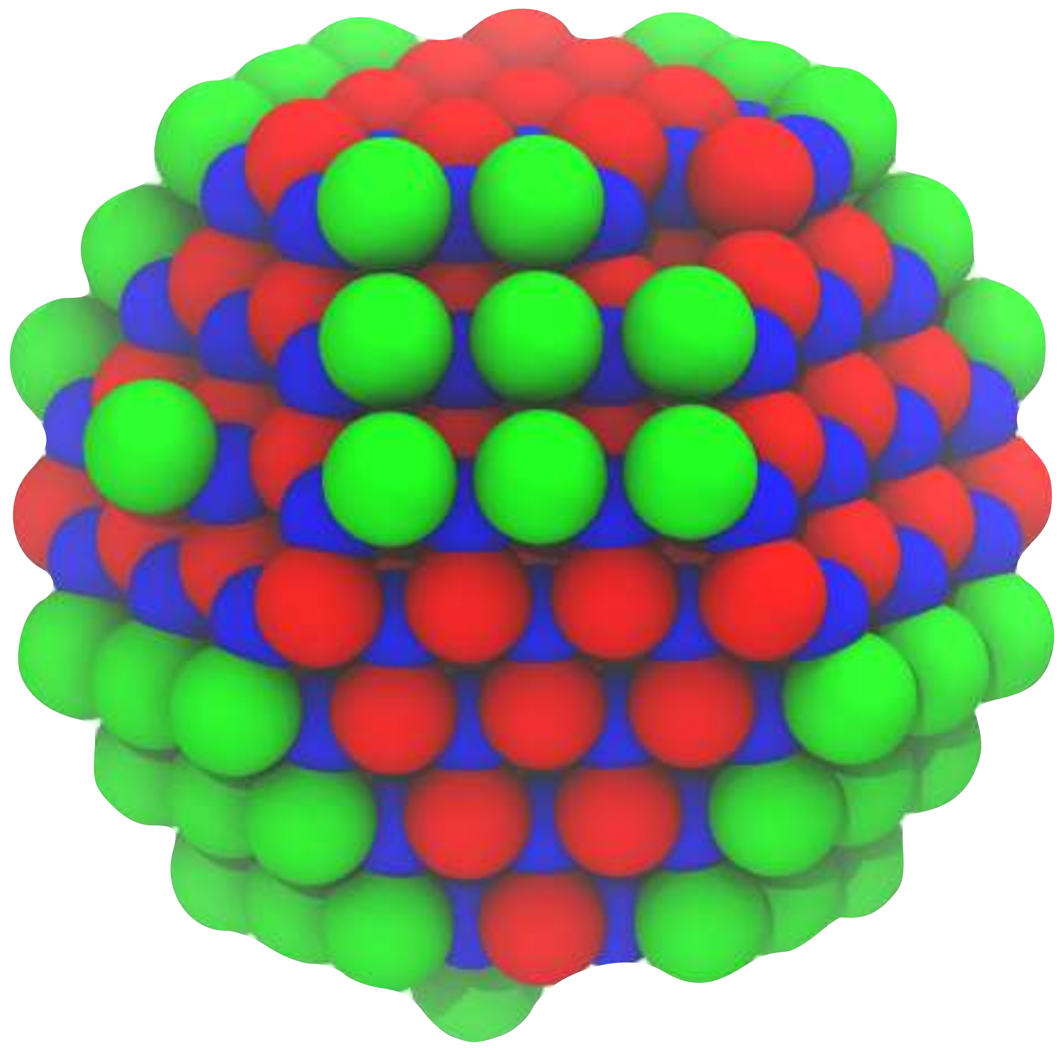
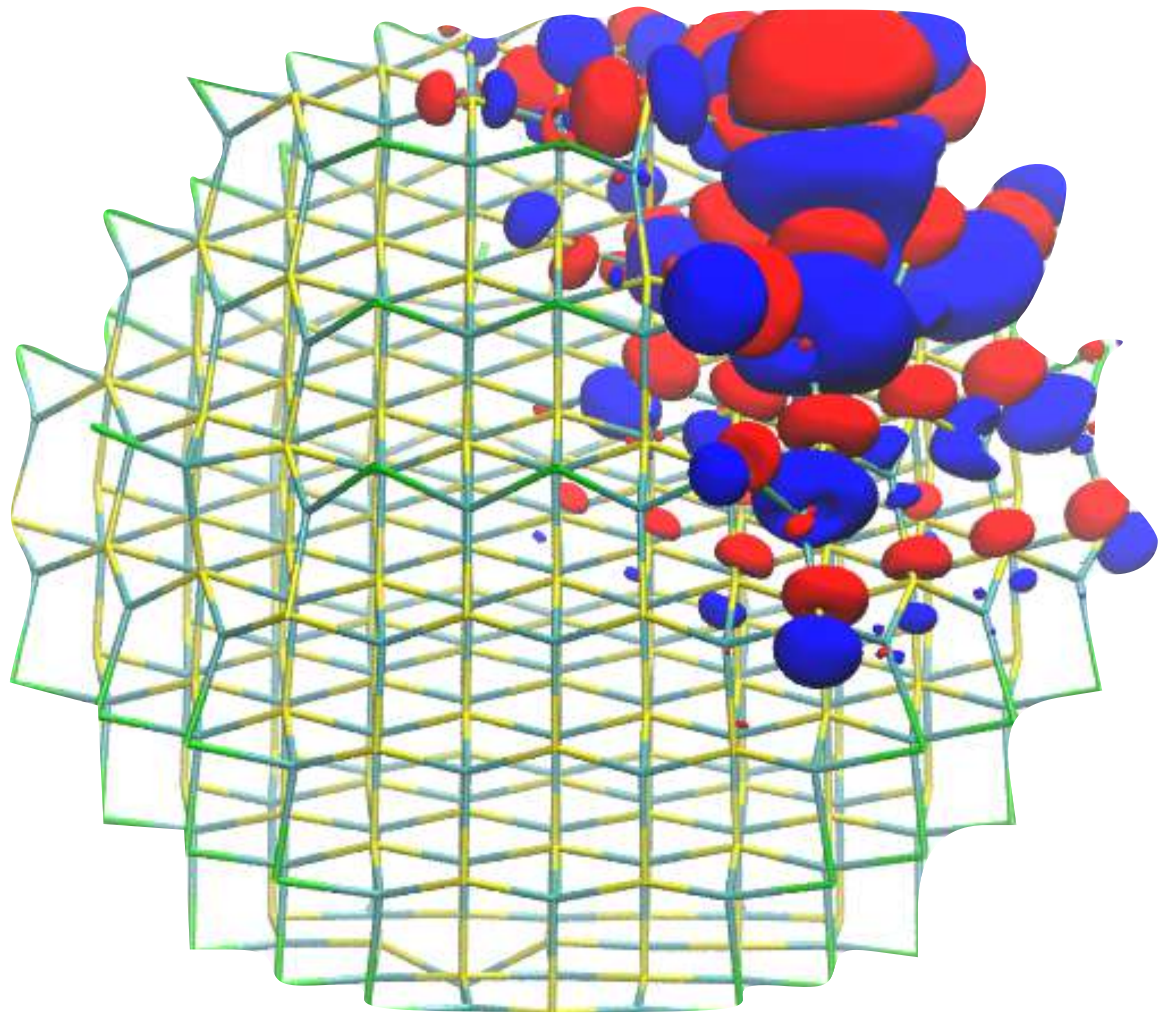
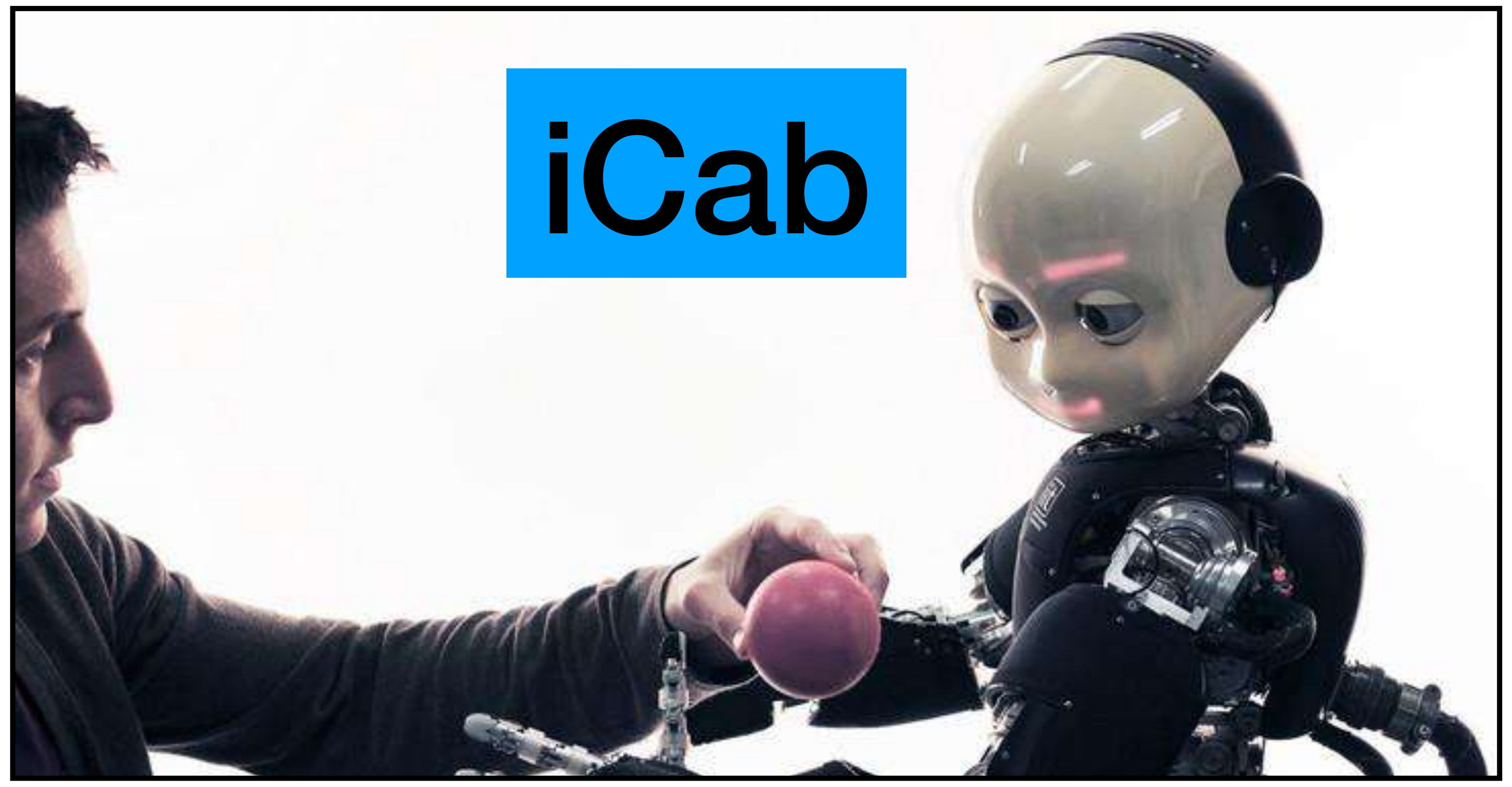




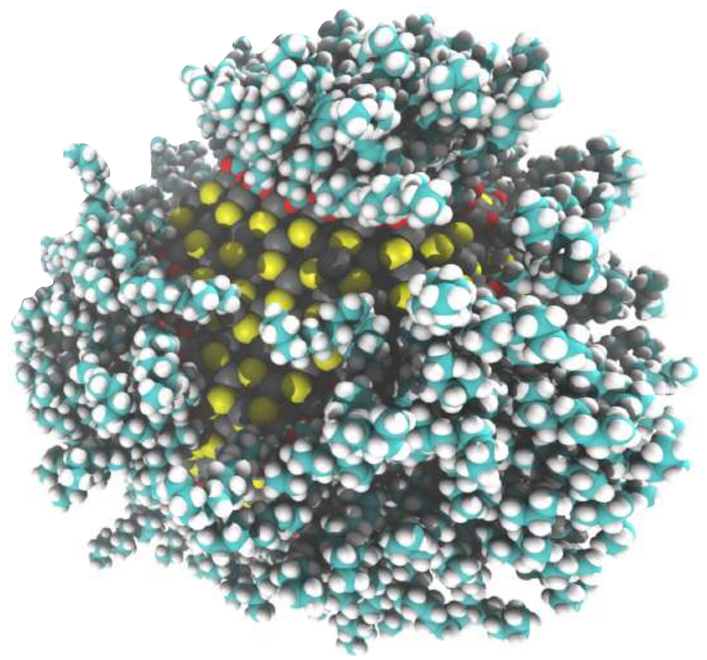
CAN WE UNDERSTAND SURFACE TRAPS IN COLLOIDAL NANOCRYSTALS AND HOW TO HEAL THEM ?

