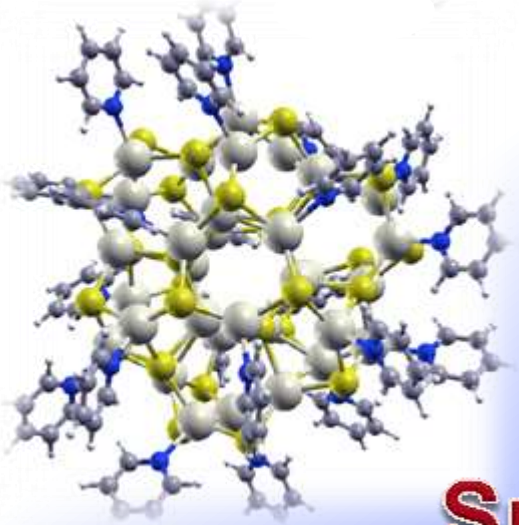

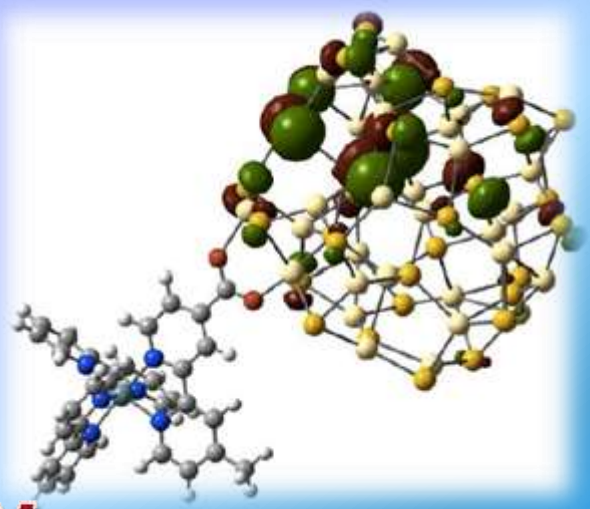

Modeling of Surface Chemistry of Quantum Dots

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North Dakota State University, Fargo

RASA, Tampa 11/9/2013

Why Nanotechnology?

Consumer products

Surface reactivity,
novel mechanical and
size-tunable optical properties

Benefits of nano: size 10^{-9} m

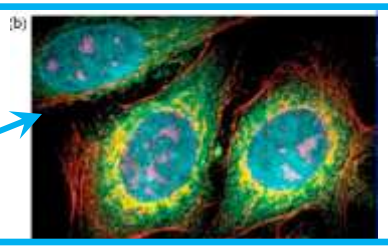
Miniaturization of devices,
low fabrication cost,
lower heat-losses

