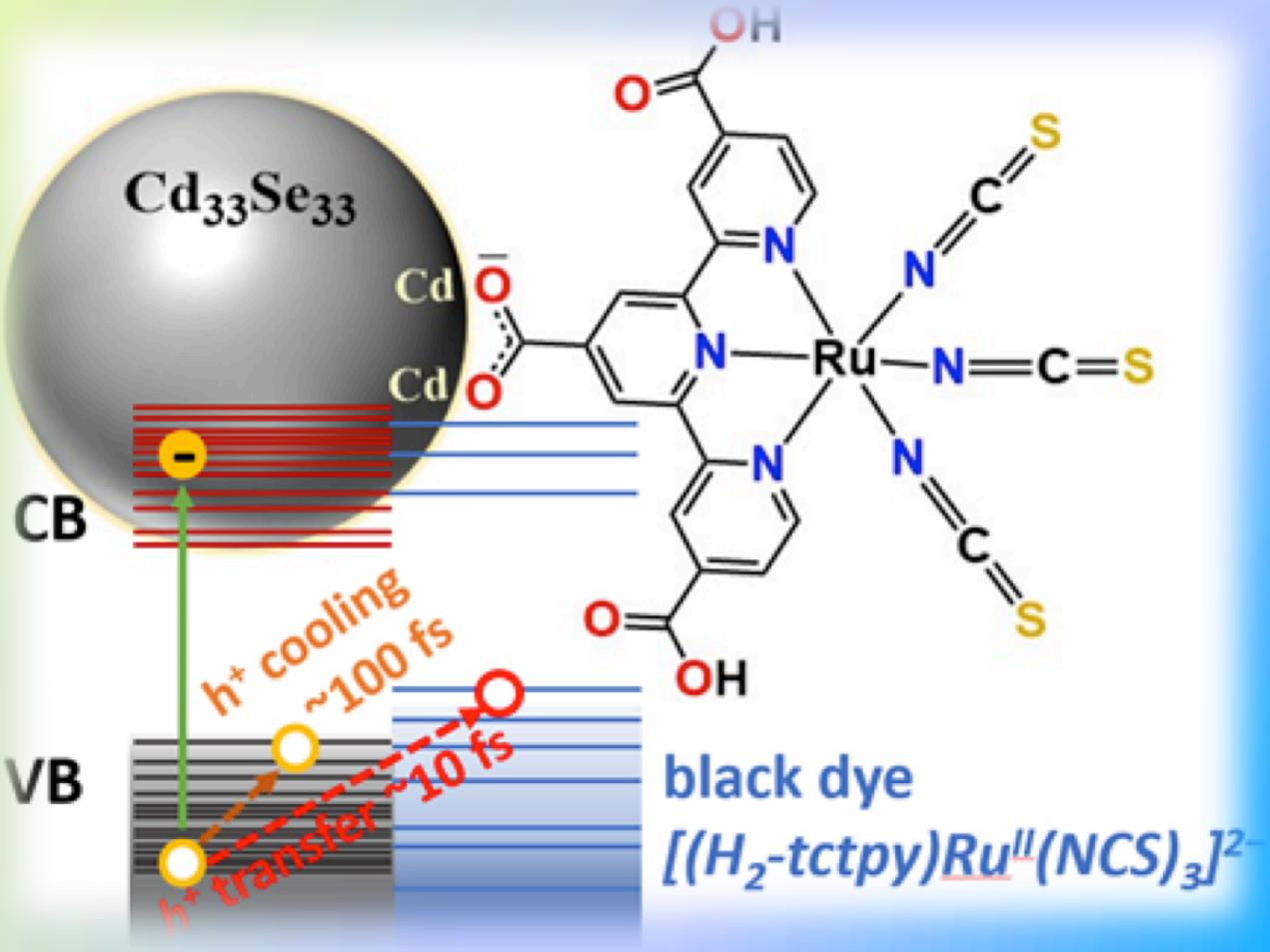
Charge Transfer between Quantum Dots and Functionalizing Dyes



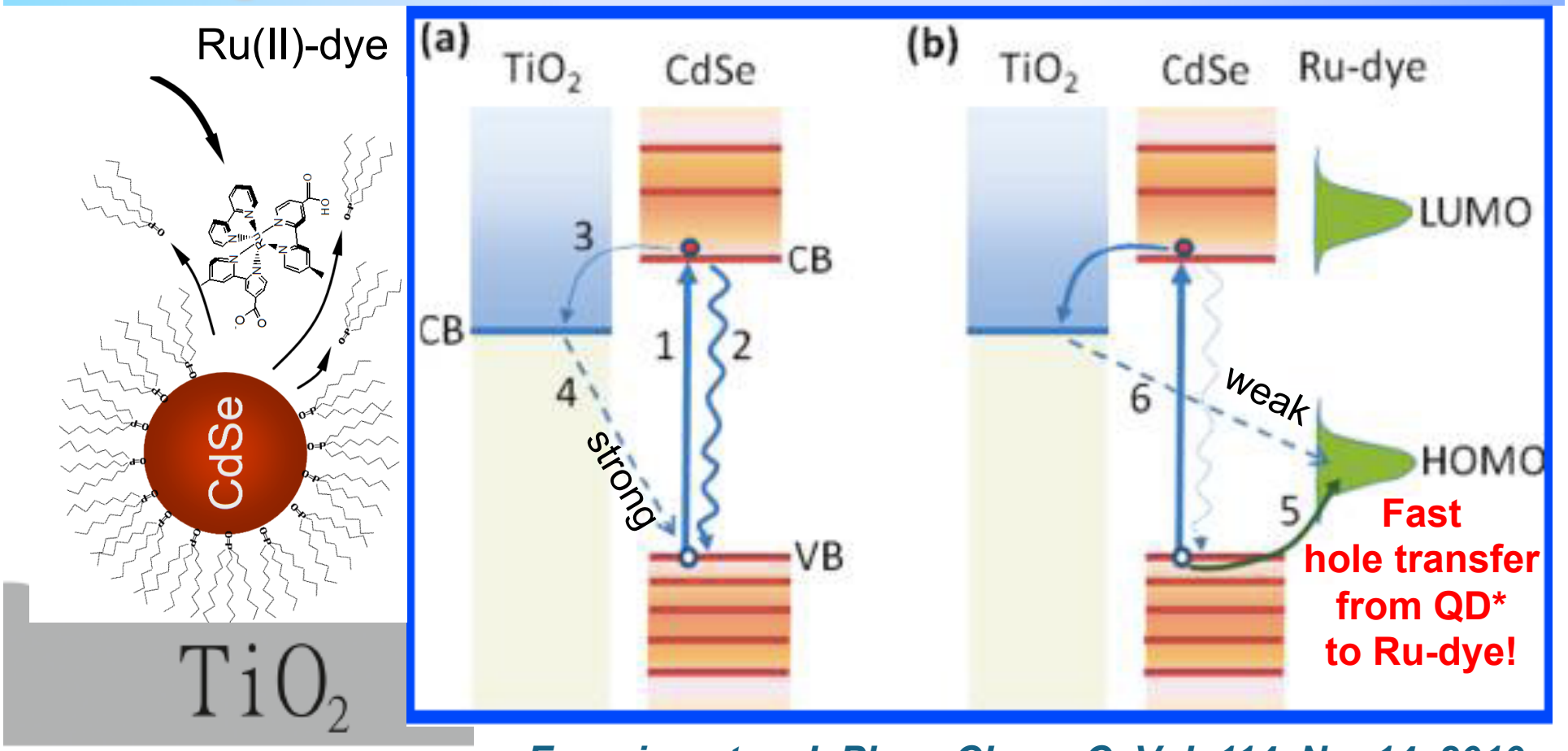
Svetlana Kilina

Dep. Chemistry & Biochemistry,

North Dakota State University,

Fargo, ND, 58108

Quantum Dot-Sensitized Solar Cells



Experiment: *J. Phys. Chem. C, Vol. 114, No. 14, 2010*
J. Appl. Phys. 110, 014314 (2011)

QD-sensitized solar cell: Efficiency is low of ~14%, due to fast internal electron-hole re-combinations => Introduce hole-accepter

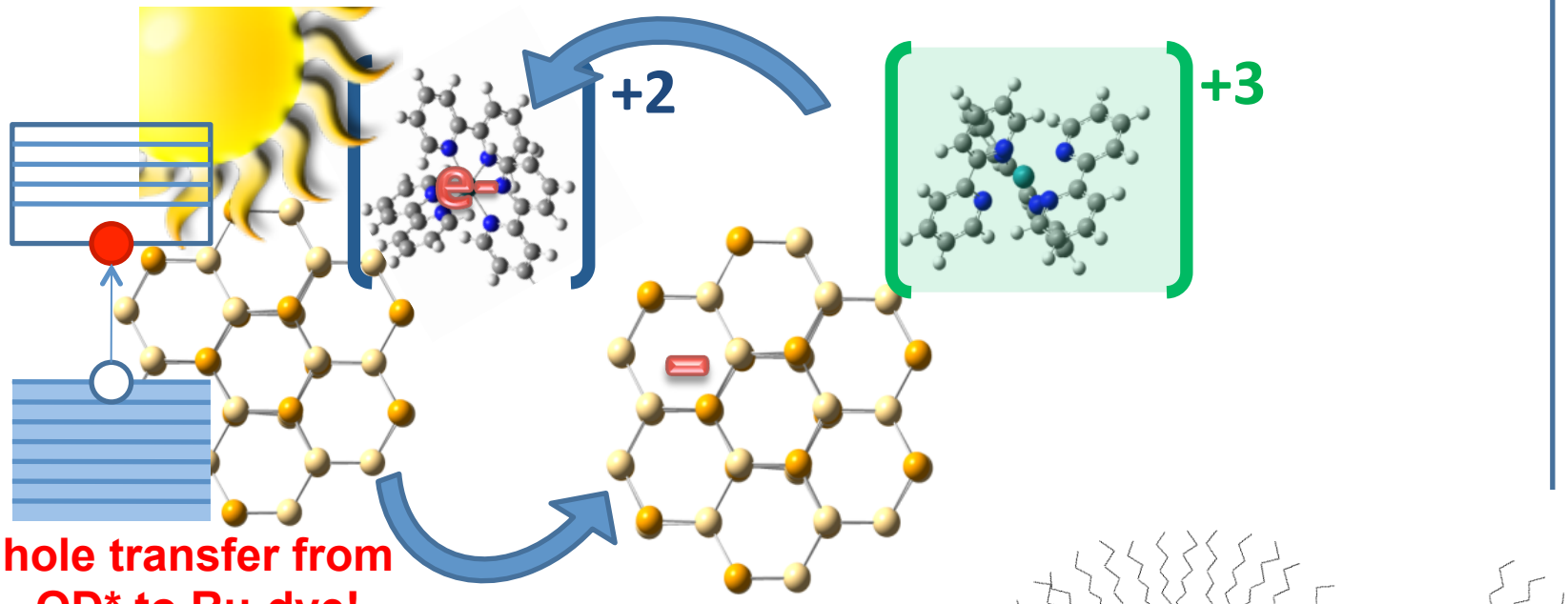
Our DFT predictions: *J. Phys. Chem. C 2013, 117, 18216;*
J. Phys. Chem. Lett. 2014, 5, 3565; ACS Appl. Nano Mater. 2018, 7, 3174