Ivan Infante

ISTITUTO ITALIANO DI TECNOLOGIA



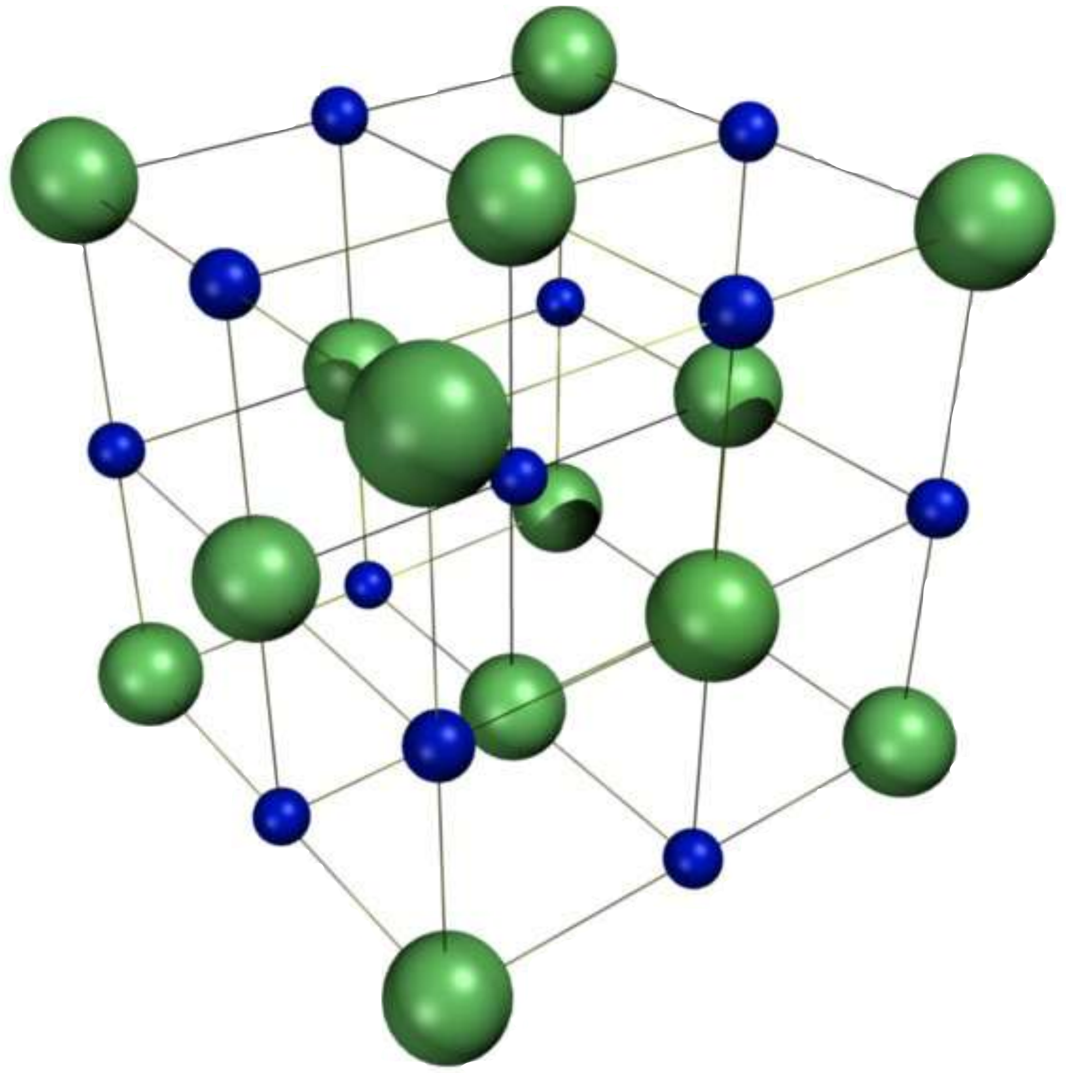
Nanochemistry Department
(Manna Group)



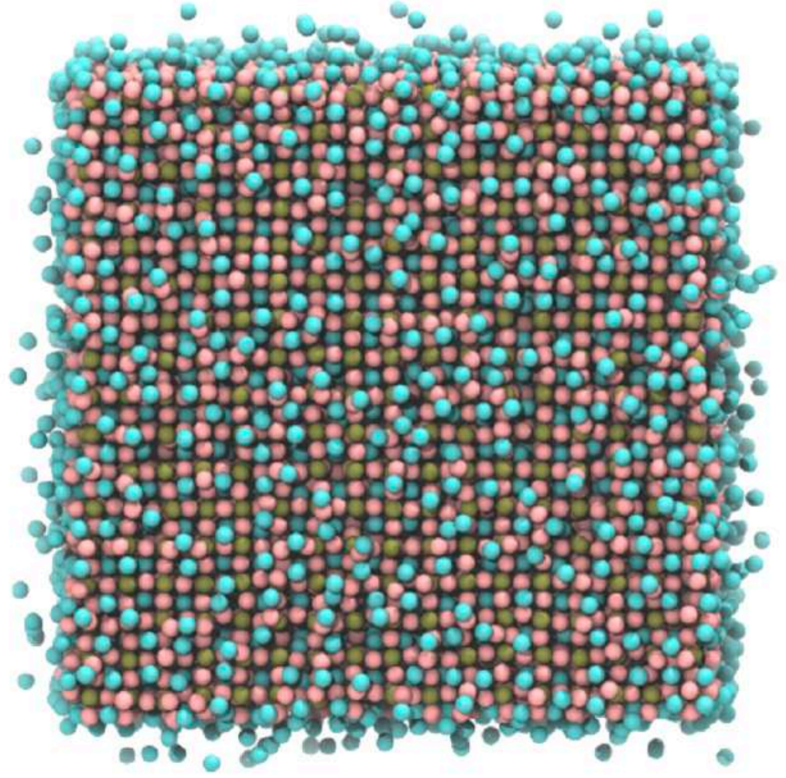
Modelling since 2018

What are Colloidal Nanocrystals ?

