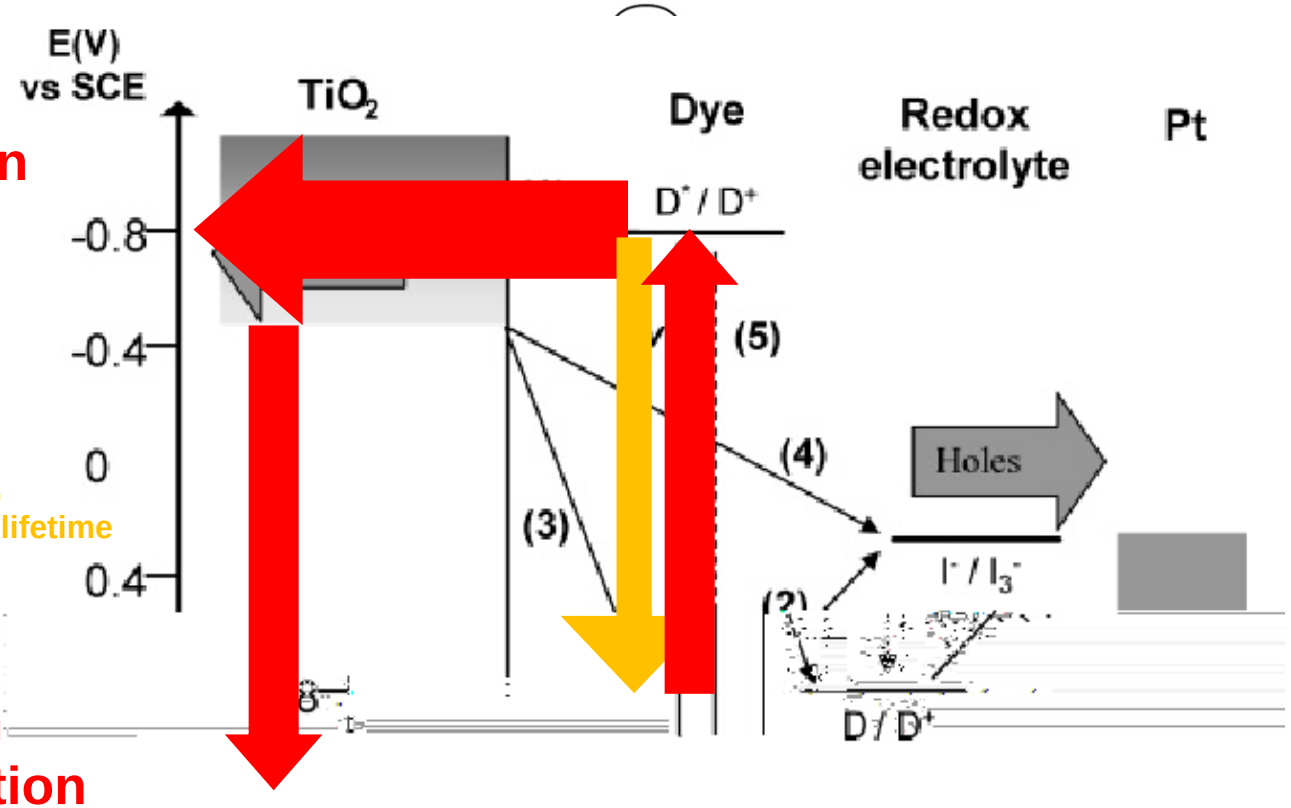
$$V = \frac{k_B T}{q}\ln\left(\frac{J_{sc} - I}{I_S} + 1\right) \qquad I_S = \frac{J_{SC}}{\exp(qV_{OC}/k_B T) - 1}$$

1. Absorption

2. Injection

inj inj / $T_{lifetime}$

3. Collection /Recombination



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

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

PANDORA: Predictive algorithms for nano device operation rate assessment

PANDORA

PCE η

J_{SC}

$J_{SC} = \quad h \; e \quad)] \quad {}_{\text{in}} \quad {}_{\text{b}} \; d$

LHE: $(E) \quad \lambda \; = \int \varepsilon\rho \quad \mathrm{d}(-\varepsilon\rho x) \; x$

$\Phi_{\text{in}} : \Phi_{\text{in}} = 1 \Big/ \left(1 + \frac{\tau_{\text{in}}}{\tau_{\text{ke}}}\right)$

$\eta_{\text{b}} : \eta_{\text{b}} = 1 \Big/ \left(1 + \frac{\tau_{\text{a}}}{\tau_{\text{e}}}\right)$

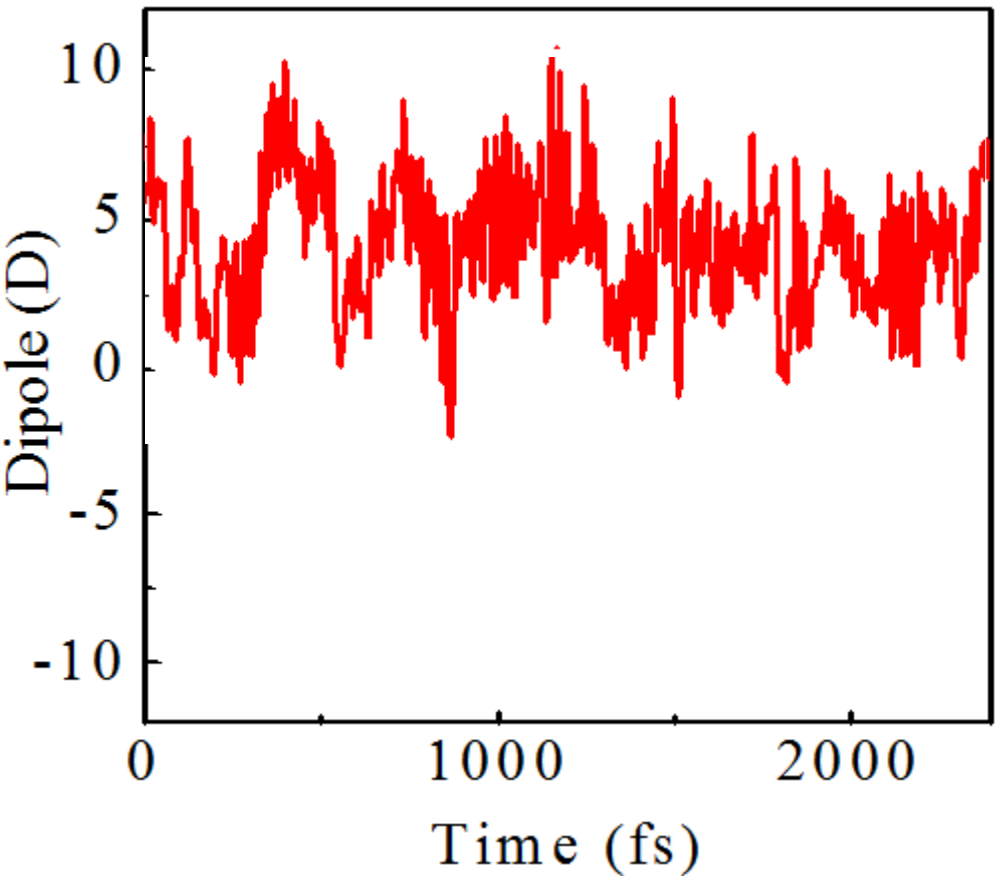
V_{OC}

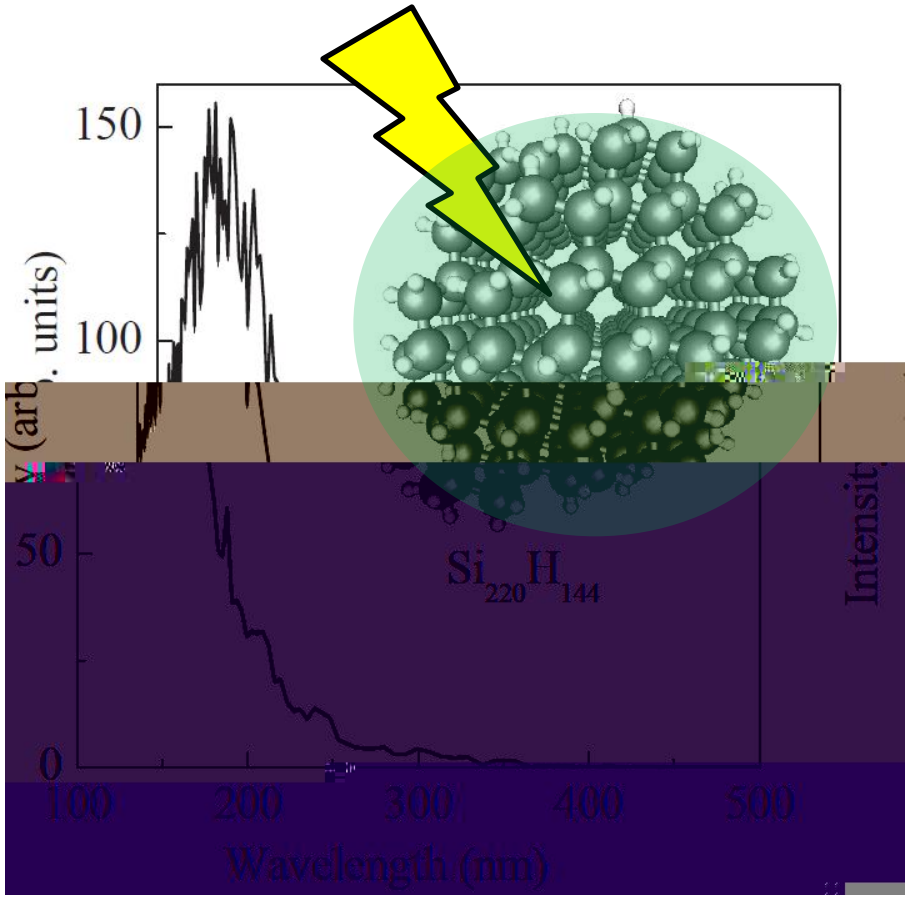
$V_{\text{O}} = \frac{kT_B}{\beta' q} \ln \frac{\beta R \, J_{0\;\text{S}}}{kT_B}$

$R_0 = \frac{\sqrt{\pi\lambda kT_B}}{q d^2 k \gamma c_{\text{ex}} N_{\text{s}}} \exp\left(\gamma \frac{E_{\text{M}} - E_{\text{e}}}{kT_{\text{B}}} \quad \frac{}{kT_{\text{B}}} + \frac{\lambda}{4}\right)$

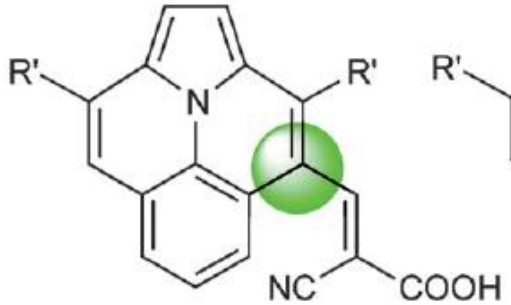
FF → *I*-*V* curve

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

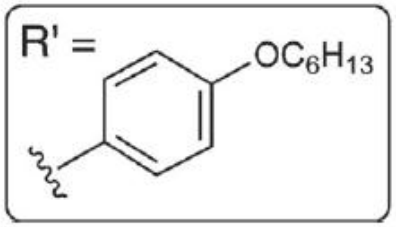

10
5
0
-5
-10
Dipole (D)
0
1000
2000
Time (fs)

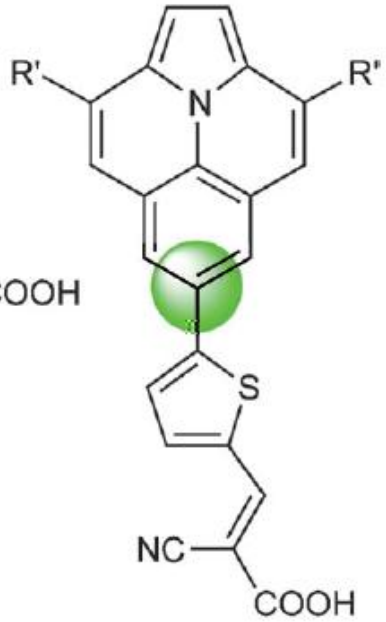

150
100
50
0
Si220H144
100
200
300
400
500
Wavelength (nm)

