First-principles calculations of electron and hole transfer rates in organic and hybrid photovoltaic devices

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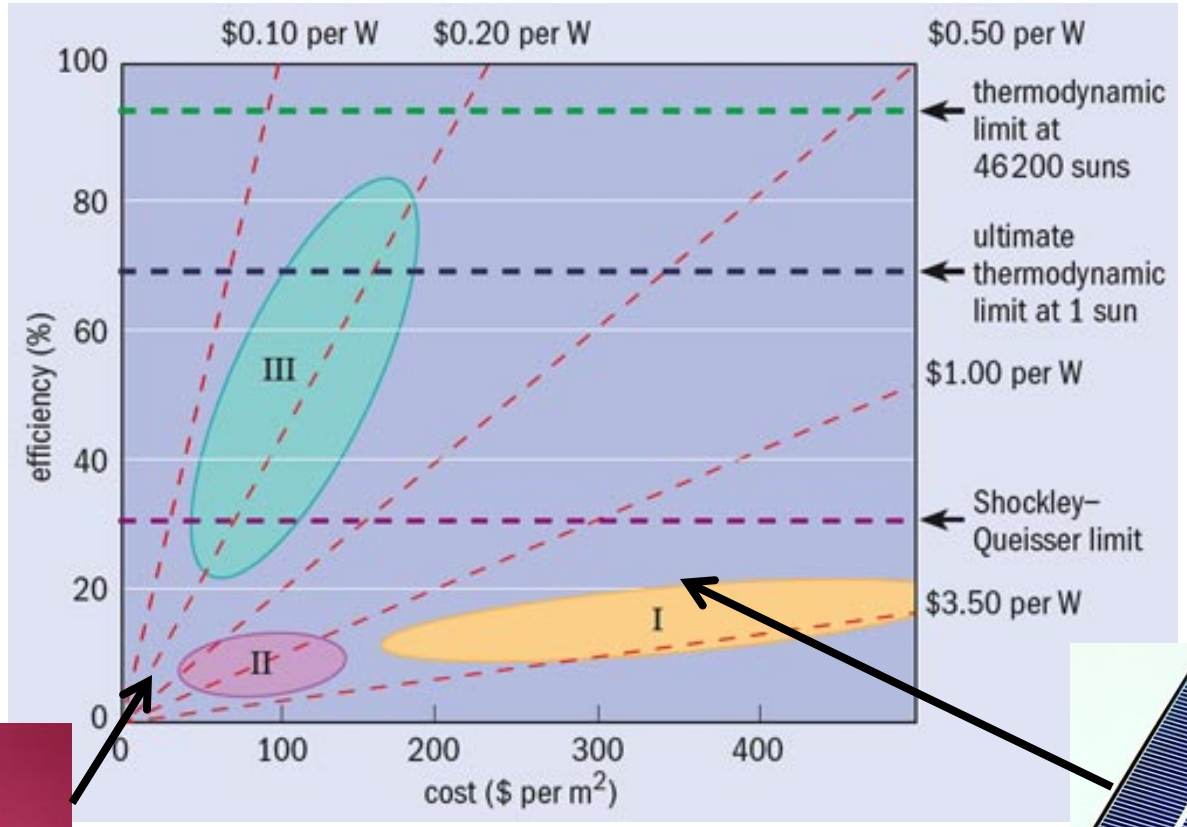
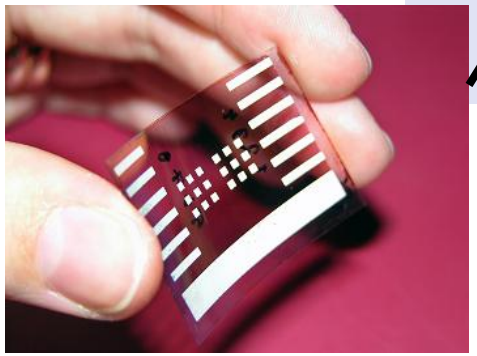
5th International Symposium on Flexible Organic Electronics (ISFOE12)

2-5 July 2012, Thessaloniki, Greece

Quest for affordable solar energy

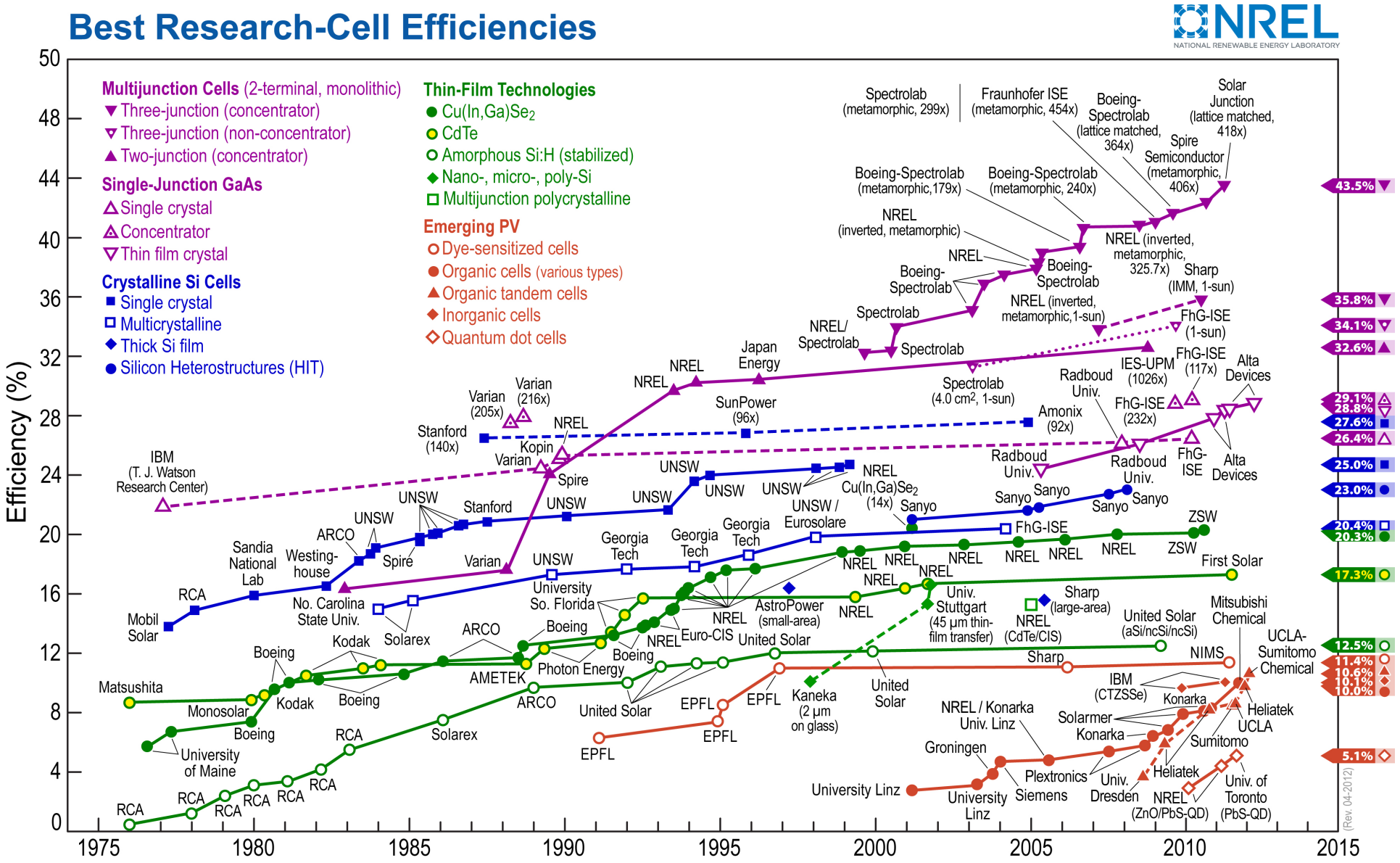




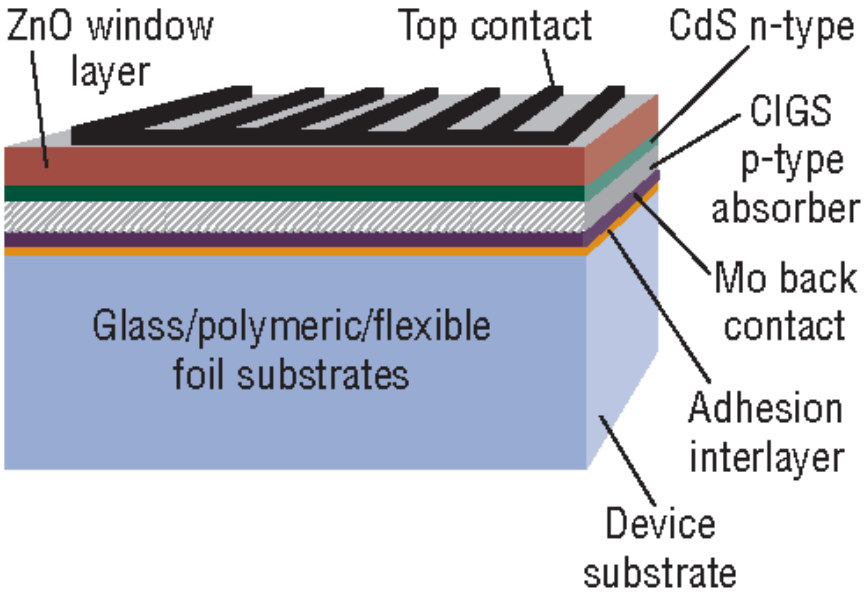
OPV

c-Si panel

Best Research-Cell Efficiencies

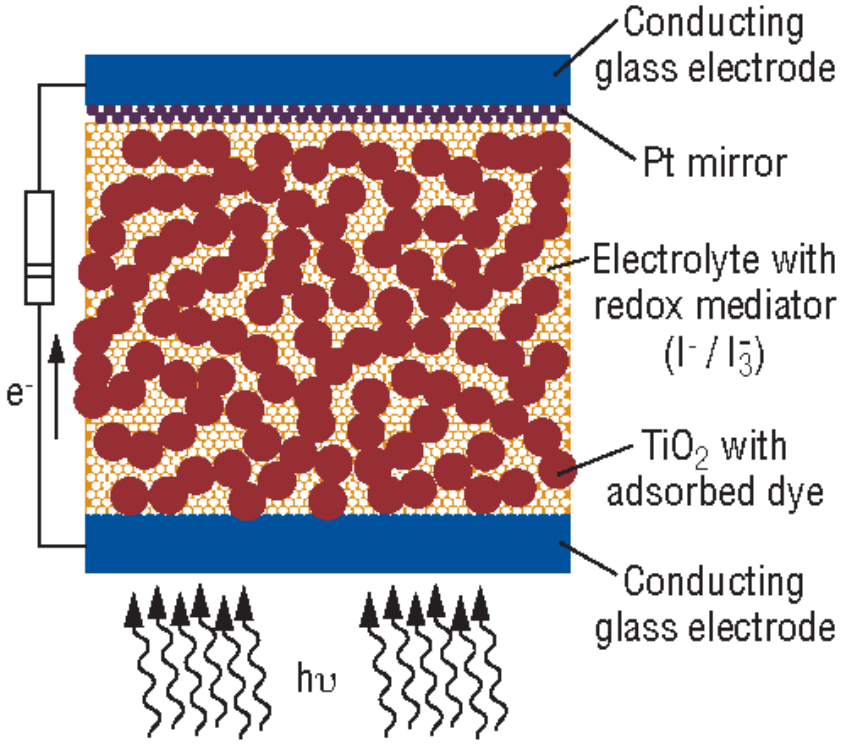


Copper-Indium-Gallium-Selenide cell



Conventional p-n junction cell (inorganic)
Physically simple, technically complex

Dye-sensitized cell (hybrid organic/inorganic)
Technically simple, physically complex

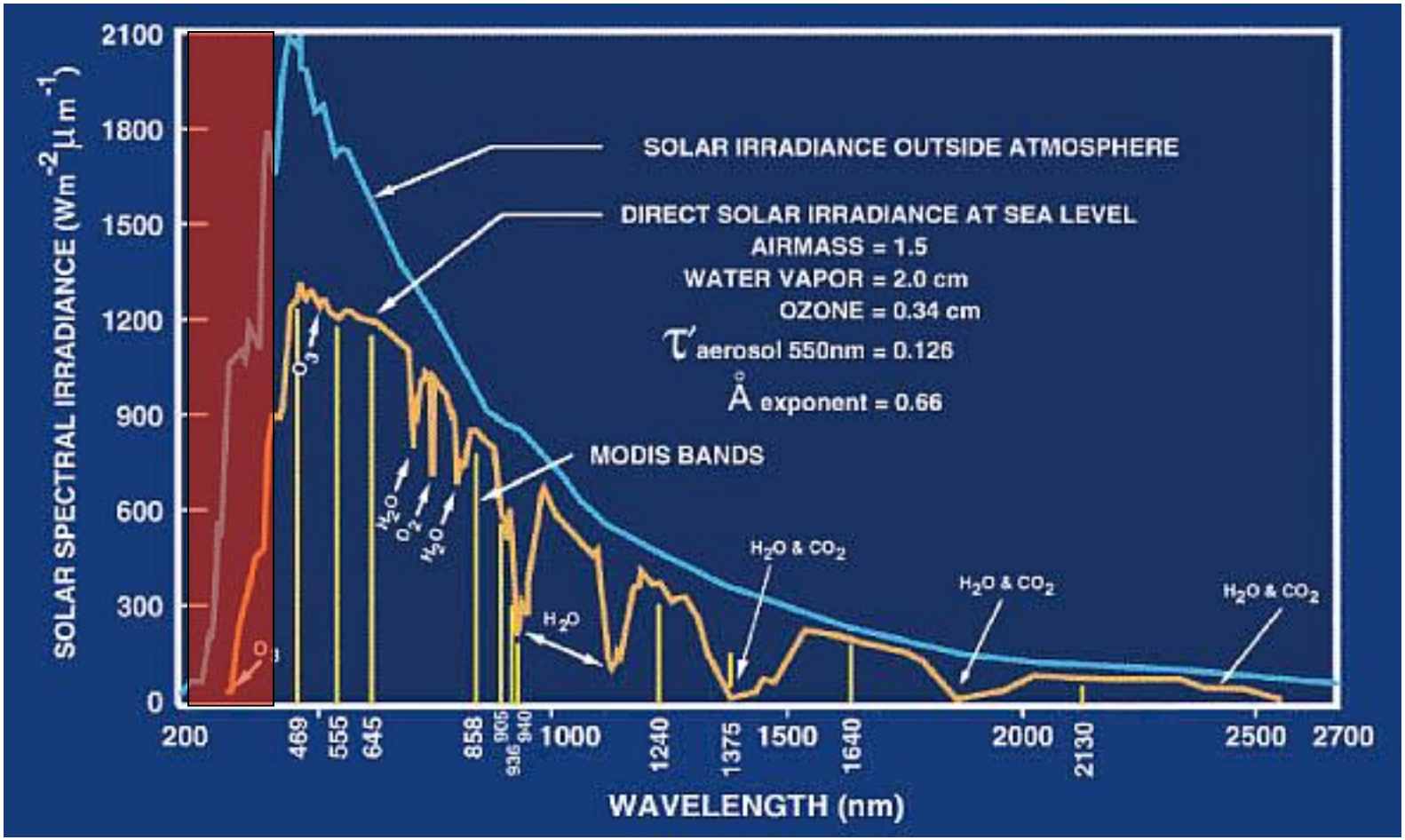


O'Regan & Graetzel, Nature (1991)