Quantum dots for photo-catalysis

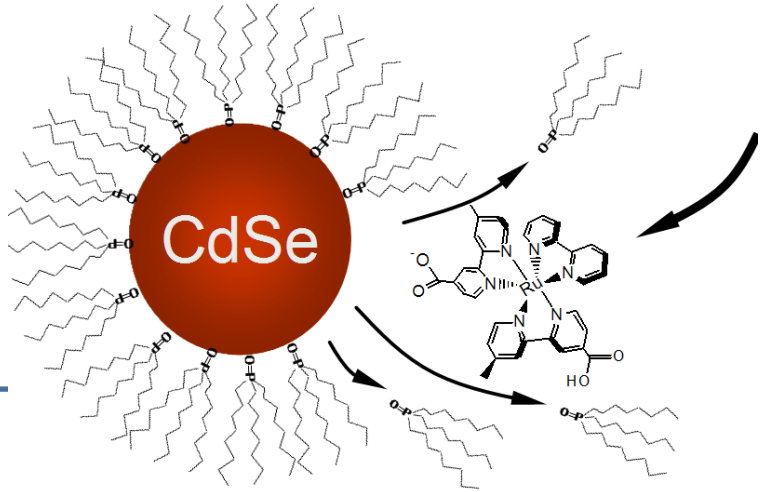
2 pathways are possible for catalysis:

① Electron transfer from the photoexcited dye: Ru*(II) => Ru(III)

② Hole transfer from photoexcited QD: Ru(II) => Ru(III)



$$2\,H_2O \Rightarrow 4H^+ + O_2 + 4\,e^-$$

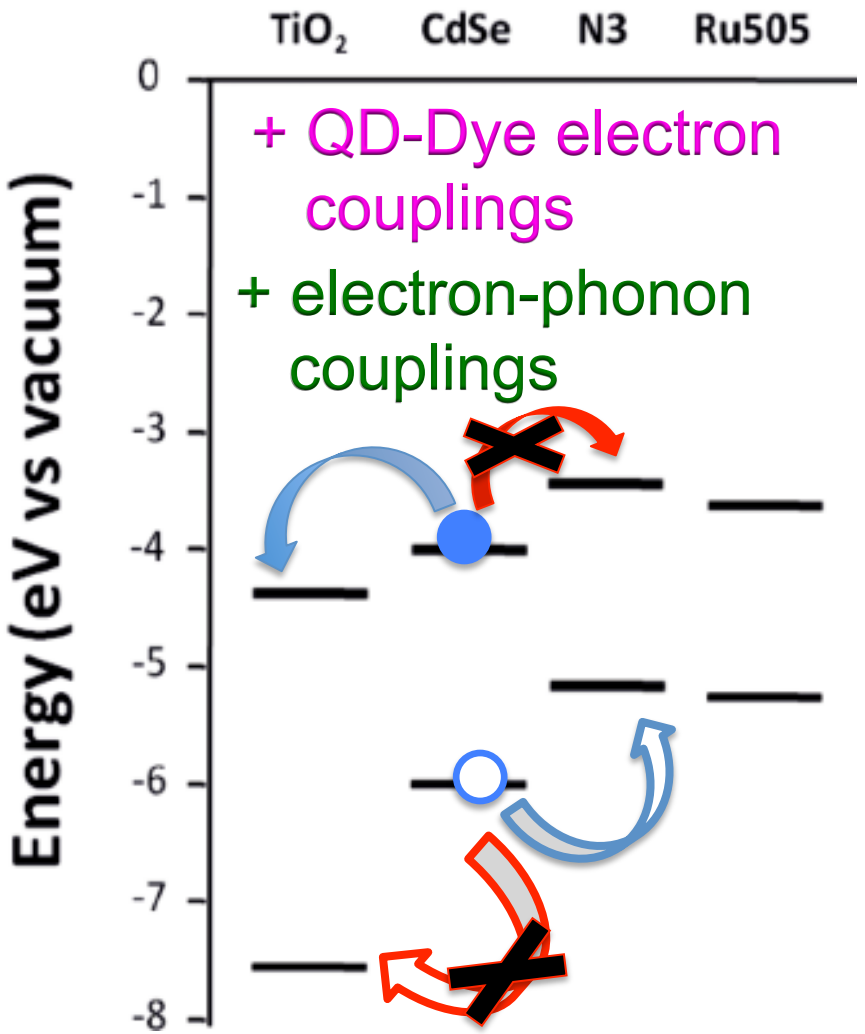


Sykora et al. ***J. Am. Chem. Soc. 2006, 128, 9984***

Charge Transfer Prerequisites

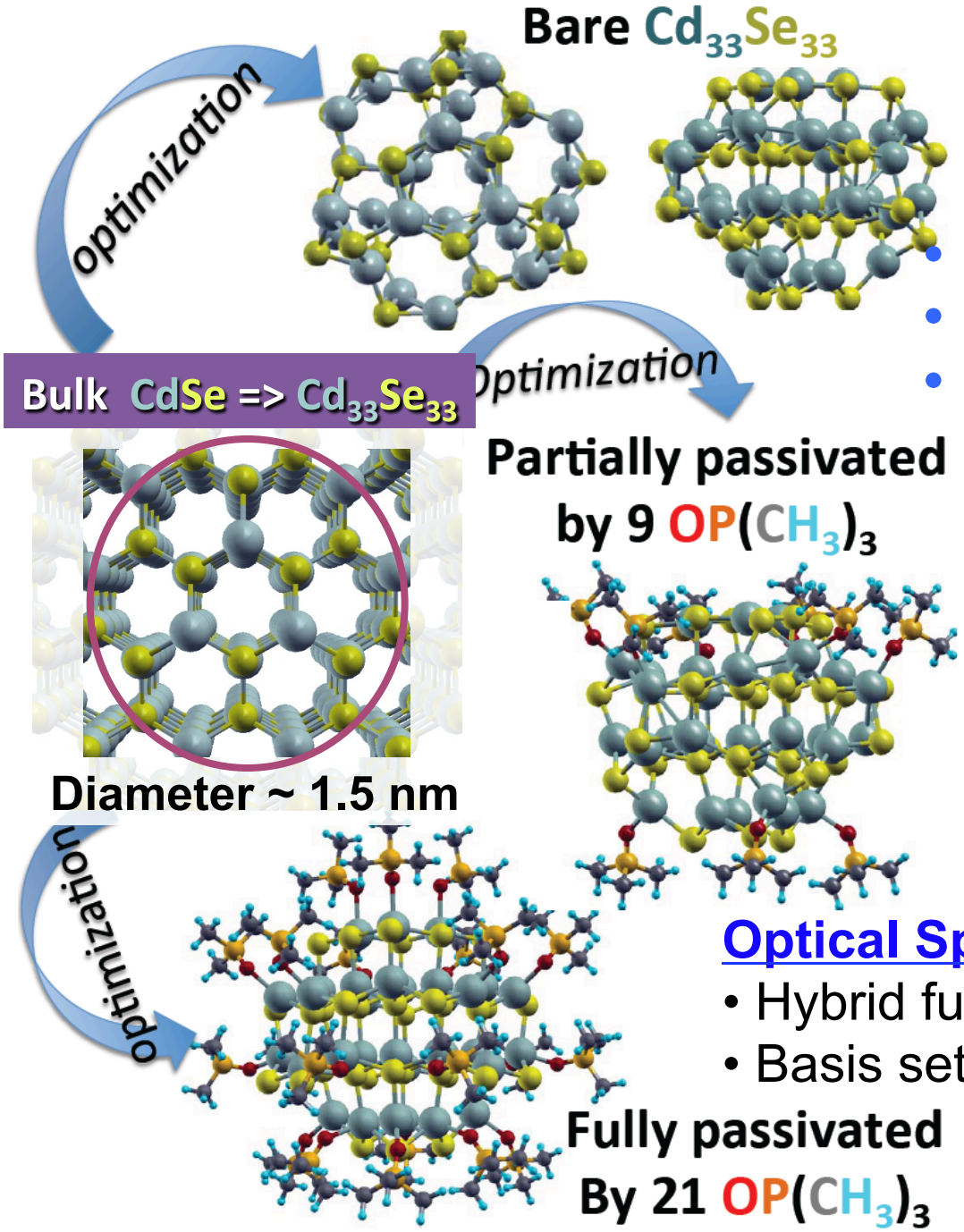
For solar energy conversion **the direction and speed of charge transfer are the key factors to increase the efficiency of a device.**

- **The alignment of electronic states** of the QD with respect to the dye is a preliminary condition determining the charge transfer mechanisms.
- **QD-size**, **dye modifications**, and **QD-Dye interactions** may change the mutual alignment of electronic states and the QD-dye couplings.



J. Appl. Phys. 110, 014314 (2011)

Computational models



Tools:

- **DFT:** Hybrid functionals PBE0
- Linear-response TD-DFT
- Non-adiabatic DFT-based dynamics + surface hopping

Geometry and Dynamics:

by VASP

- plane wave basis set;
- GGA functionals (PBE);
- Pseudo-potentials (PAW)

Optical Spectra: GAUSSIAN (TD-DFT):

- Hybrid functionals (PBE1)
- Basis set: LANL2dz (QD)/6-31G*(ligand)

Non-Adiabatic Dynamics: Time Dependent Kohn-Sham

Kohn-Sham (KS) equations of motion:

$$i\hbar\frac{\partial\varphi_p(x,t)}{\partial t} = H\left\{\varphi(x,t)\right\}\varphi_p(x,t),\ \ p=1,\ldots,N_e$$

Wavefunction in adiabatic (KS) basis $\varphi_p(x,t) = \sum_k^{N_e} c_{pk}(t)\left|\phi_k(x;R)\right\rangle$?