JD21



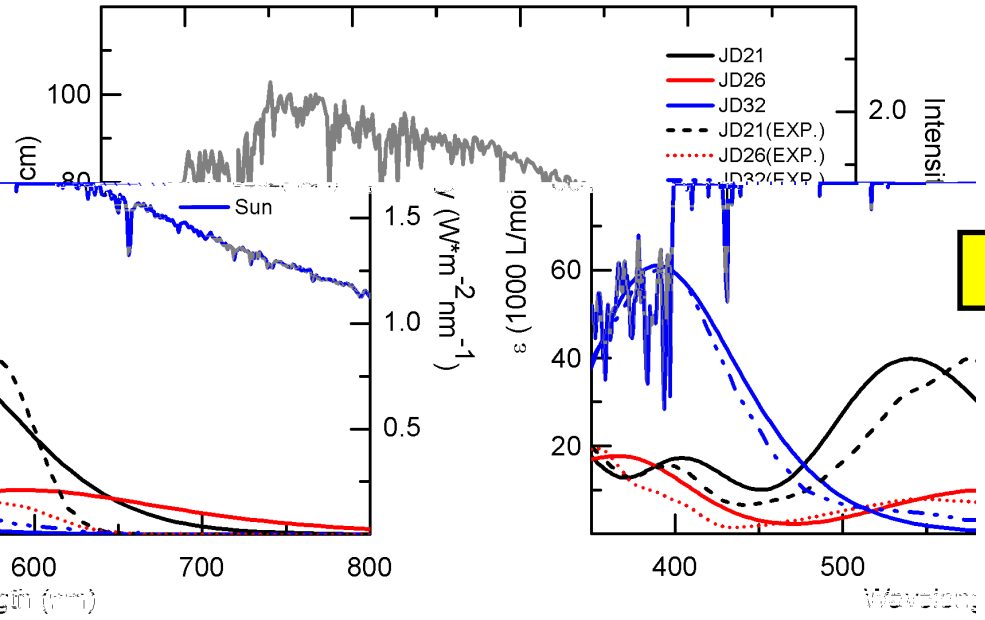
JD26

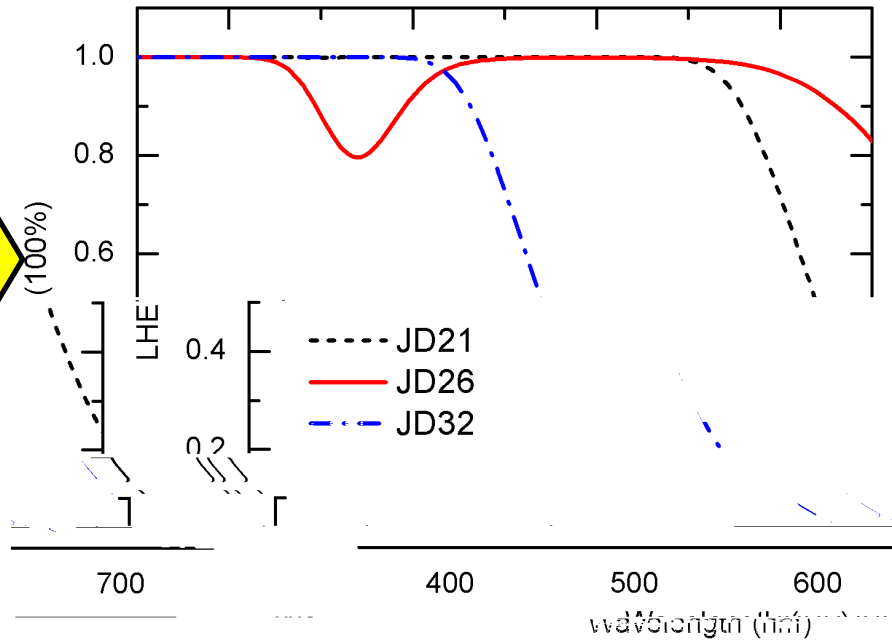




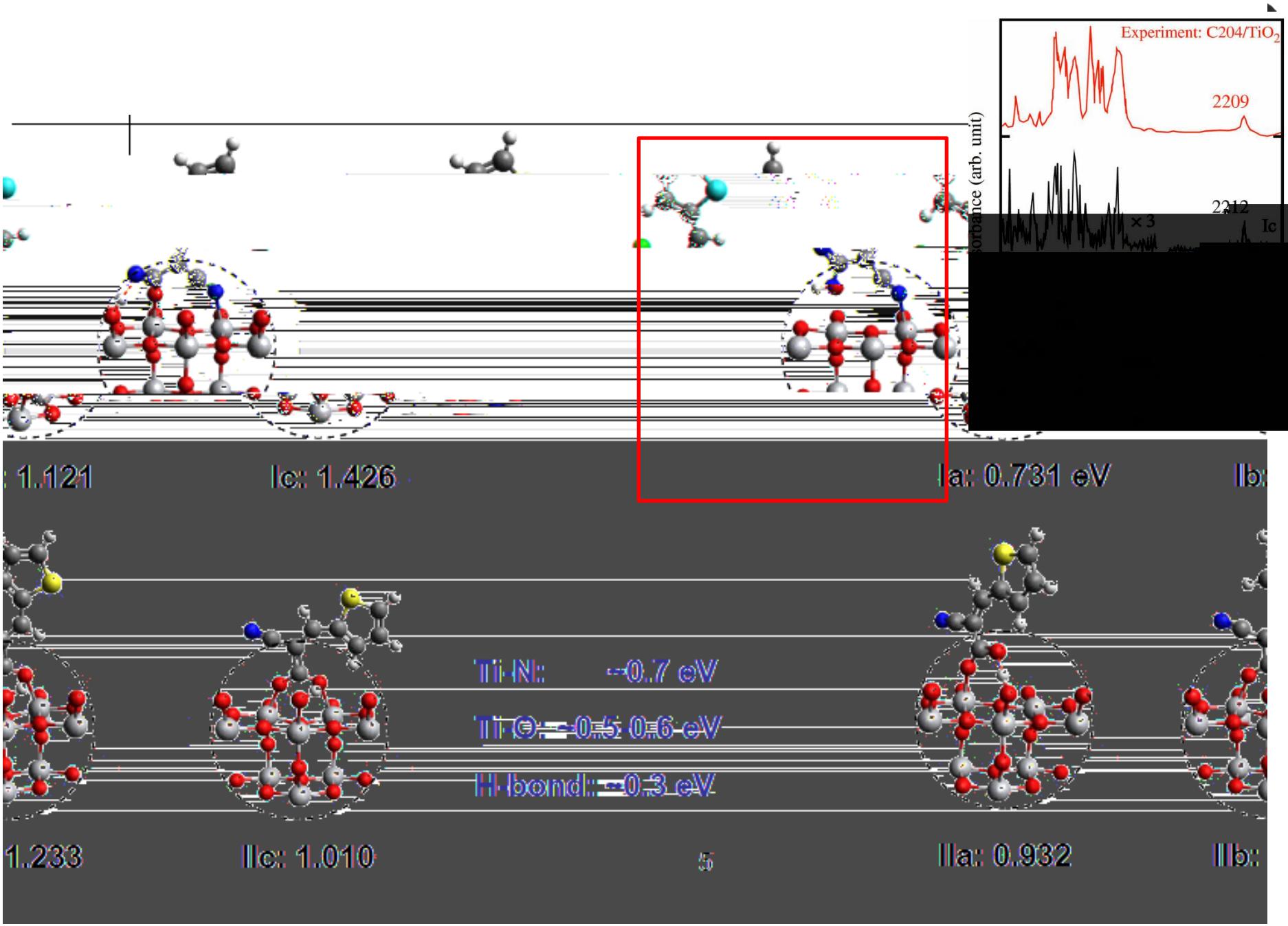
JD32

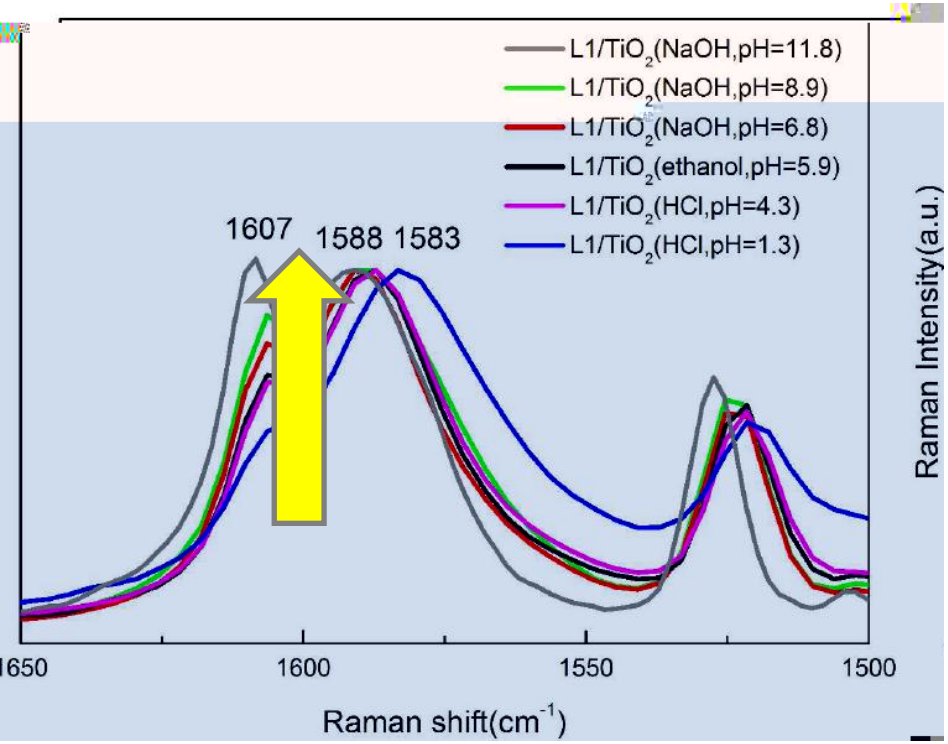
$$(H) \quad \lambda = \int \varepsilon\rho \quad \mathrm{d}(-\varepsilon\rho x) \quad x$$

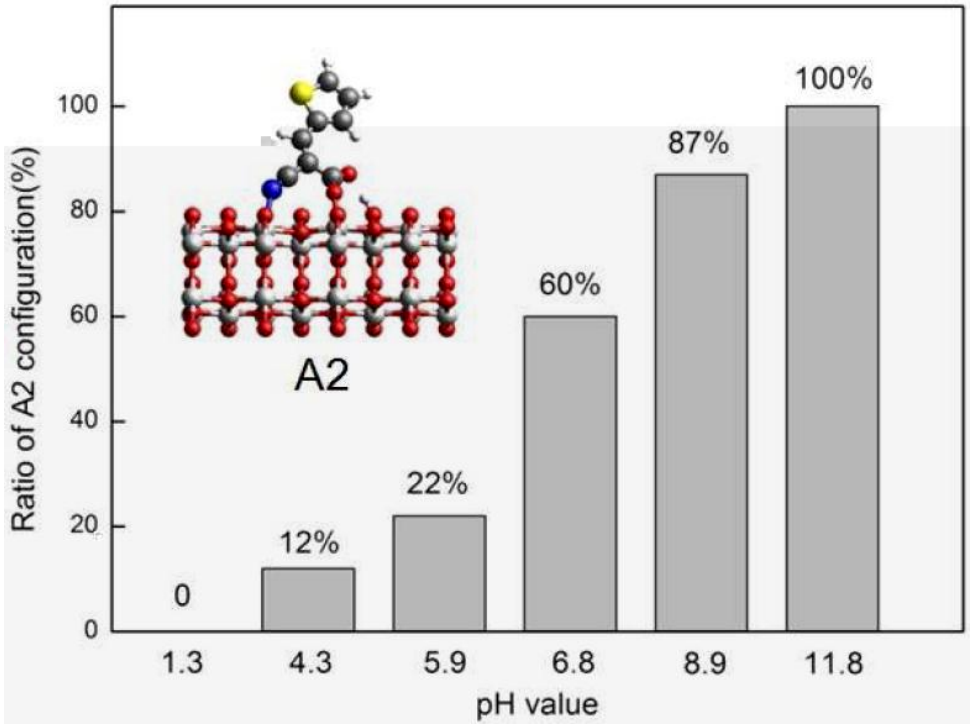




TiO_2 film thickness: d = 3
dye loading: 300 mmol/L

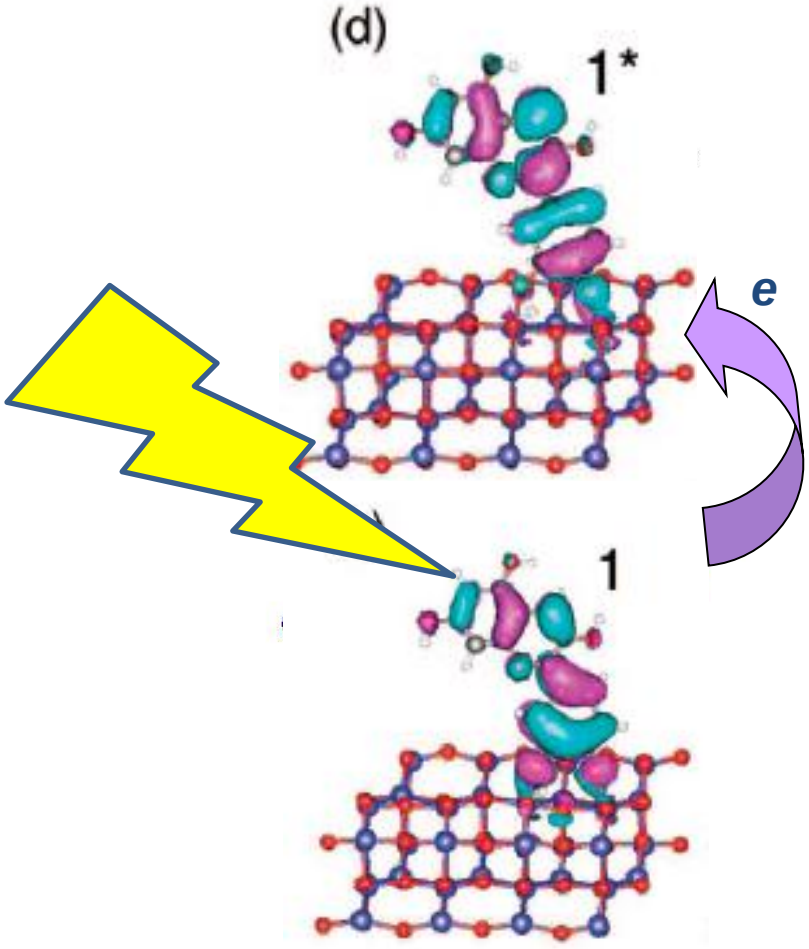

Experiment: C204/TiO2
2209
2212
× 3
Ic
orbance (arb. unit)
1.121
Ic: 1.426
Ia: 0.731 eV
Ib:
Ti-N:
-0.7 eV
Ti-O:
-0.5 0.6 eV
H-bond:
-0.3 eV
1.233
IIc: 1.010
IIa: 0.932
IIb:
5