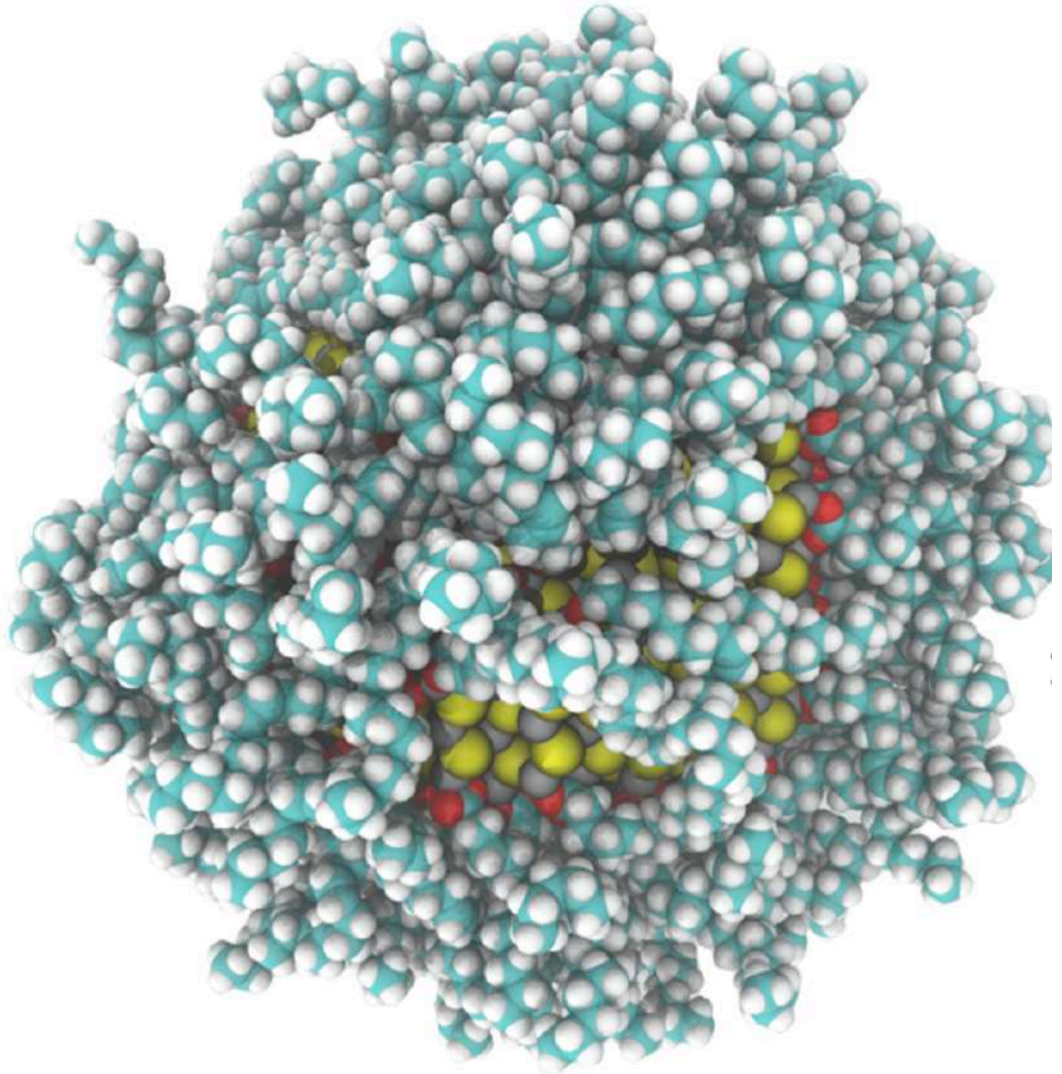
Salt



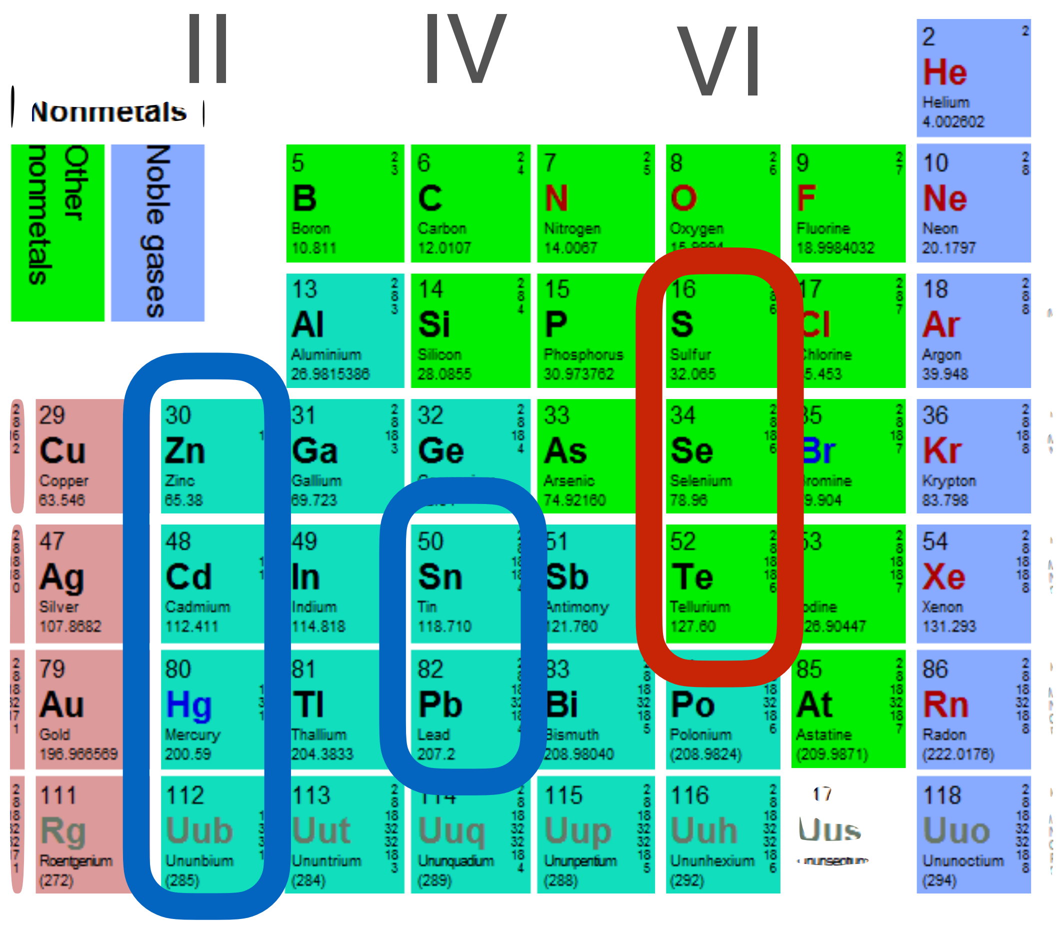
Rock-Salt
Macroscopic Crystal



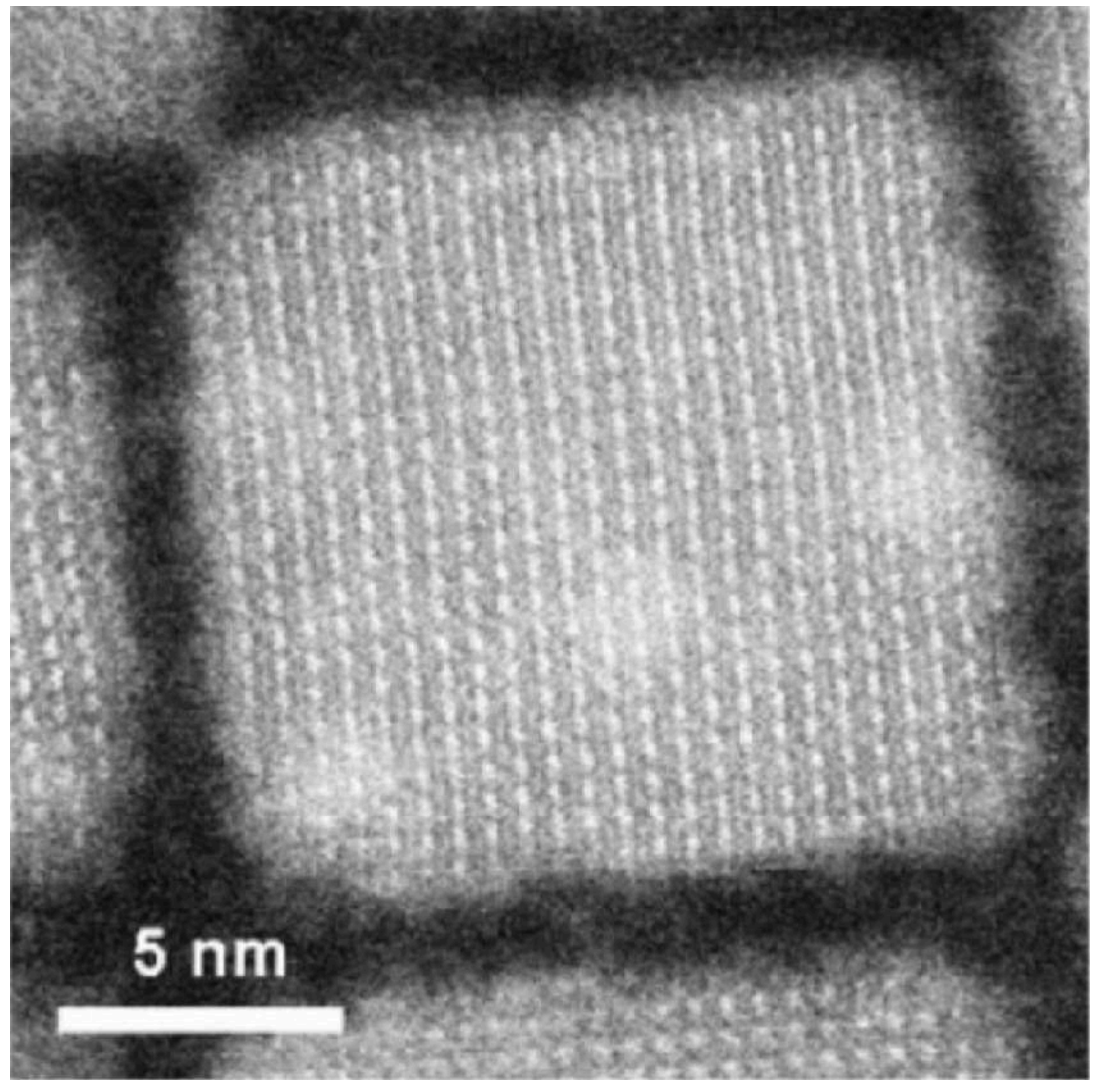
Nanocrystal



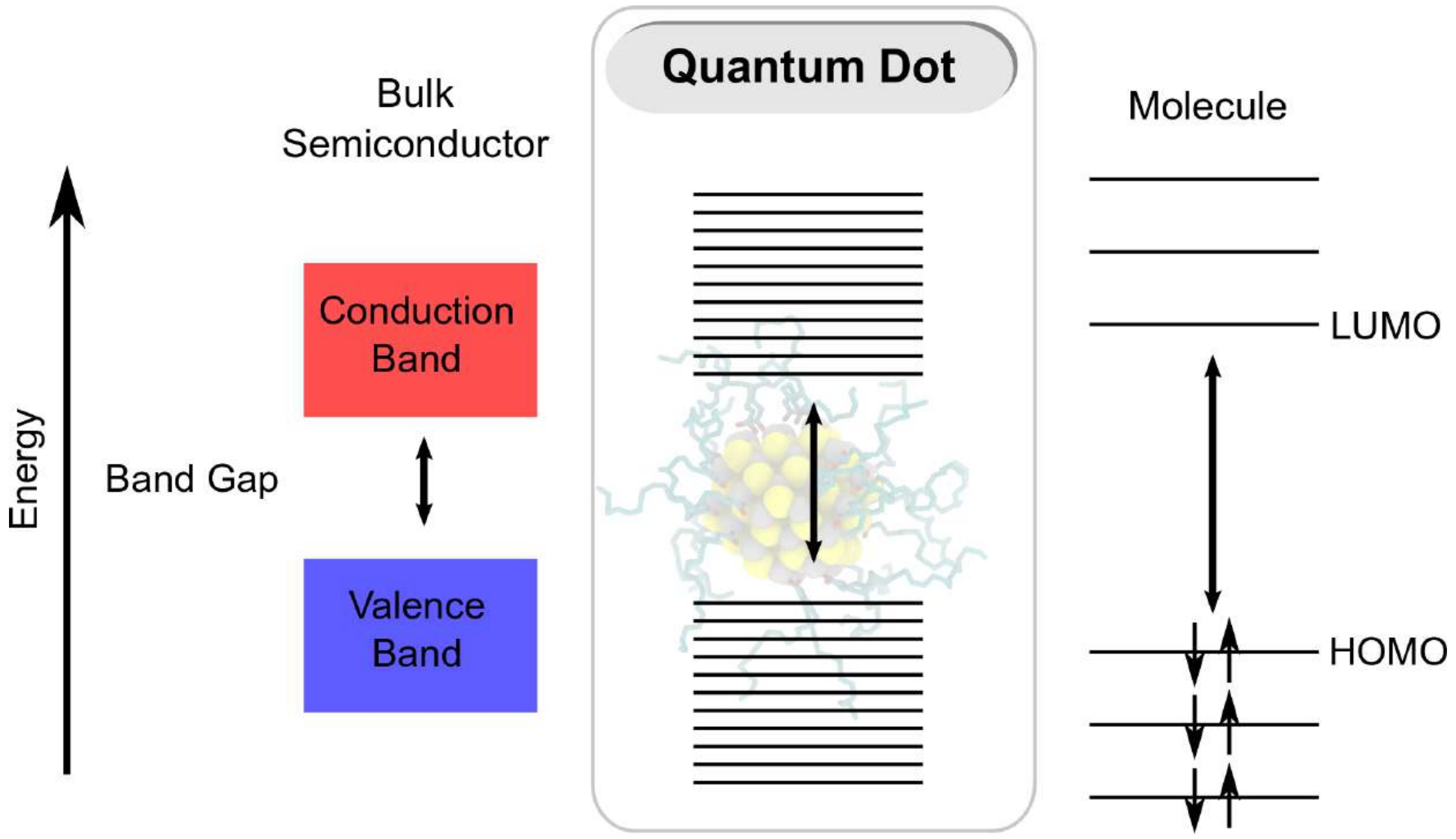
Solution Processable



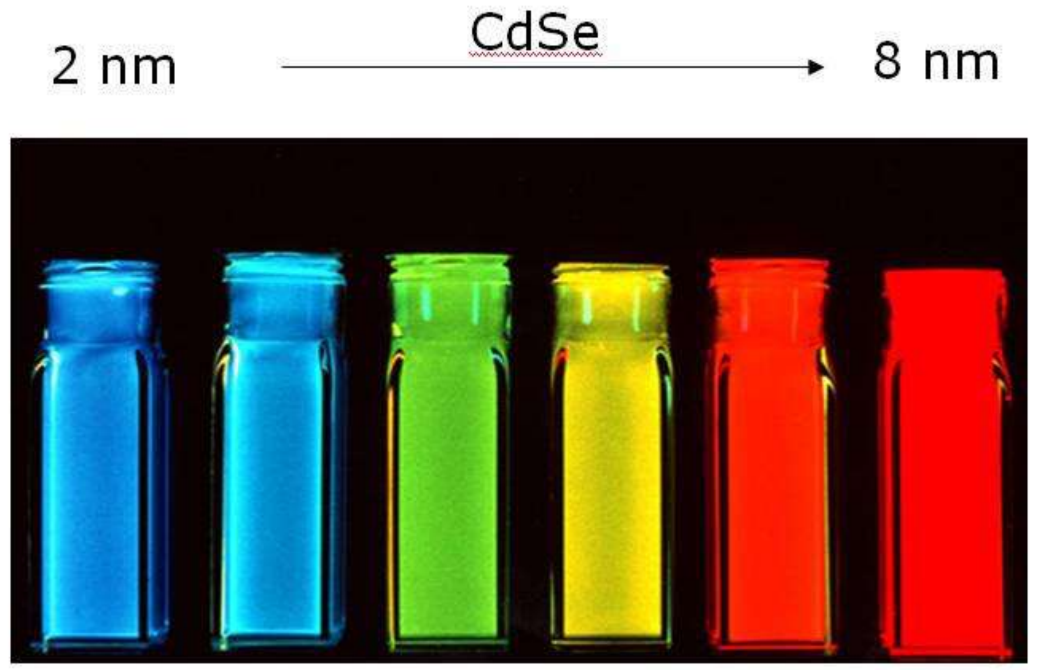
CdS, CdSe, CdTe, PbS, PbSe
(Semiconductors)