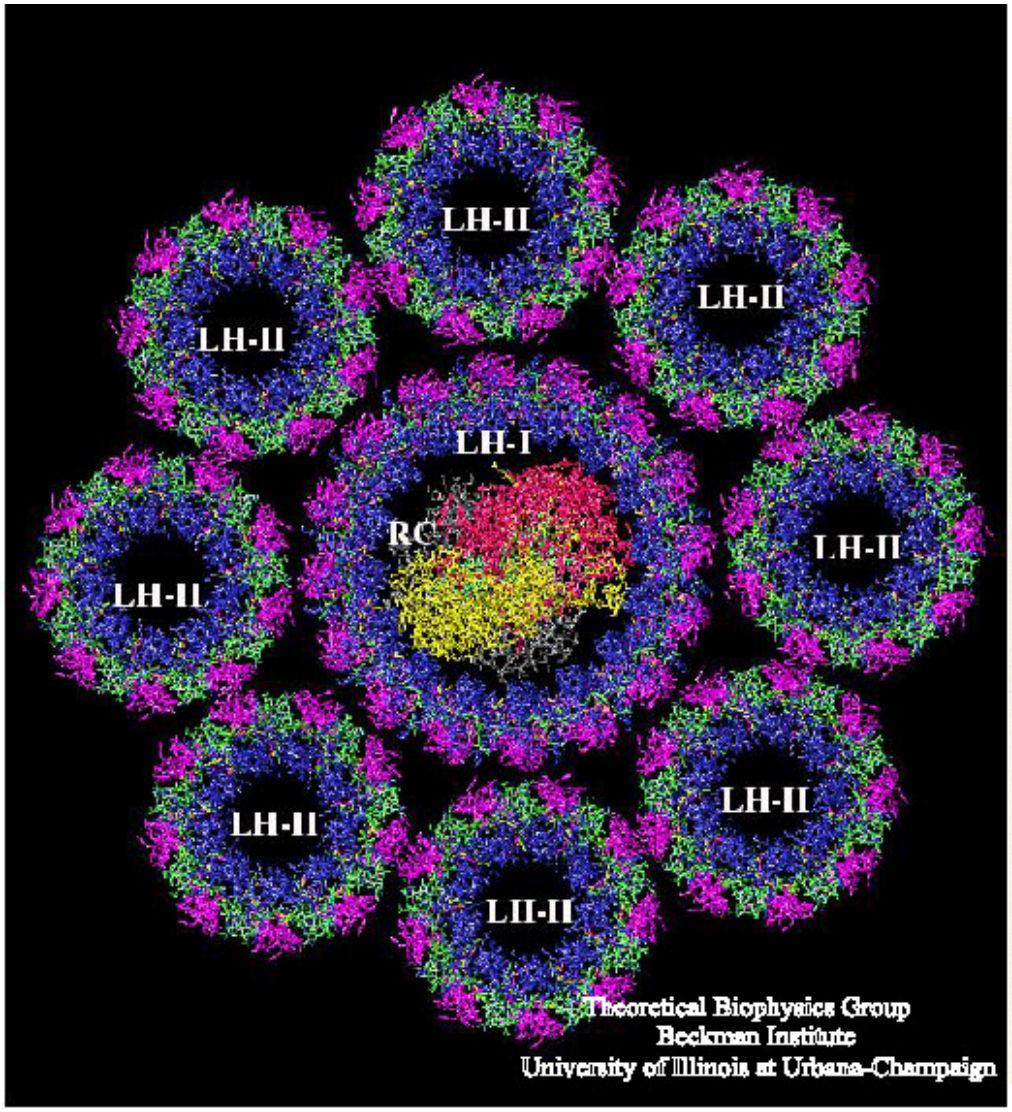
- The Problem: materials for carrier transport with large band gaps

  TiO_2 gap = 3.2 eV (200 nm < λ < 400 nm)

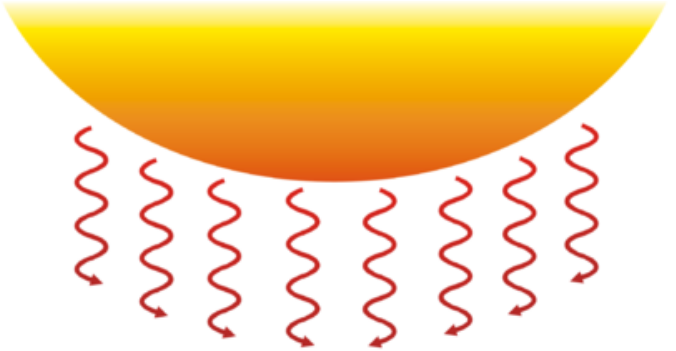
solar spectrum

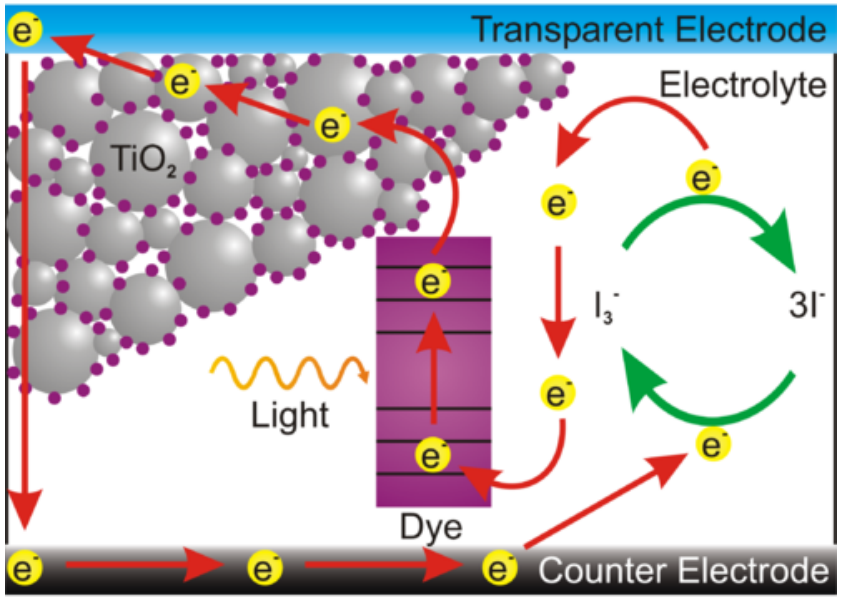


The Principle: separate light-absorption and charge collection processes



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





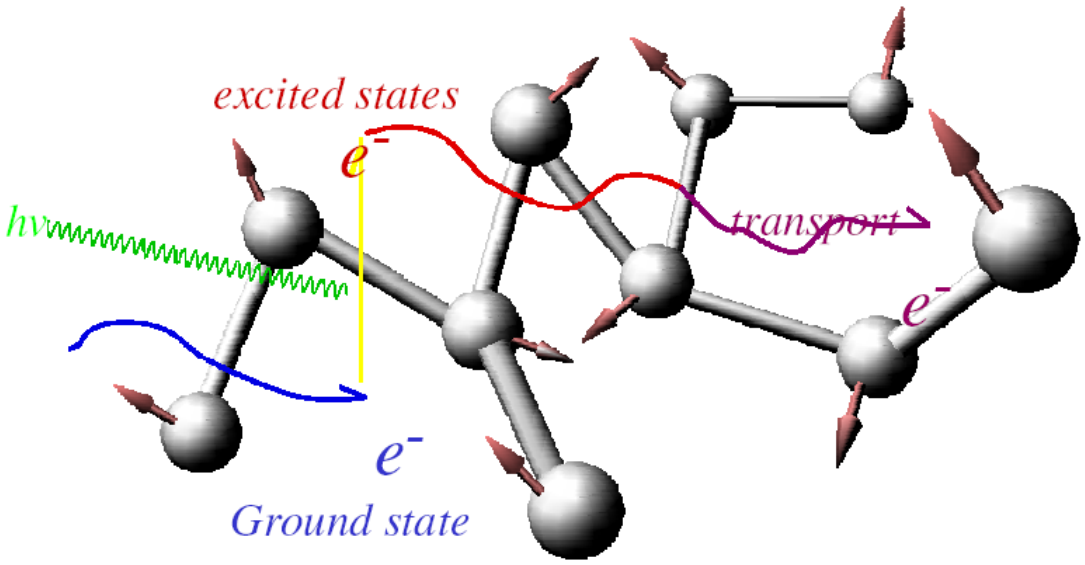
Main issue: coupled electron-ion dynamics

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

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

Coupled electron-ion dynamics

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

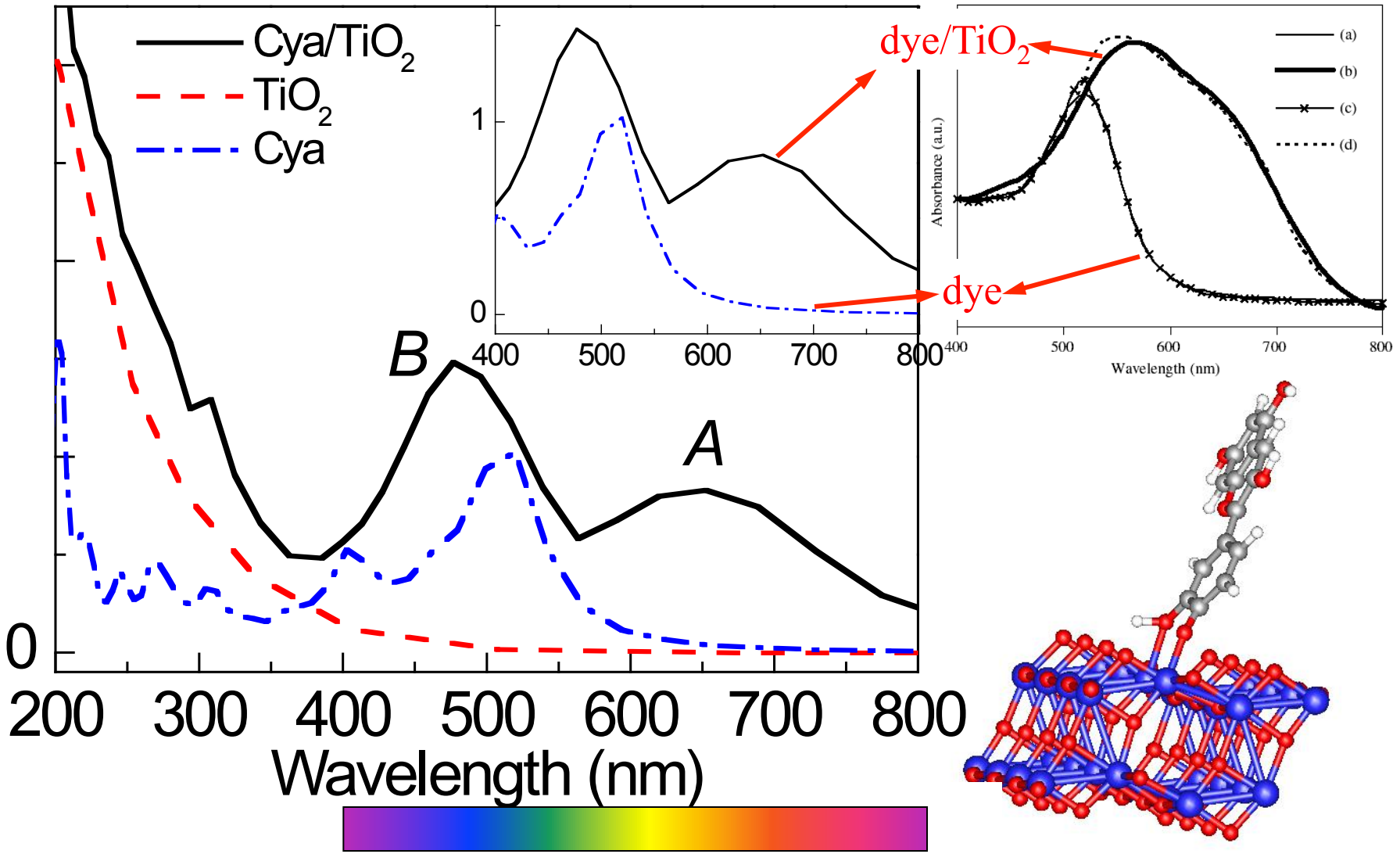
$$\begin{cases} i\hbar\dfrac{\partial\phi_j(\mathbf{r},t)}{\partial t} = \left[-\dfrac{\hbar^2}{2m}\nabla^2_{\mathbf{r}} + v_{ext}(\mathbf{r},t) + \displaystyle\int\dfrac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' - \sum_I \dfrac{Z_I}{|\mathbf{r}-\mathbf{R}^{cl}_I|} + v_{xc}[\rho](\mathbf{r},t)\right]\phi_j(\mathbf{r},t)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

Propagation of electrons in time (TDSE) + Ehrenfest dynamics for ions

Optical absorption (TDDFT)