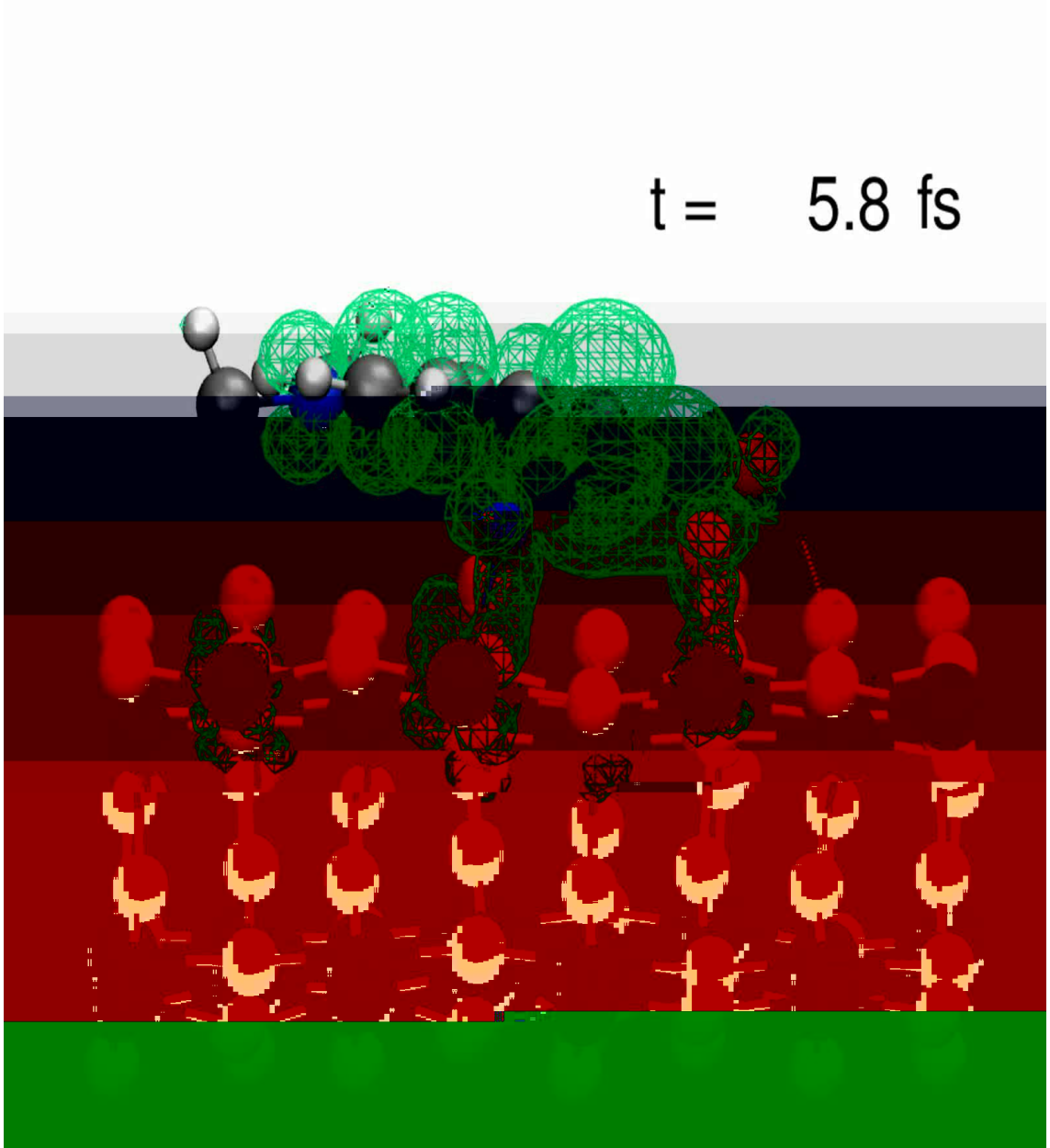


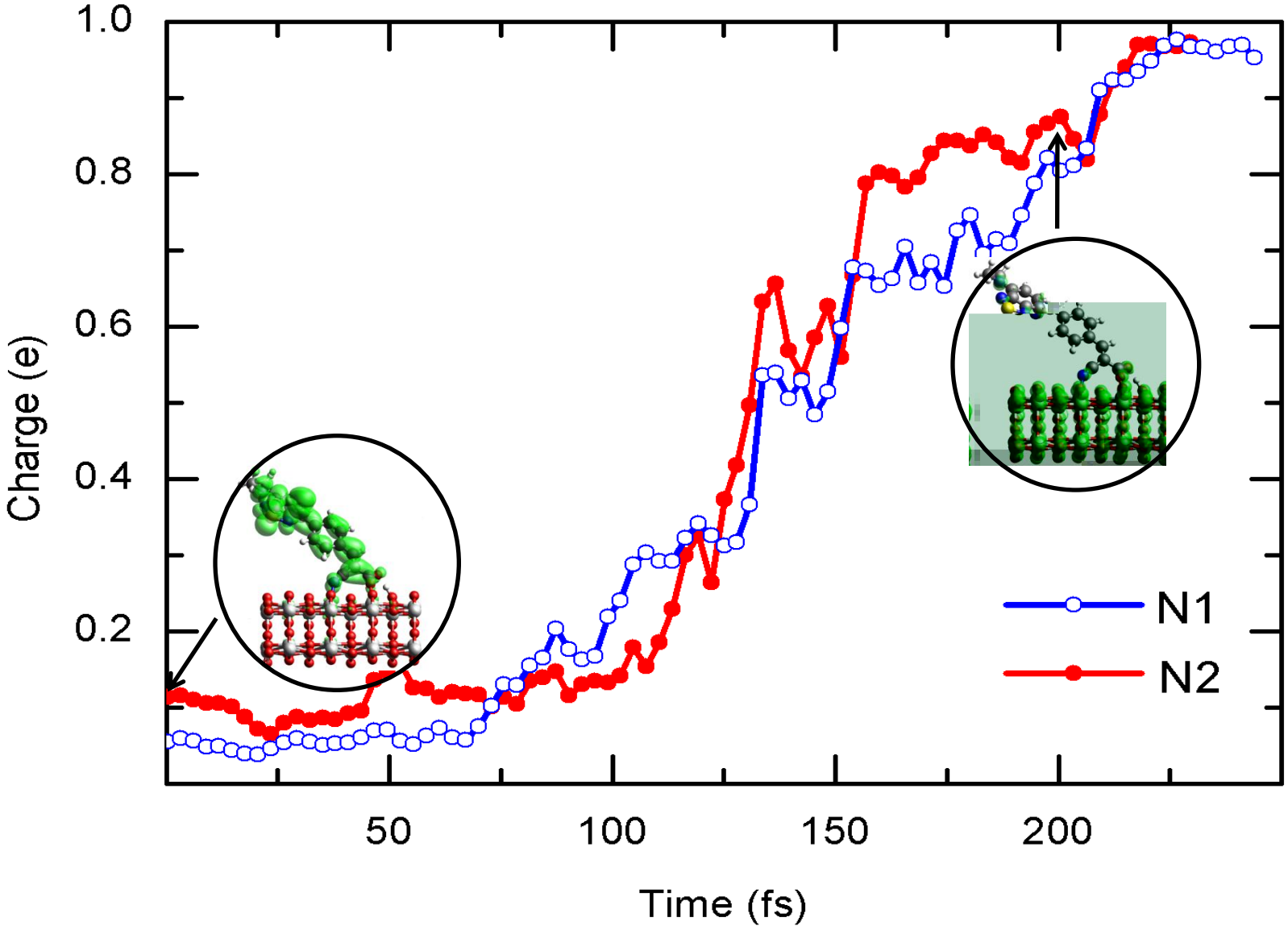
Zhang, Ma, Jiao, Wang, Shan, Li, Lu, Meng, ACS Appl. Mater. Interface (2014).

Electron Injection Dynamics



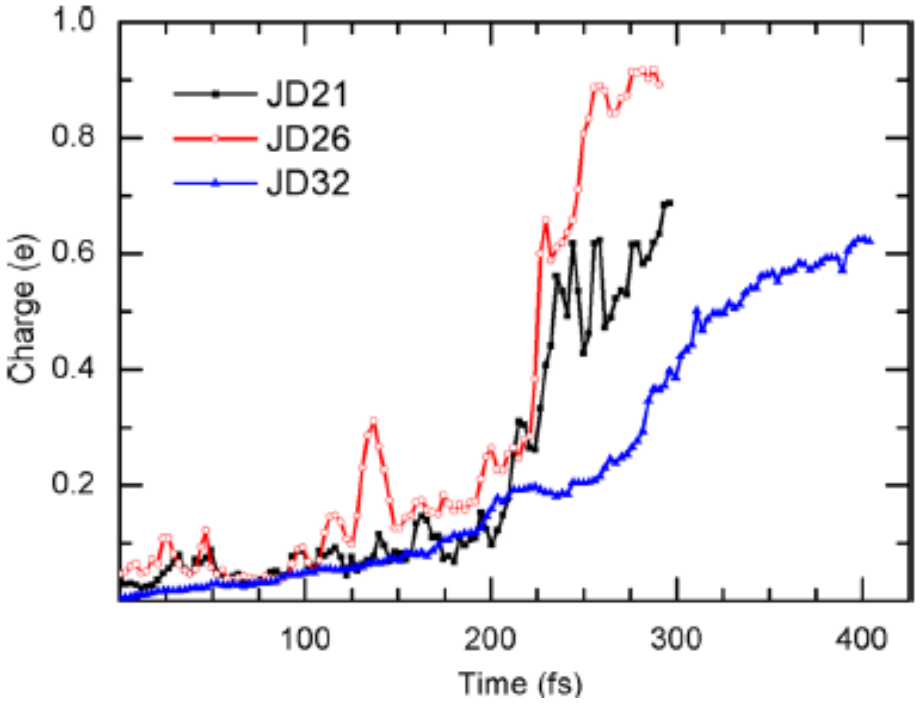
Electron Injection Dynamics




1.0
0.8
0.6
0.4
0.2
Charge (e)
50
100
150
200
Time (fs)
N1
N2

Electron Injection Efficiency

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



Φ			

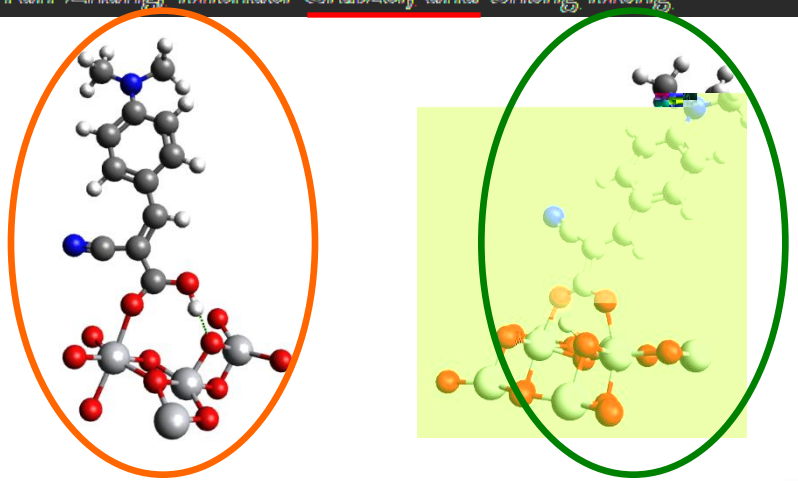
Jiao, Zhang, Gratzel, Meng, Adv. Funct. Mater. (2013).

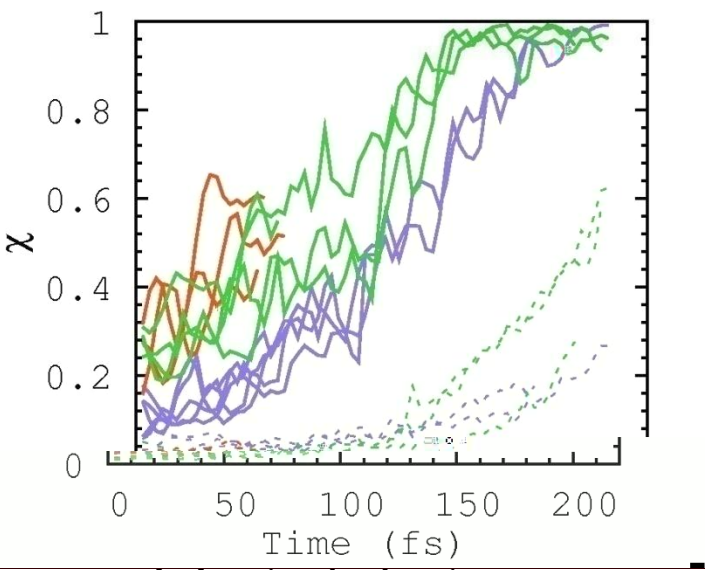
Ma, Jiao & Meng, J. Phys. Chem. C (2014).

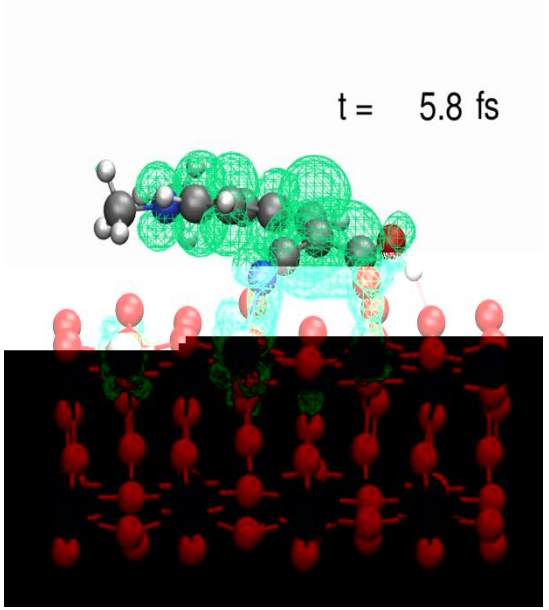
Materials Views
www.MaterialsViews.com
ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de