Pre-Restoration

Post restoration

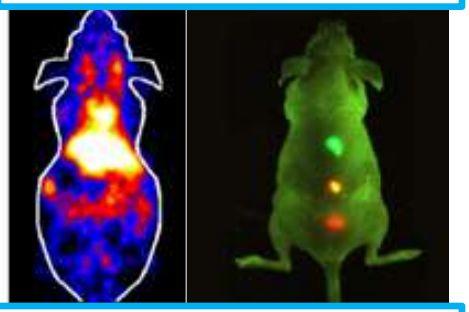
Restoration of Art

Electronics and opto-electronics



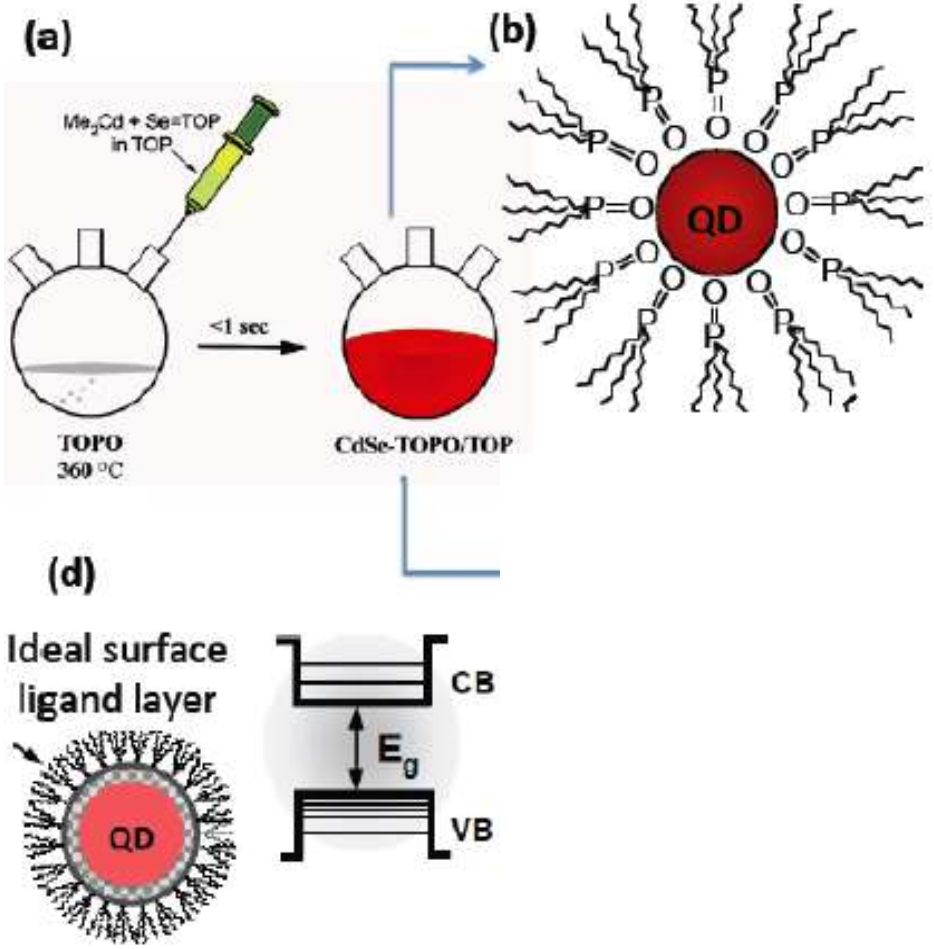
Drug delivery and therapy

Photovoltaics



Bio-imaging and diagnostic agents

Surface of Colloidal Quantum Dots



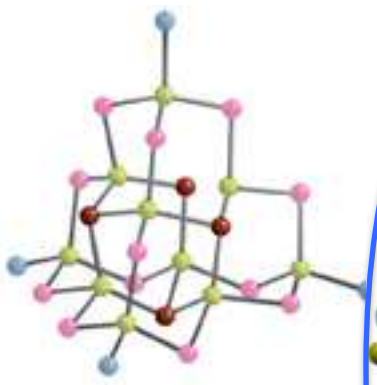
Role of ligands:

- ☺ Increase QD solubility
- ☺ Prevent QD-QD interaction
- ☺ Reduce chemical reactivity
- ☺ Increase luminescence yield

- ☹ Lead to surface defects
- ☹ Add the additional surface and trap states to the gap
- ☹ Affect both radiative and non-radiative dynamics

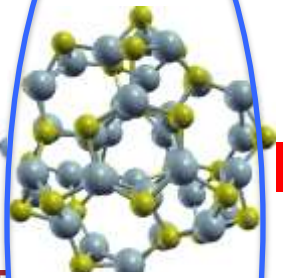
The main obstacle on the path to development of efficient QD-based energy materials is our limited understanding of the QD surfaces, its interaction with passivated ligands, and their role in photoexcitation of QDs.