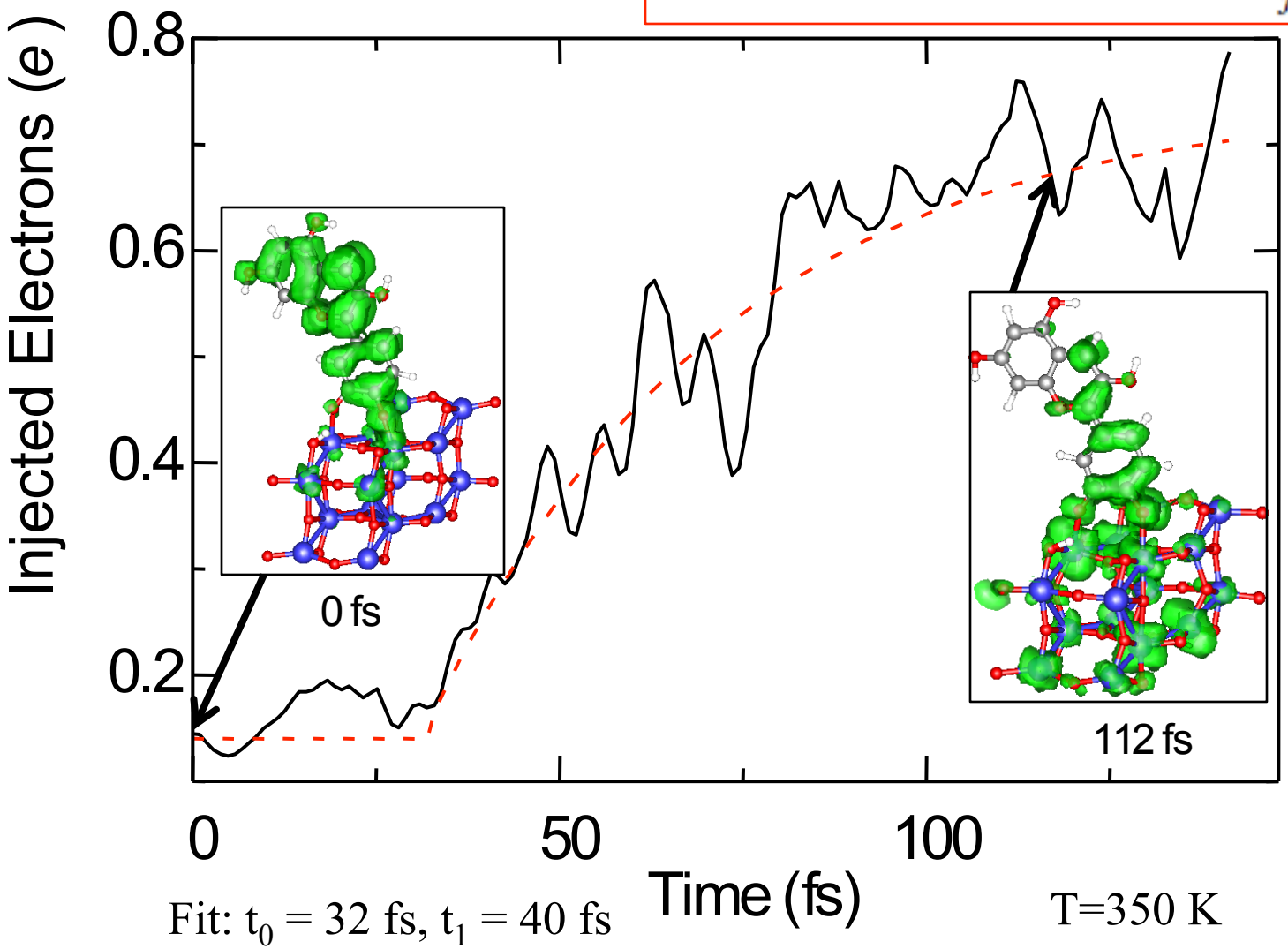
Calculated

Experiment (Wongcharee et al., 2007)



Charge injection dynamics:

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



Fit: t_0 = 32 fs, t_1 = 40 fs

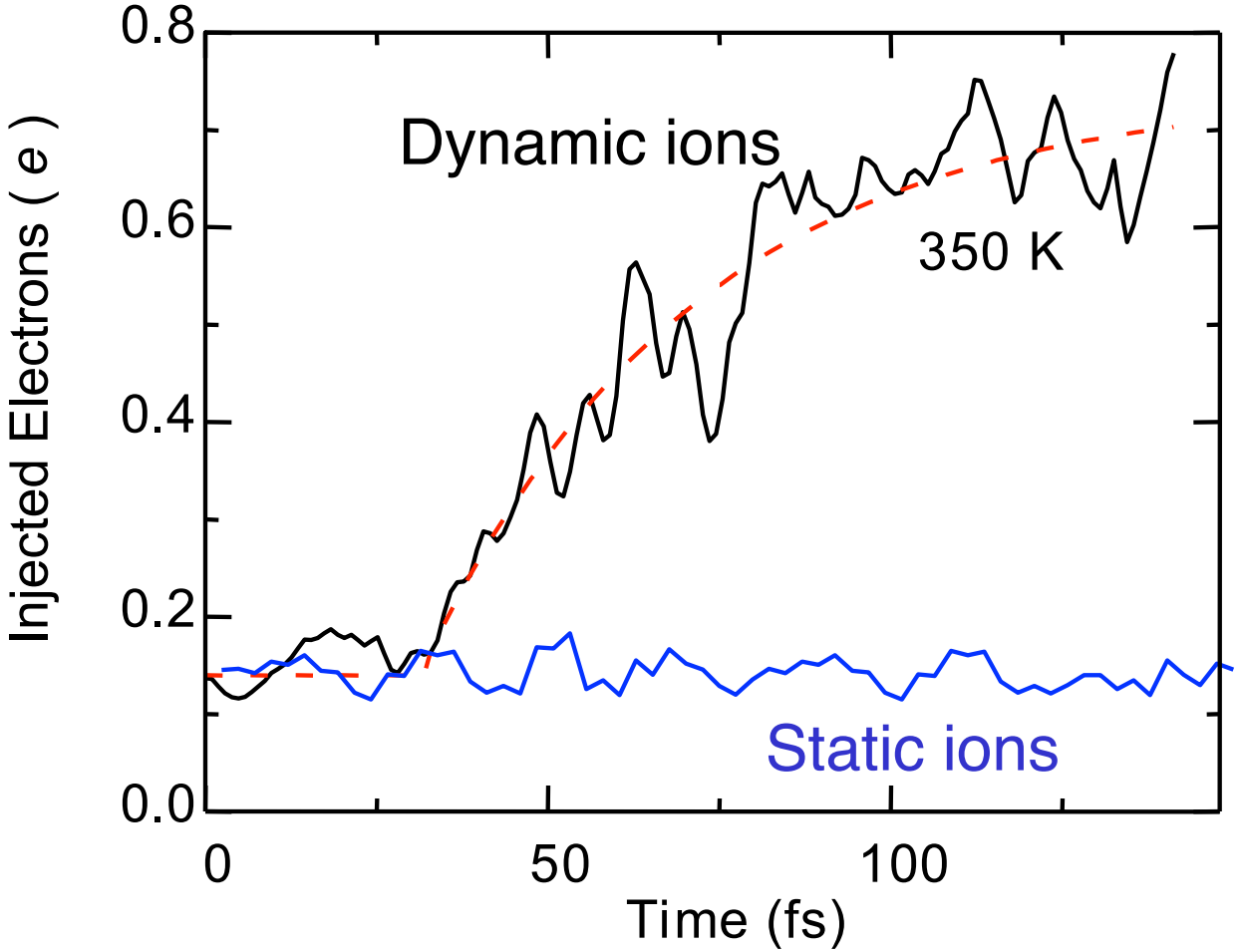
Expt.[a] : <100 fs

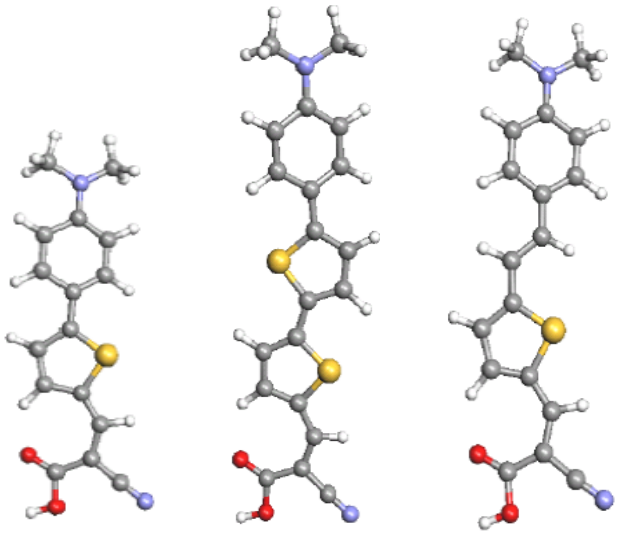
T=350 K

δt=0.02419 fs

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

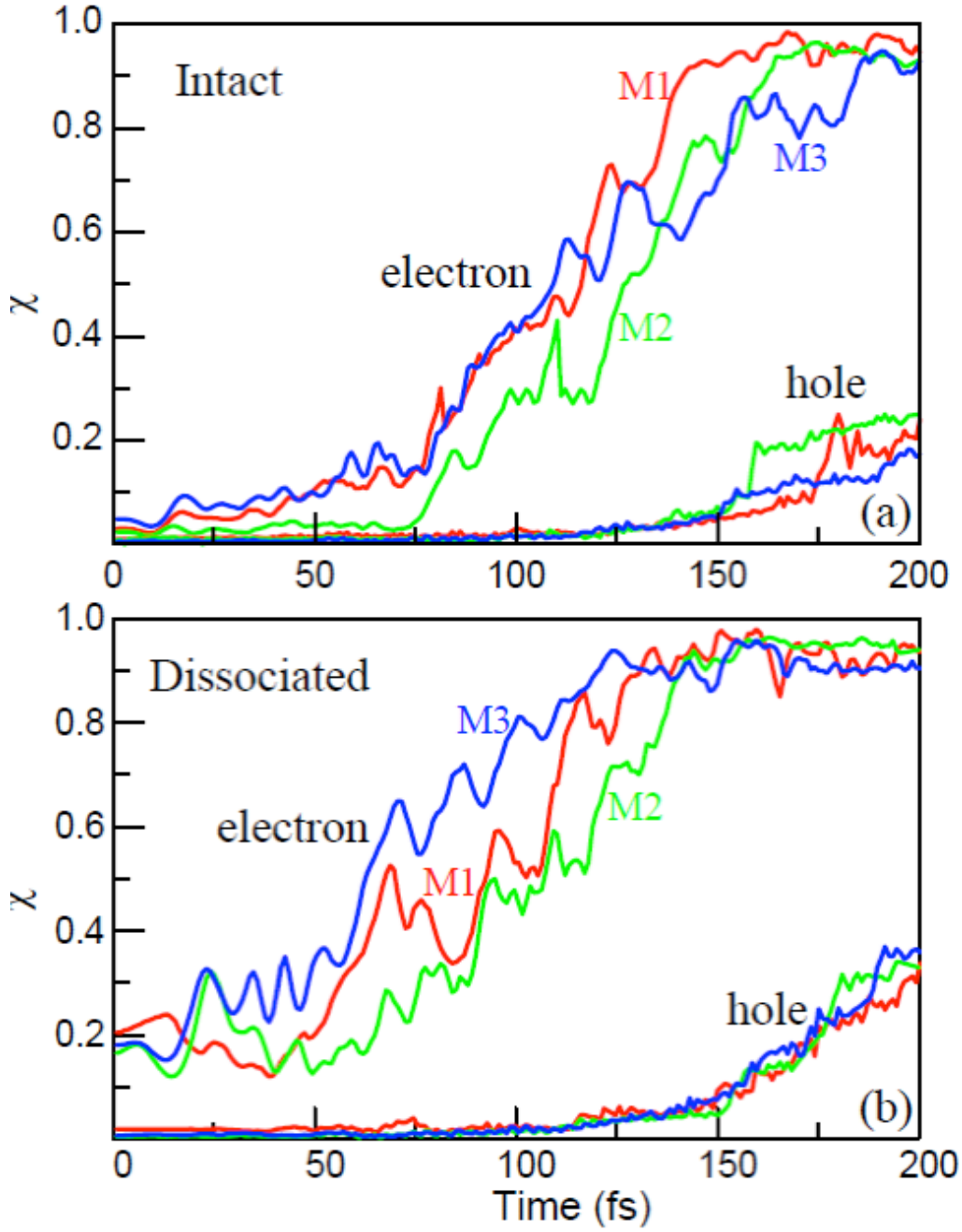
Importance of coupled e-ion dynamics



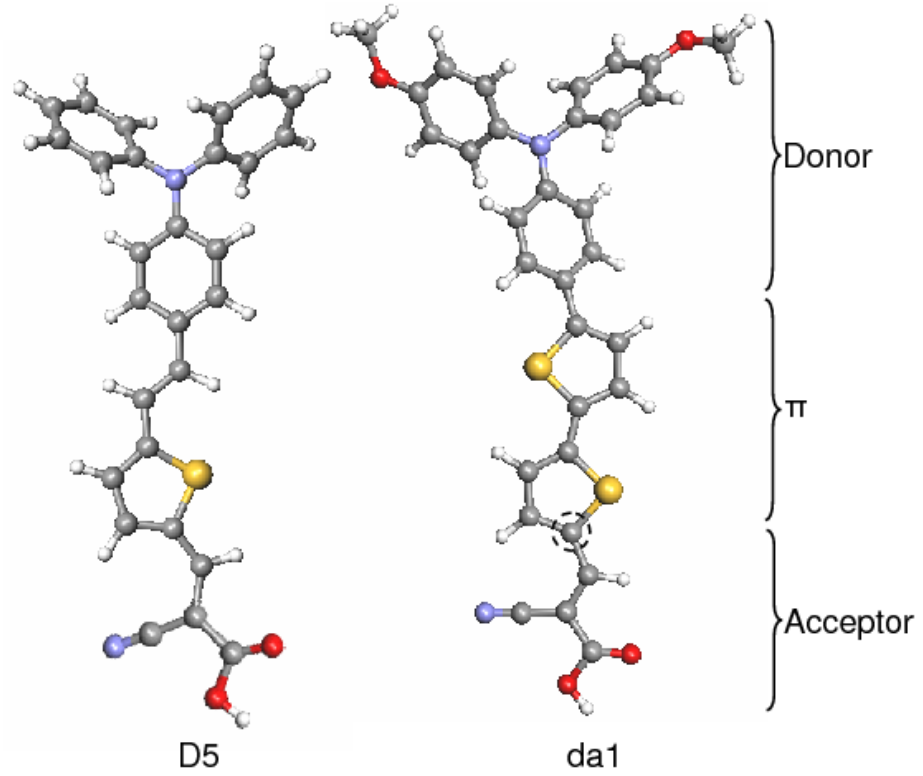


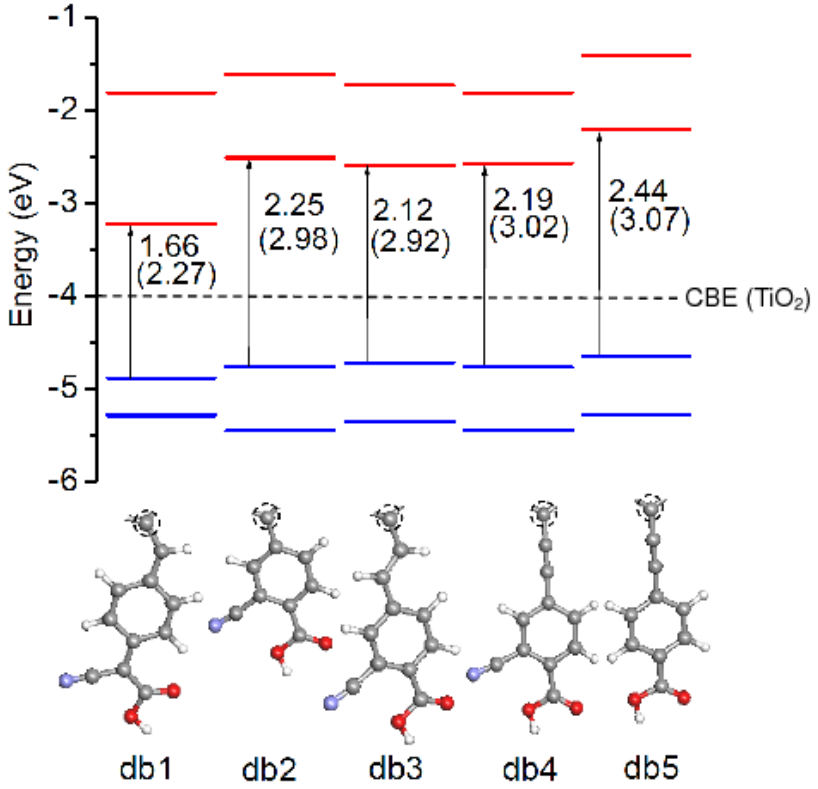
M1 M2 M3

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



Design of new dyes (not yet tried in experiments)