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

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

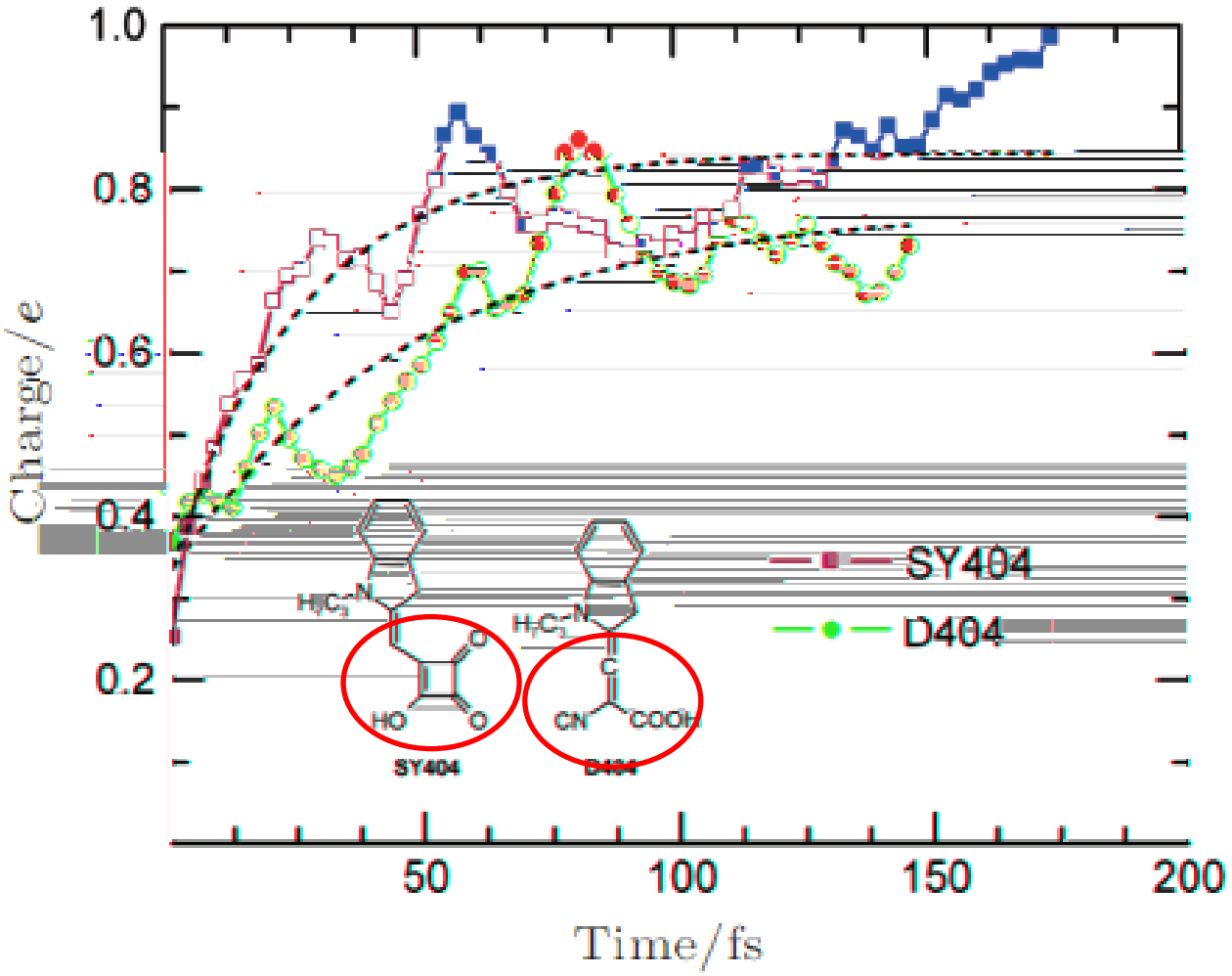






: injected electron

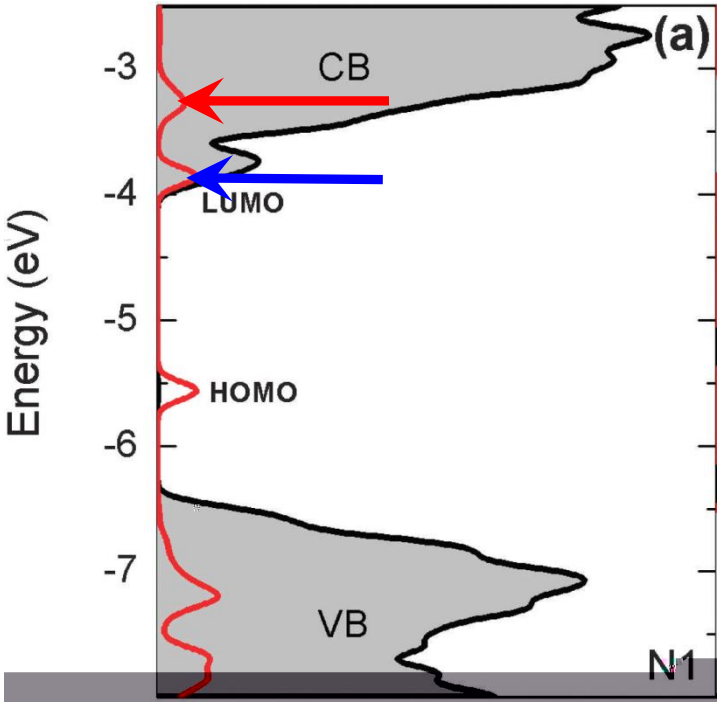
Different anchors

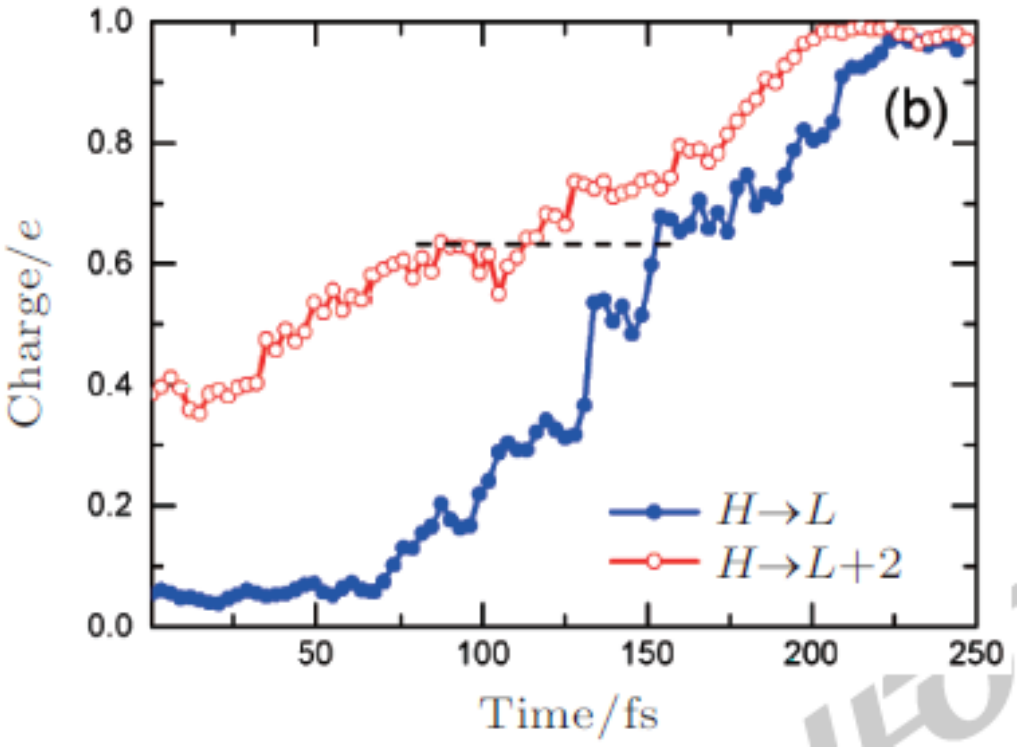


	SY404	D404
Theory	33 fs	60 fs
Expt. [a)]	50 ± 13 fs	

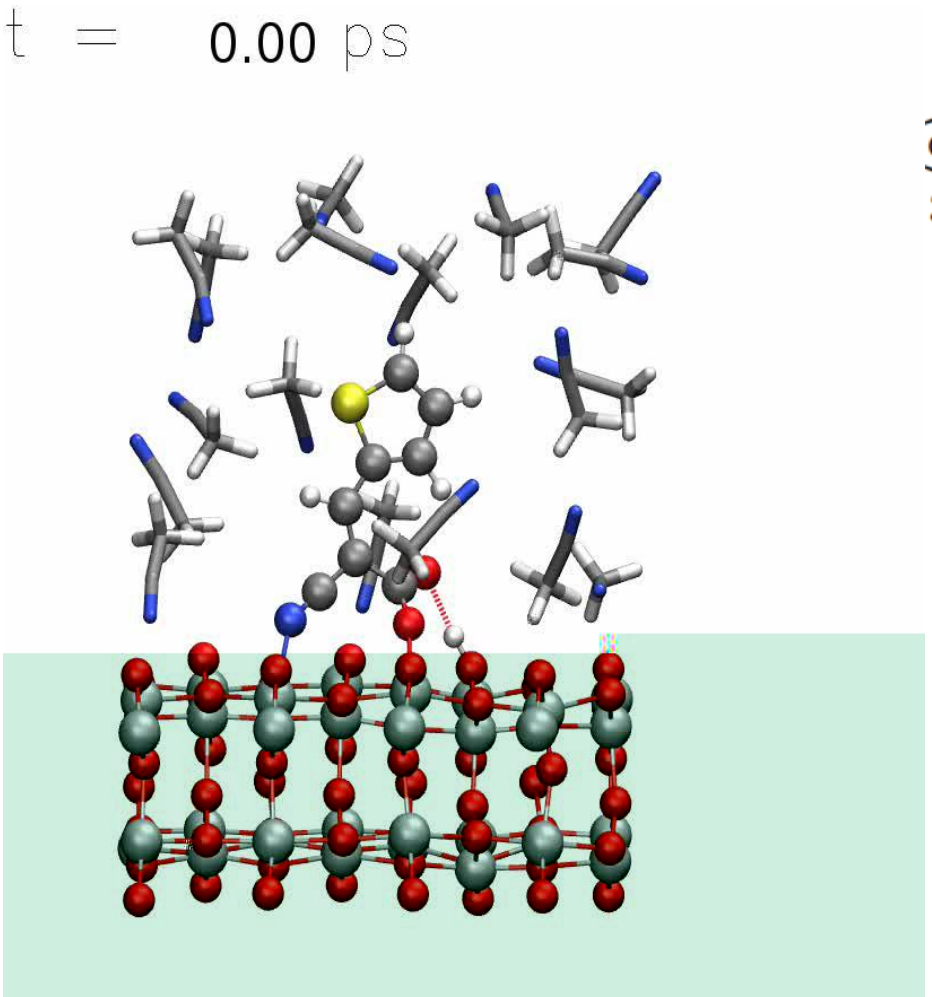
a) Bartelt et al. JPCC (2014).