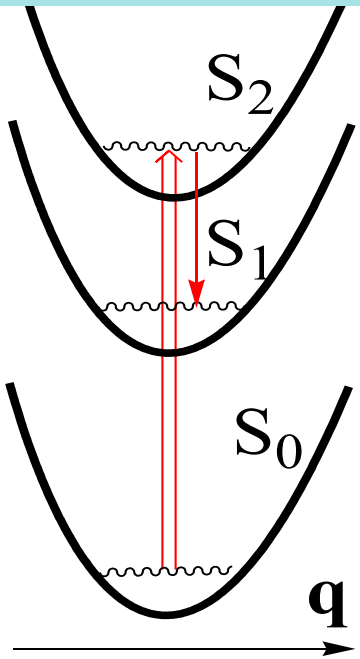
Nuclei

Evolution of wavefunction coefficients:

$$\dot{c}_j \equiv \frac{dc_j}{dt} = -\sum_k c_k\left(\mathbf{d}_{jk}\cdot\dot{\mathbf{R}} + \frac{i}{\hbar}\langle\phi_j|H_q|\phi_k\rangle\right)$$

KS orbitals at each moment *t, k=j*

non-adiabatic coupling: $\mathbf{d}_{jk}\dot{\mathbf{R}} = -i\hbar\left\langle\phi_j\right|\frac{\partial}{\partial t}\left|\phi_k\right\rangle$ $d_{jk}(R) = \langle\phi_j(r,R)|\nabla_R|\phi_k(r,R)\rangle$



Tully's fewest switches hopping techniques

Hopping probability ~ nonadiabatic coupling

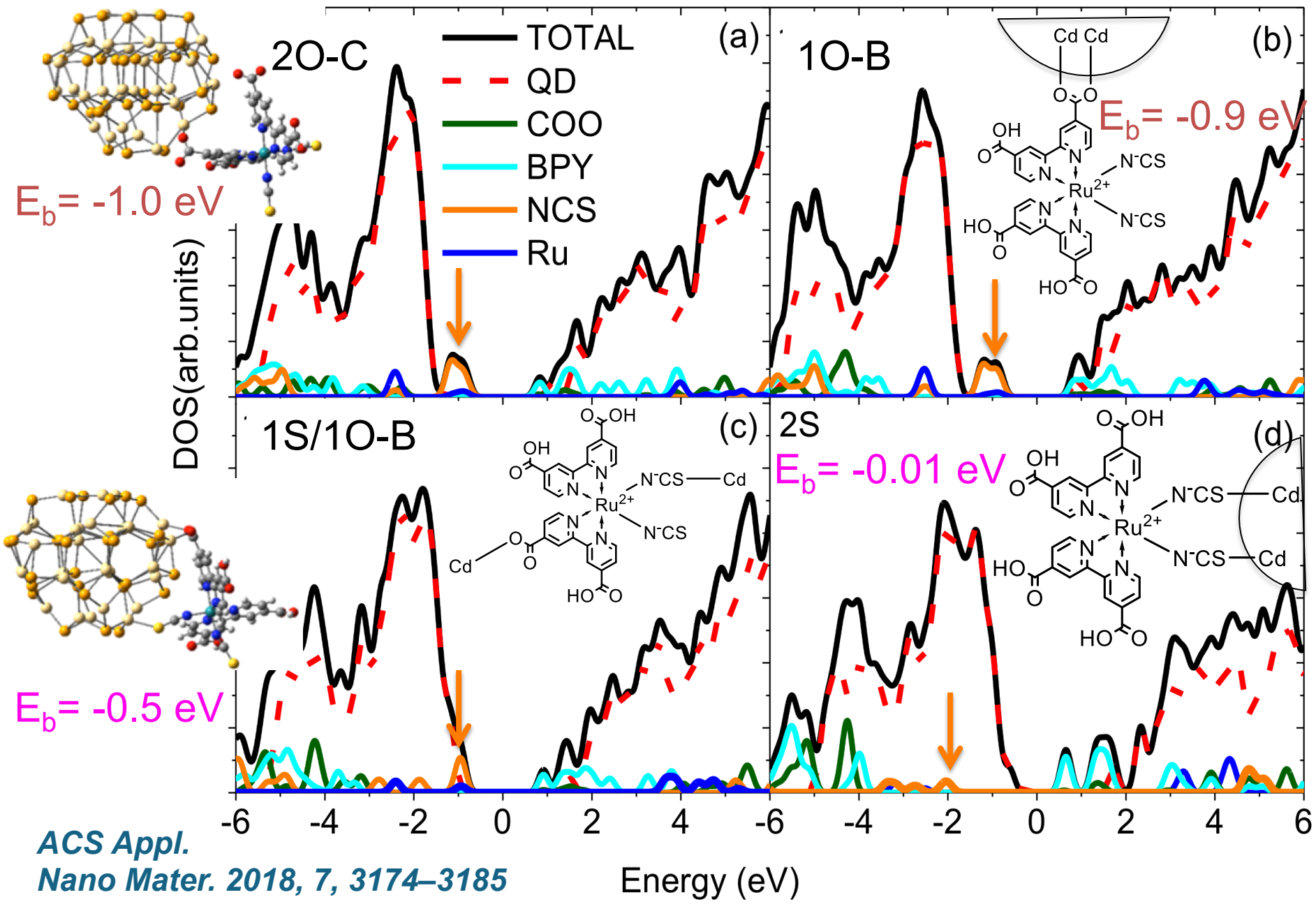
$$P_{kj}(t,dt) = 2\,\mathrm{Im}\left(\frac{a_{kj}}{\hbar}\langle\phi_k|H_q|\phi_j\rangle\right) - 2\,\mathrm{Re}(a_{kj}\mathbf{d}_{kj}\cdot\dot{\mathbf{R}}),$$

density matrix coefficient

S. Kilina et al, J. Phys. Chem, 111, 4871, 2007

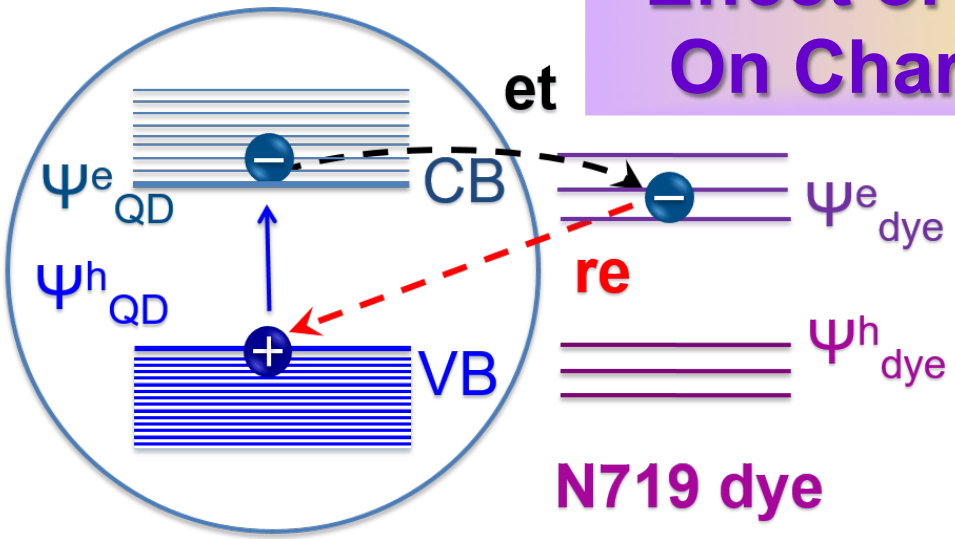
S. Kilina and O. Prezhdo, ACS Nano, 2009

Effect of Dye Binding Geometry on DOS of QD/N719



ACS Appl. Nano Mater. 2018, 7, 3174–3185

Effect of Dye Binding Geometry On Charge Transfer Couplings



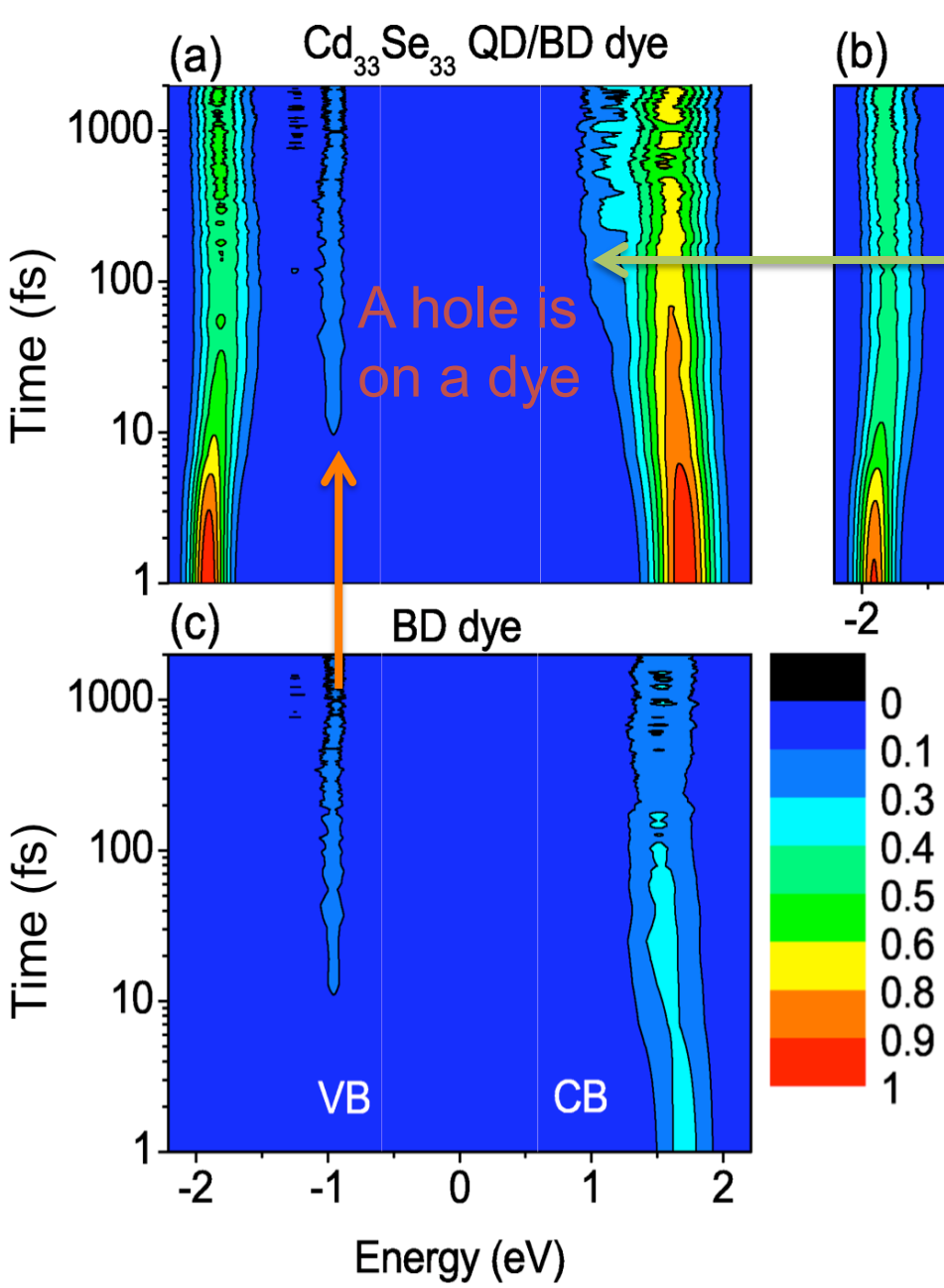
Constrained DFT (CDFT) is used for the electronic couplings.