Excitation in QDs: Size and Confinement



$Cd_{10}Se_4(SePh)_{12}(P$

100 atoms
2 nm



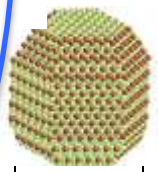
$Cd_{33}Se_{33}$

Clusters

DFT simulations

Quantum Dot Regime

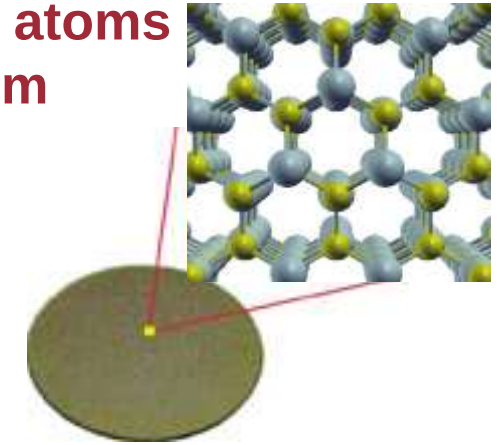
10 nm



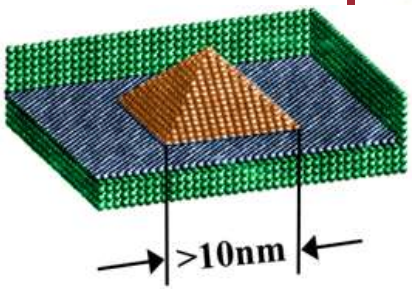
2R
<10 nm

Nanocrystals and Colloidal Quantum Dots

100,000 atoms
20 nm



Bulk CdSe

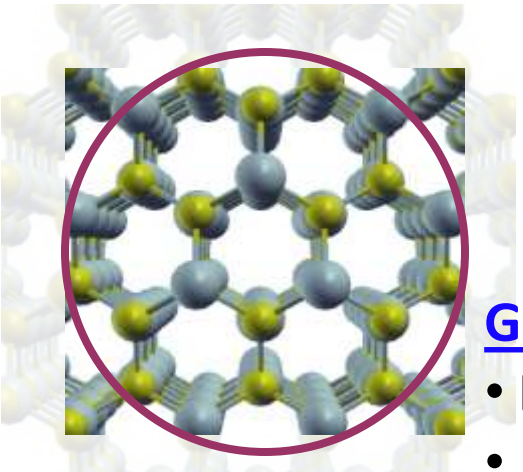


>10nm

Epitaxial Quantum Dots

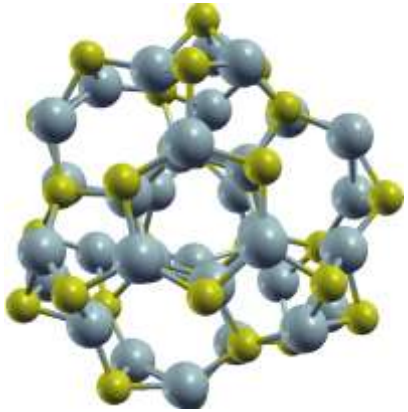
Atomic models: Comparison with experiment

Bulk CdSe => $Cd_{33}Se_{33}$



Diameter ~ 1.5 nm

Relaxed $Cd_{33}Se_{33}$



Tools:

- Density Functional Theory (**DFT**)
- Non-adiabatic Kohn-Sham Dynamics + surface hopping

Geometry and dynamics: by VASP

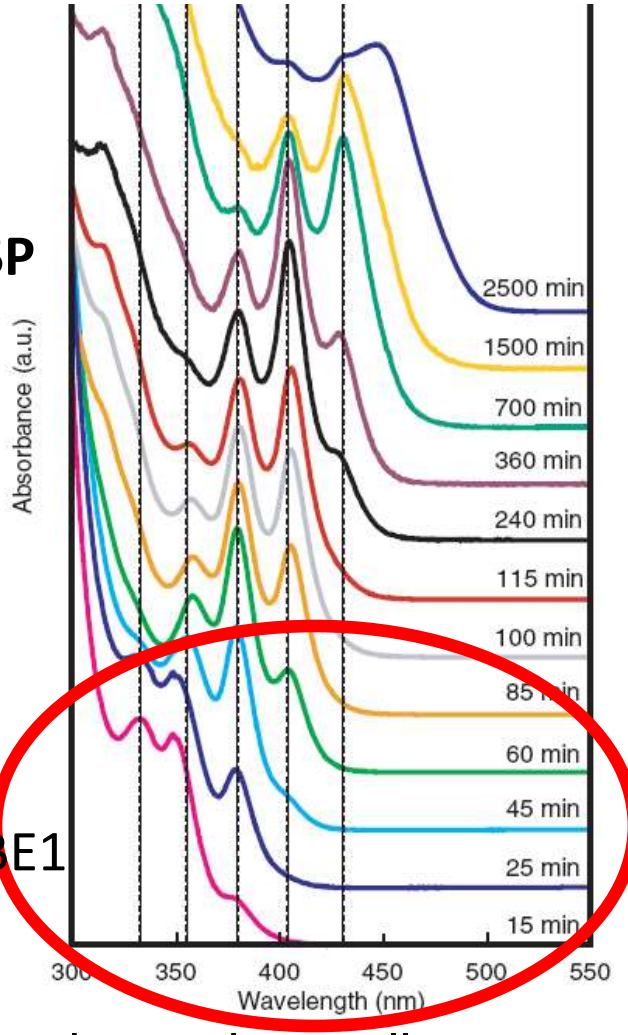
- **DFT** with plane wave basis set;
- PW91 GGA functional;
- Ultrasoft pseudo-potentials for core electrons.