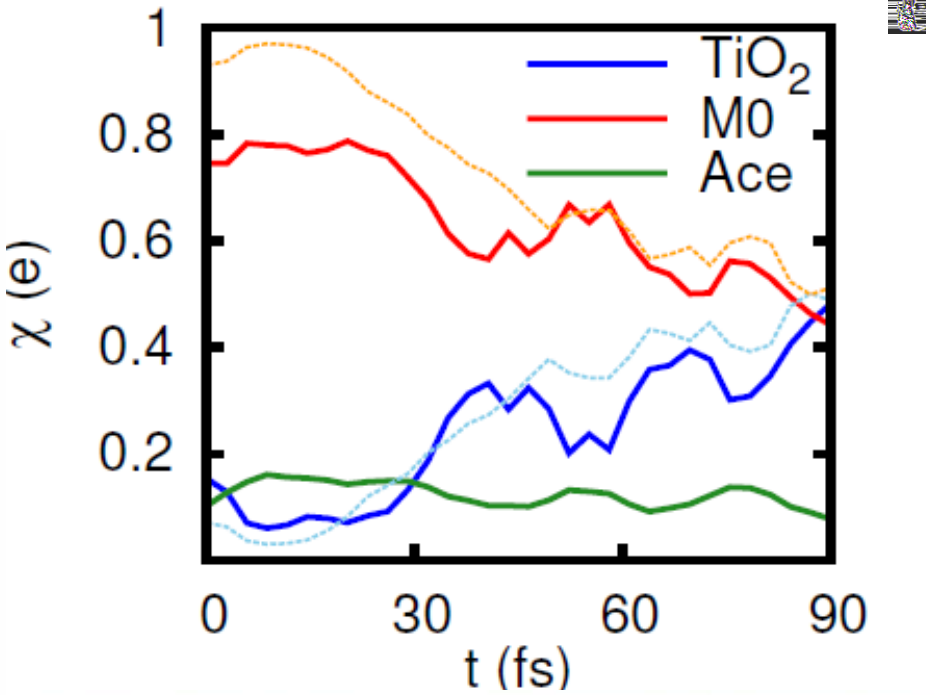
Hot electron effect

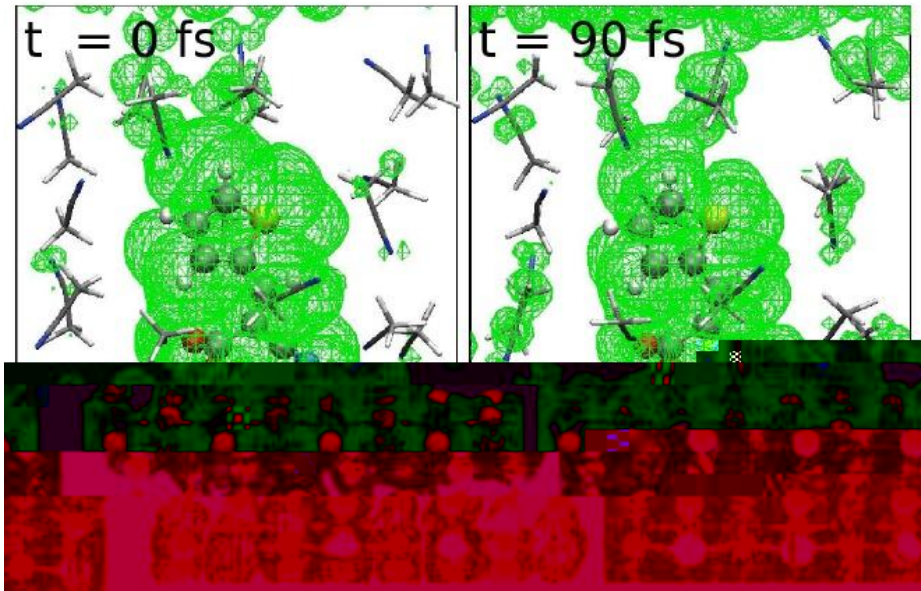


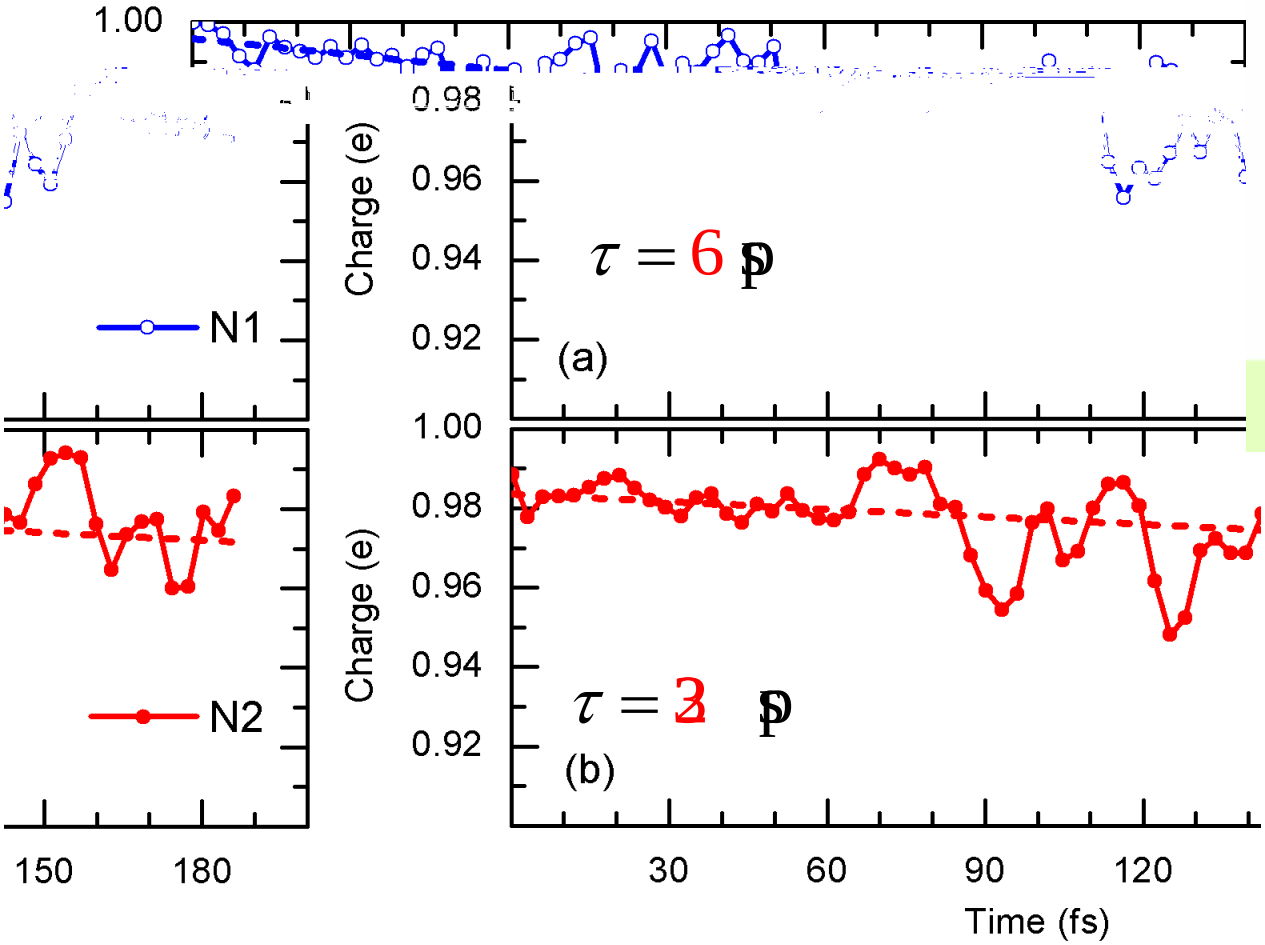


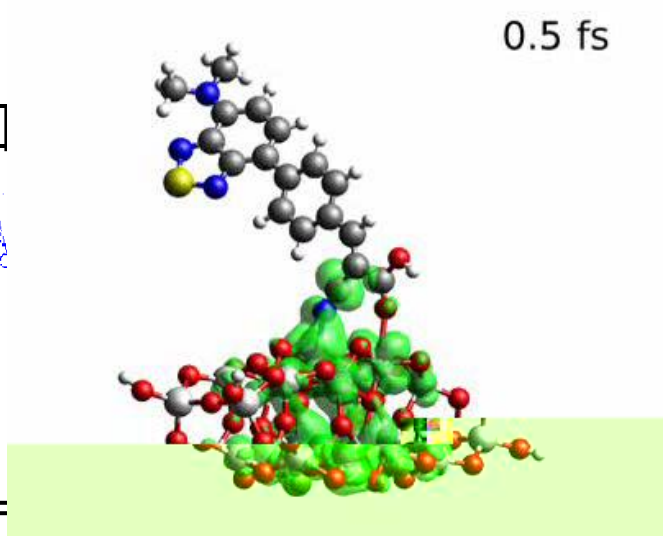
Solvent effect







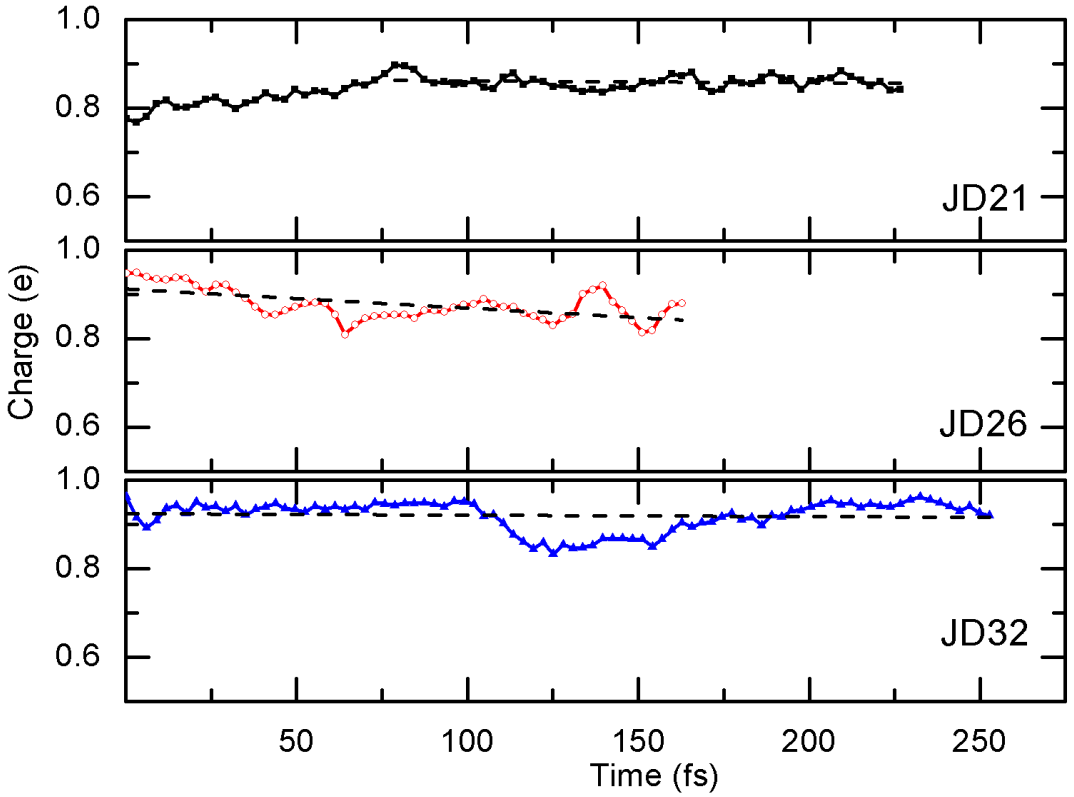


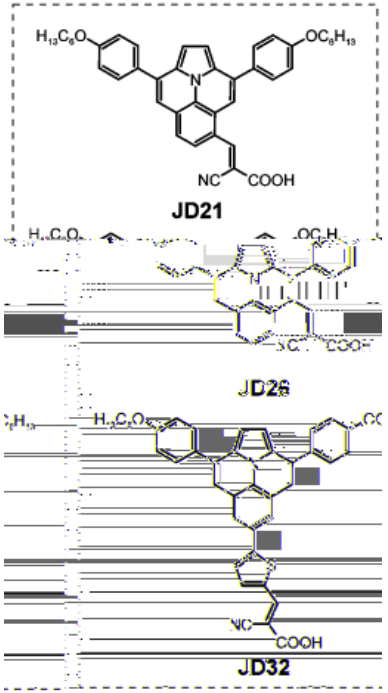


Experiment: 5 times difference using ultrafast laser photolysis.

Ma, Jiao, Meng, PCCP (2013).

Electron Collection Efficiency





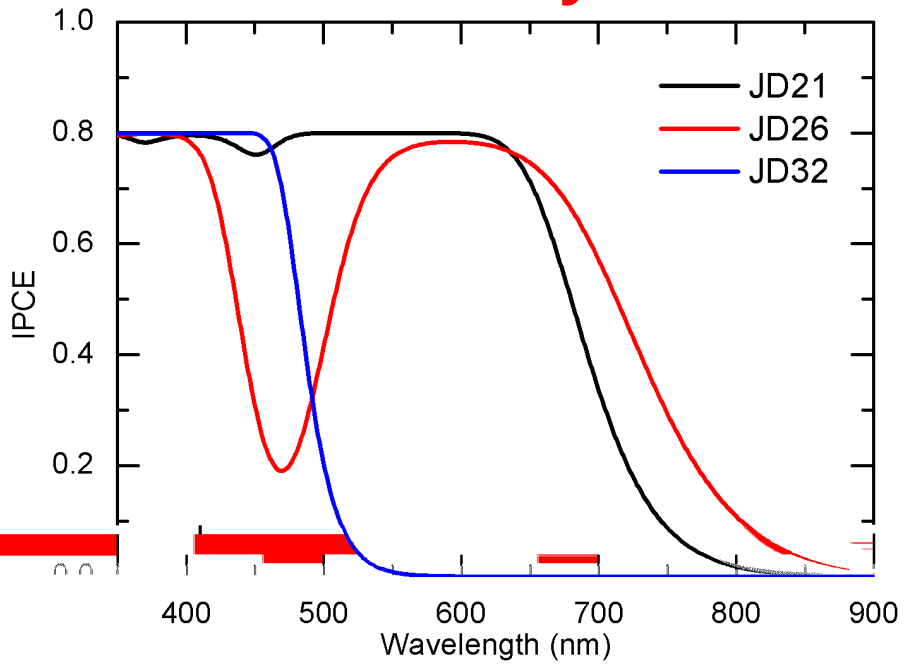
$$\eta_{b} = 1 \Big/ \left(1 + \frac{\tau_{a}}{\tau_{e}} \right)$$

$$a = 5\ P(\quad)$$

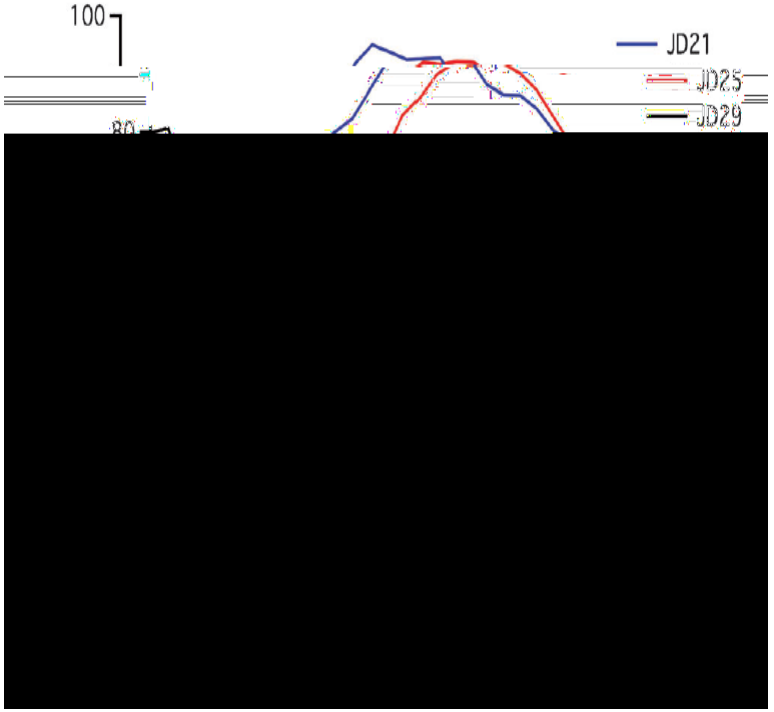
η			

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

Theory



Experiment



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

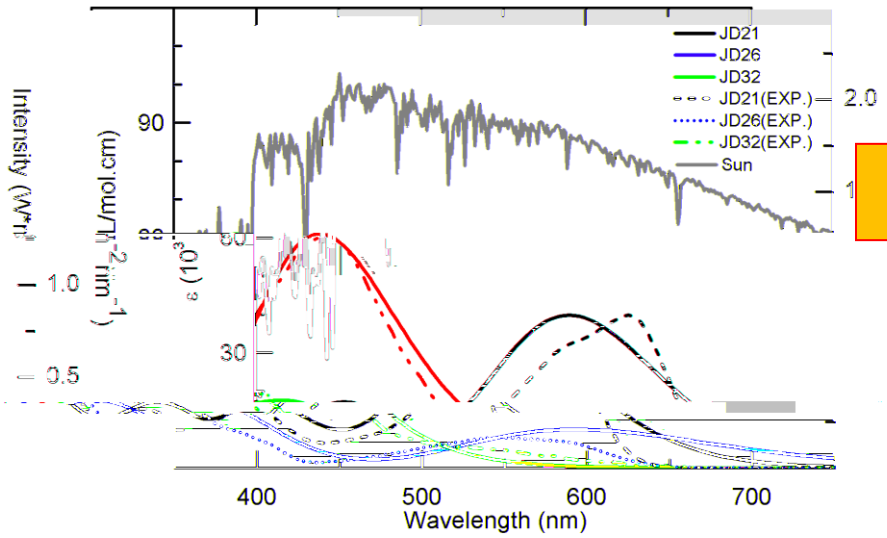
Estimating the V_{OC}

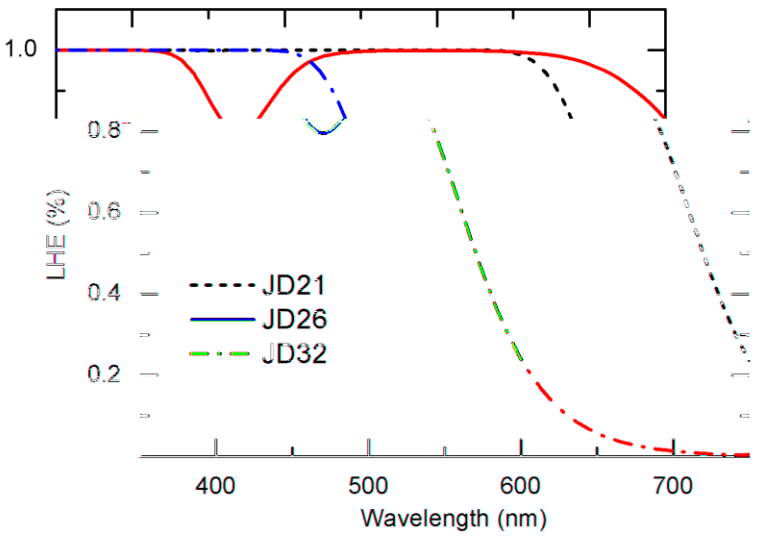
$$V_O = \frac{kT_B}{\beta' q} \ln \frac{\beta' q J_{0\,sc}}{kT_B}$$

$$R_0 = \frac{\sqrt{\pi \lambda k T_B}}{q^2 k \gamma c_{ex} N_s} \left(\gamma \frac{E_{ex} - E_F}{kT_B} + \frac{\lambda}{4} \right) \qquad k_{ex} = 1$$

D	k^{-1}_{in} (s)	k^{-1}_{ex} (ps)	J_{sc} / (mA cm^{-2})	V_{OC} (mV)	FF	J_{sc} (mA cm^{-2})	V_{OC} (mV)	(%)		
D	0	3	8	7	0	4	9	0	8%	8%
D	0	2	6	9	0				2%	
D	0	8	4	6	0	3	5	0	1%	1%