		Electronic coupling (Hartree)	
		et	*re*
I	2O-A	1.29×10^{-6}	2.32×10^{-7}
	2O-B	3.60×10^{-8}	1.84×10^{-8}
	2O-C	8.28×10^{-7}	1.73×10^{-8}
II	1O-D	3.84×10^{-8}	3.57×10^{-8}
	1O-E	2.29×10^{-6}	4.20×10^{-9}
III	1S/1O-A	8.08×10^{-8}	1.92×10^{-5}
	1S/1O-B	3.41×10^{-4}	1.32×10^{-2}
	2S/1O	4.60×10^{-4}	2.09×10^{-2}
	1S/2O	3.22×10^{-6}	1.78×10^{-6}
IV	2S	7.30×10^{-2}	1.36×10^{-2}

Weak **et** and **re** couplings provide better conditions for QD*-to-dye hole transfer!

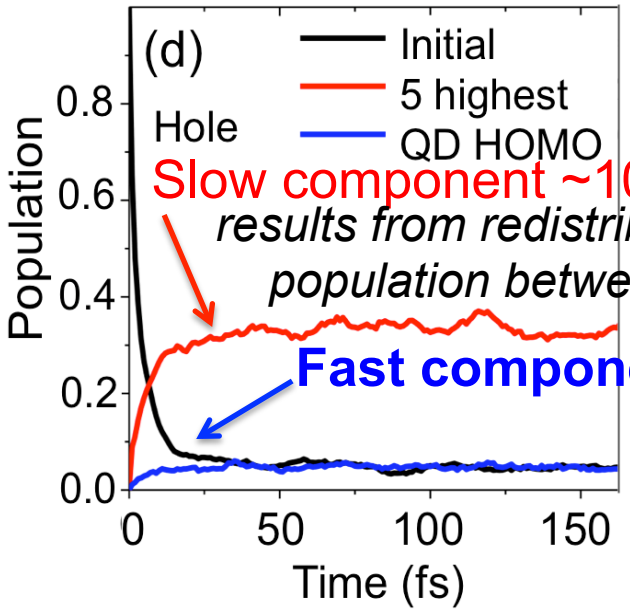
Strongest electron couplings ⇔ fast QD*-to-dye e-transfer and e-recombination

Charge Transfer from QD to Black Dye



Dr. Peng Cui

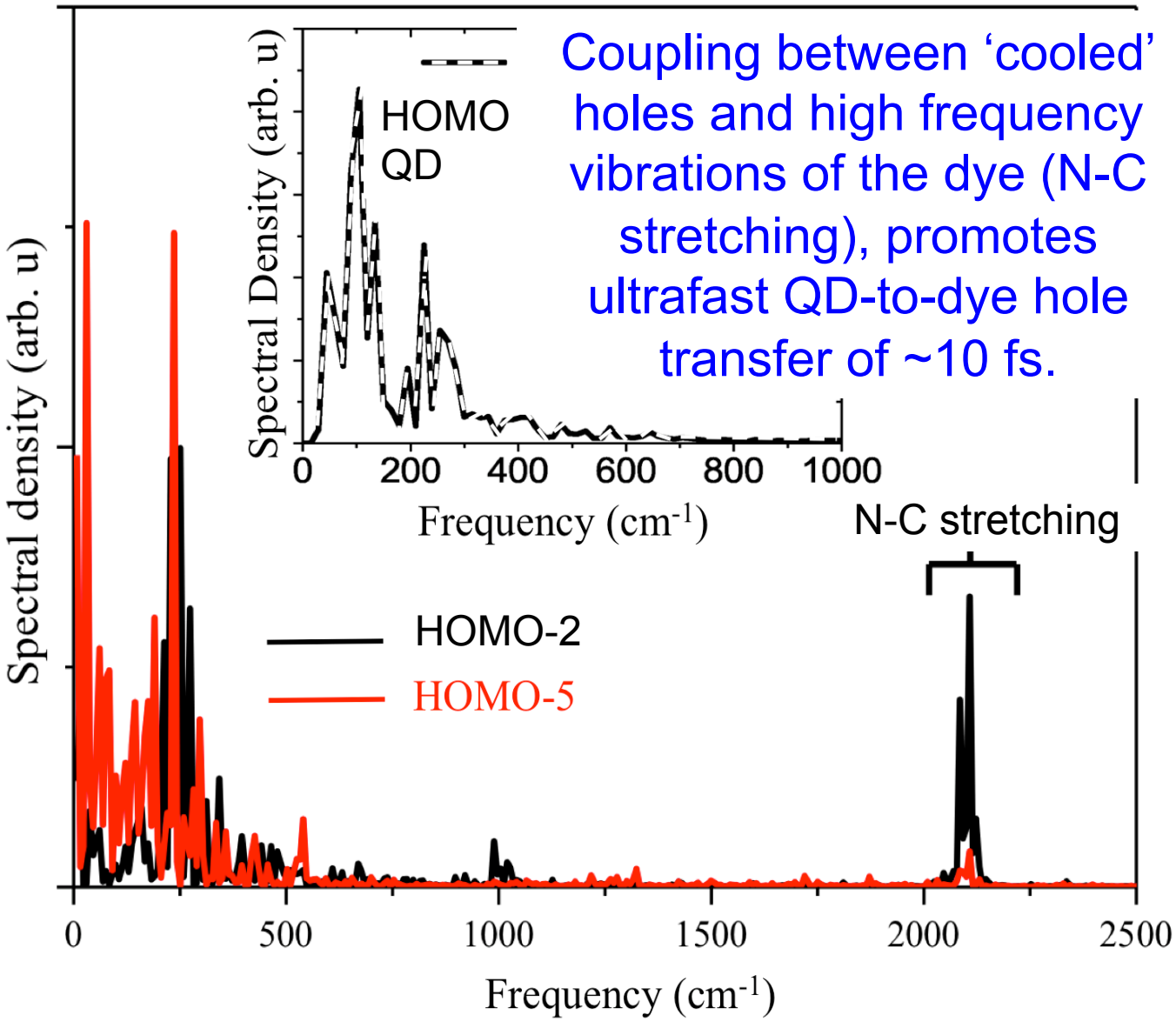
Dr. Jabed Mohammed



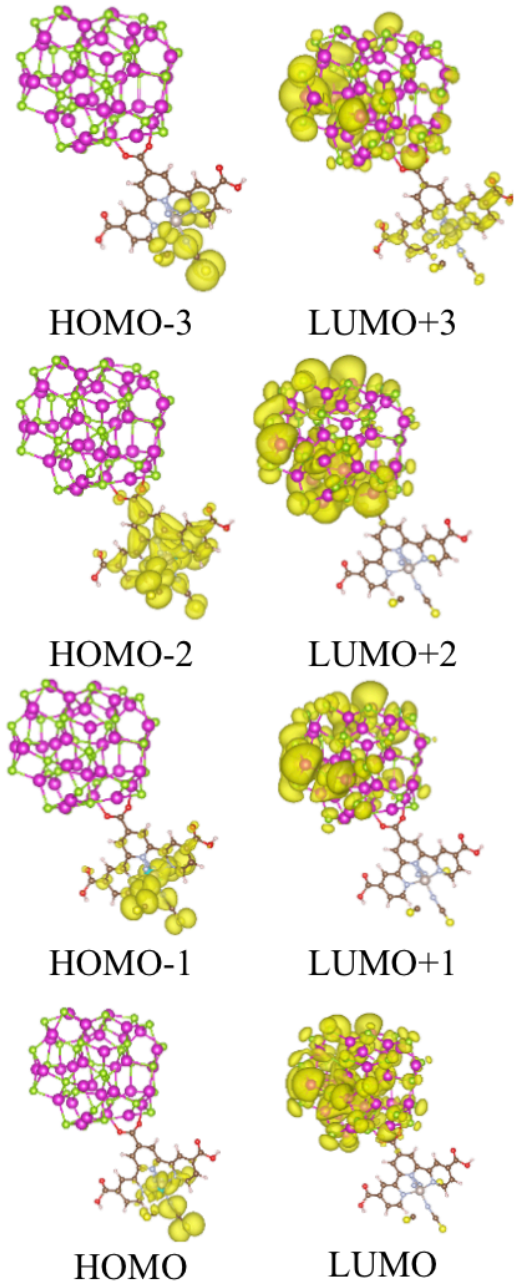
Slow component ~100 fs
results from redistribution of population between ***QD states***

Fast component ~10 fs
results from ***QD-to-dye*** *hole transfer*

Phonon Modes Coupled to Holes

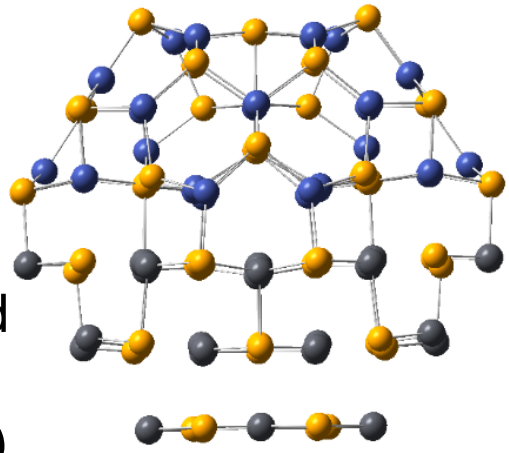


Coupling between 'cooled' holes and high frequency vibrations of the dye (N-C stretching), promotes ultrafast QD-to-dye hole transfer of ~10 fs.