Electronic structures and Optical spectra: by GAUSSIAN

TDDFT:

- Hybrid functional B3LYP and PBE1
- Localized basis set LANL2dz

Sequential Growth of Magic-Size CdSe QDs



Small Magic-size ($Cd_{33}Se_{33}$) nanocrystals were observed experimentally

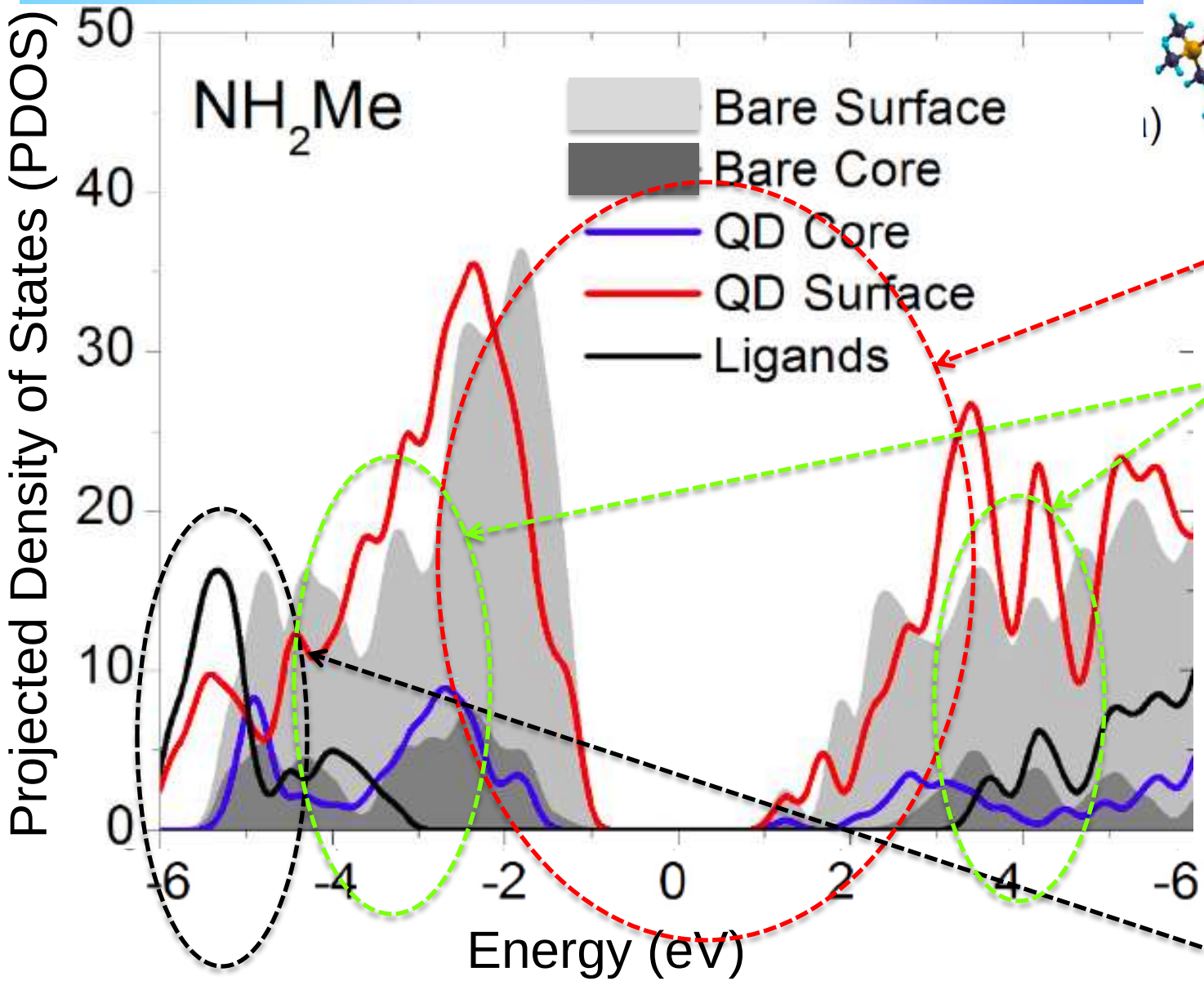
Nature Mat. 3, 99 (2004); S. Kudera et. al. Adv. Mater. 19, 548–552 (2007)