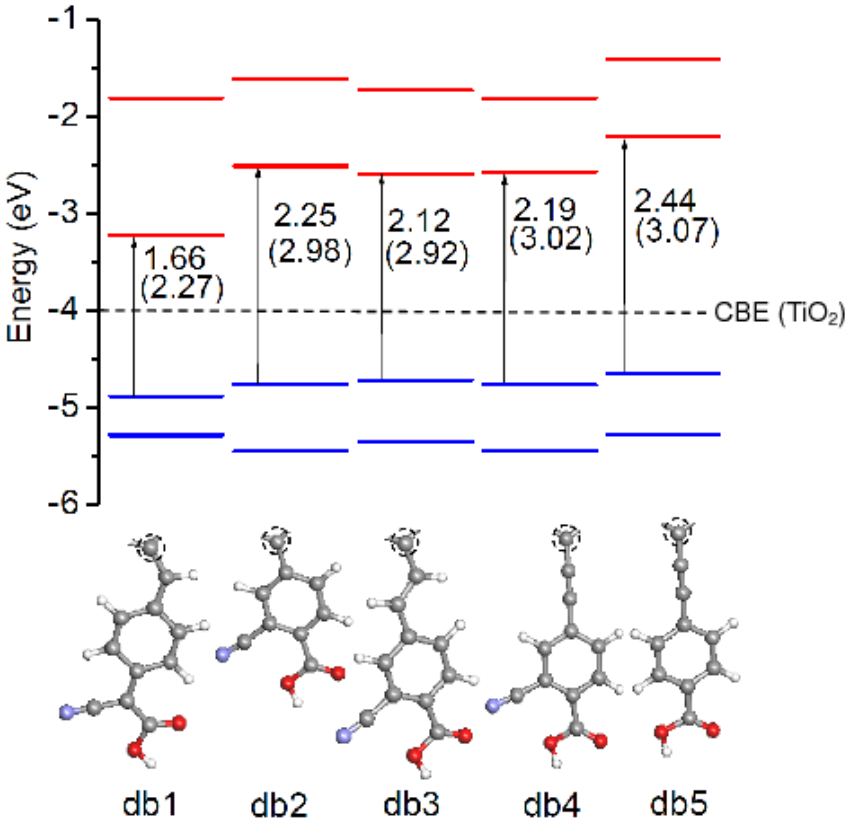


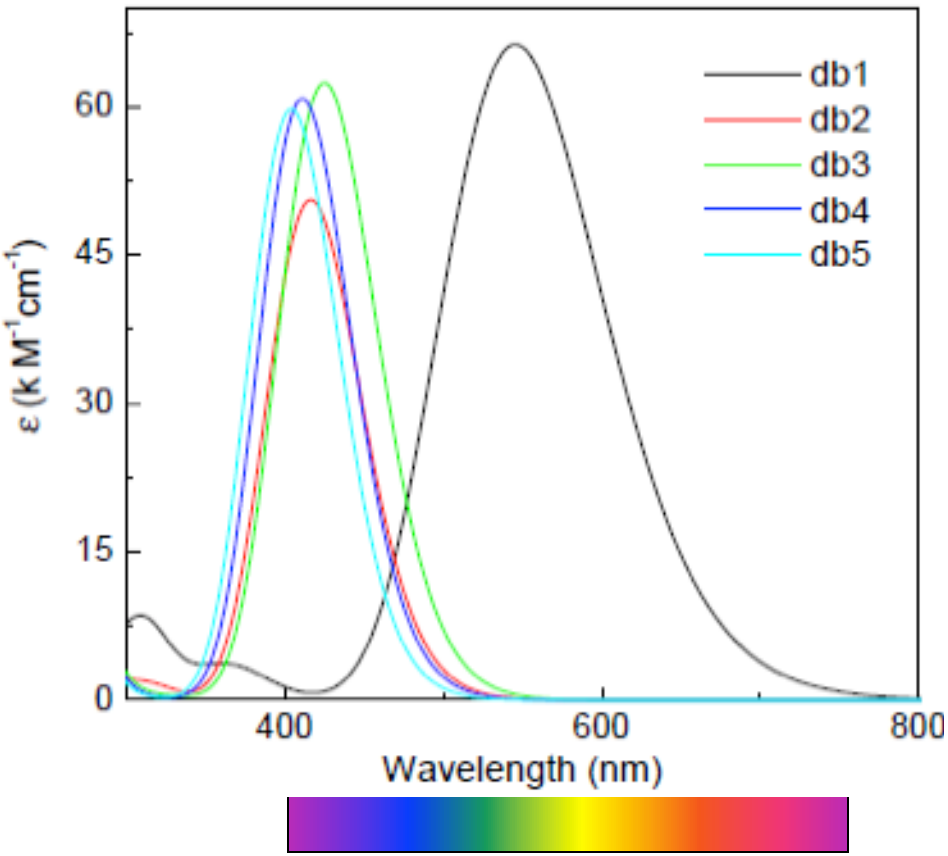


Design of Dye Acceptors for Photovoltaics from First-Principles Calculations

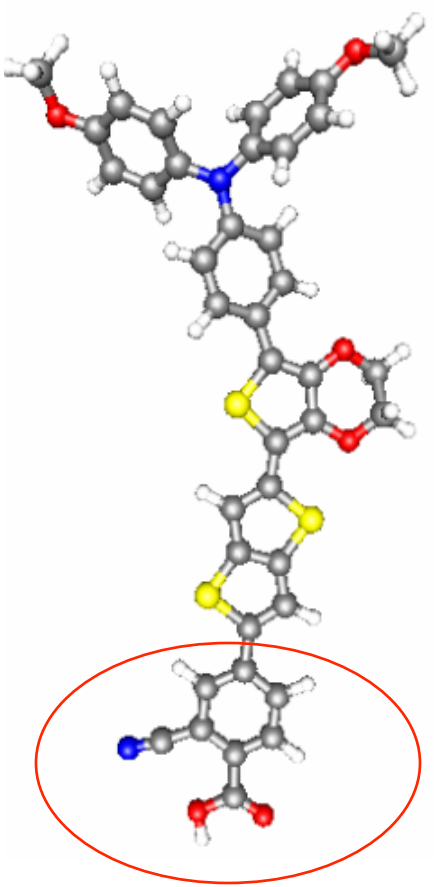
Sheng Meng, Efthimios Kaxiras, Md. K. Nazeeruddin, and Michael Gratzel

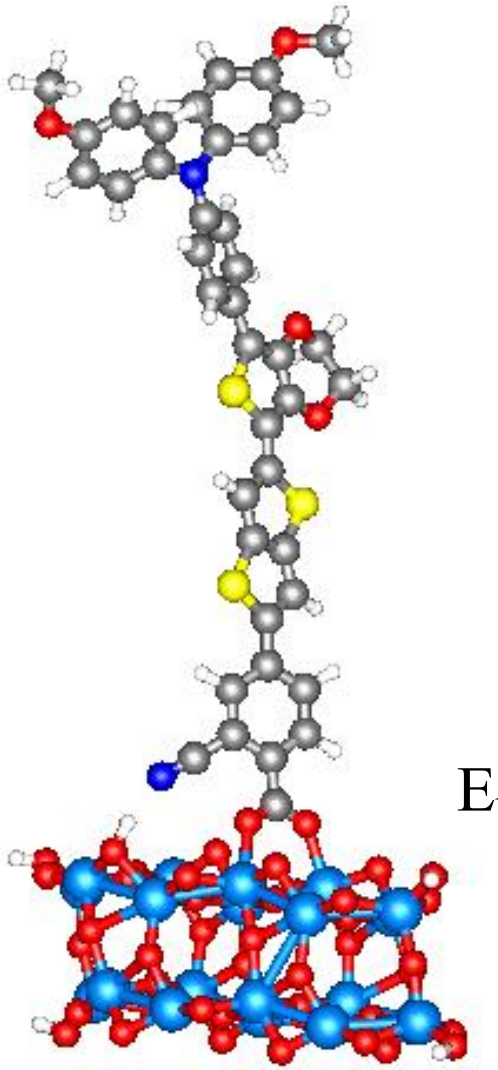
J. Phys. Chem. C 2011, **115**, 9276–9282


Energy (eV)
-1
-2
-3
-4
-5
-6
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)
60
45
30
15
0
400
600
800
Wavelength (nm)
db1
db2
db3
db4
db5

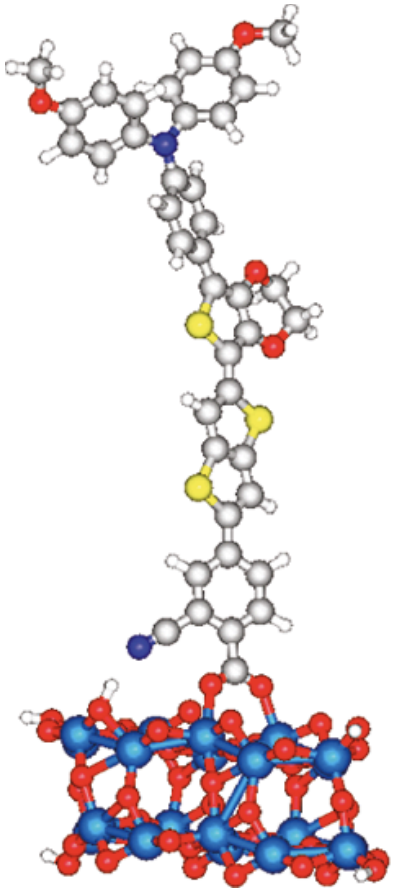
Enhanced dye binding to TiO_2

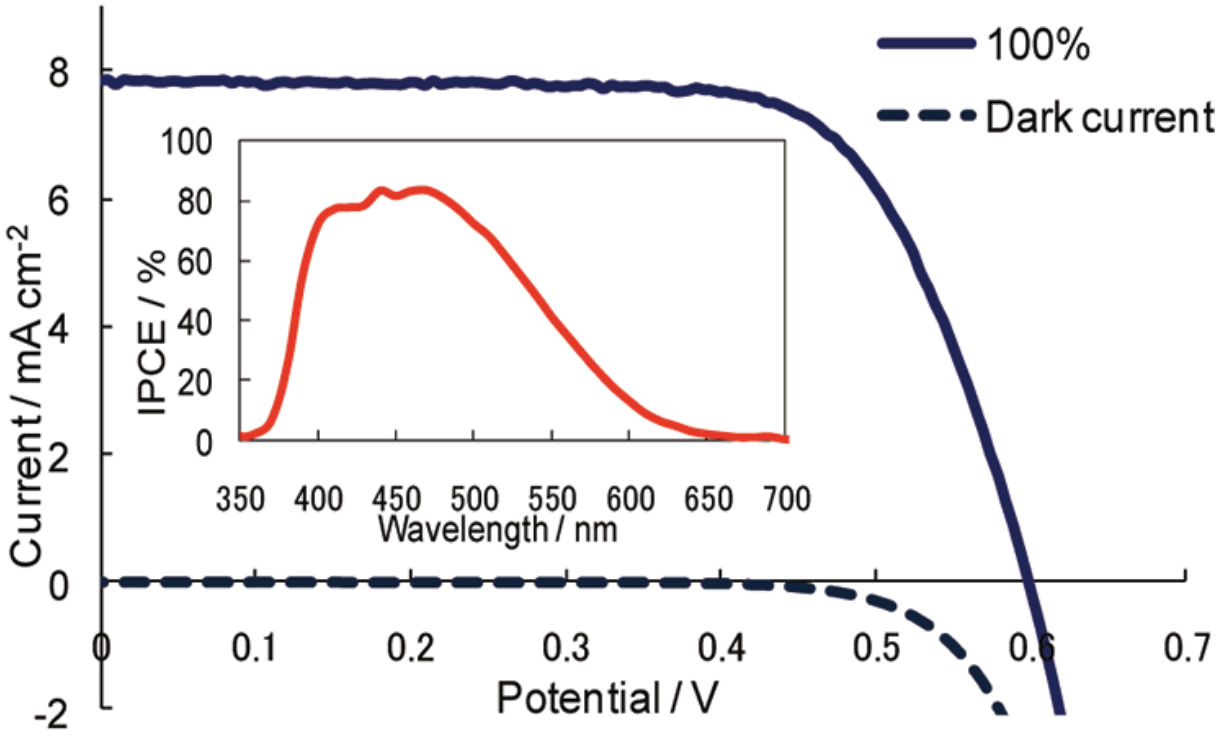




E_b=1.52 eV

84% Incident Photon to Current Efficiency,
3.3% Electric Power Conversion Efficiency