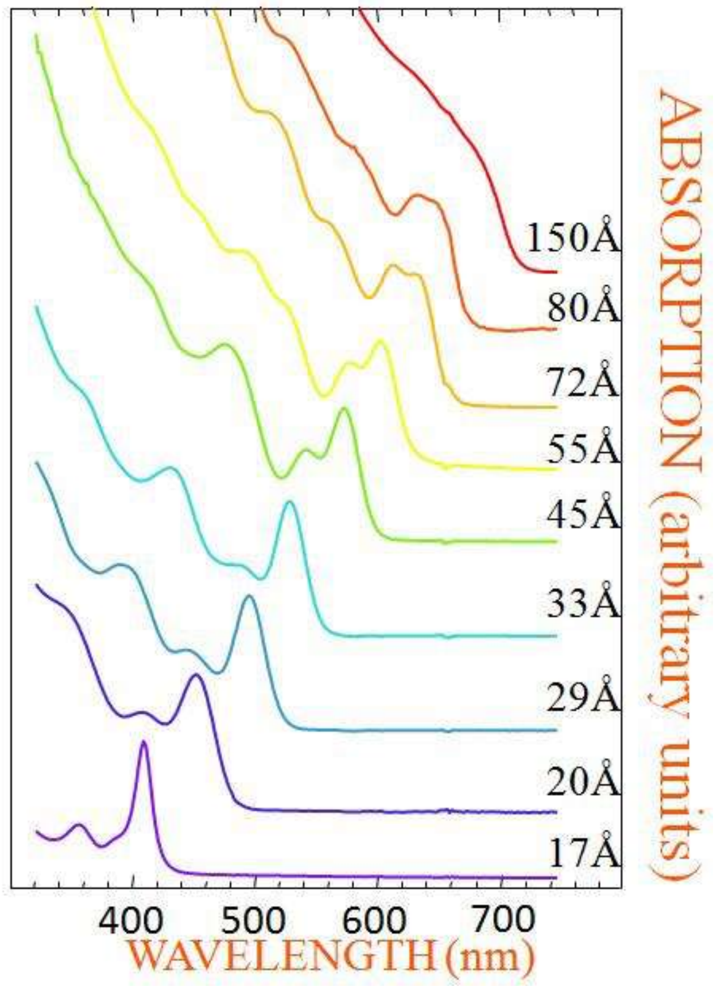


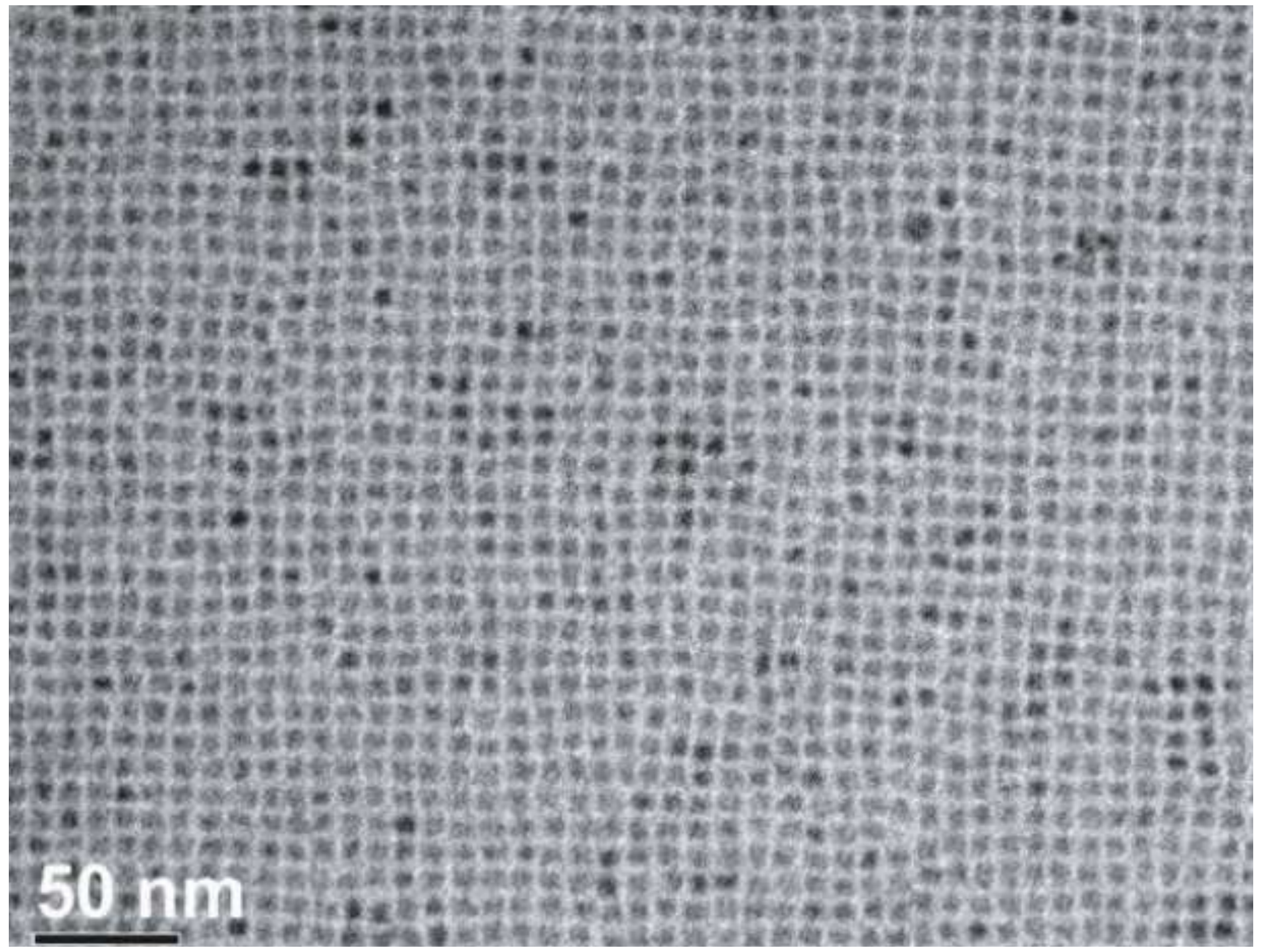
$CsPbBr_3$



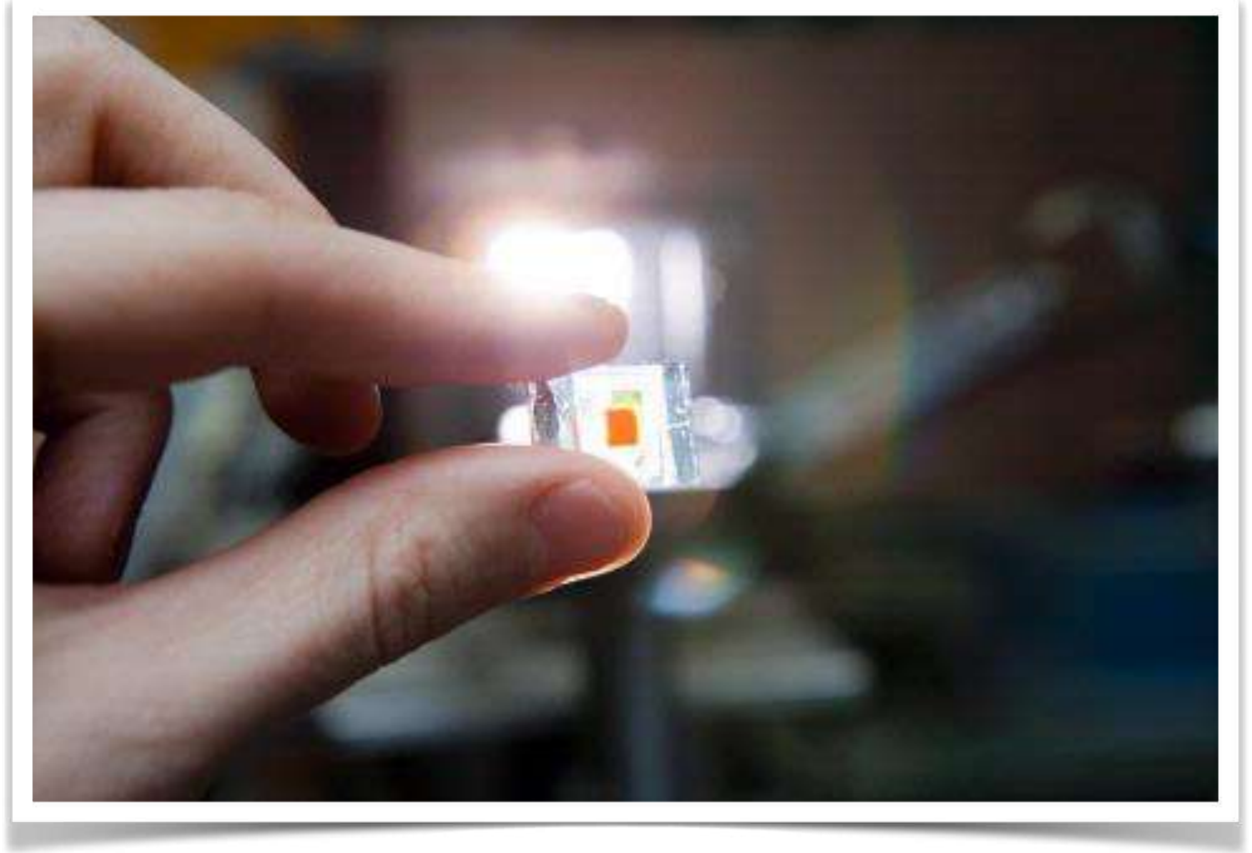
Quantum Confinement



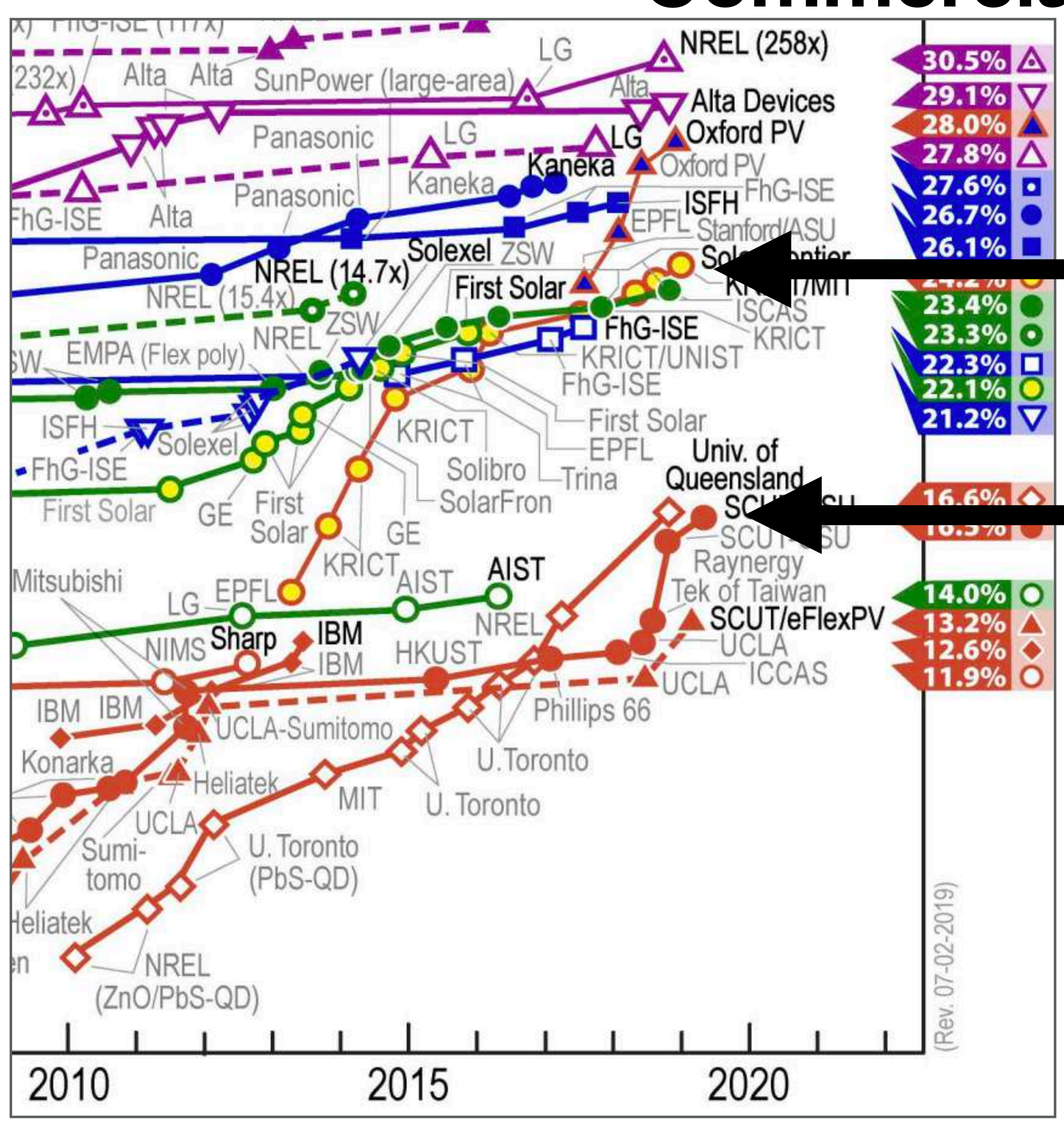




Photovoltaics



Commercial Si PV: ~ 15%

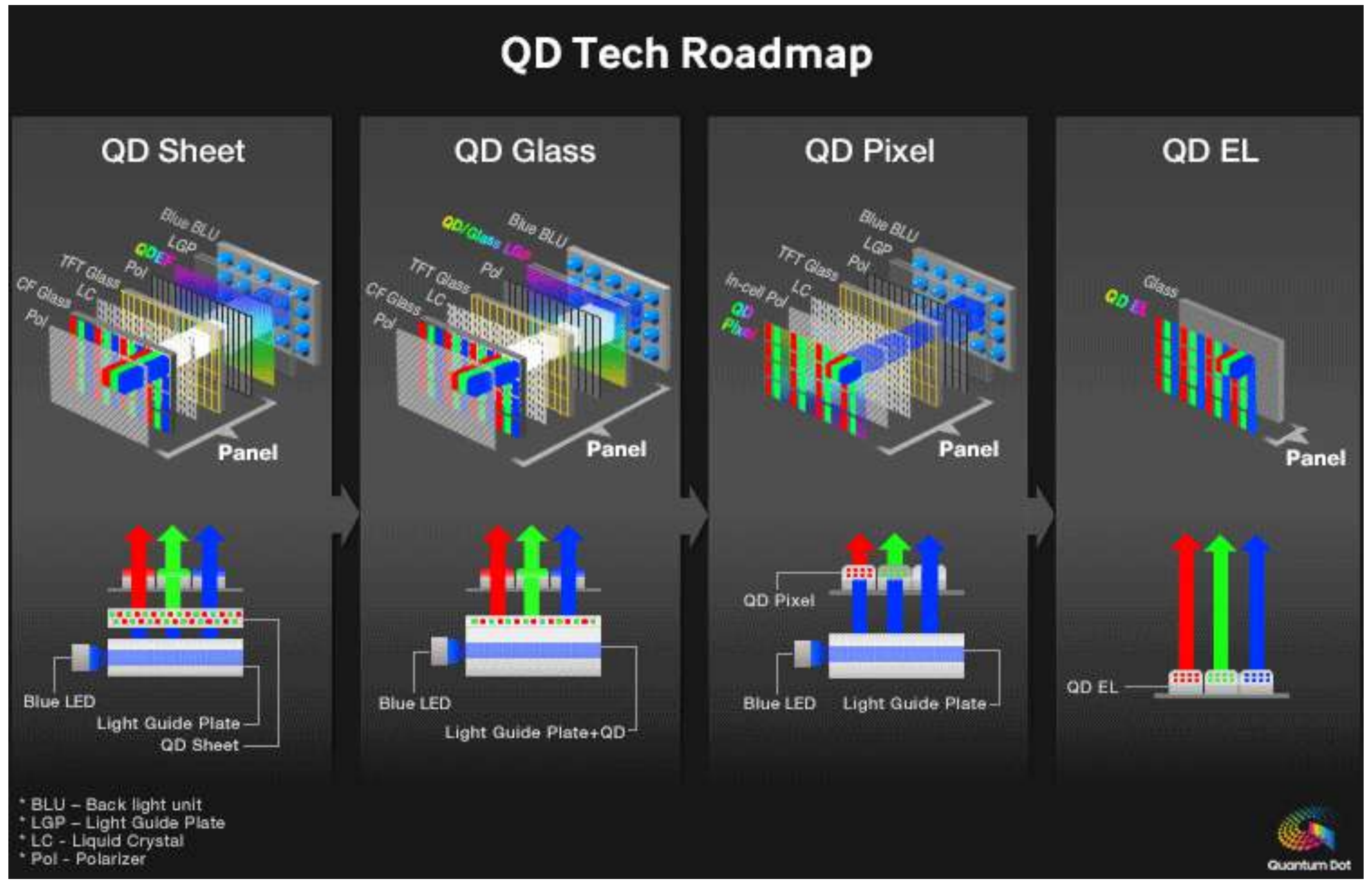


24.2%