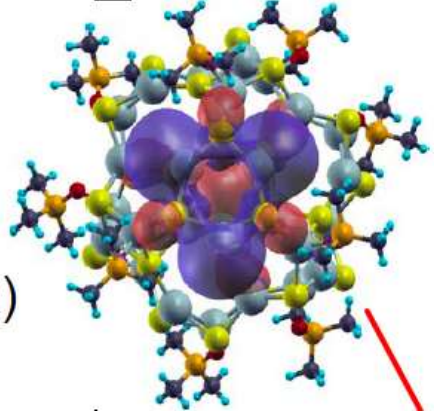
What Can We Learn from DFT Simulations?

Effect of surface defects and ligands:

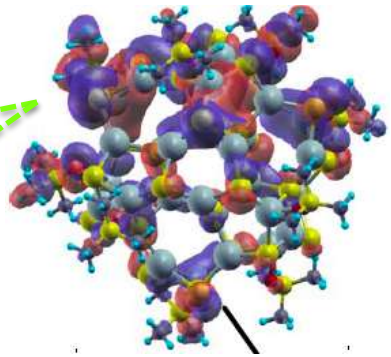
1. **QD-ligand interactions**:
   Do they strongly interact?
2. **Ligand states**:
   Localized or delocalized?
   Where they are located relative to the QD states?
3. **Excitation of an electron-hole pair**:
   Do ligand states contribute to optical transitions?
4. **Relaxation of excitation**:
   Do ligands enhance or hinder energy dissipation?
   Do ligand vibrations contribute to the electron-phonon coupling?

Where are ligand states?

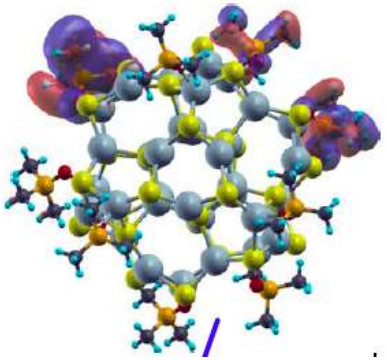




QD MO



hybrid MO

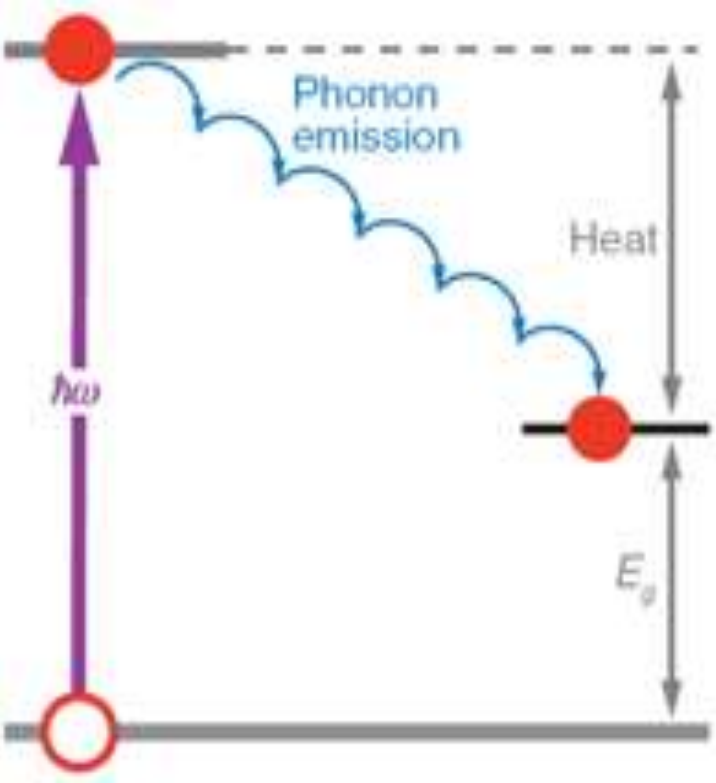


Ligand MO

S. Kilina, et al., 131, 7717 (2009)

Relaxation of Excitation in Quantum Dots

Excitation + Relaxation



Strong confinement => Discrete energies:

$E_{splitting} >> E_{phonon}$ => ***Phonon bottle neck*** ⇔ very long relaxation time

But it was not observed experimentally:

$t_{QD} \sim t_{bulk}$

Phys. Rev. Lett. 2005, 95, 19640;
Phys. Rev. Lett. 2007, 98, 177403

except for giant core/shel QDs

Science 2008, 322, 929

Mechanisms of fast relaxation

1) Auger relaxation (?)