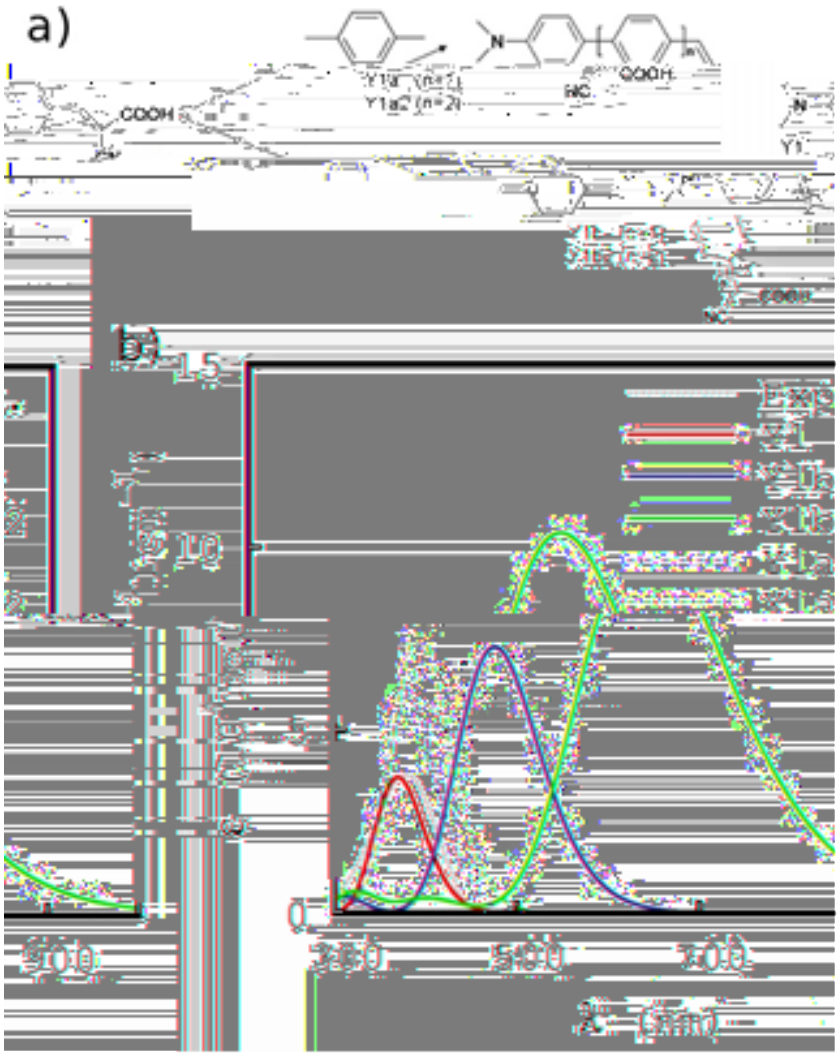
Red: Theory Blue: Experiment

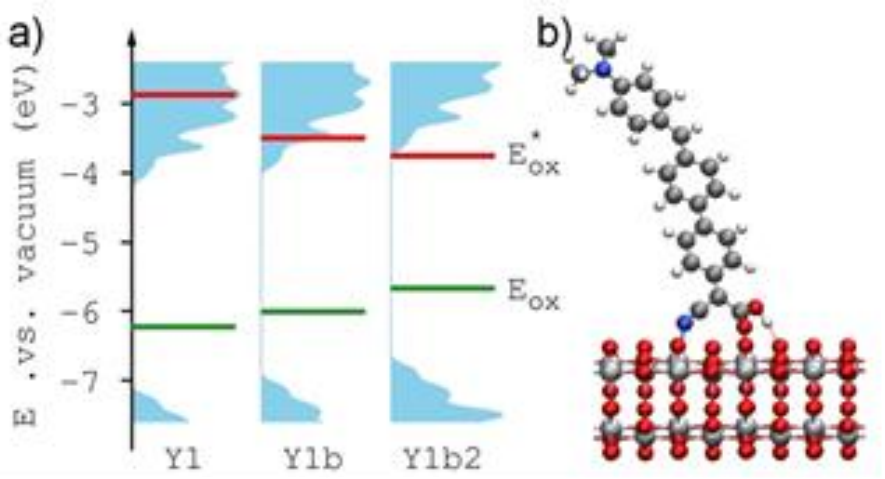




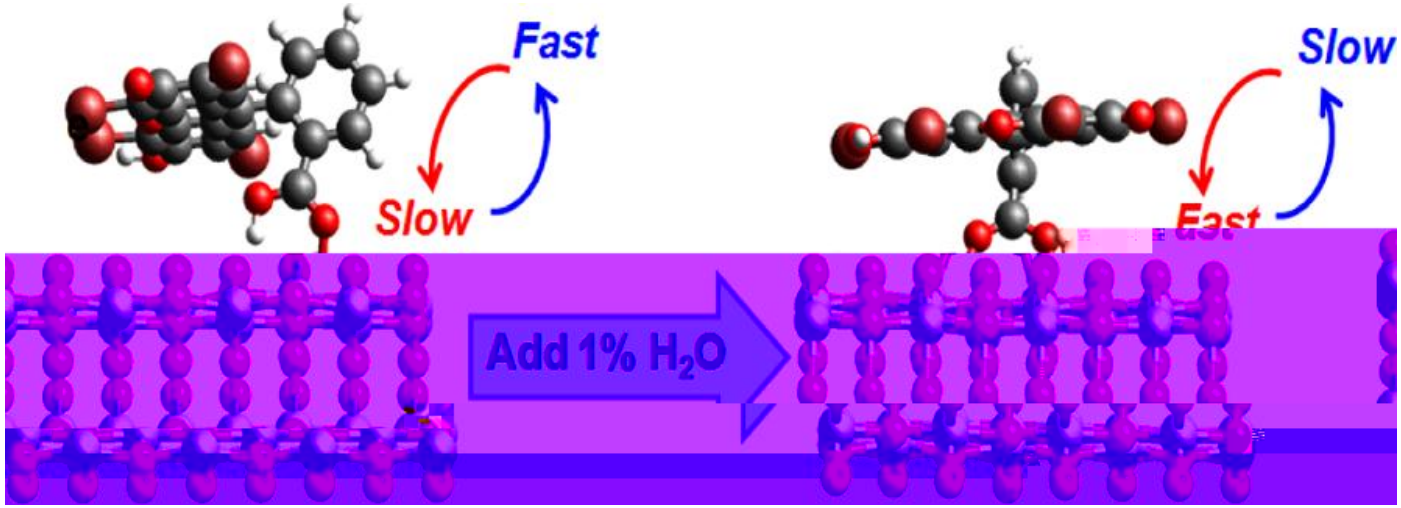
Quantum mechanics based, parameter free

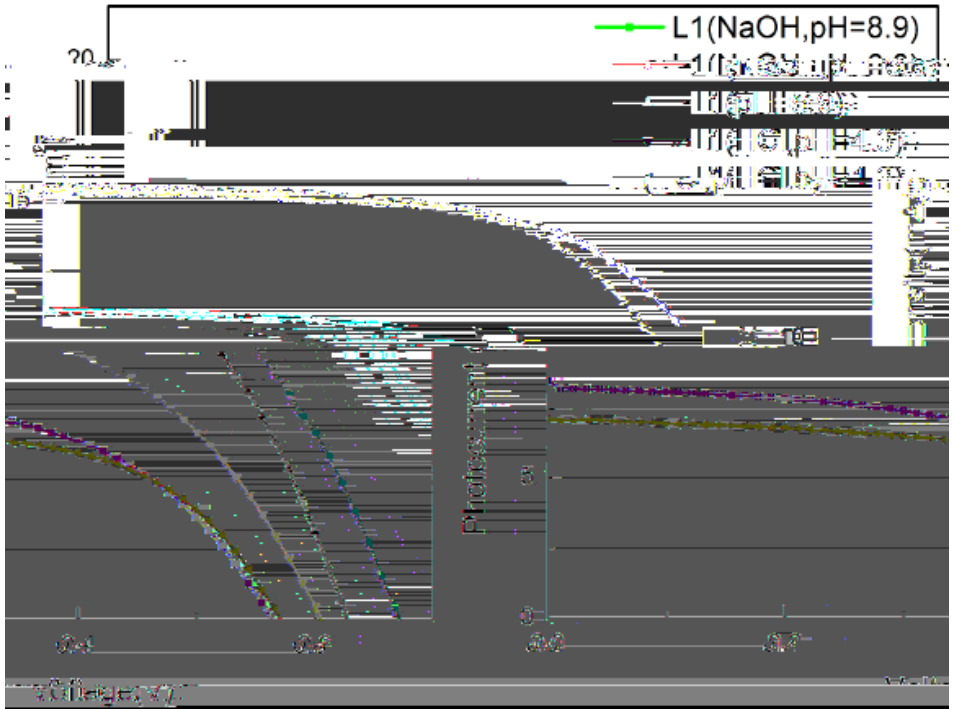
Close to experiment values:1-2%





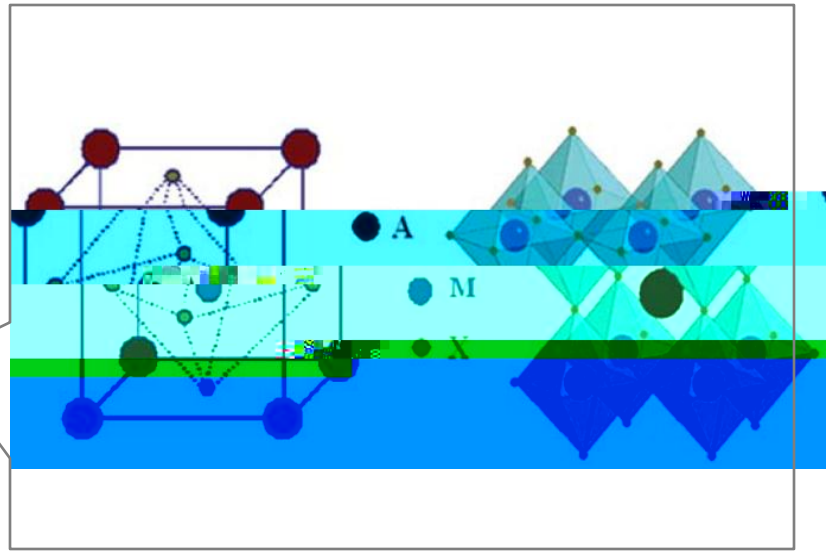
Jiao, Ma, Meng , Chem. Phys. Lett. (2013).

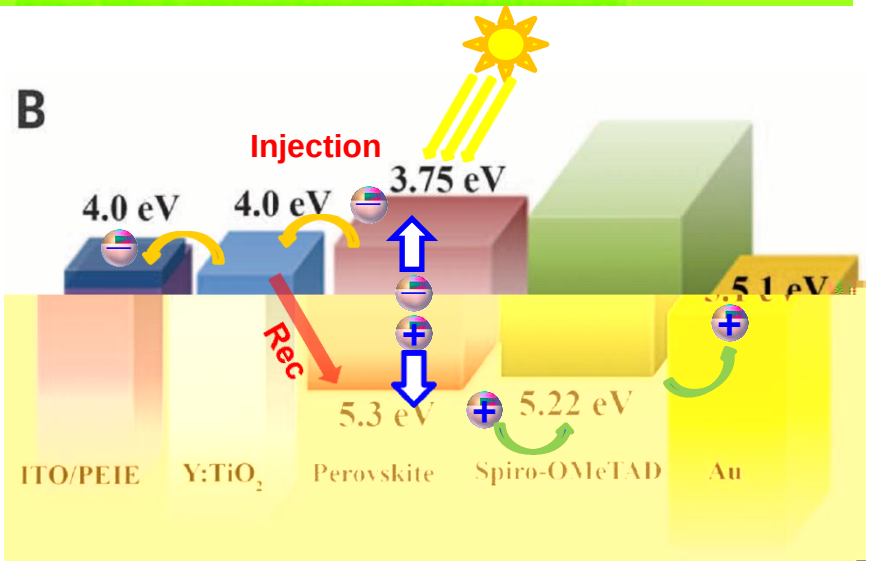




η 2.4% 6.1%

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





Problems:

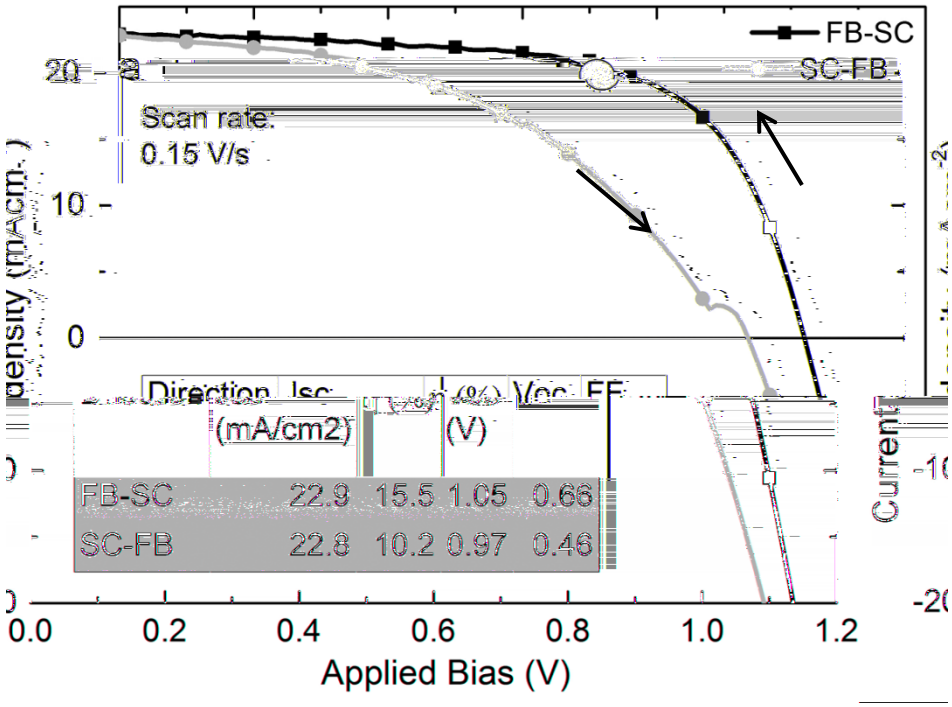
1.Pb

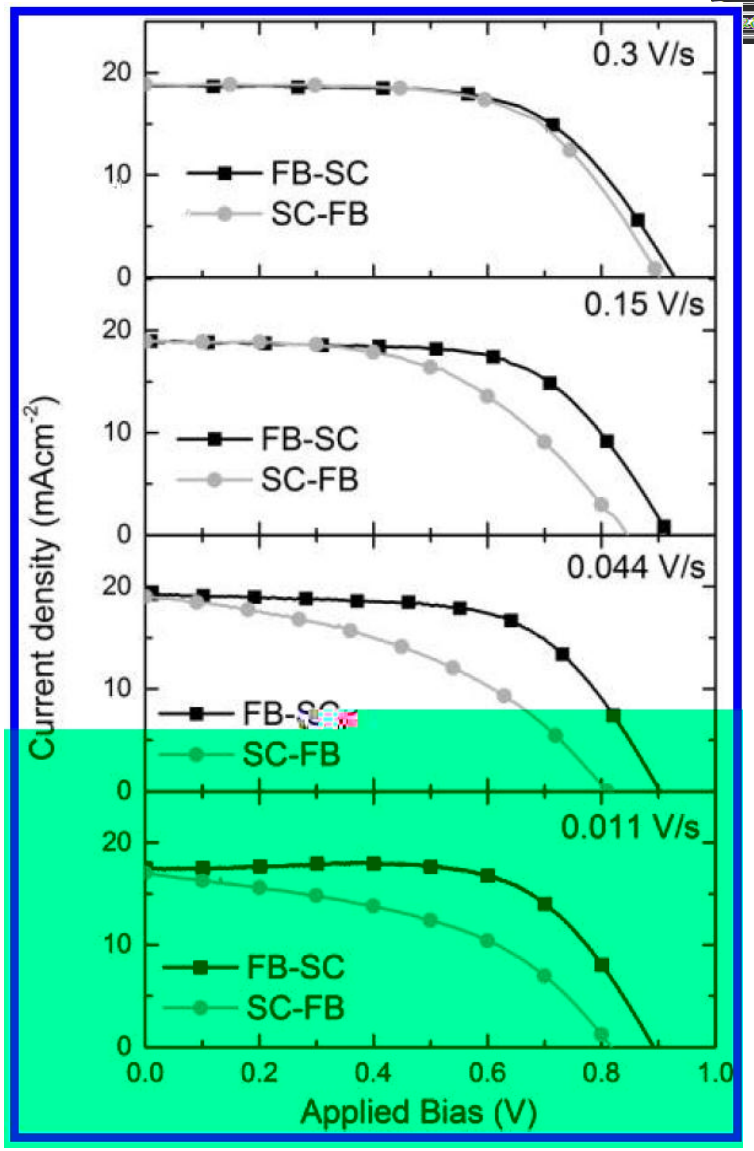
2. Unstability

3. Hysteresis

Perovskite solar cell $\eta = 20.1\%$

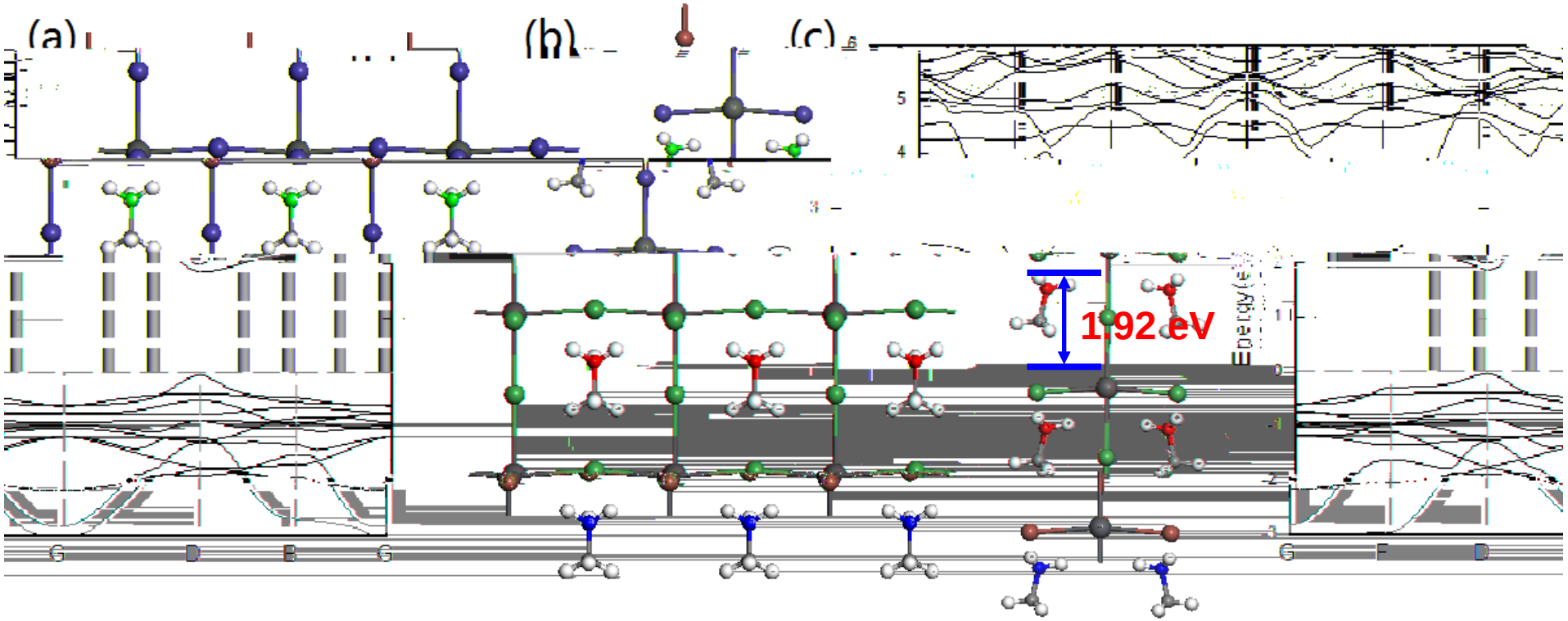
Anomalous hysteresis

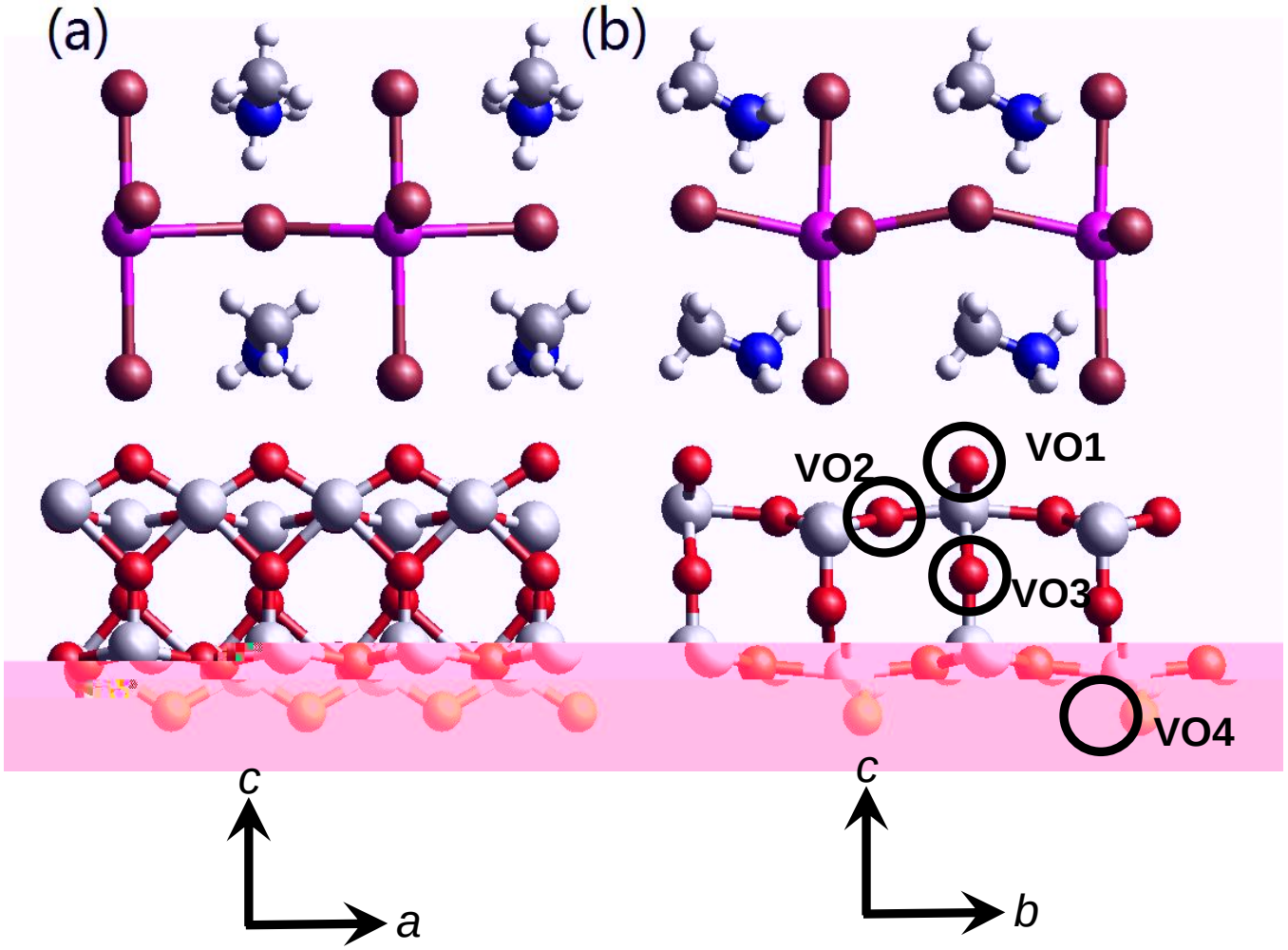


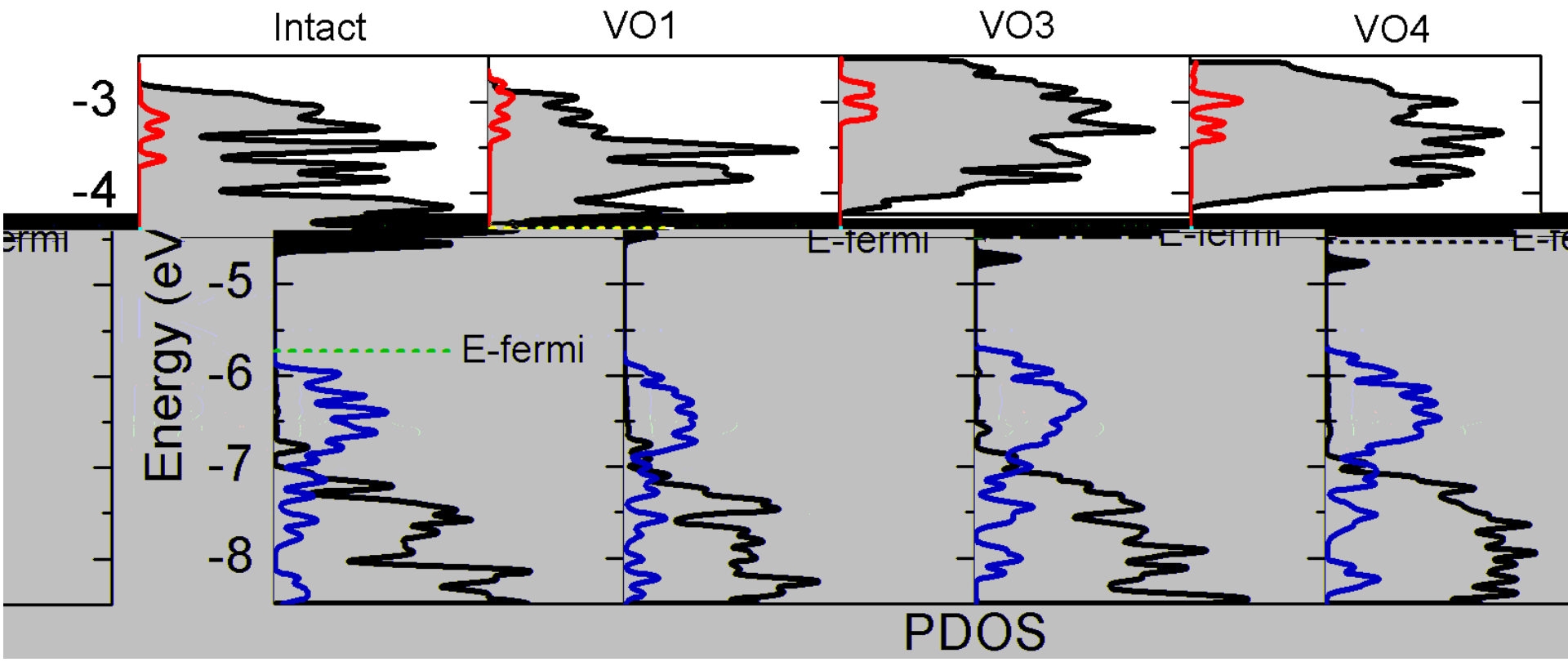


Snaith et al. JPCL (2014).

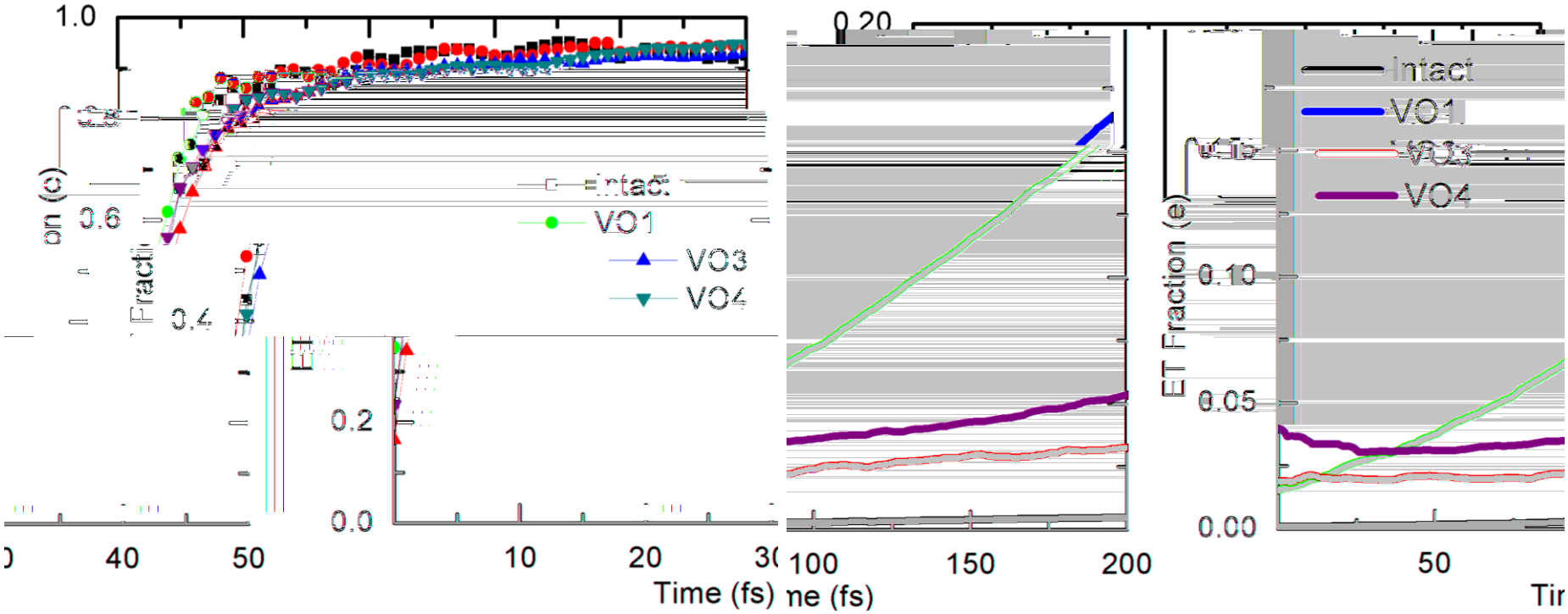
Band Structure




(a)
(b)
VO2
VO1
VO3
VO4
c
a
c
b

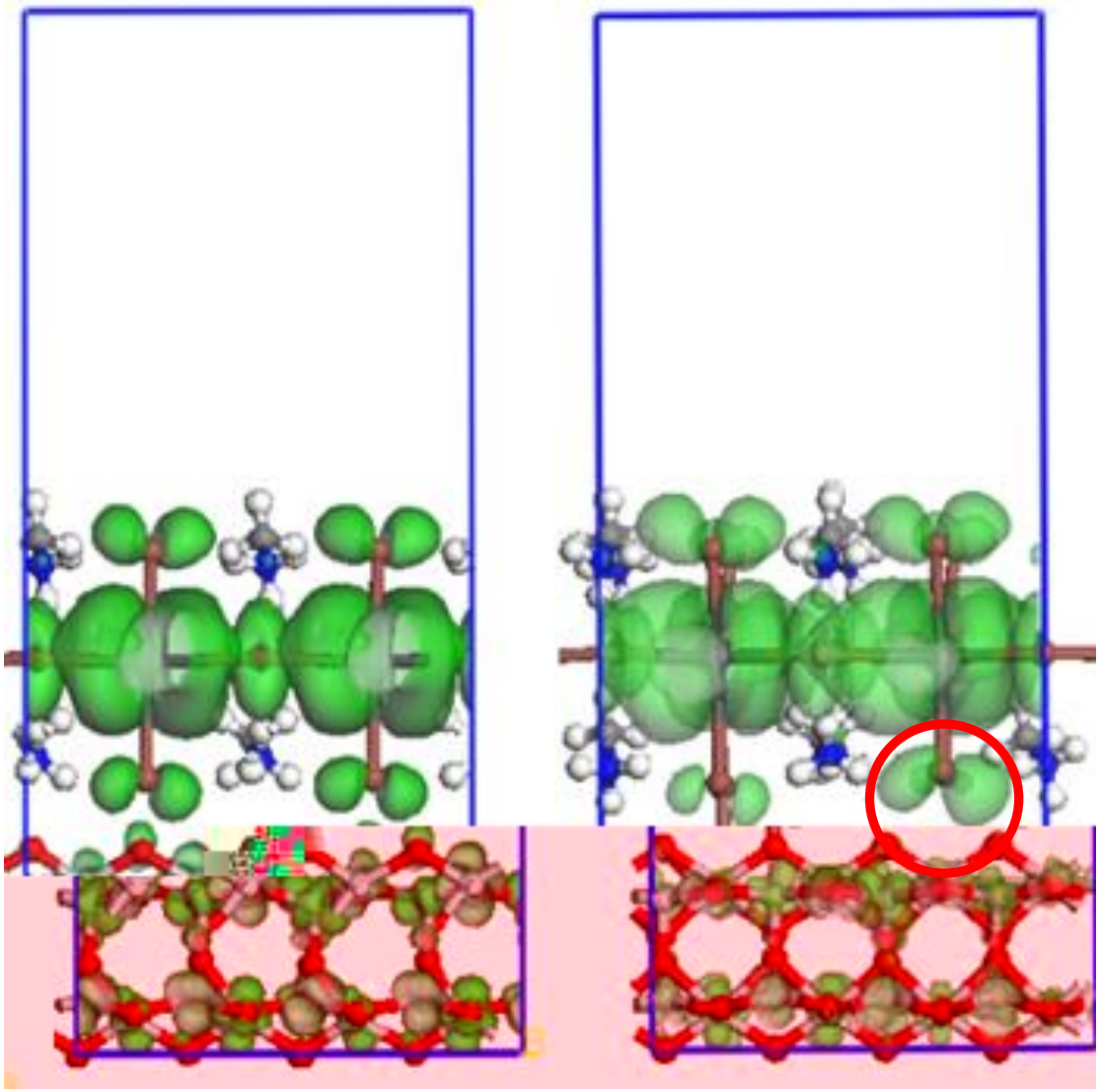

Intact
VO1
VO3
VO4
-3
-4
-5
-6
-7
-8
Energy (eV)
E-fermi
E-fermi
E-fermi
PDOS

DFT+U (U=4.2 eV)