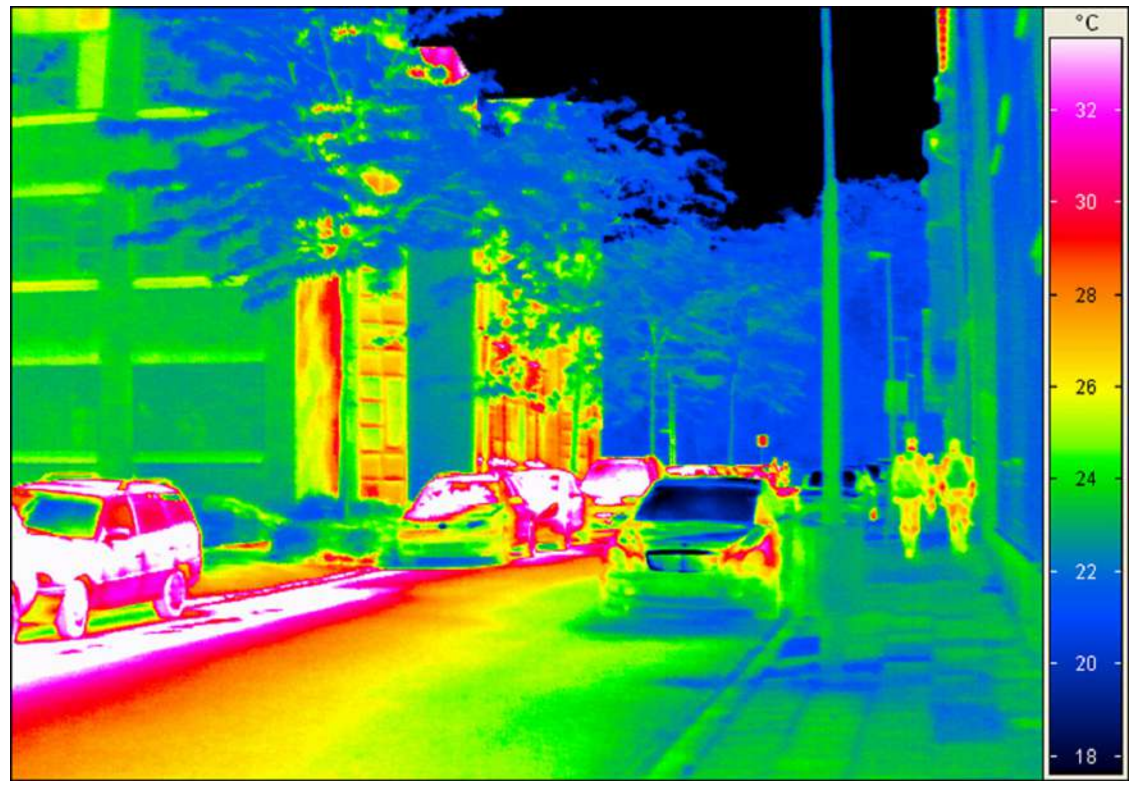
16.6 %

Bio-imaging

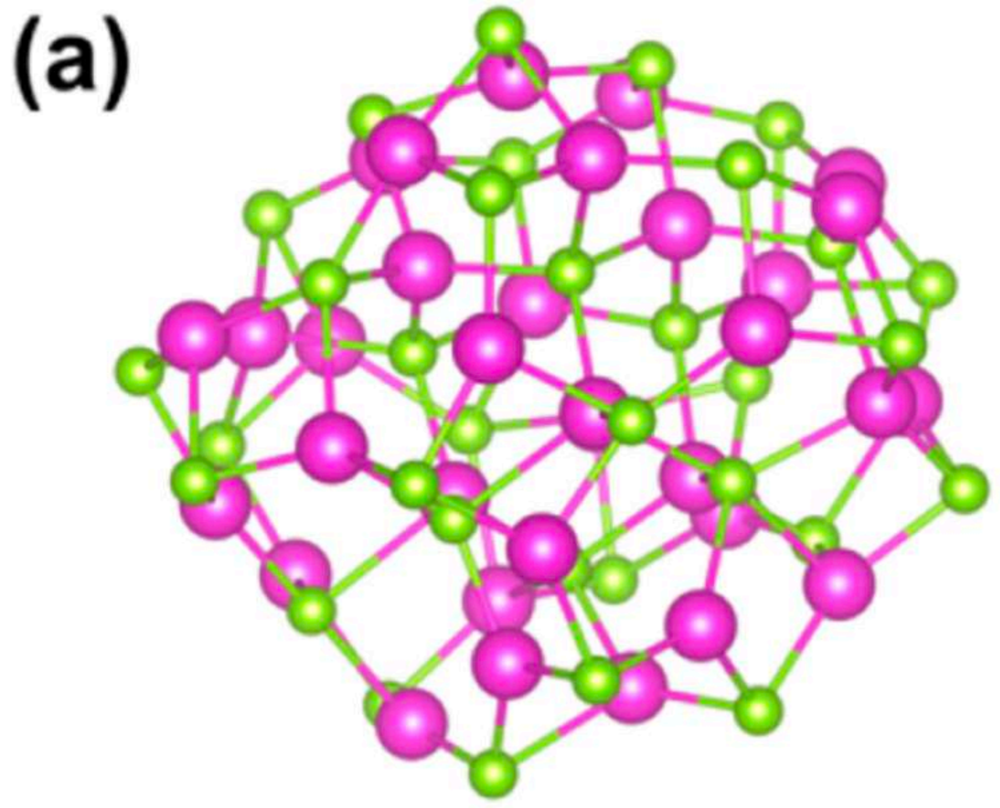
QLED (TV DISPLAYS)



IR Photodetectors



Calculations on CdSe Nanocrystals



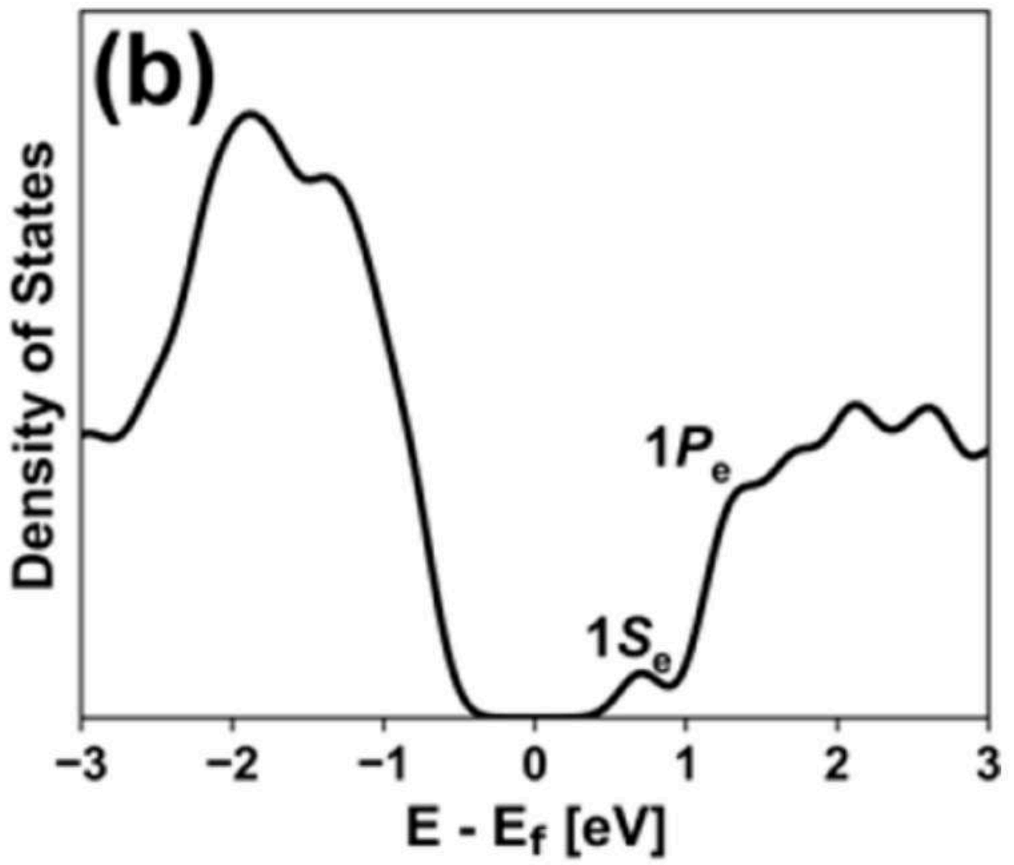
The Effect of Organic Ligand Binding on the Growth of CdSe Nanoparticles Probed by Ab Initio Calculations