Efros A. et. al., Solid State Com. 1995, 93, 281-284

2) Non-adiabatic channel:
Through surface and ligand states (?)

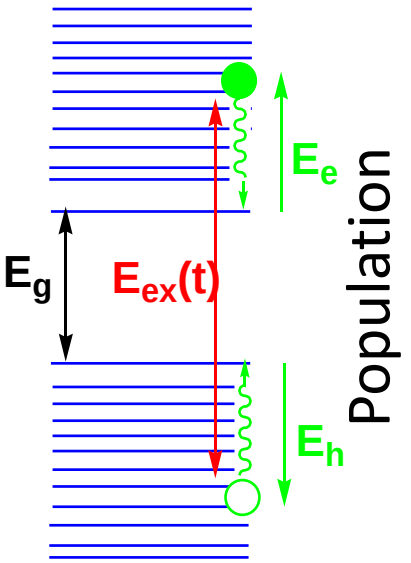
M. Beard et. al. Nano Lett. 2009, 9, 1217
A. Pandey et.al. Science 2008, 322, 929

Exciton Cooling: Relaxation of Energy

Non-adiabatic dynamics:

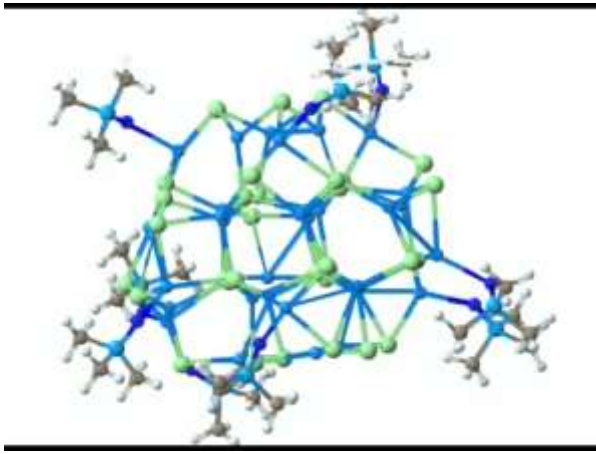
Exciton cooling: Evolution of excited wave packet