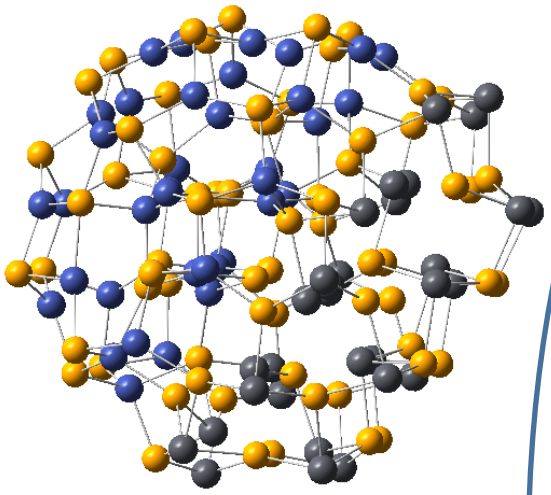


Janus PbSe|CdSe QDs: Structures

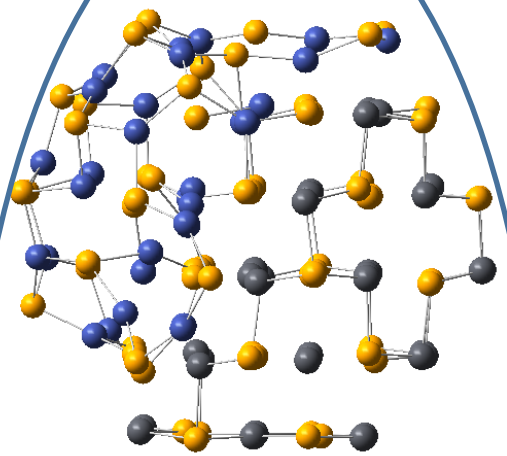
Dr. Jabed Mohammed (former Grad. Stud)



$(PbCd)_{34}Se_{68}$ *(100)*
symmetric



$Pb_{31}Cd_{37}Se_{68}$ *(111)*
Cd-enriched

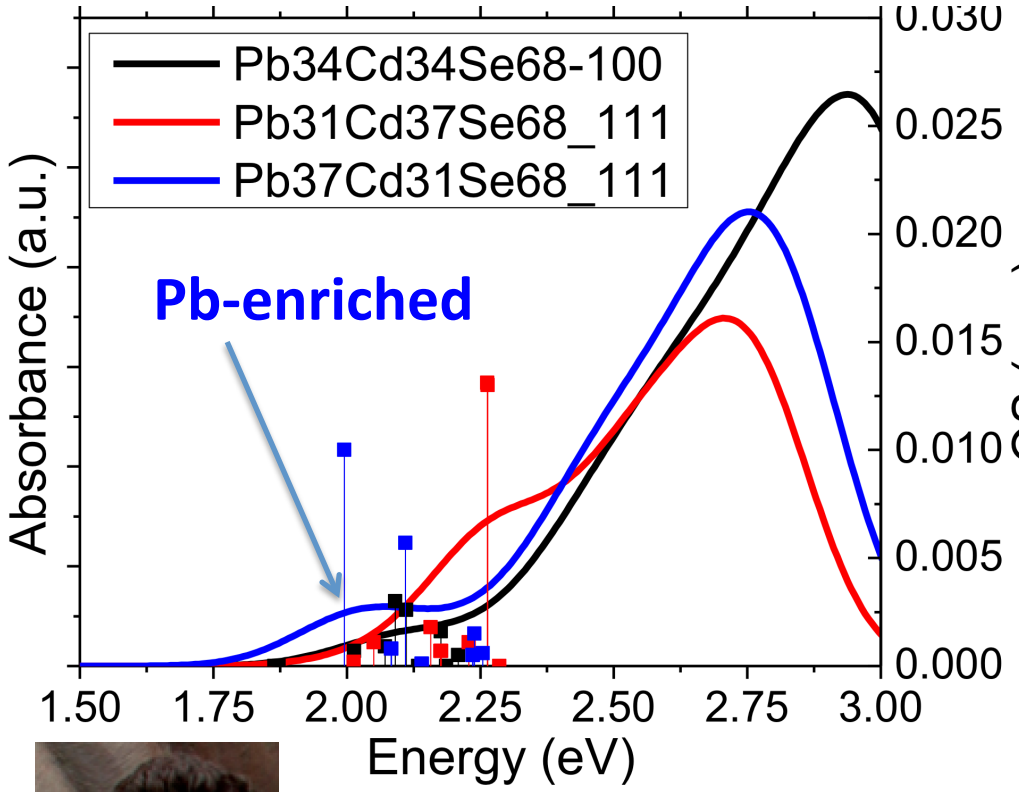


$Pb_{37}Cd_{31}Se_{68}$ *(111)*
Pb-enriched

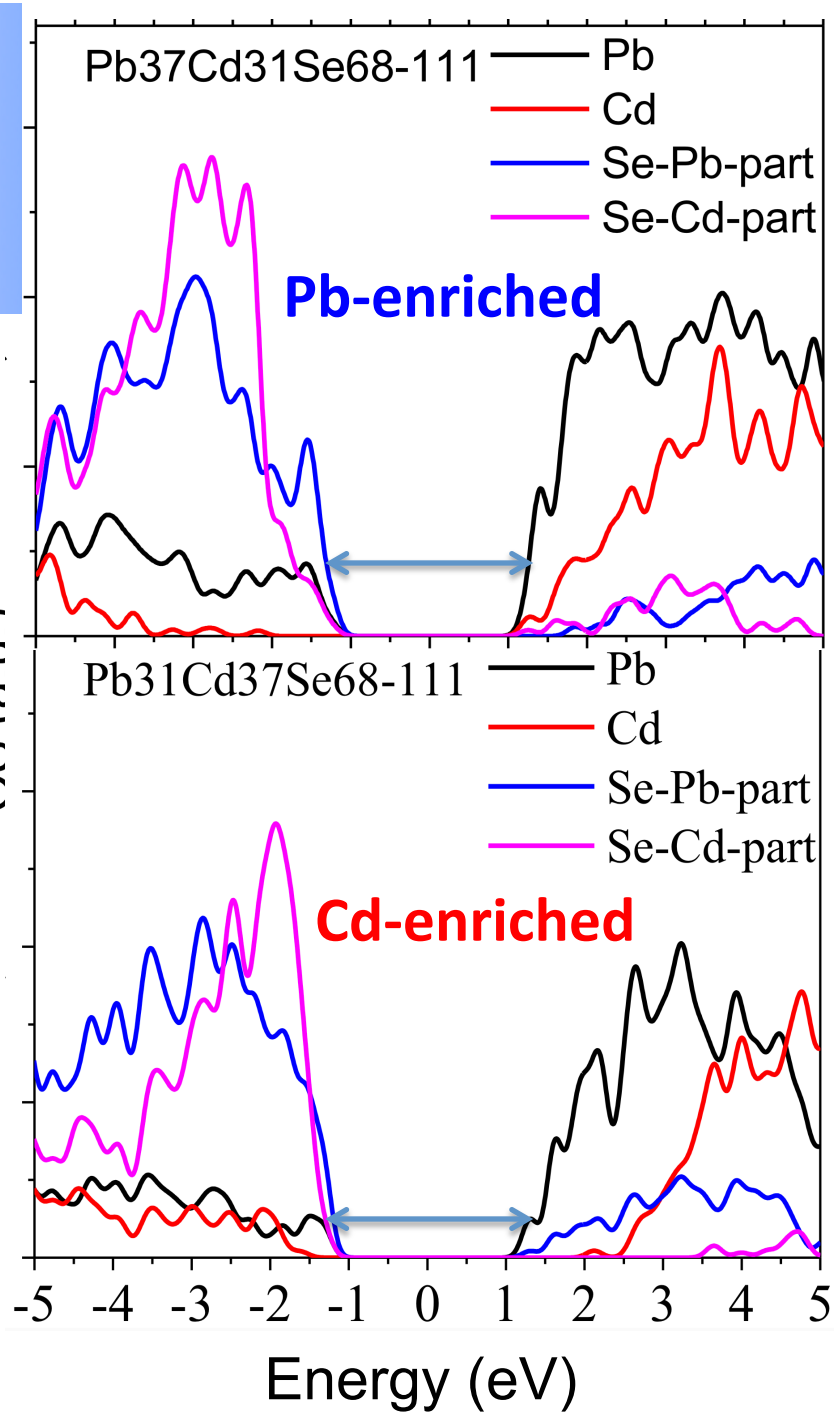
Dipole, D (toluene)	**11.0**	**26.8** (19.1)	**13.9** (13.1)
Pb-Se, Ang (toluene)	**2.90**	**2.91** (2.95)	**2.96** (2.95)
Cd-Se, Ang (toluene)	**2.69**	**2.74** (2.76)	**2.73** (2.73)

Experiment: Nano Lett. 2017, 174, 2547-2553

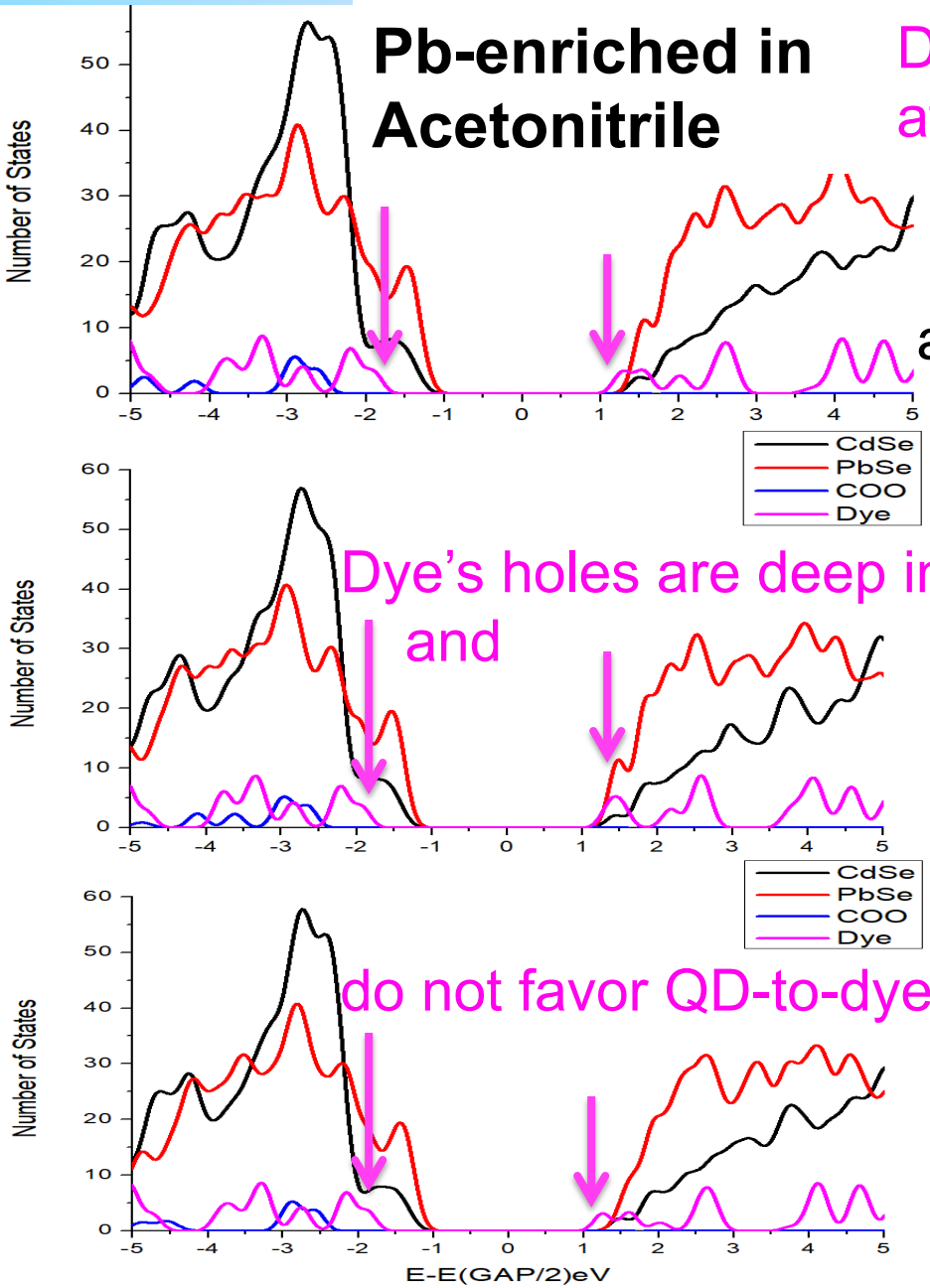
Janus PbSe|CdSe QDs: Absorption and Electronic Structure