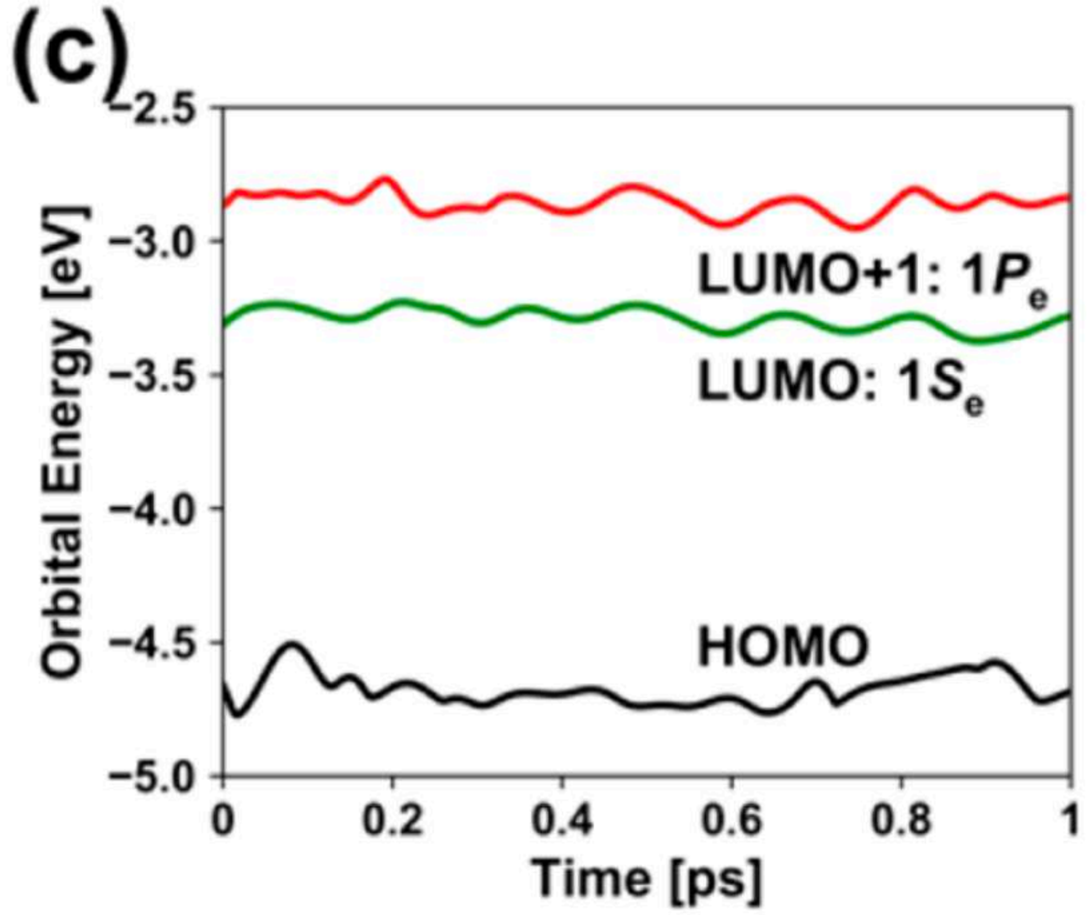
Aaron Puzder, Andrew J. Williamson,* Natalia Zaitseva, and Giulia Galli

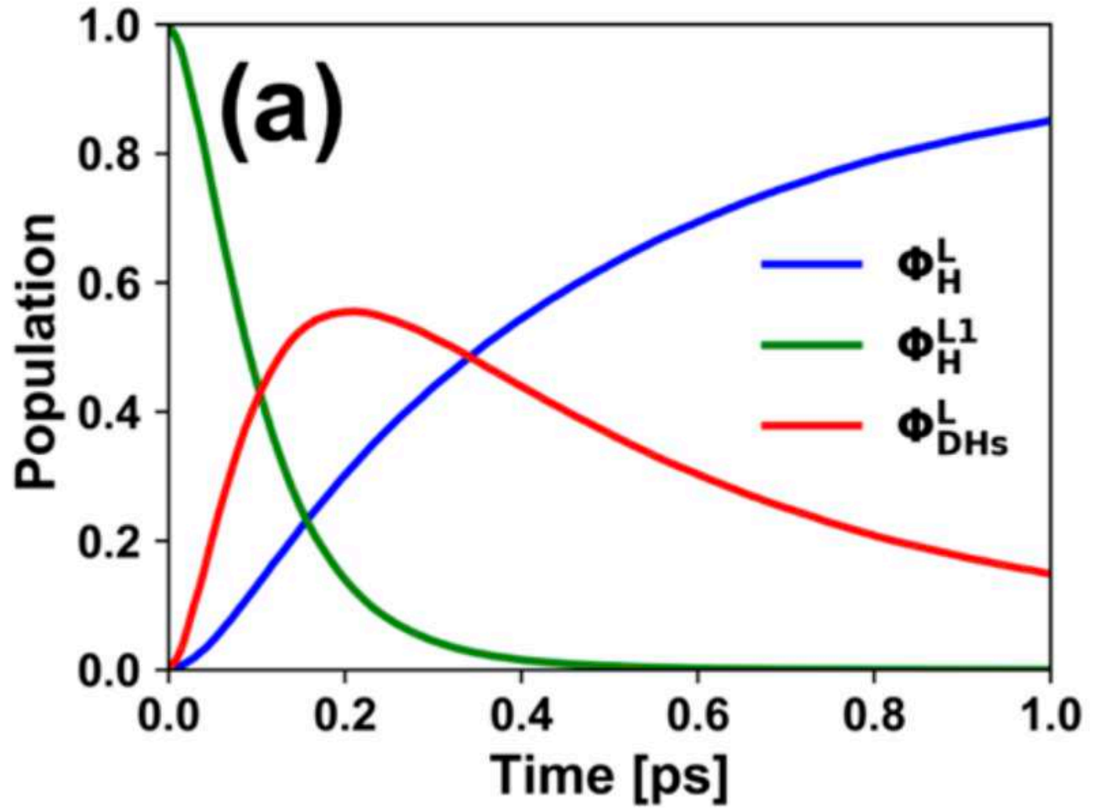
Lawrence Livermore National Laboratory, Livermore, California 94550

Liberato Manna† and A. Paul Alivisatos

Lawrence Berkeley National Laboratory, Berkeley, California





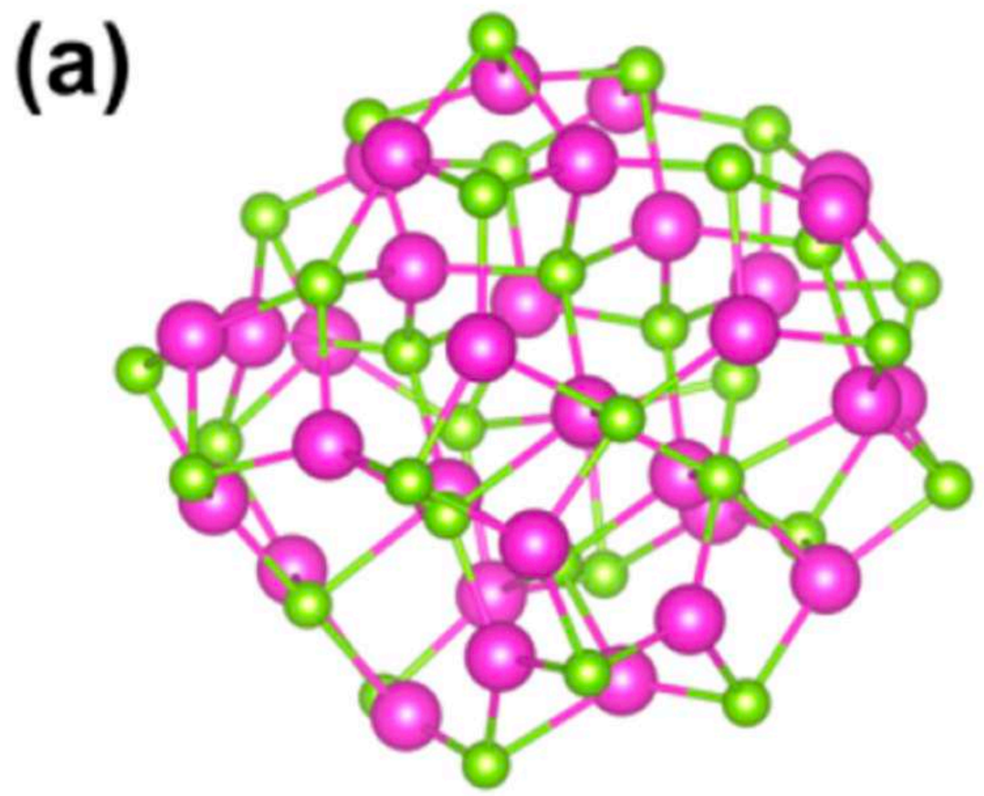


Many works by Prezhdo, Kilina, Tretiak, etc.

Modeling Auger Processes with Nonadiabatic Molecular Dynamics

Guoqing Zhou, Gang Lu, and Oleg V. Prezhdo*

Cite This: *Nano Lett.* 2021, 21, 756−761 Read Online



Became a Standard

Insights on Electronic Structure

Easy to calculate: MD of about 10ps

Became a Standard

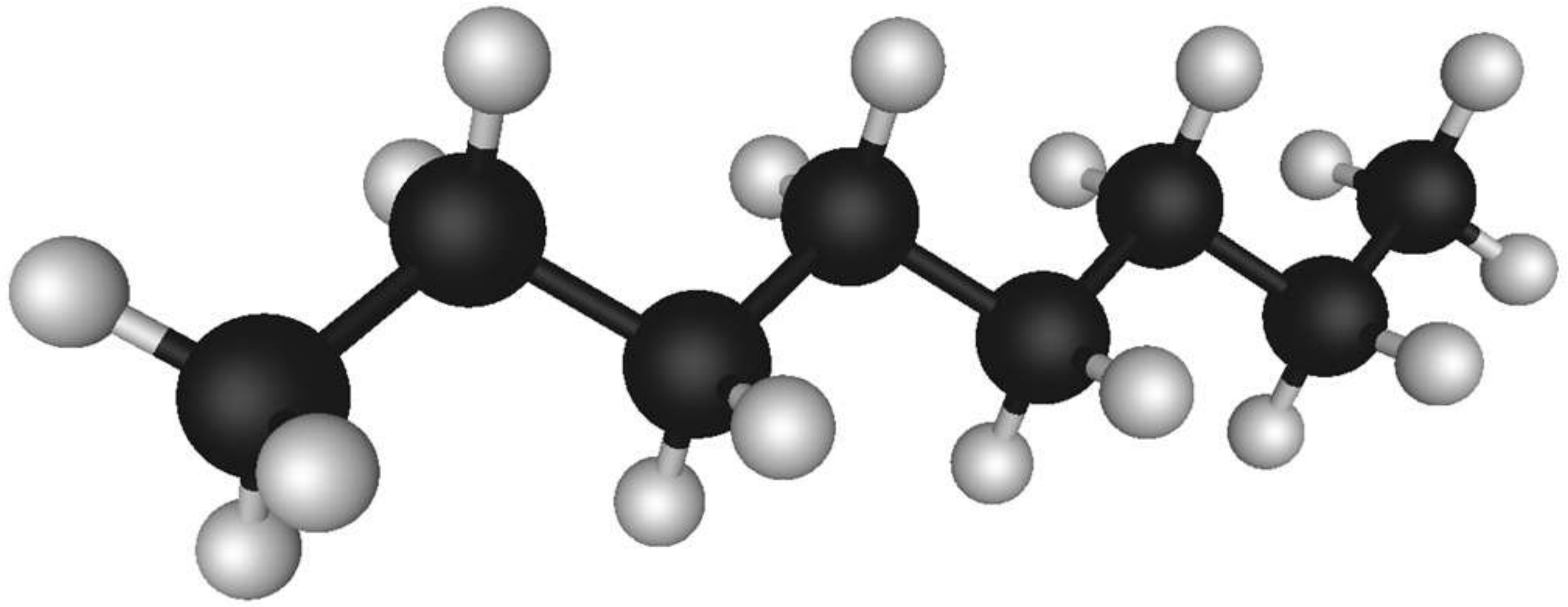
Not Scalable with Size

Too small (approx. 1nm)