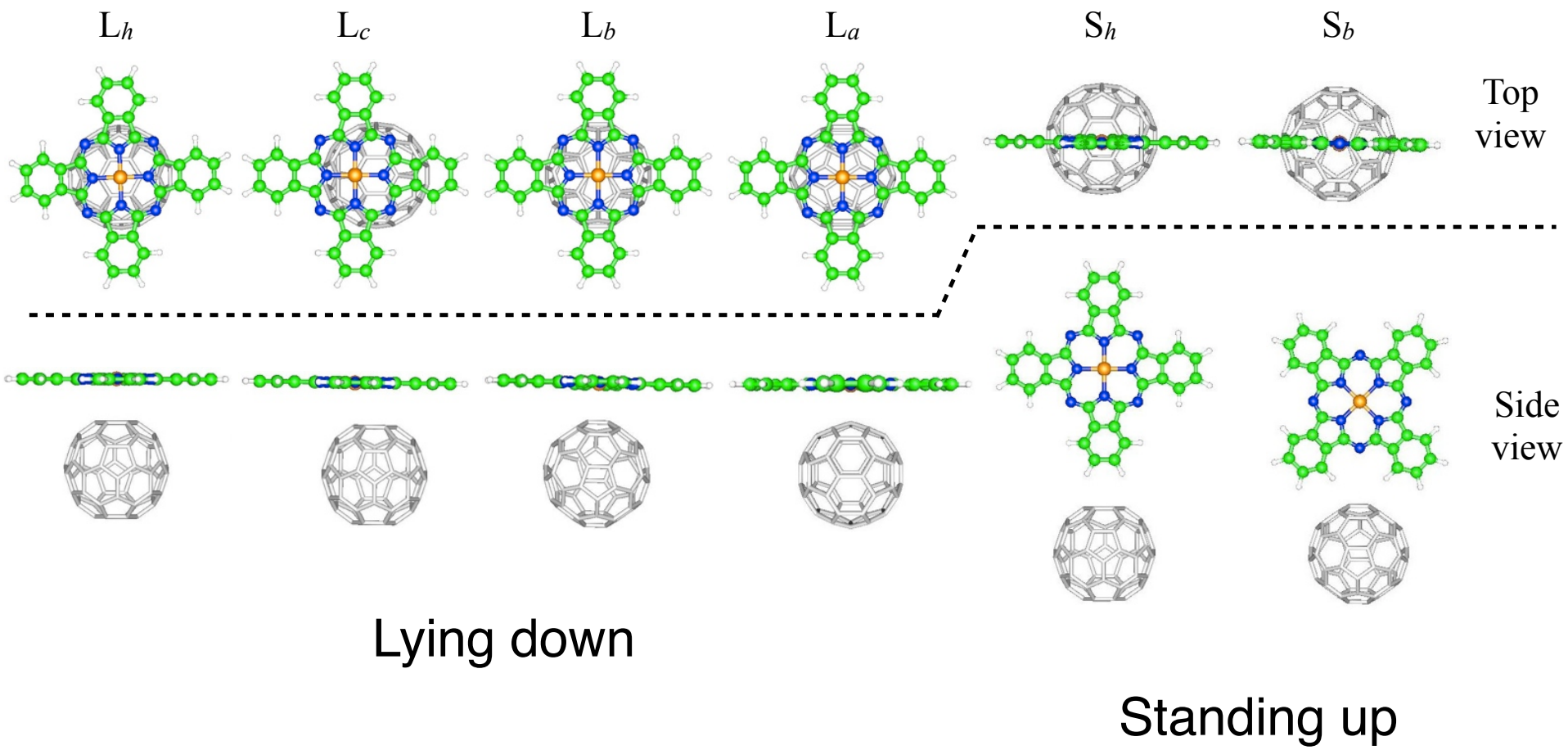
D-π-A Dye System Containing Cyano-Benzoic Acid as Anchoring Group for Dye-Sensitized Solar Cells

Masataka Katono, Takeru Bessho, Sheng Meng, Robin Humphry-Baker, Guido Rothenberger ,Shaik M. Zakeeruddin, Efthimios Kaxiras, and Michael Gratzel

Langmuir 2011, **27**, 14248–14252

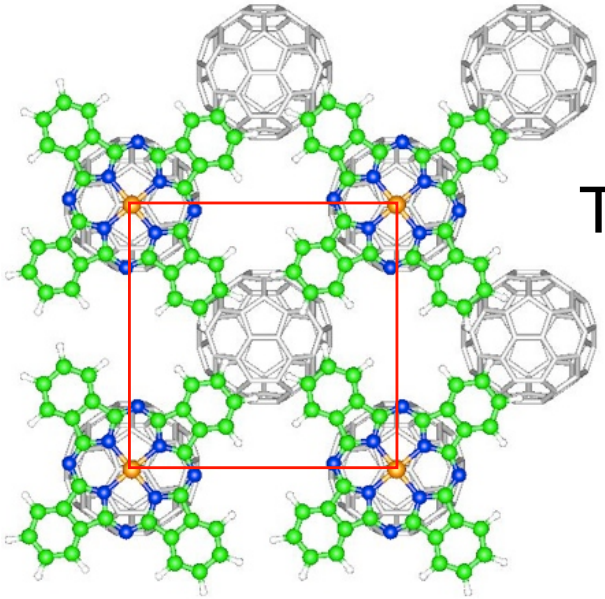
Current focus: organic PV cells

The Cu phthalocyanine / C_{60} system: prototypical OPV



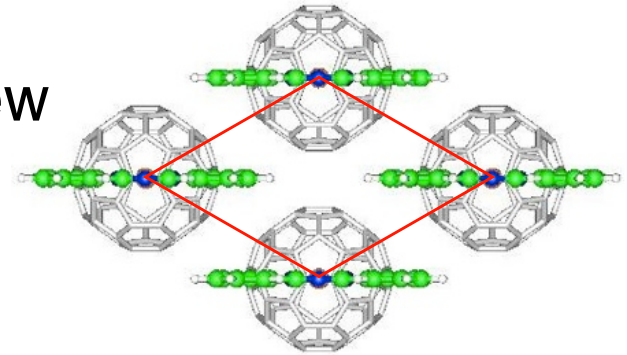
Periodic structures:

on (100) surface of C_{60} film



Top view

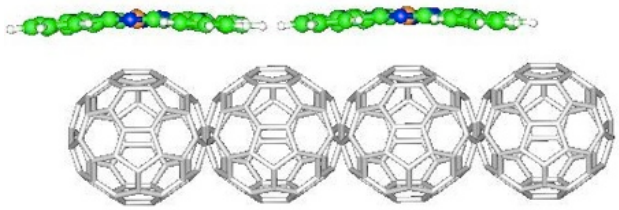
on (111) surface of C_{60} film

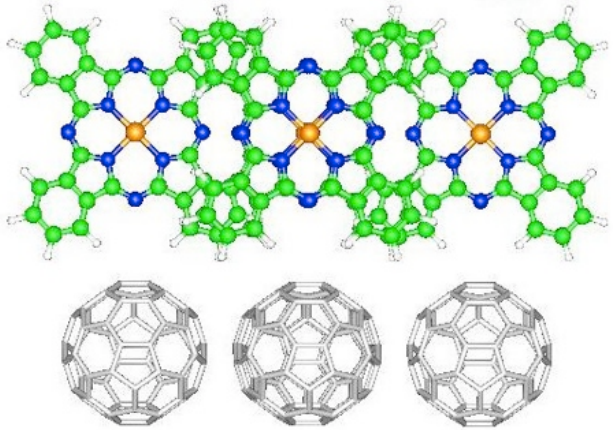


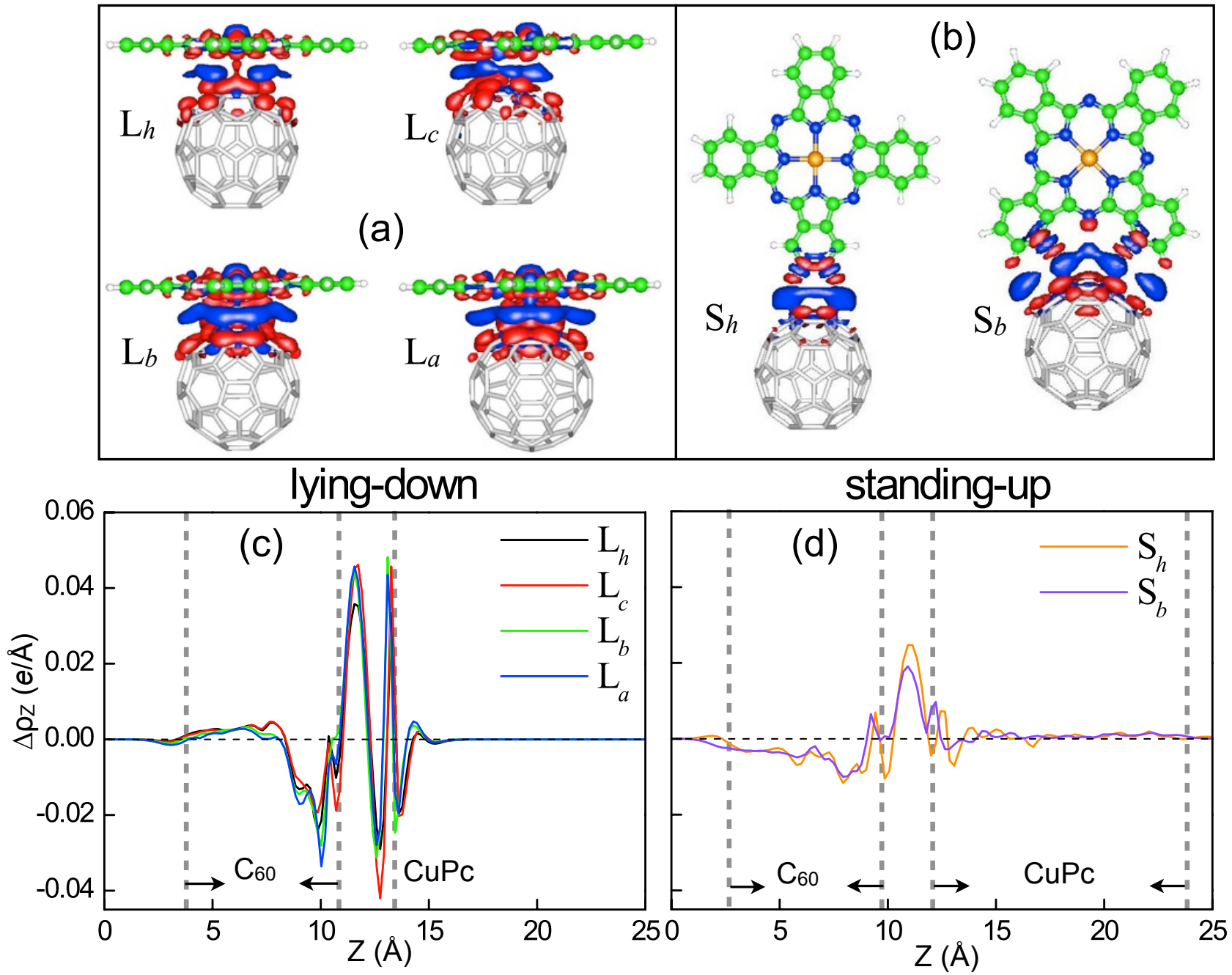
(a)

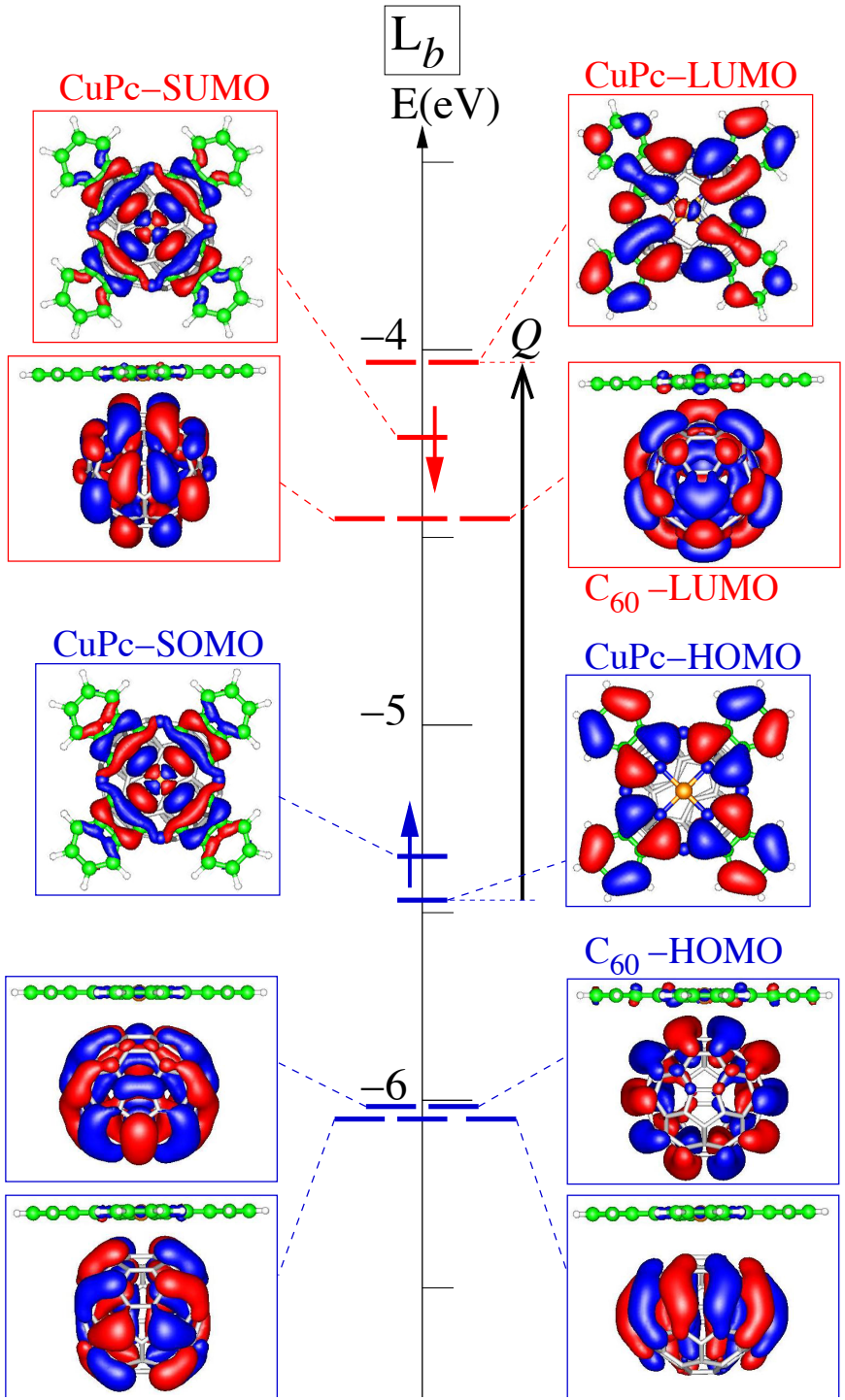
(b)