Jabed Mohammed
(Former Grad. Stud)

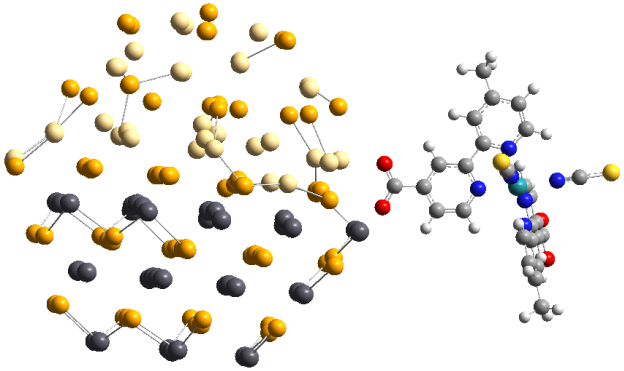


N719 Dye on Janus PbSe|CdSe QDs

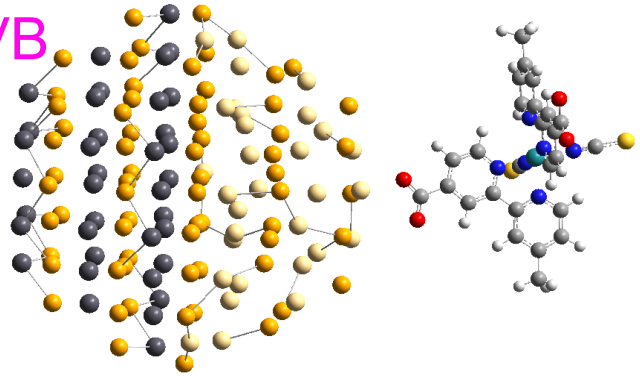


Dye's electron states are more affected by linking than holes.

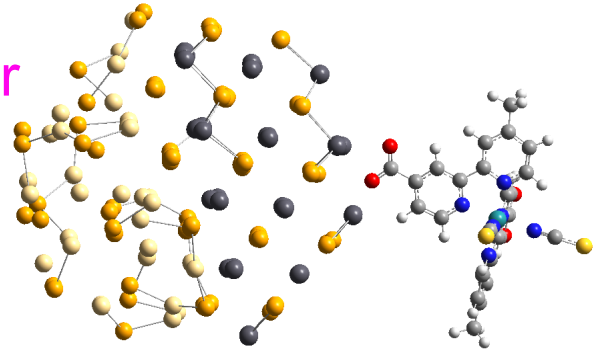
Interface attachment



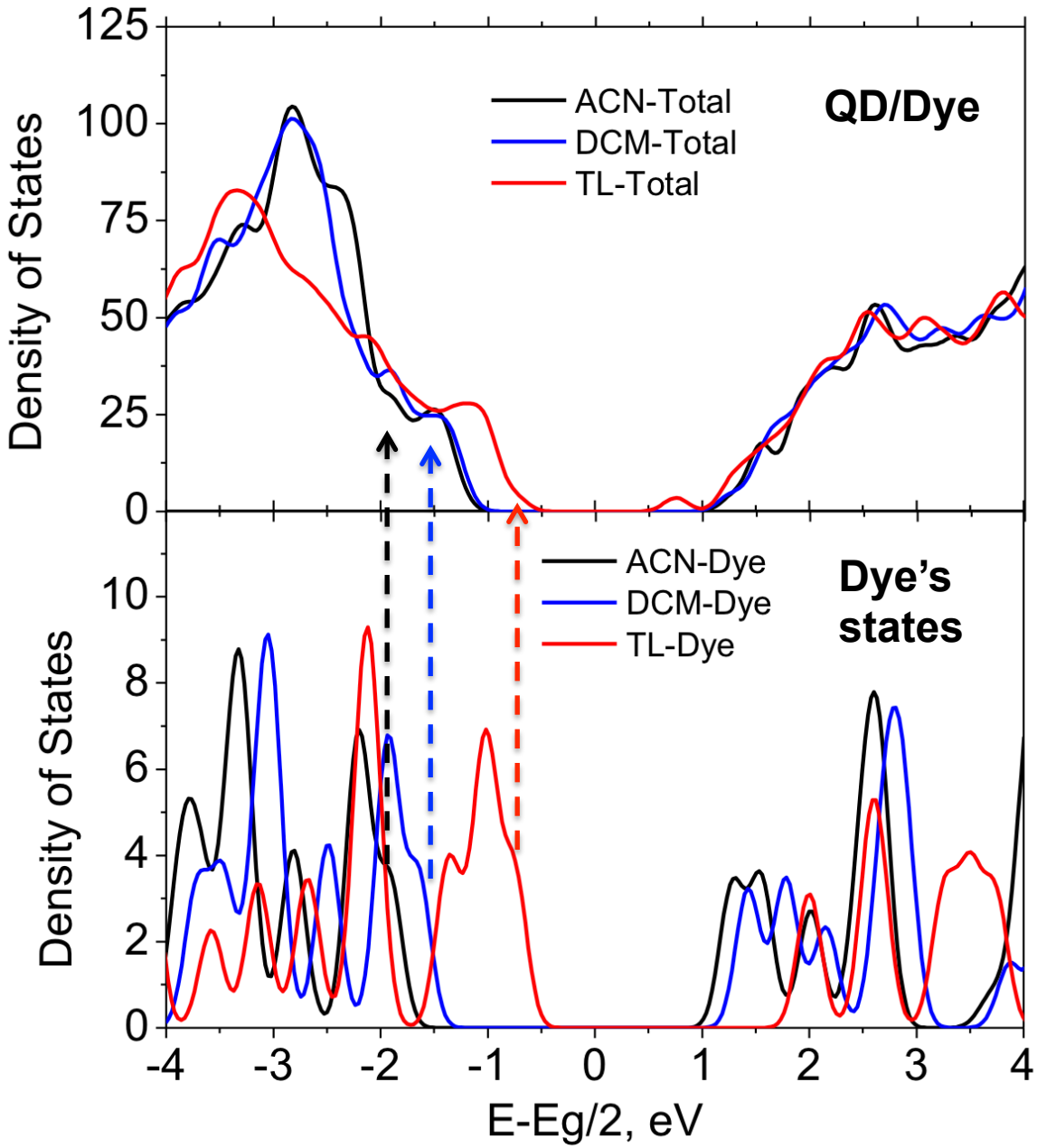
Cd-site attachment



Pb-site attachment



Solvent effect: N719 Dye on Janus QD



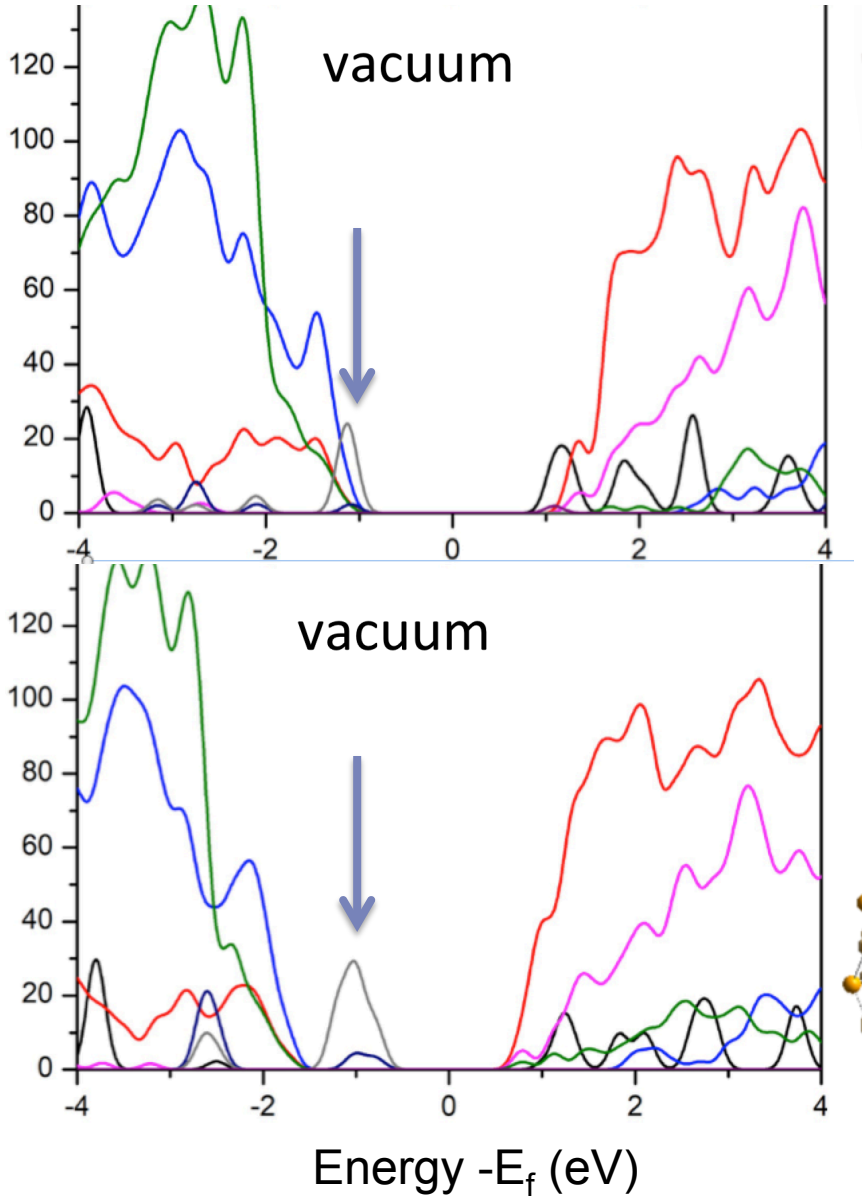
Pb-enriched Interface attachment of N719

Ben Geffree (undergrad)

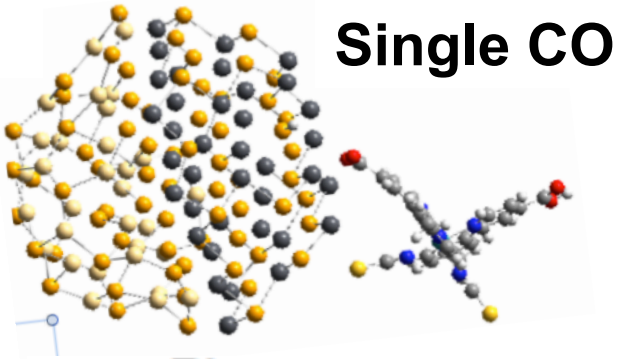
A nonpolar solvent destabilizes dye hole states moving them to the edge of the QD VB.