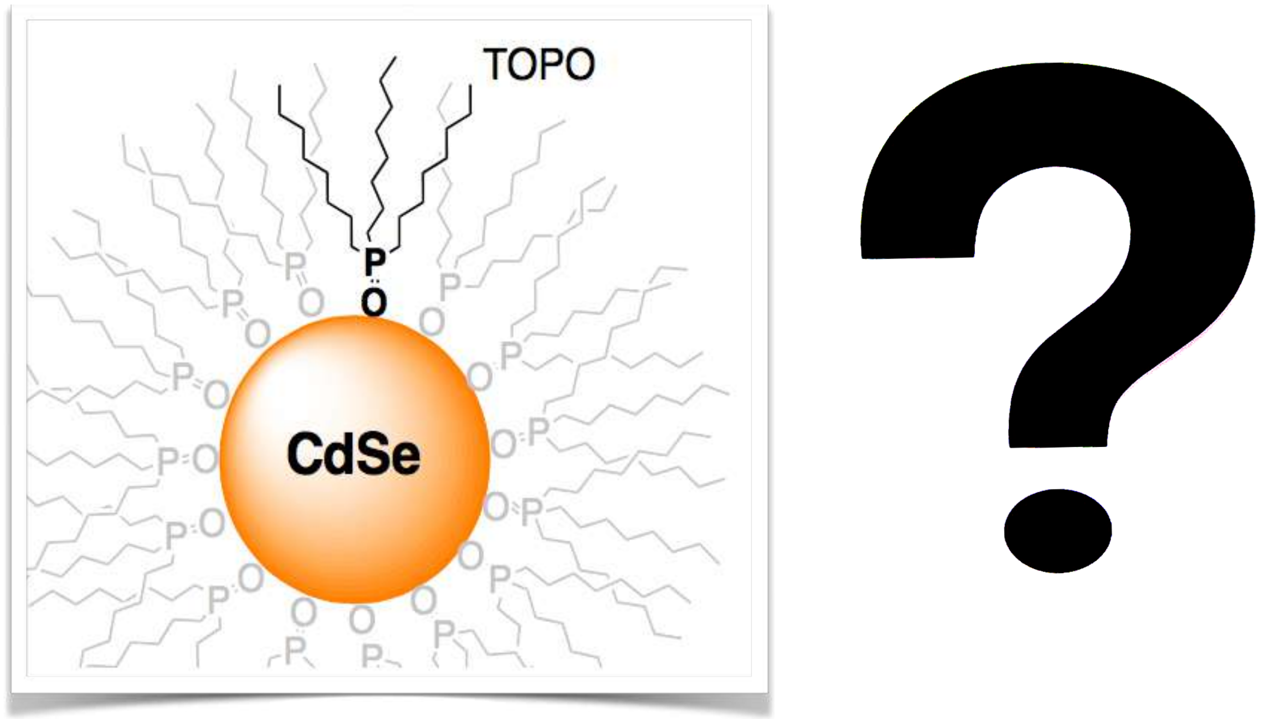
Too flexible

Disadvantages of Colloidal Nanocrystals ?

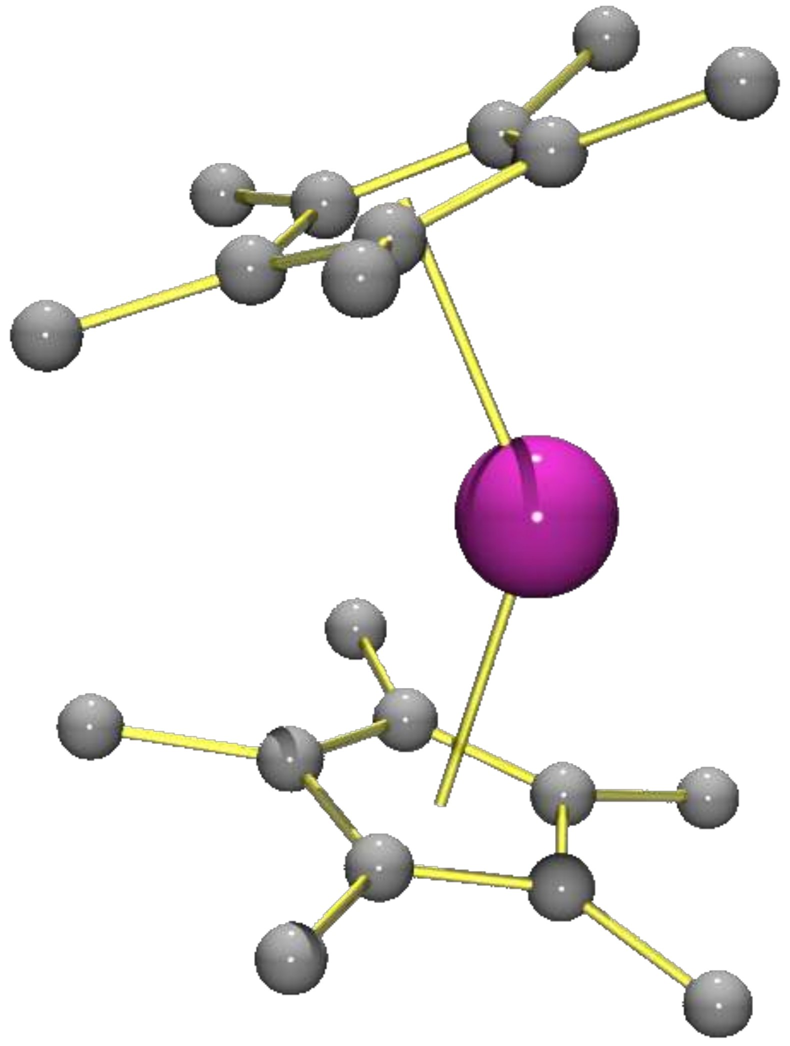
Organic Molecules



Colloidal Nanocrystals



Organometallic Molecules

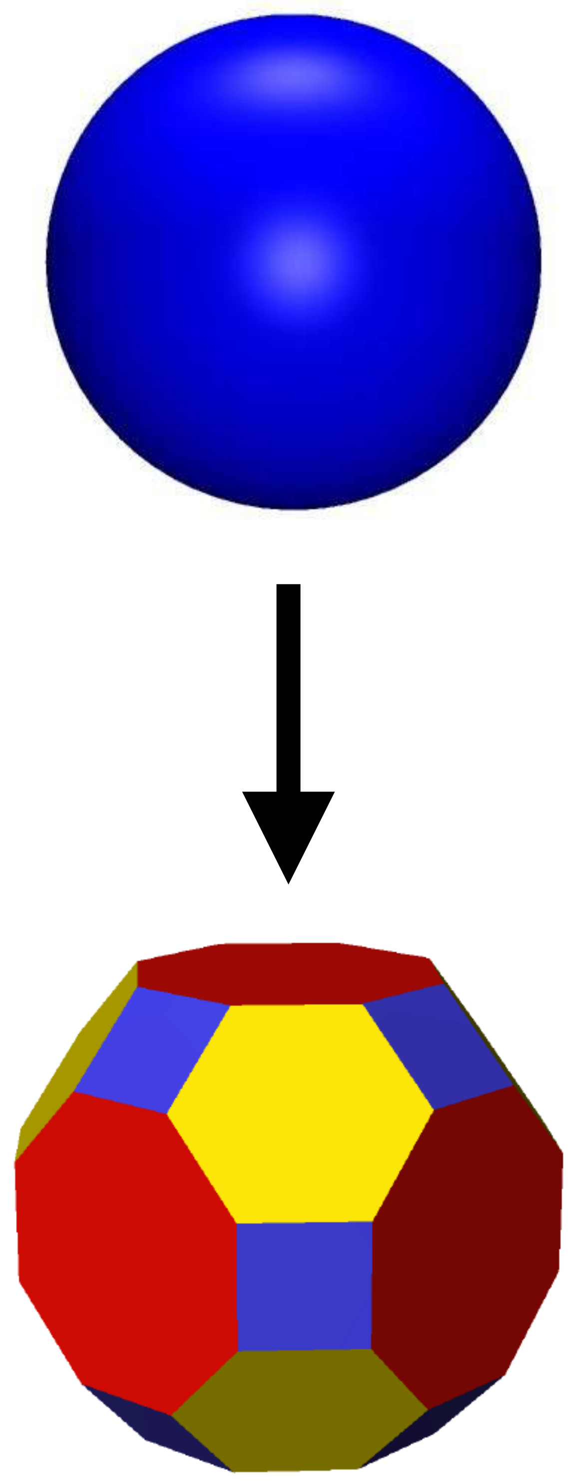


Stoichiometry
how many Cd or Se ?

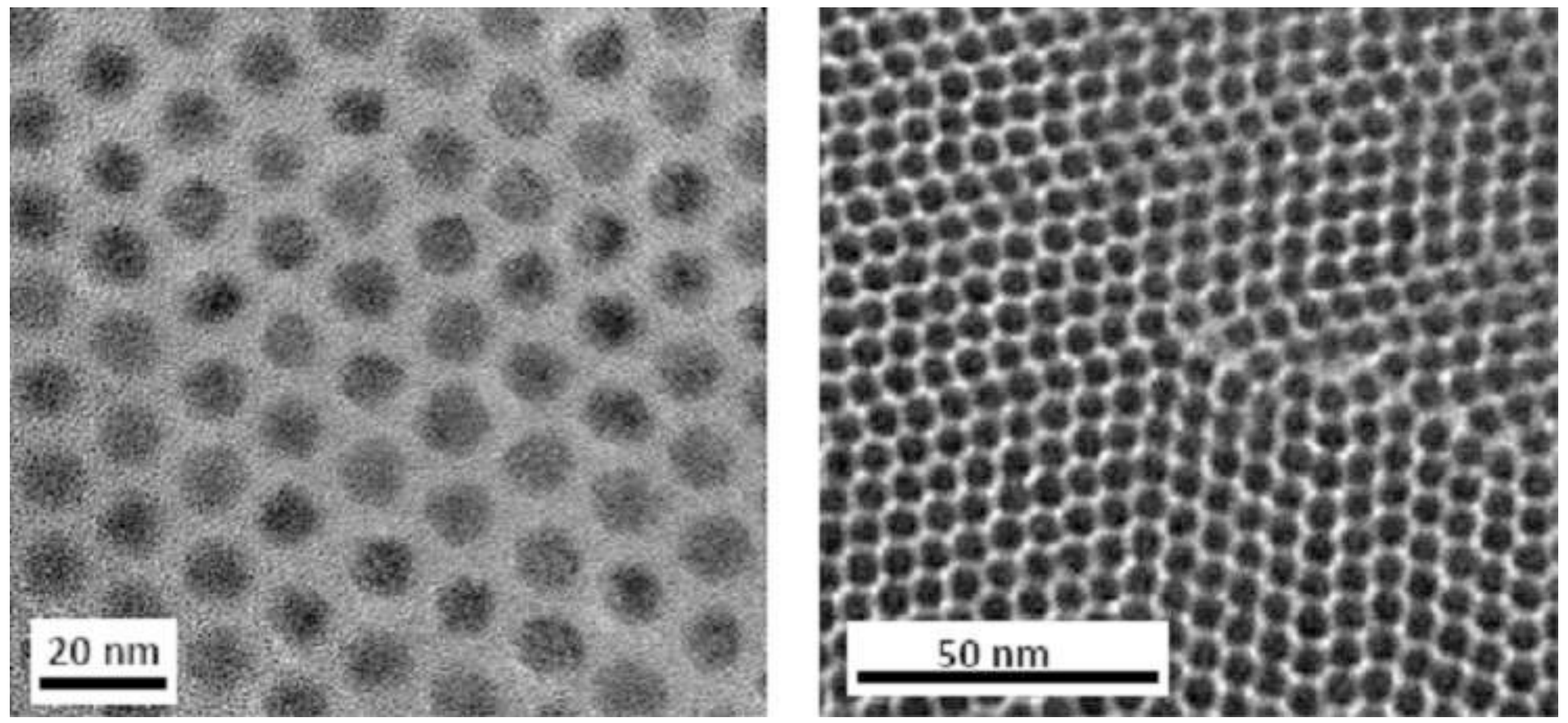
Surface
what shape ?