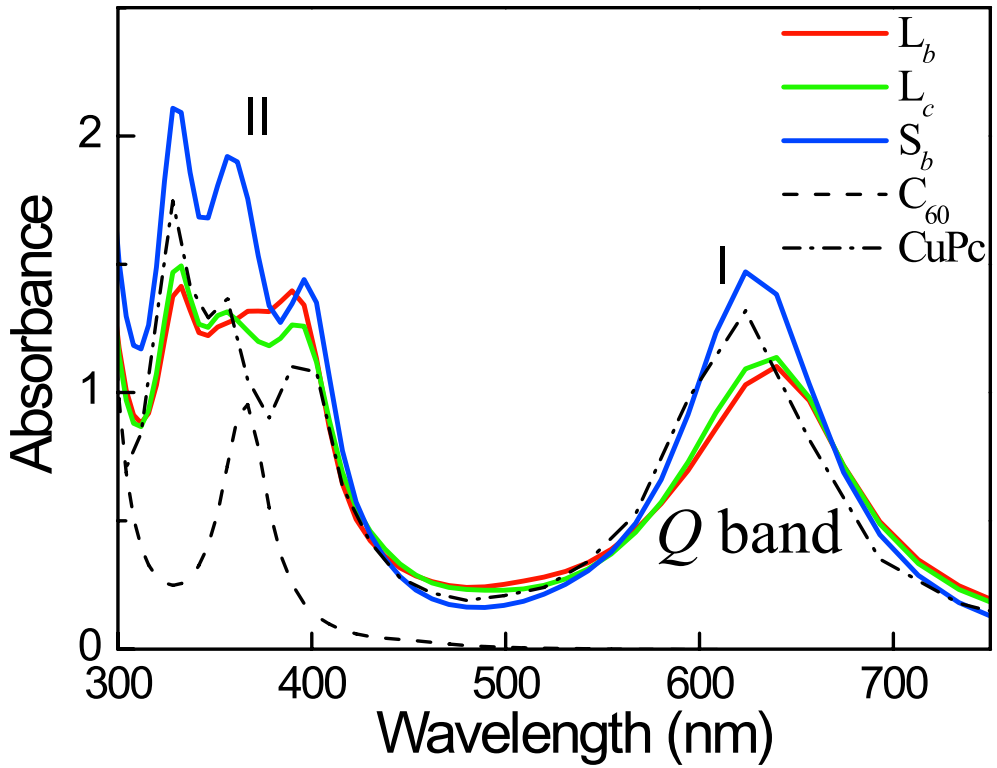
Side view

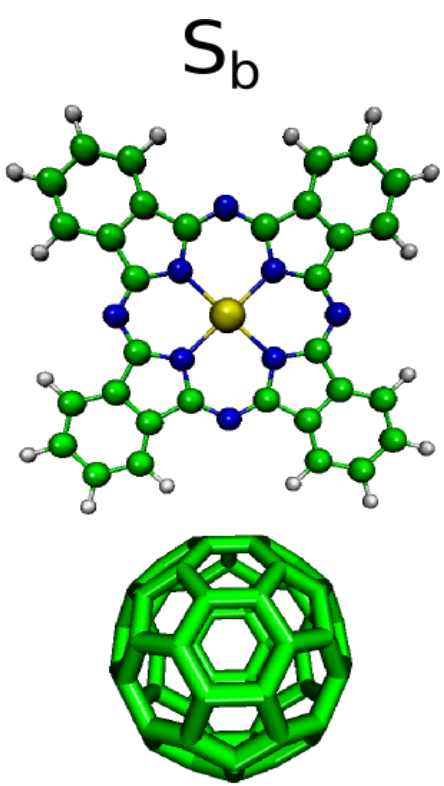


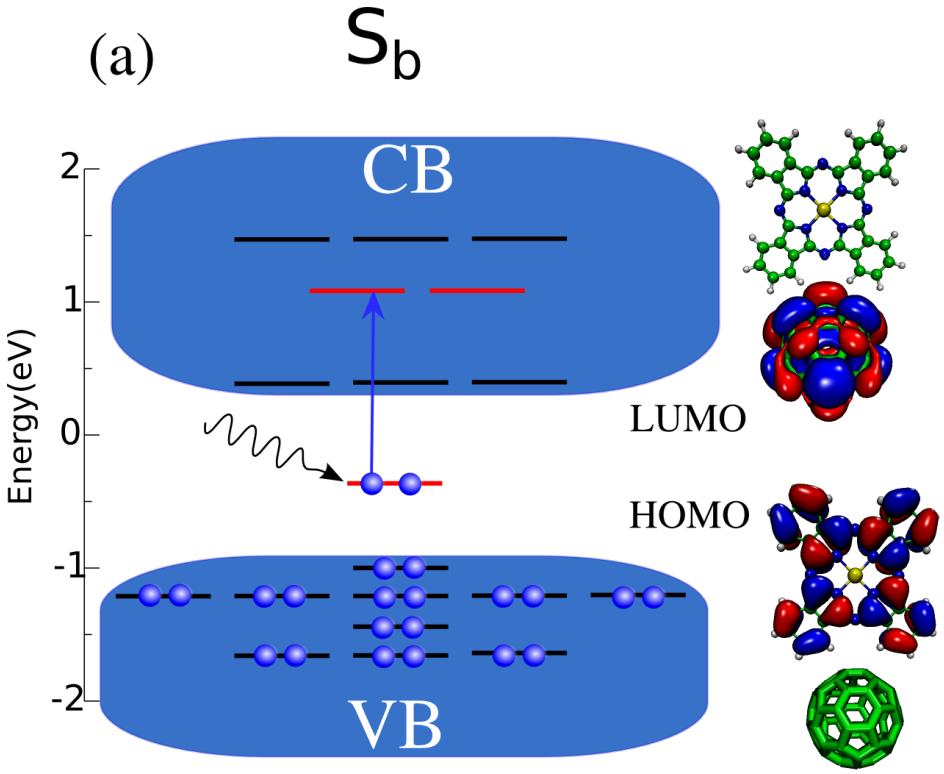



(a)
L_h
L_c
L_b
L_a
(b)
S_h
S_b
lying-down
standing-up
(c)
(d)
L_h
L_c
L_b
L_a
S_h
S_b
C60
CuPc
Δρz (e/Å)
Z (Å)
0.06
0.04
0.02
0.00
-0.02
-0.04
0
5
10
15
20
25

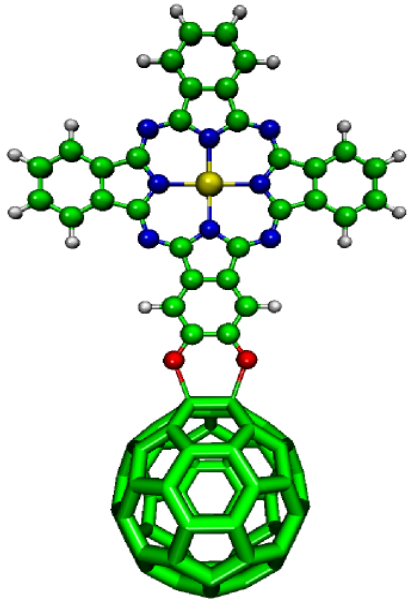

L$_b$
E(eV)
CuPc–SUMO
CuPc–LUMO
–4
Q
C$_{60}$ –LUMO
CuPc–SOMO
CuPc–HOMO
–5
C$_{60}$ –HOMO
–6


L$_b$
L$_c$
S$_b$
C$_{60}$
CuPc
II
I
Q band
Absorbance
Wavelength (nm)
0
1
2
300
400
500
600
700