Solvent effect: N719 Dye on Janus QD

Pb-enriched QD/N719

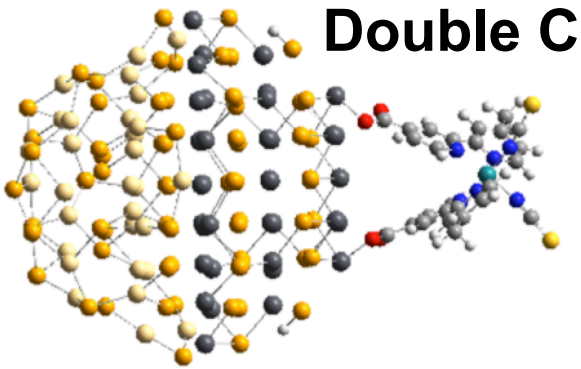


Single COO-attachment

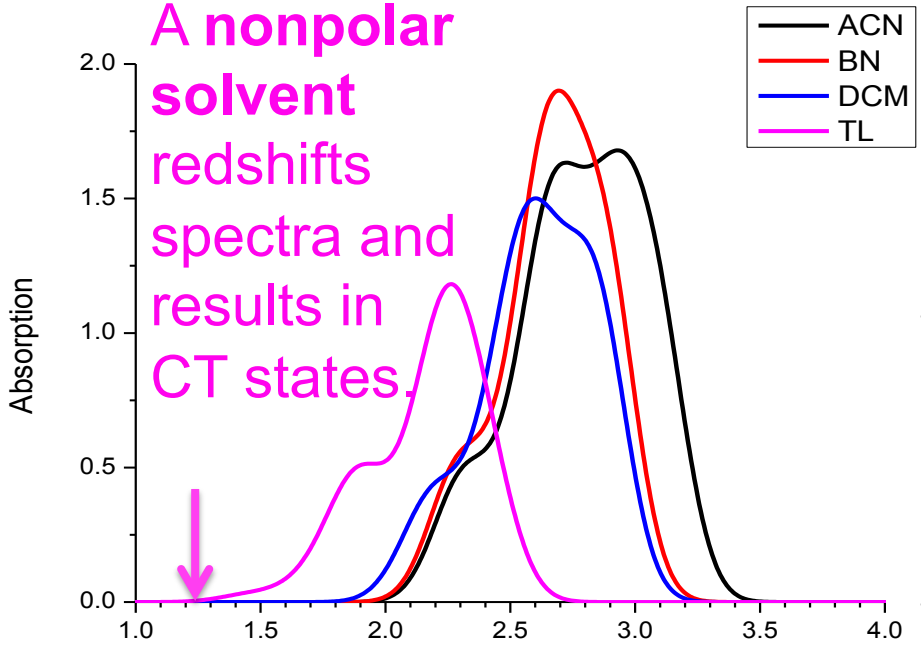


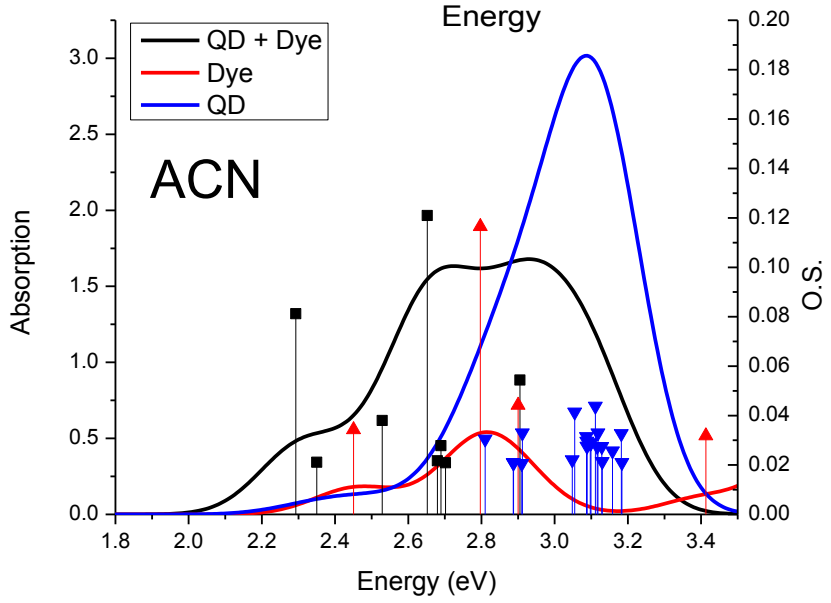
Pb
Se (Pb)
Cd
Se (Cd)
Ru(II)
Isothiocyanate
Carboxyl

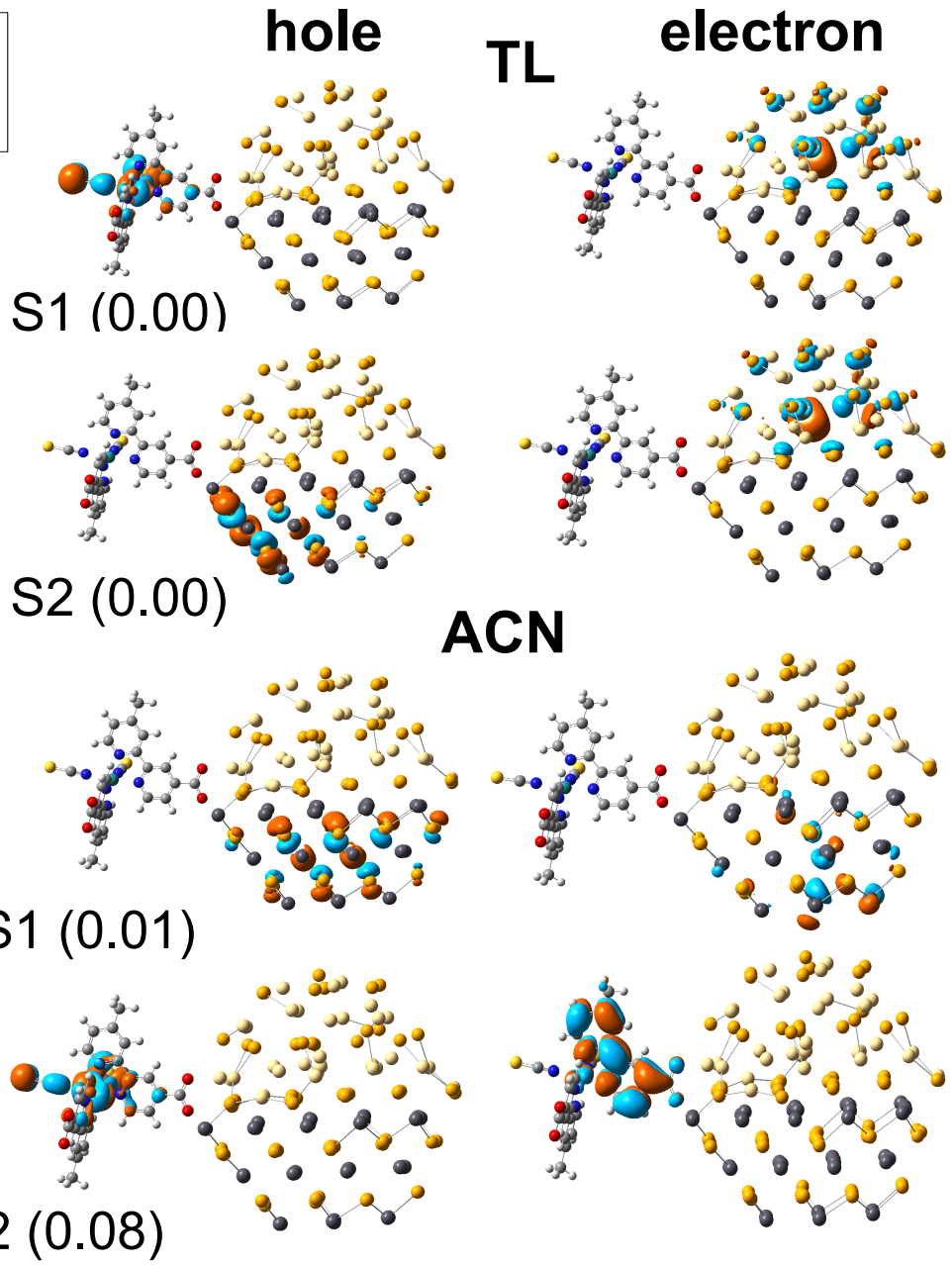
Double COO-attachment



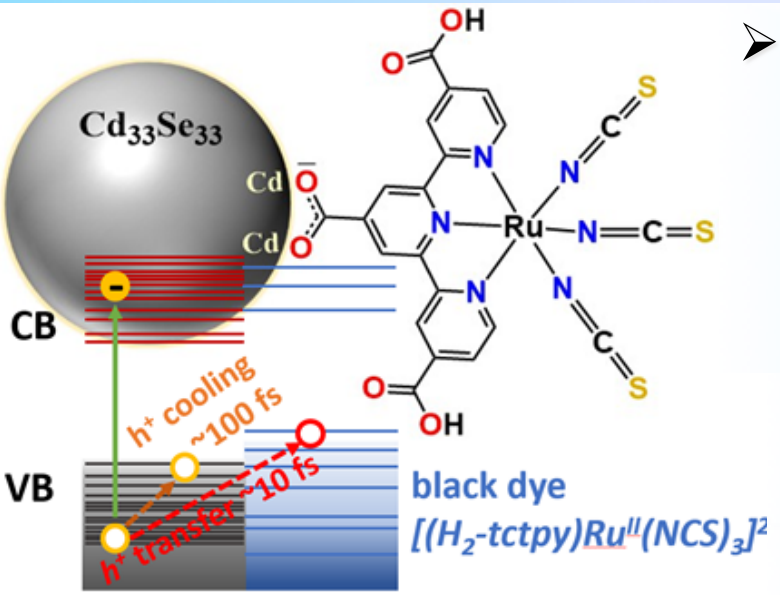
Absorption Bands: N719 Dye on Janus QD





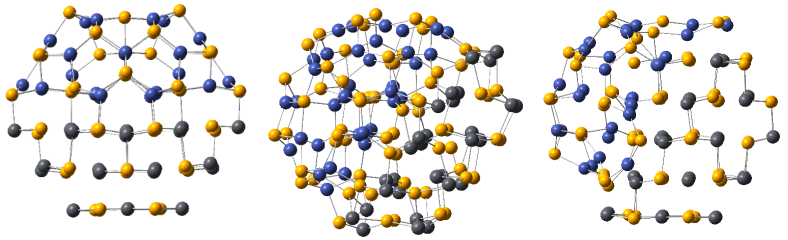


Conclusions



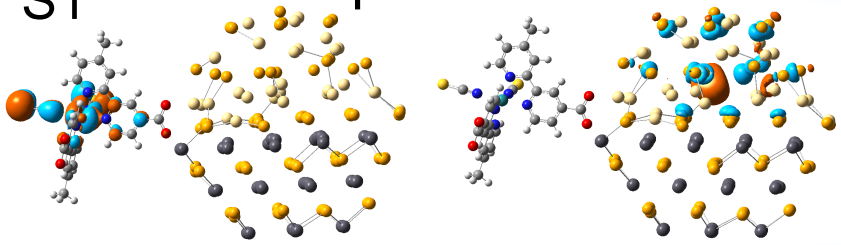
- Binding via isothiocyanates is not stable.
  - It leads to strong electronic couplings favoring QD-to-Dye electron transfer
  - It stabilizes dye orbitals deep inside the VB unfavoring QD*-to-dye hole transfer.
- Binding via carboxyl is stable and favors QD*-to-dye hole transfer
- Two passways for QD*-to-dye hole transfer
  - Ultrafast (~10 fs) is facilitated by coupling with C-N stretching phonon
  - Slower component (~100 fs) originates from the QD inter-band relaxation.