$Cd_{33}Se_{33}$ + 9 $OP(CH_3)_3$



Initial excitation: Ee=Eh

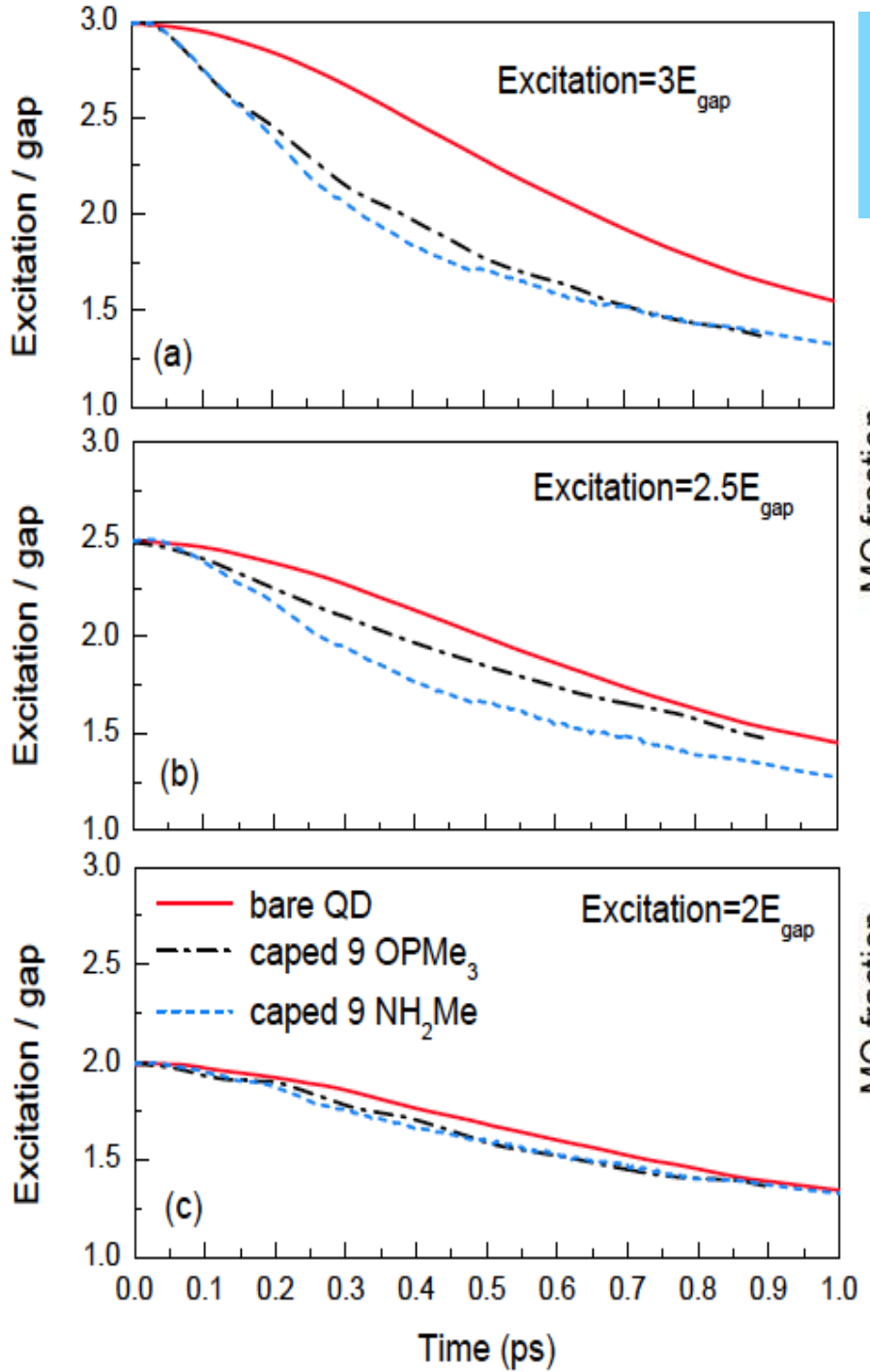
Adiabatic dynamics: Thermal motion

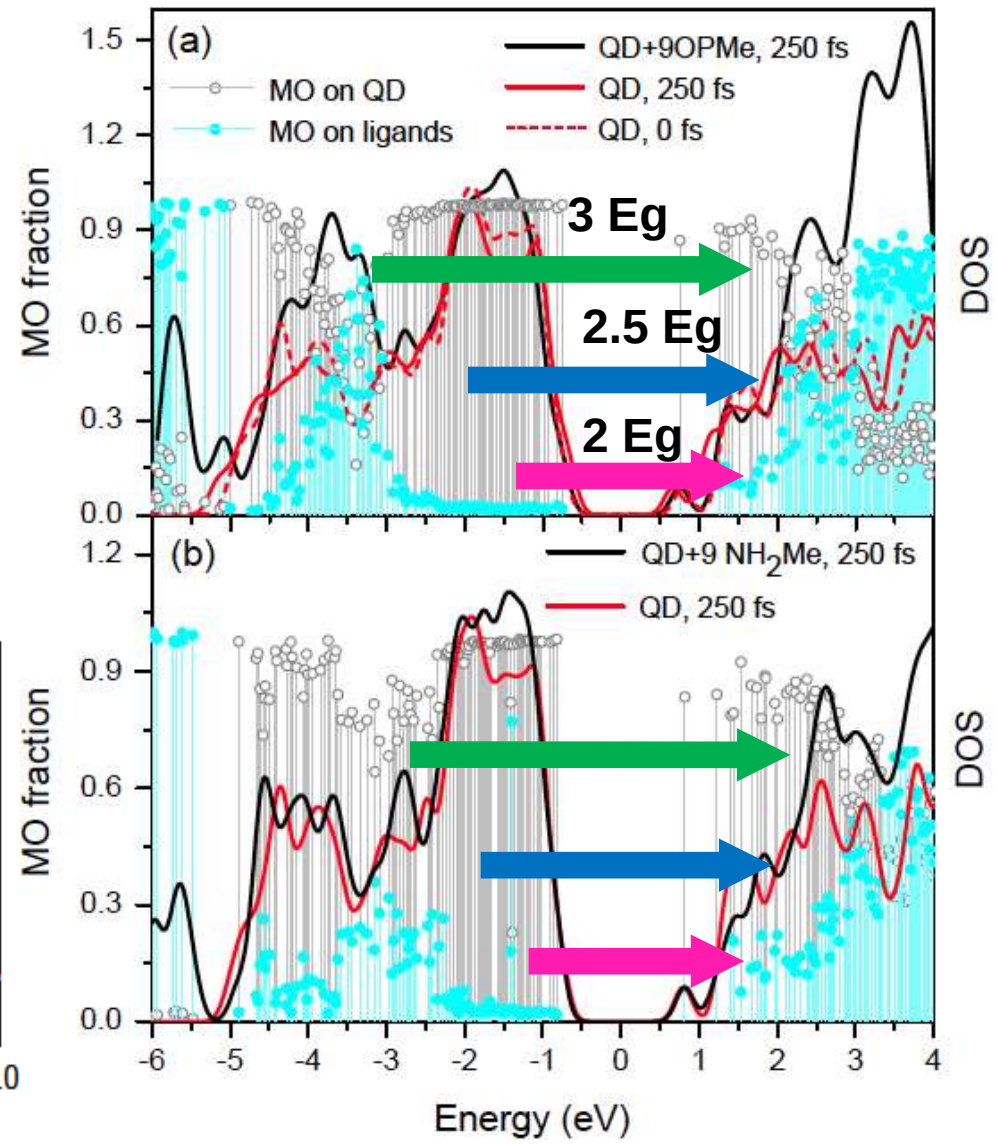


- No phonon bottle neck: relaxation is nearly done in a few ps
- Slow relaxation is seen only between a few electron states at the edge of CB
- Surface states speed up relaxation

- *S. Kilina et al*, ***ACS Nano, 3, 93 (2009)***; *S. Kilina et al*, ***JPC C, 111, 4871 (2007)***

Exciton Cooling: Relaxation of Energy

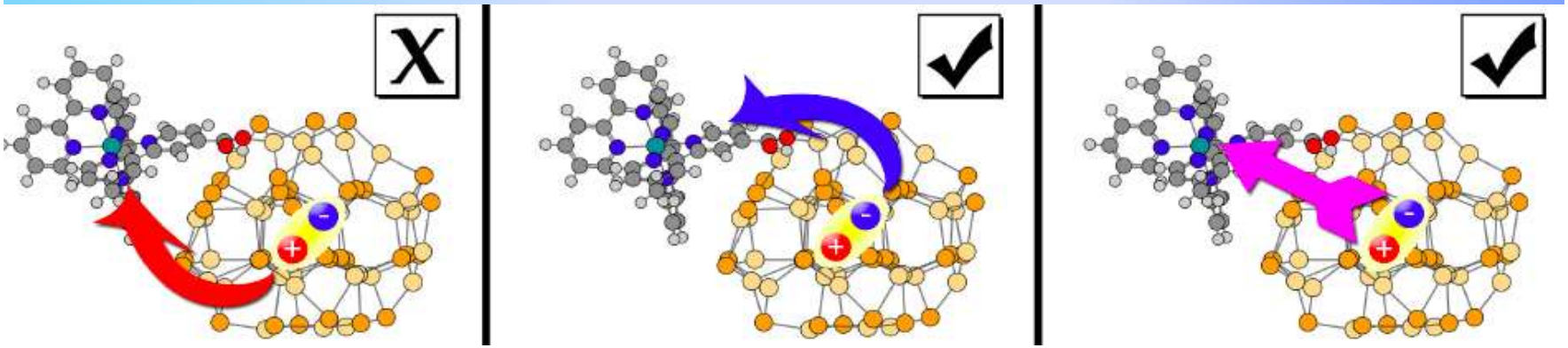




Conclusions

- Ligands exhibit strong binding with the QD surface.
- Many ‘hybridized’ surface-ligand orbitals appear upon ligation at energies > 2Eg. Most of these states are optically inactive, but contribute to relaxation.
- Ligands substantially increase relaxation rates of high energy photo-excitations >3Eg due to strong non-adiabatic coupling with both ligand and QD phonons.

Future Directions



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(Los Alamos National Lab)

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- ***Center for Nonlinear Studies (CNLS)***
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