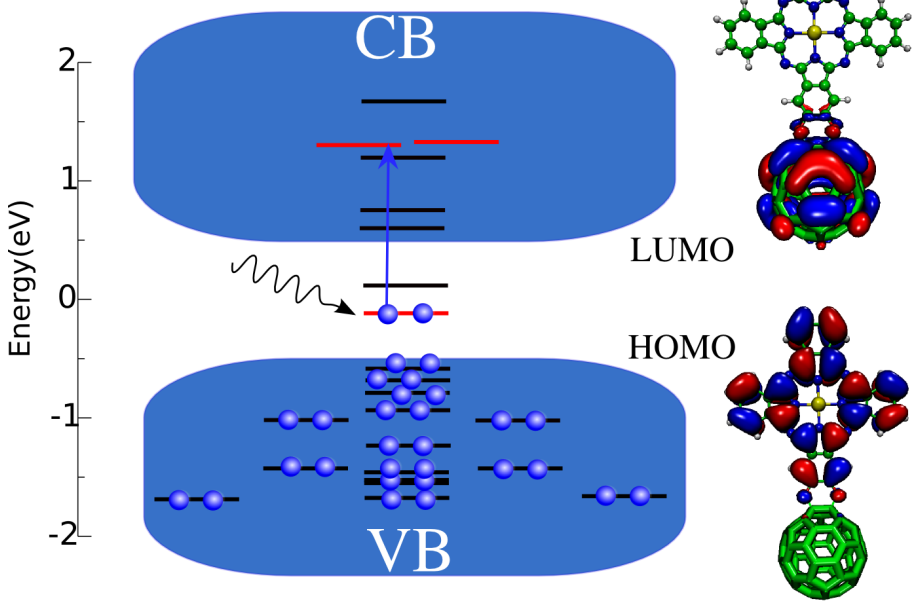

Sb


(a)
Sb
CB
VB
LUMO
HOMO
Energy(eV)
2
1
0
-1
-2

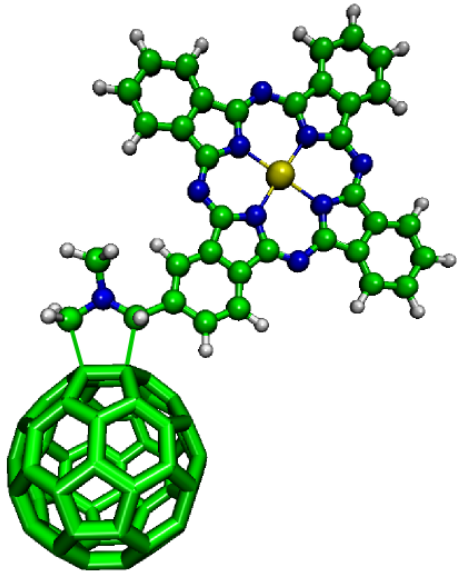
S_h-bond 1



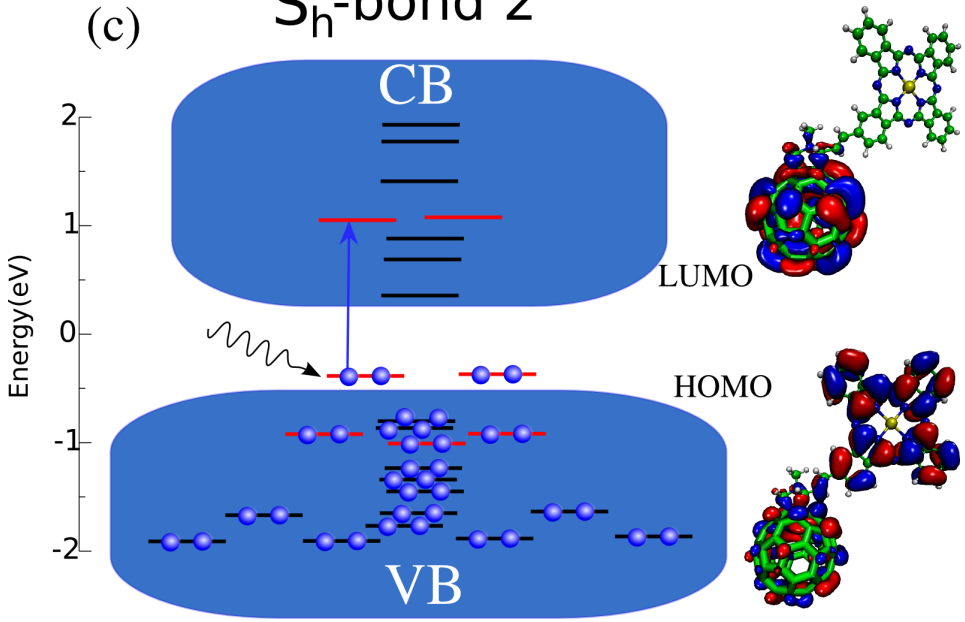
(b) S_h-bond 1

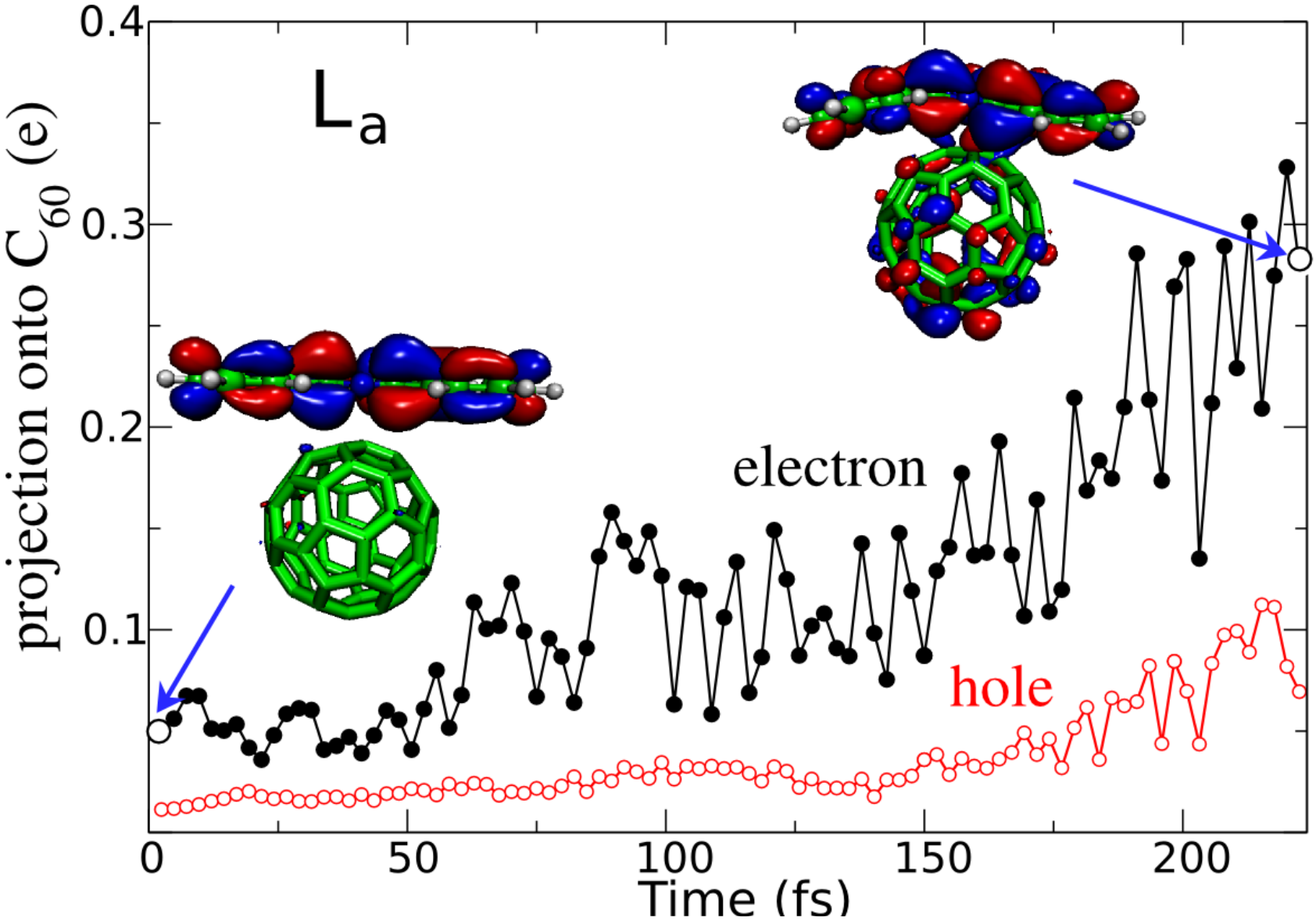


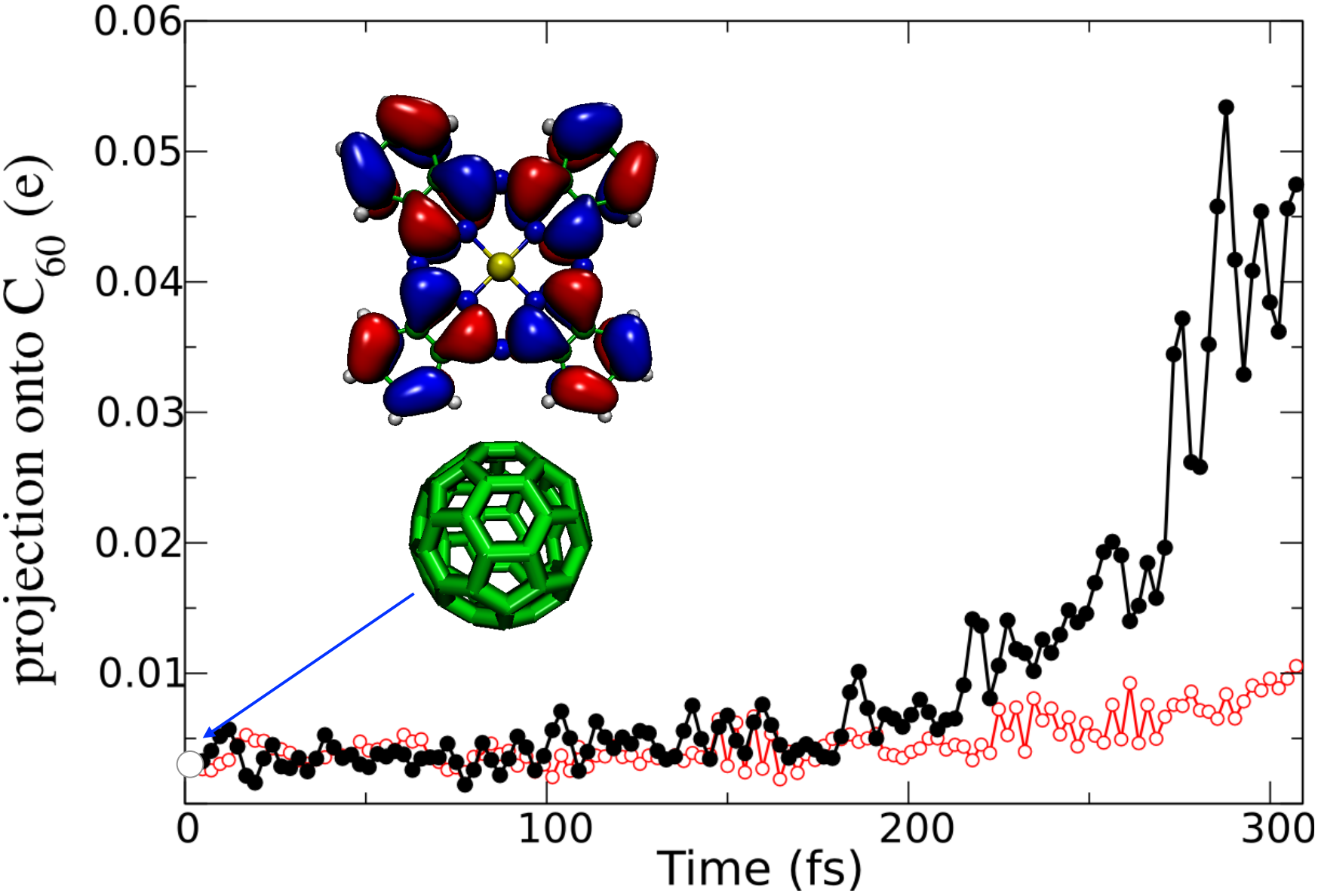
S_h-bond 2

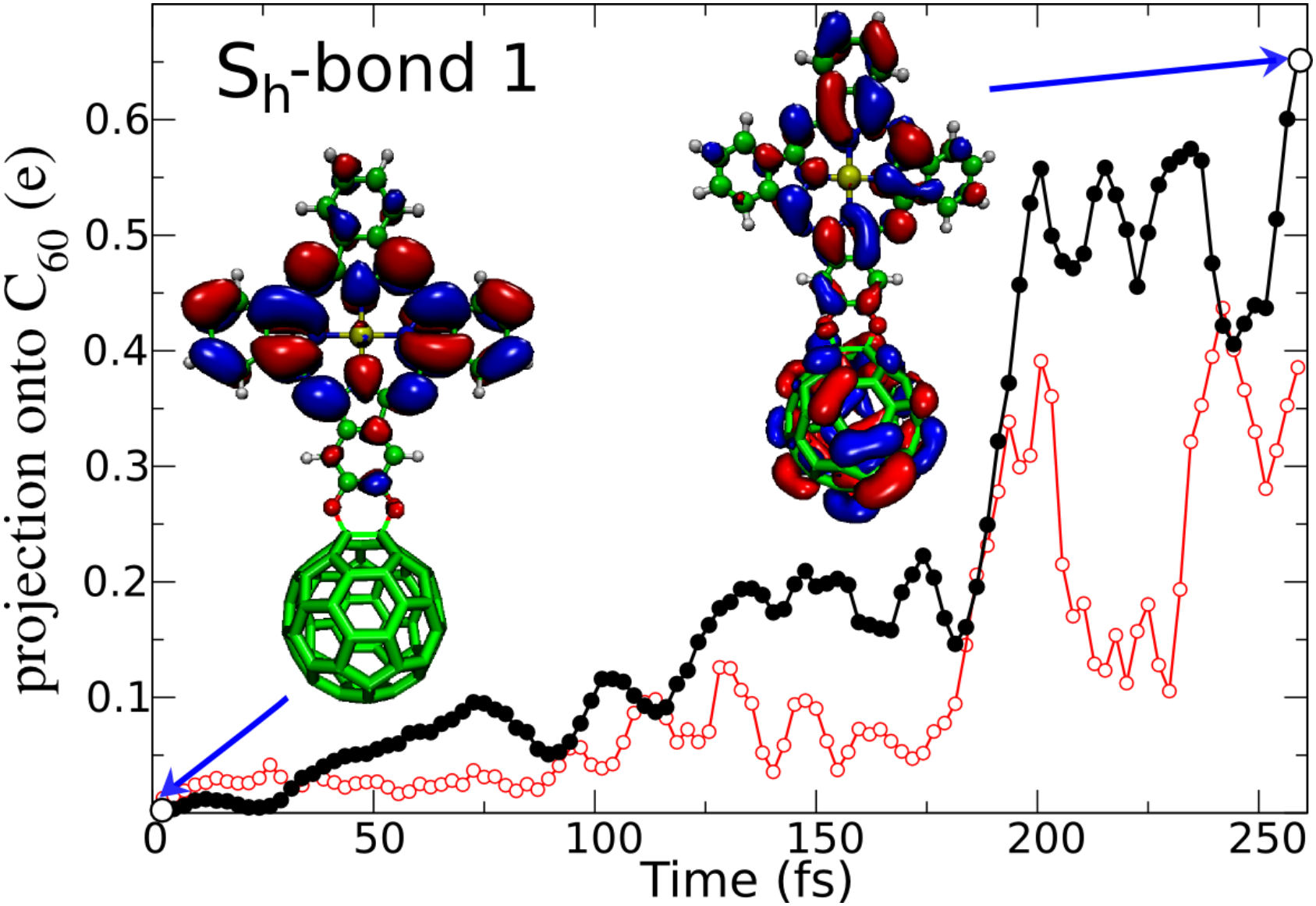


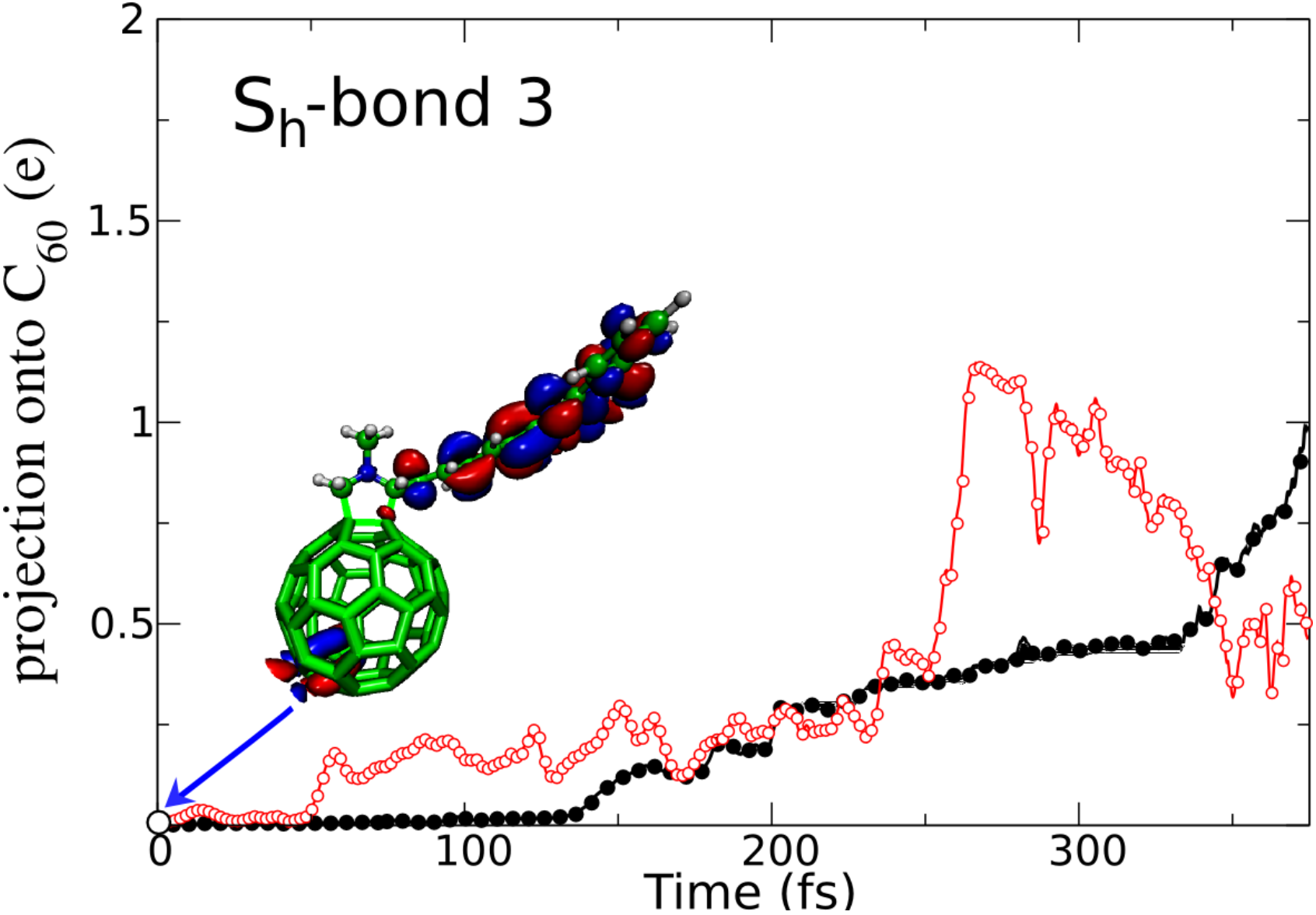
(c) S_h-bond 2



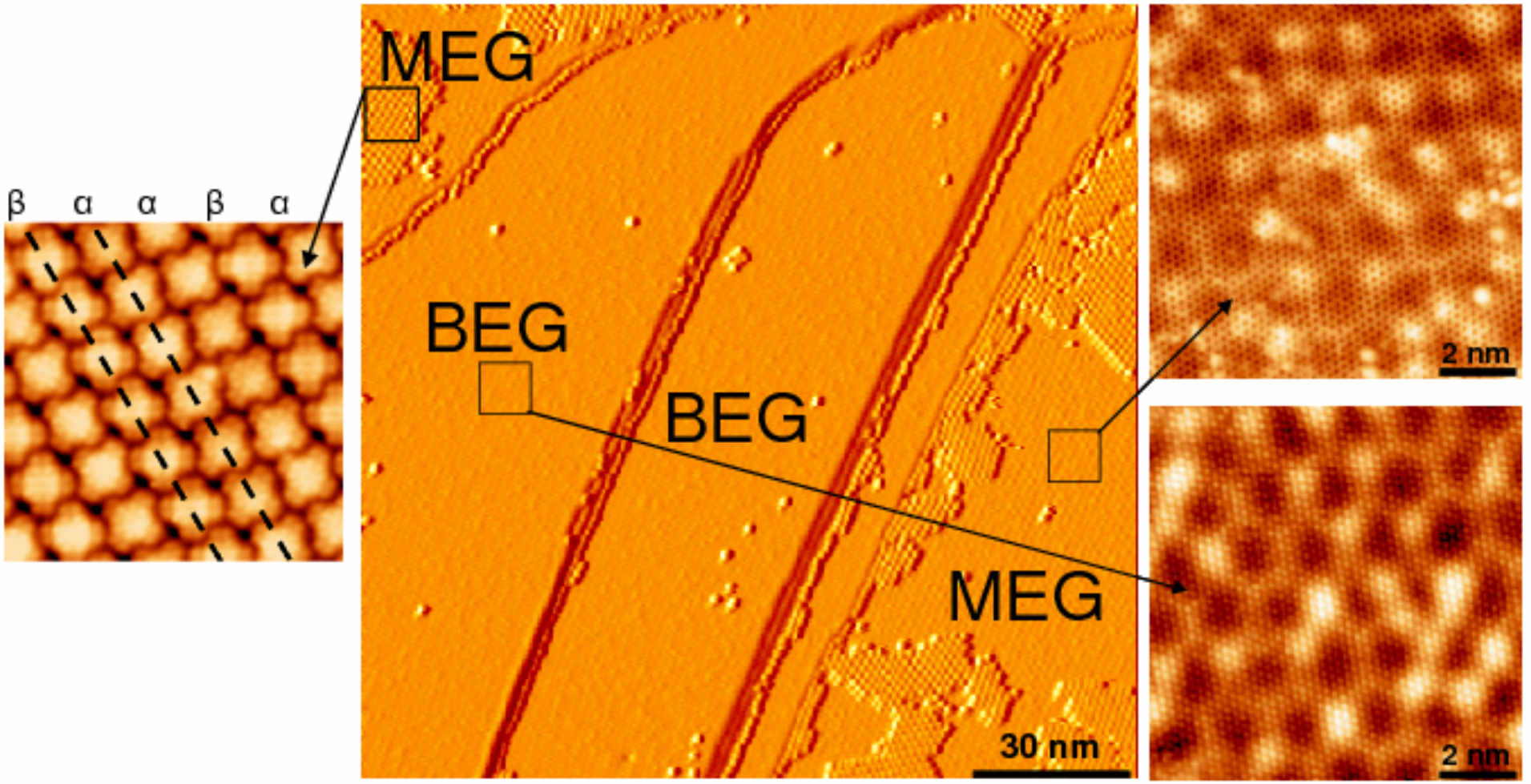

L_a
electron
hole
projection onto C_60 (e)
Time (fs)
0.4
0.3
0.2
0.1
0
50
100
150
200