Janus QDs



non-polar solvent

S1



Hole **Electron**

- Electronic structure **of Janus QDs** is adjustable by dye's linking and media/ solvent polarity:
  - Non-polar solvent results in charge-transfer (CT) optical transitions.

Acknowledgments

Los Alamos NATIONAL LABORATORY

Dr. Kirill Velizhanin
(Los Alamos National Lab)

Dr. Sergei Tretiak
(Los Alamos National Lab)

Dr. Sergei Ivanov
(Los Alamos National Lab)

Dr. Sean Robertson
(UT, Austin)

- **National Science Foundation** grant no. 2004197
- **DOE grant no** DE-SC0021287
- **DOE grant no** DE-SC0022239

Dr. Peng Cui
(former GS, 2012-16)

Jabed Muhamed
(GS, NDSU; 2014-20)

Benjamin Geffre
(URA NDSU, 2018-20)

Steven Westra
(GS NDSU, 2021)

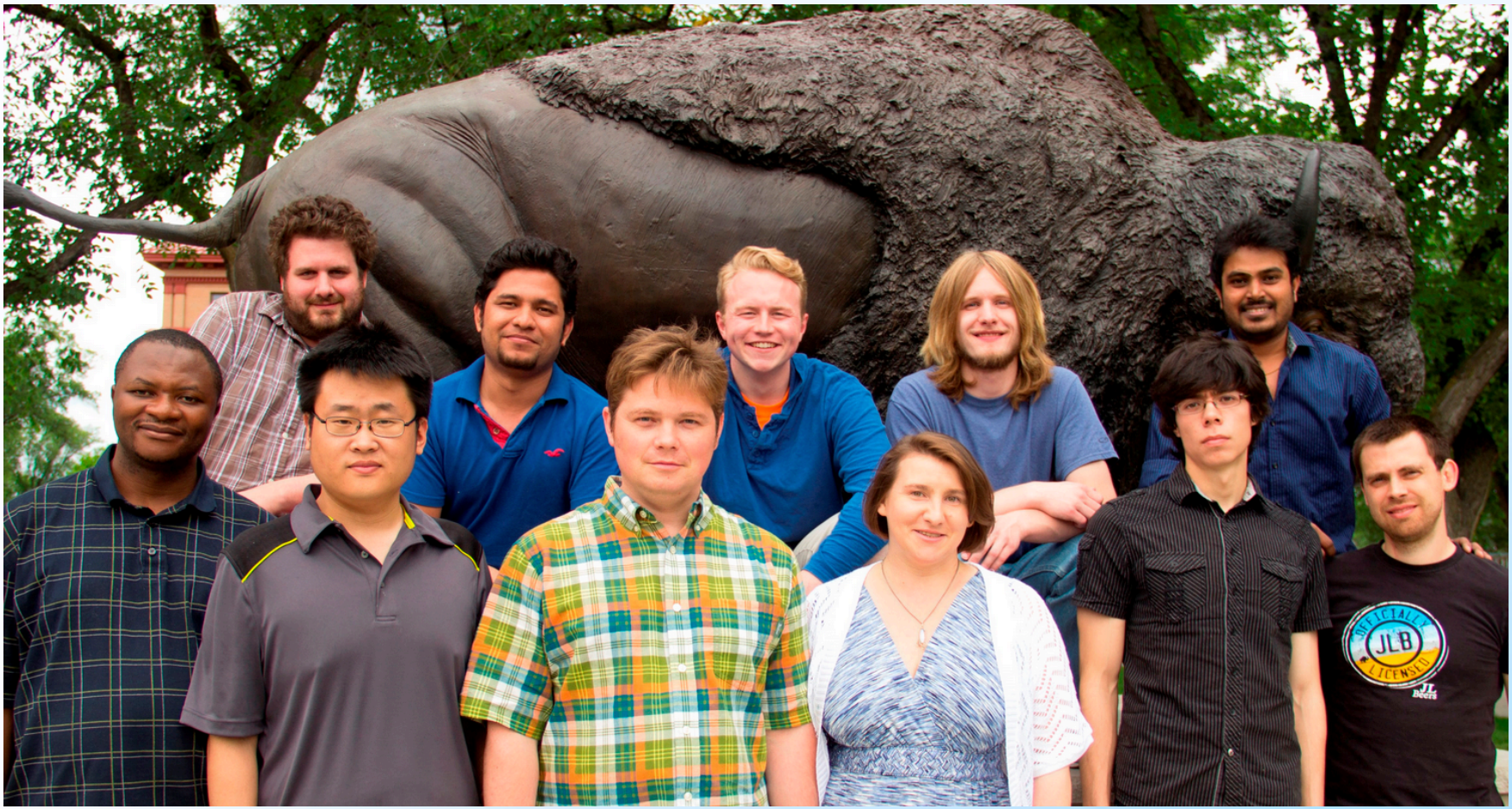
Prof. D. Kilin (NDSU)

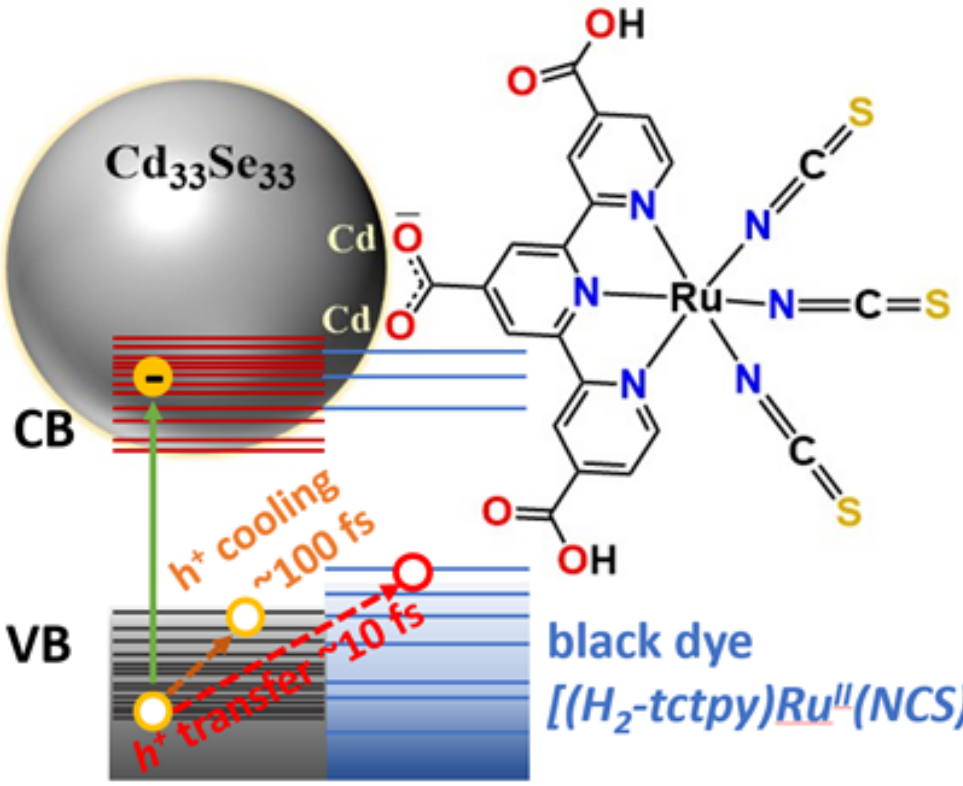
Prof. W Sun (NDSU)

Computational Facilities:

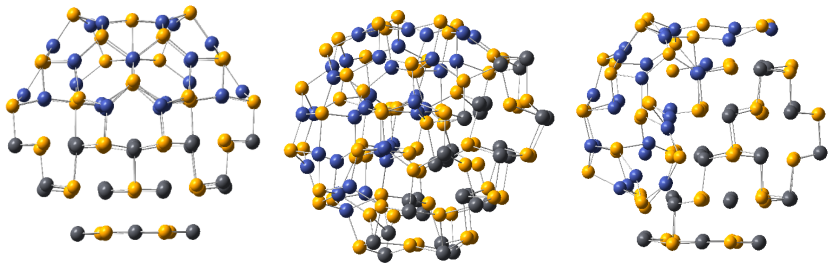
- ***CCAST at NDSU (NSF, ND-EPSCoR)***
- ***Center for Integrated Nanotechnologies (CINT), LANL, (DOE BES)***
- ***NERSC (DOE BES);***

Thanks to my group and NDSU collaborators!

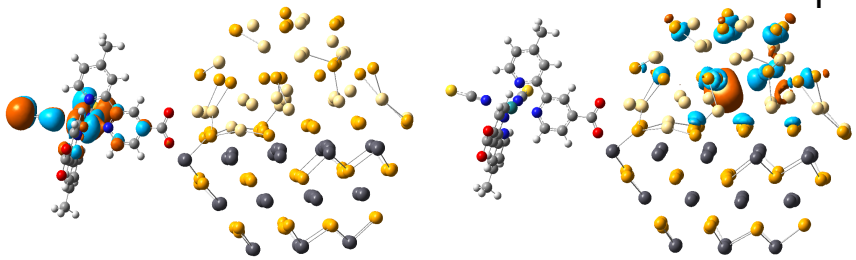




Janus PdSe|CdSe QDs



The lowest excited state S_1



Hole **Electron**