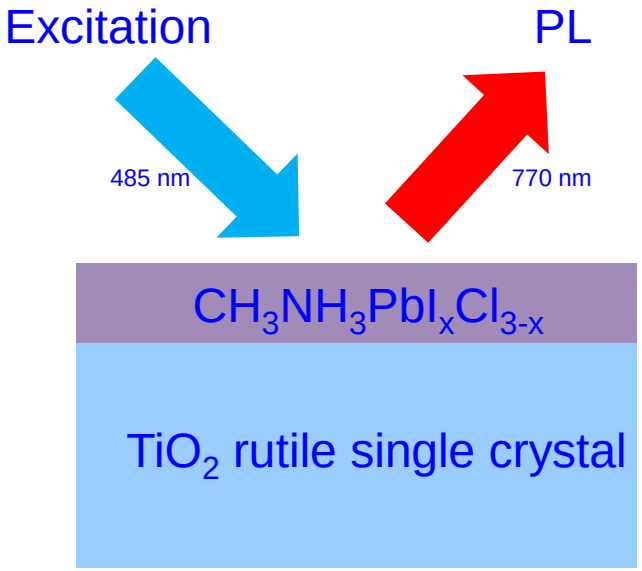

1.0
0.6
0.4
0.2
0.0
Intact
VO1
VO3
VO4
40
50
10
20
Time (fs)
0.20
0.10
0.05
0.00
ET Fraction (e)
100
150
200
50

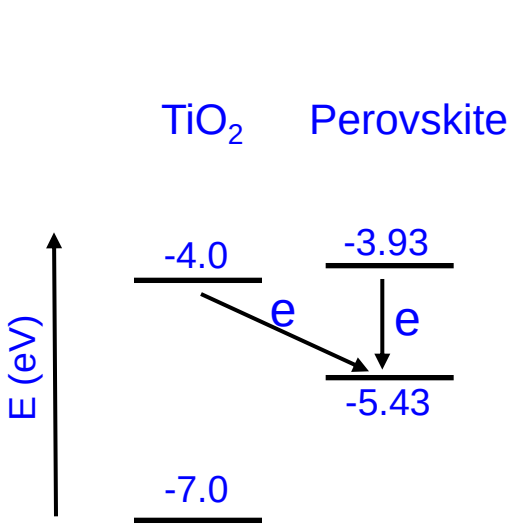
perfect

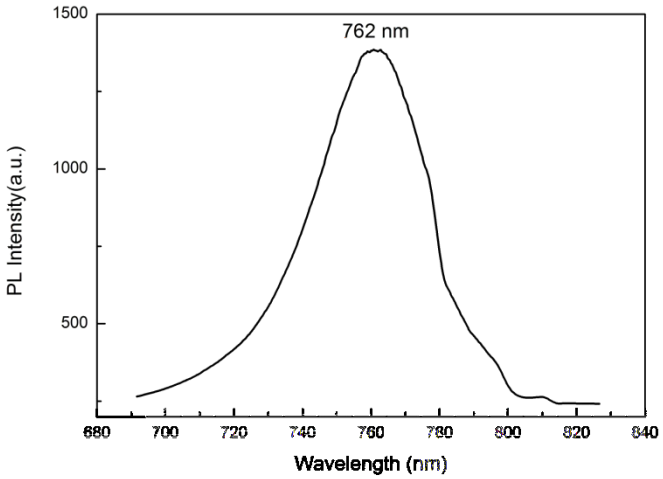
with Vo



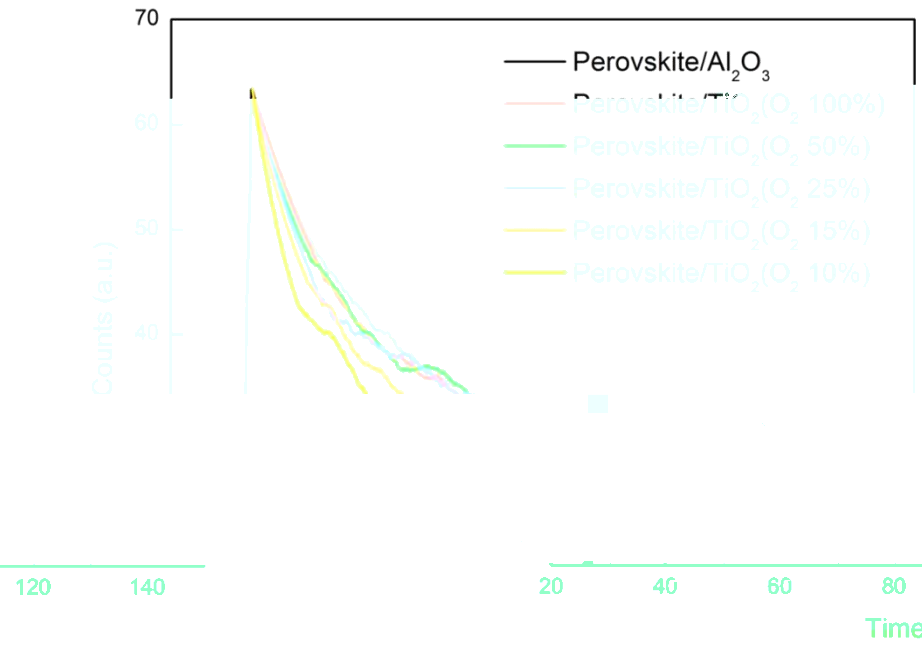
Experiment: Photoluminescence Spectra







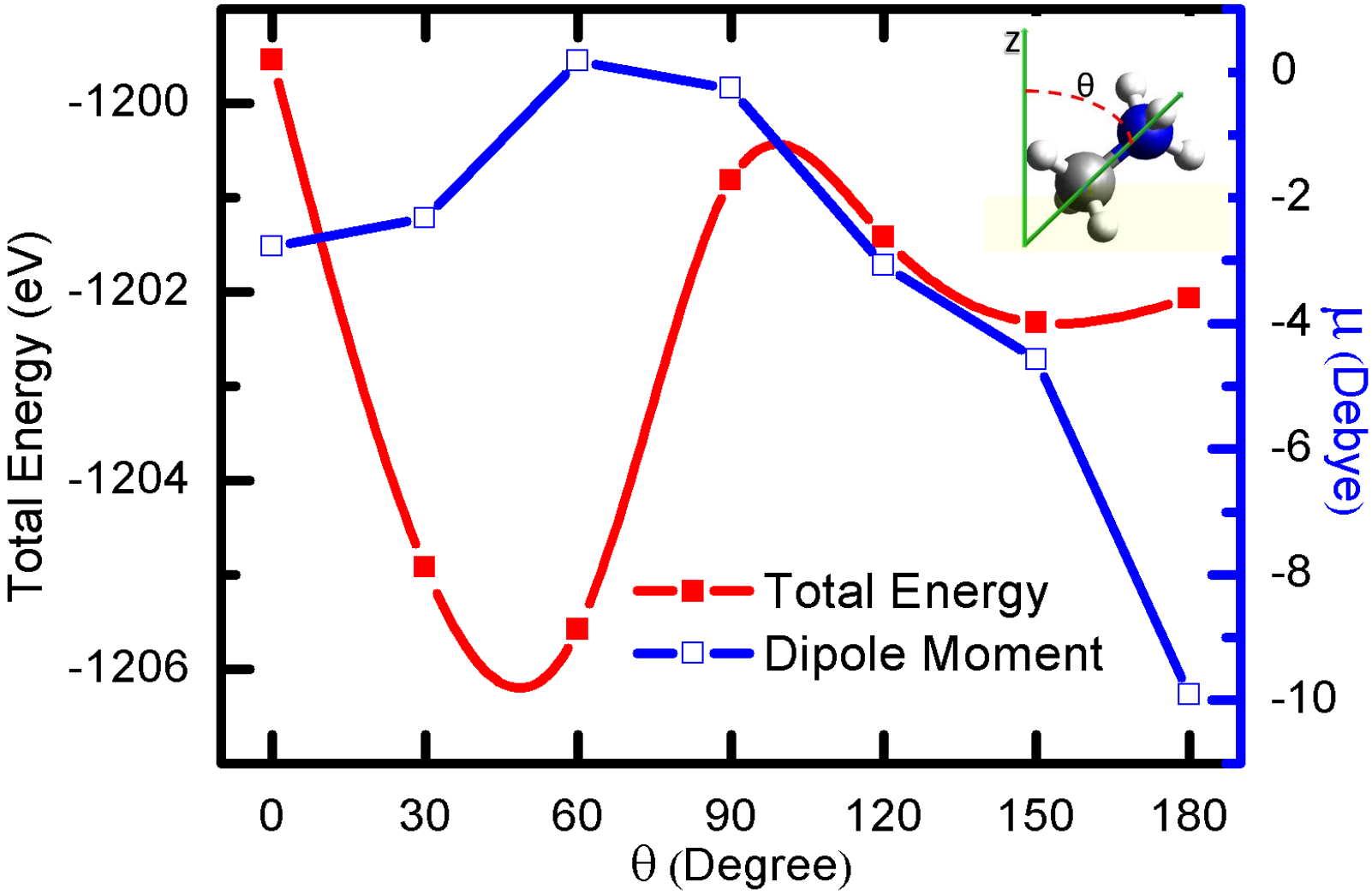
PL spectra (532 nm excitation)



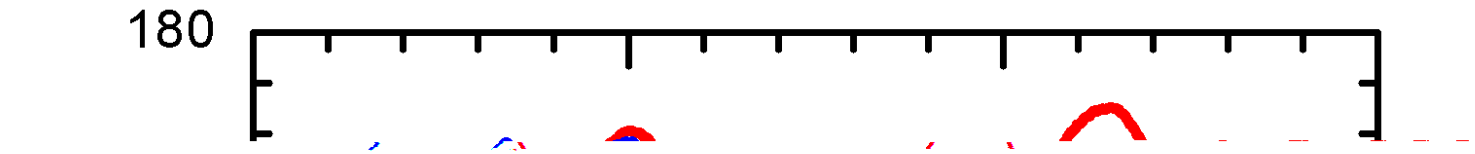
O_{vac}

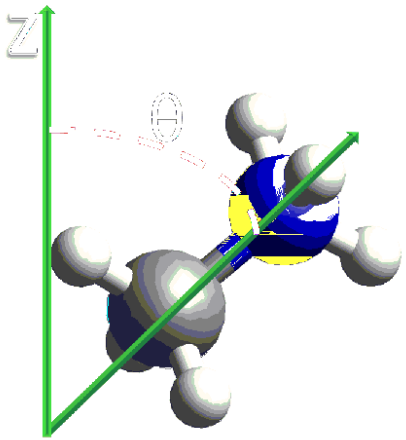
增加

MA Orientation



Molecular Dynamics Simulation at 350 K

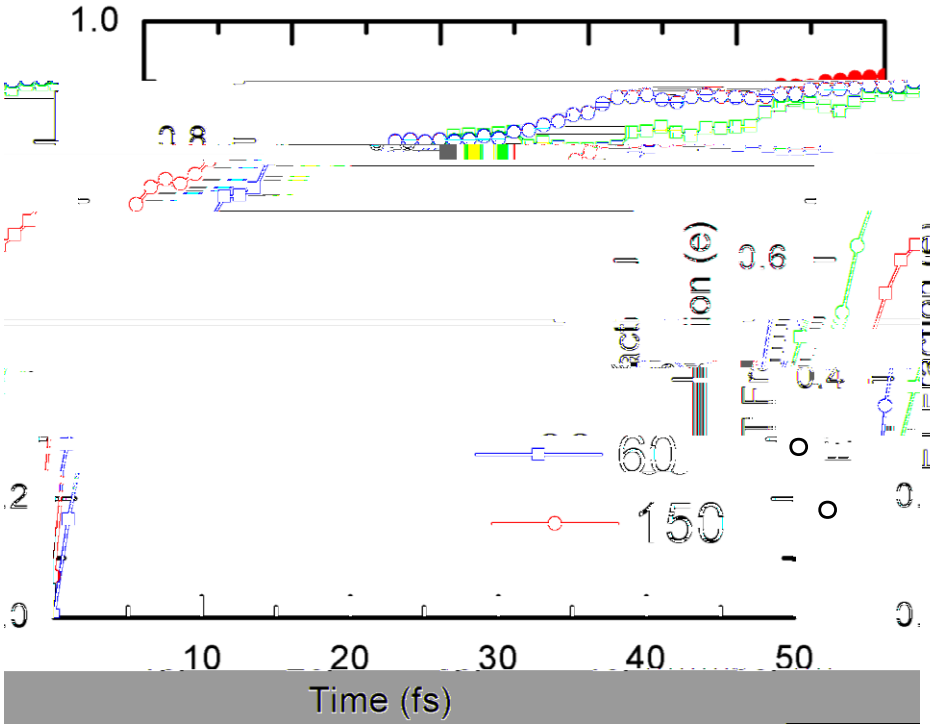


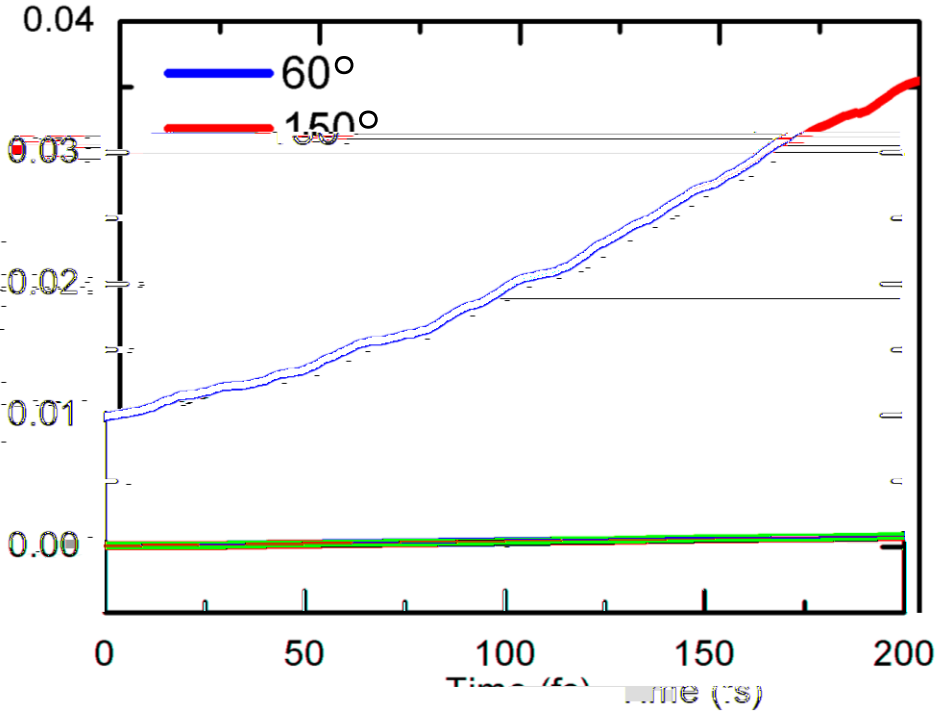


500 1000 1500

Time (fs)

Injection and Recombination Dynamics





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

-
- 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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