0.06
0.05
0.04
0.03
0.02
0.01
projection onto C_{60} (e)
0
100
200
300
Time (fs)


S_h-bond 1
projection onto C_{60} (e)
0.1
0.2
0.3
0.4
0.5
0.6
0
50
100
150
200
250
Time (fs)


S_h-bond 3
projection onto C_{60} (e)
Time (fs)
0
100
200
300
0.5
1
1.5
2

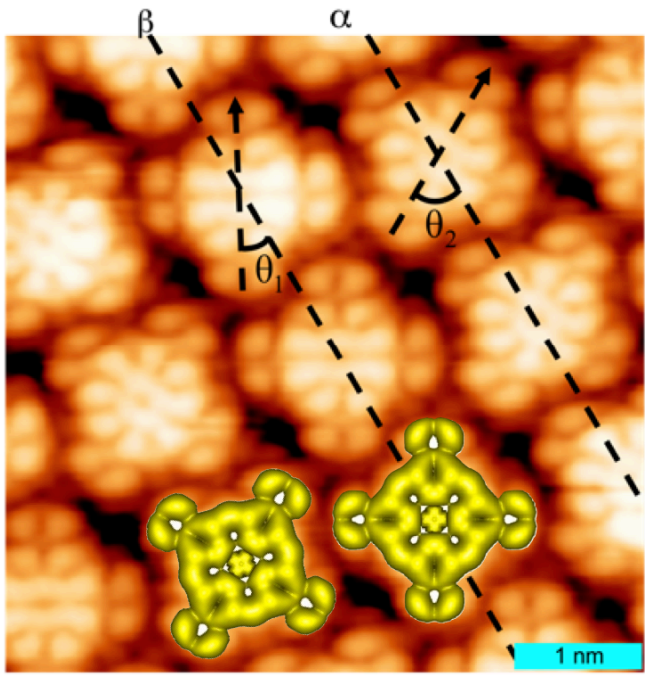
Graphene as a substrate for M-Pc films:

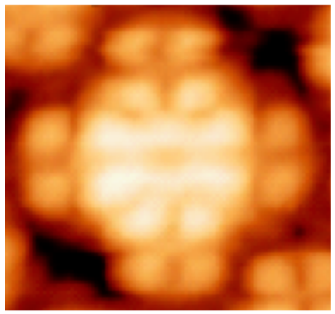


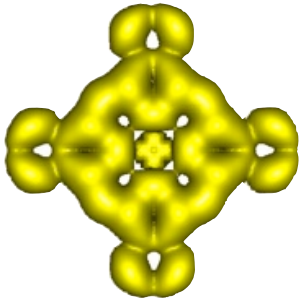
Selective adsorption and electronic interaction of F16CuPc on epitaxial graphene

Yi-Lin Wang, Jun Ren, Can-Li Song, Ye-Ping Jiang, Li-Li Wang, Ke He, Xi Chen, Jin-Feng Jia, Sheng Meng, Efthimios Kaxiras, Qi-Kun Xue, and Xu-Cun Ma

PHYSICAL REVIEW B **82**, 245420 (2010)





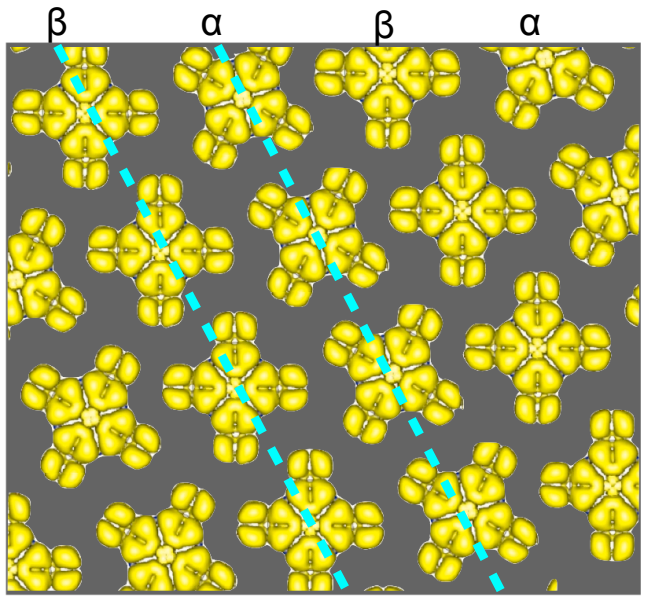


Properties of copper (fluoro-) phthalocyanine layers deposited on epitaxial graphene

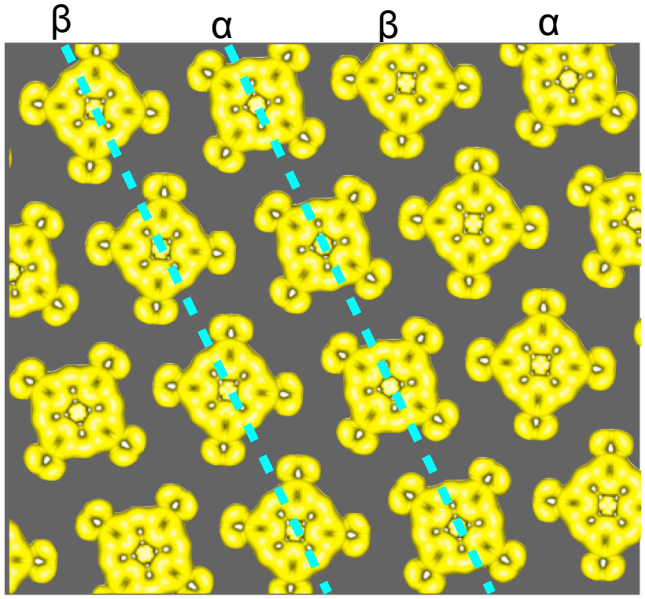
Jun Ren, Sheng Meng, Yi-Lin Wang, Xu-Cun Ma, Qi-Kun Xue, and Efthimios Kaxiras

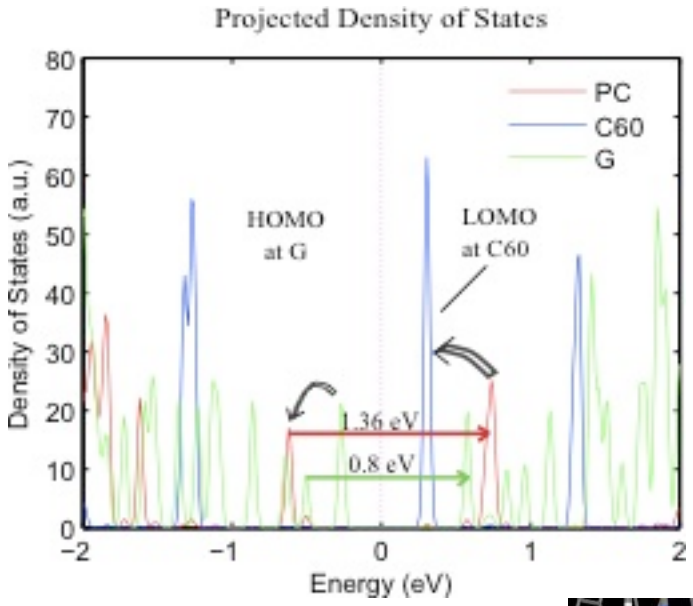
JOURNAL OF CHEMICAL PHYSICS **134**, 194706 (2011)

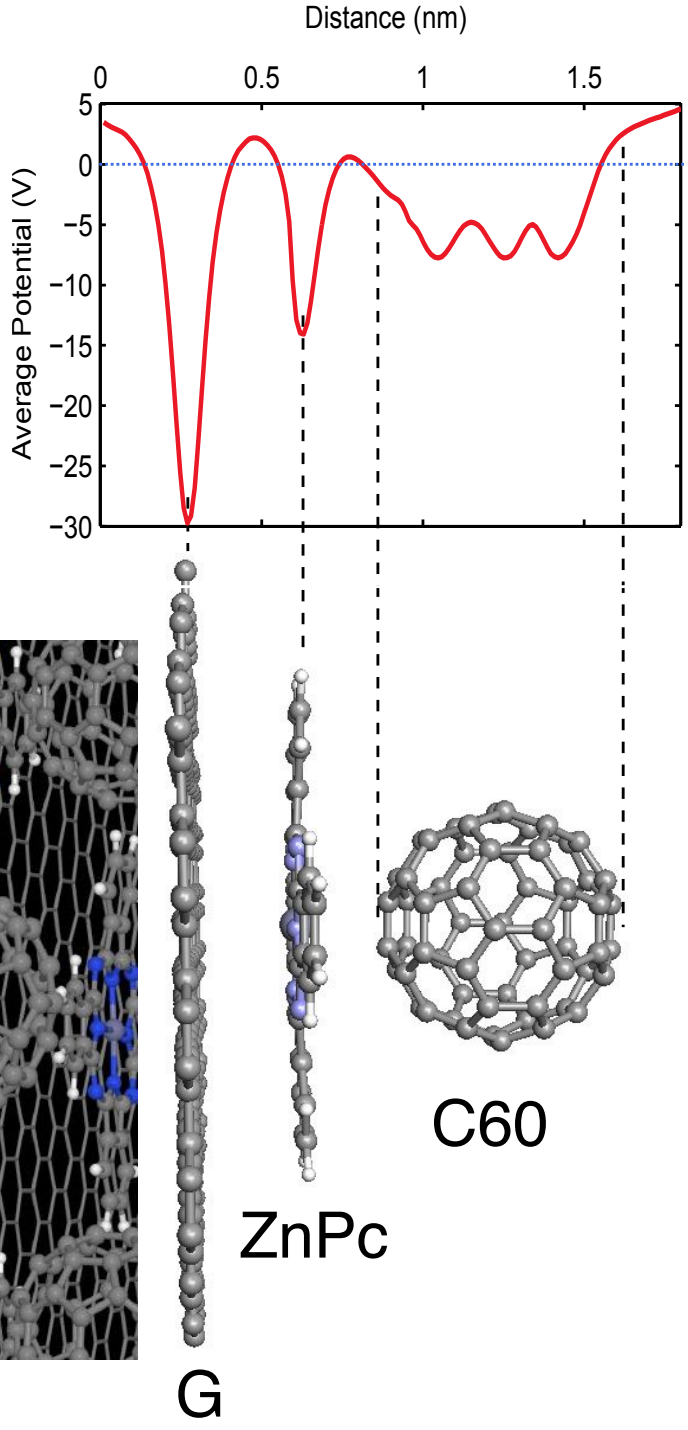
HOMO

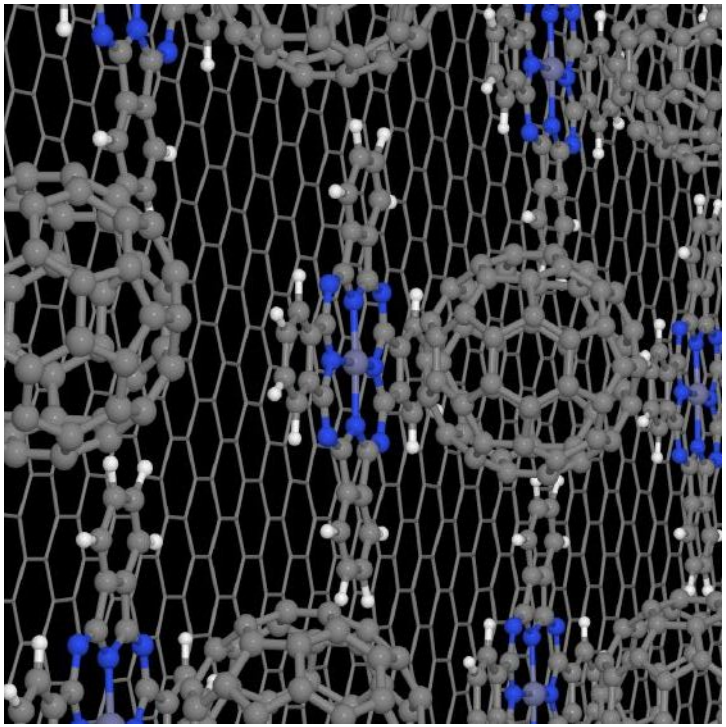


LUMO









In collaboration with:

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GRAPHENEA (Spain)

Highlights:

- Efficient theoretical tool for modeling OPV or hybrid systems
- Insights and predictions for charge transfer in DSSC's
- Insights into Zn-Pc/C_{60} system (excitation, charge transfer)
- Prediction for Graphene/Zn-Pc/C_{60} hybrid system

Support:

U.S. Dept. of Energy

Mass. Green High Performance Computing Center