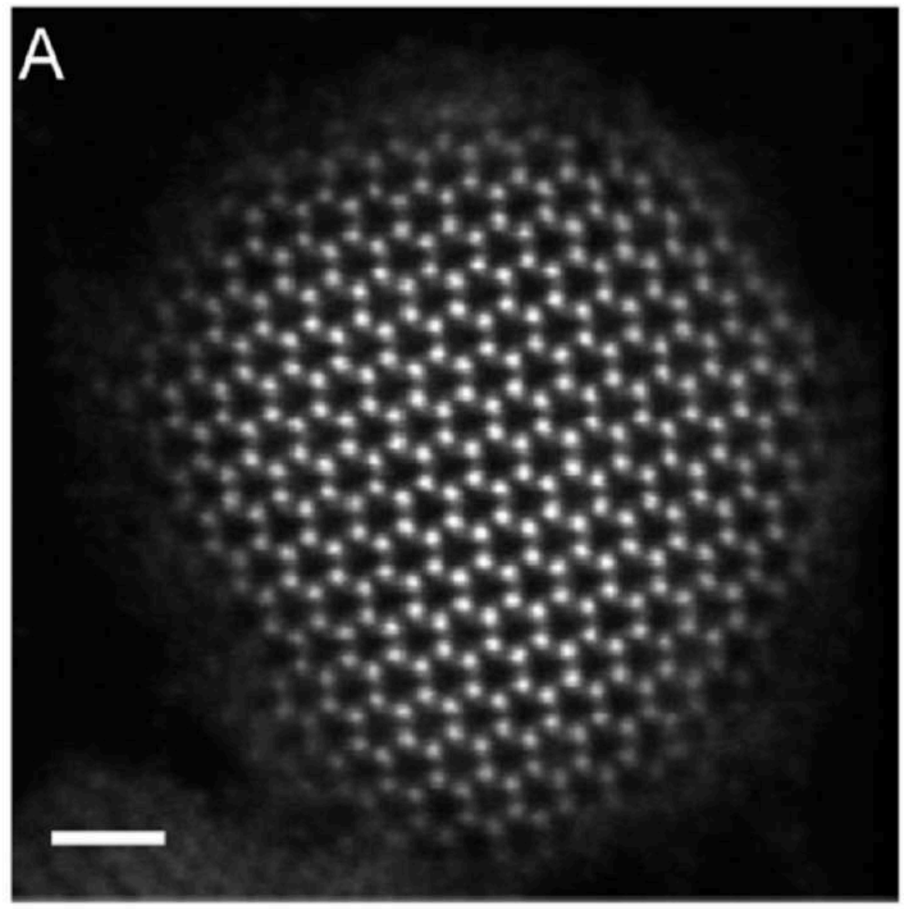
Ligands
where ? how many ?

SHAPE

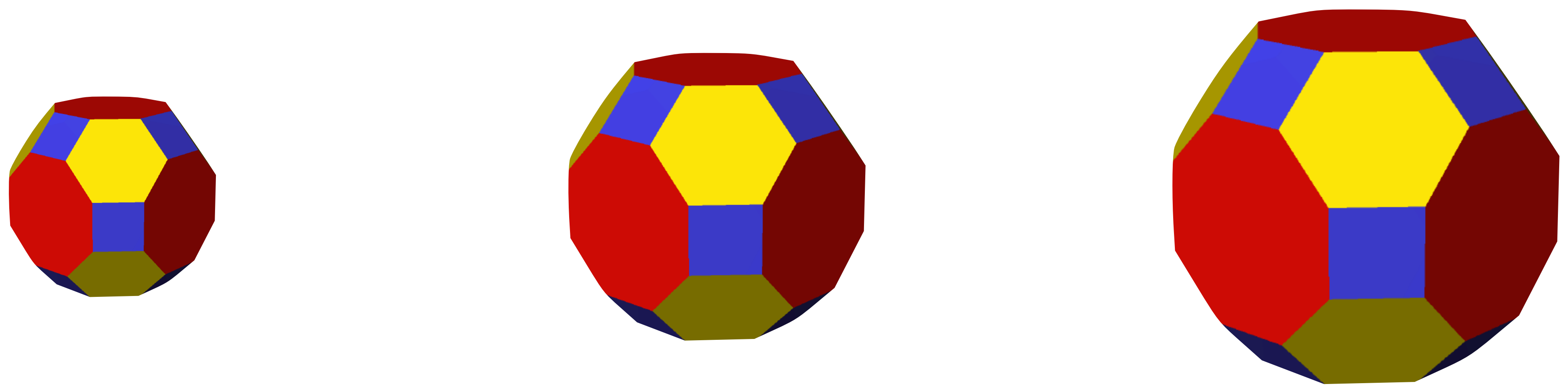


Transmission Electron Microscopy (TEM)

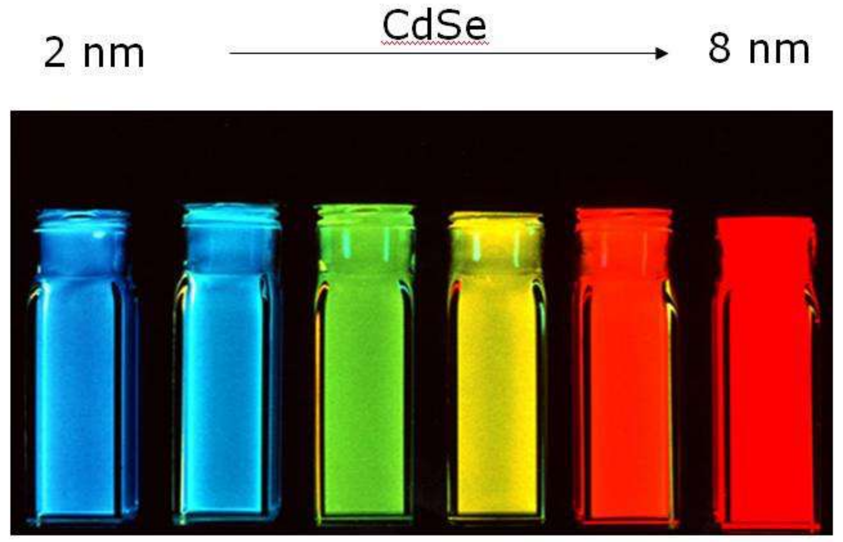


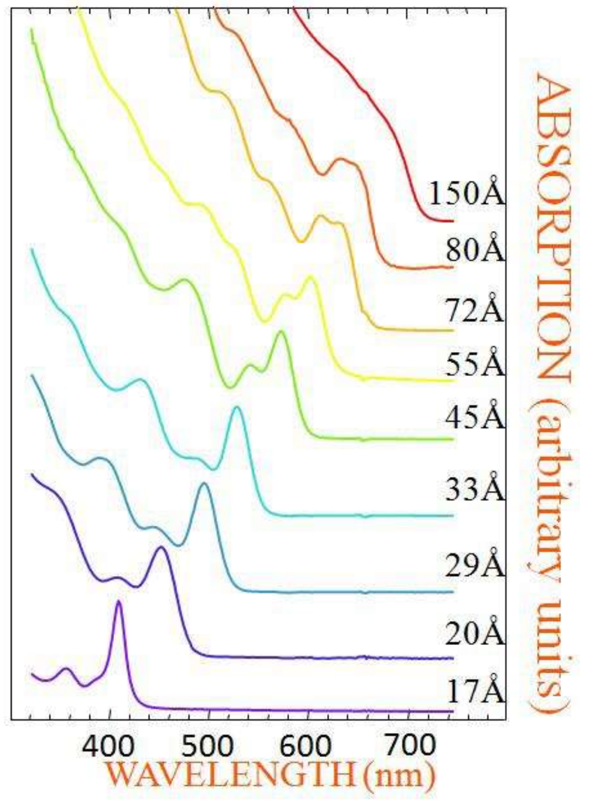


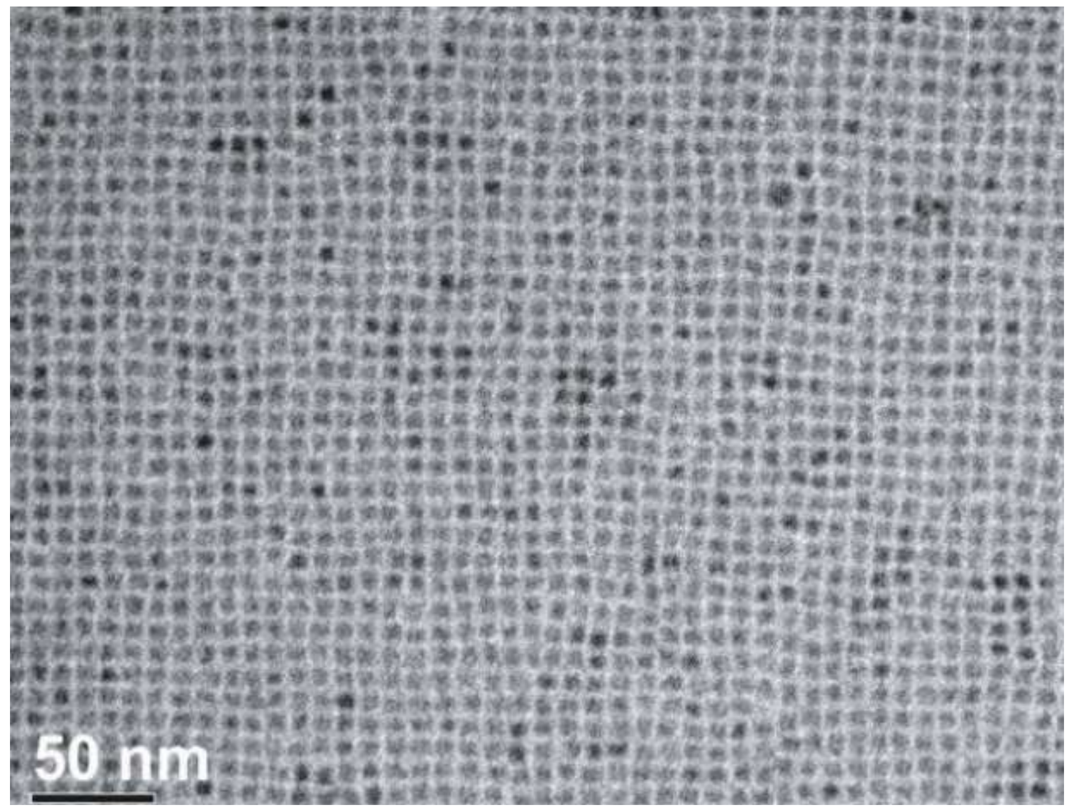
SIZE

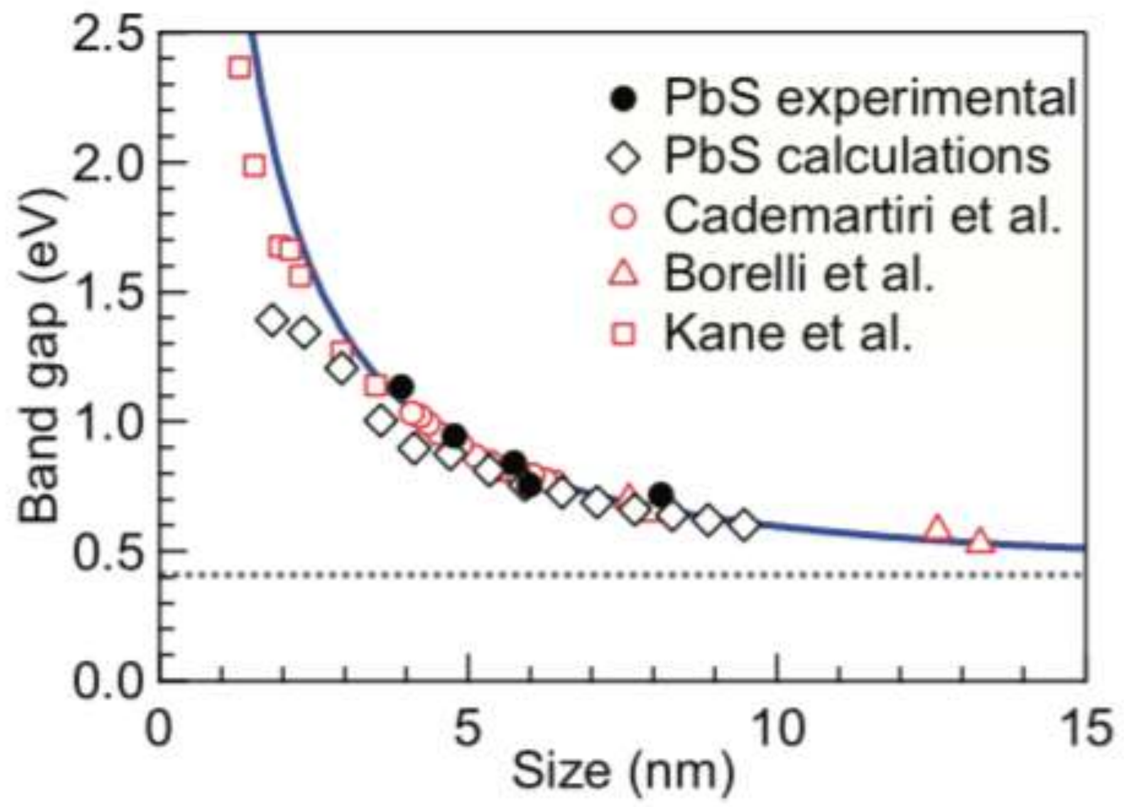


Quantum Confinement





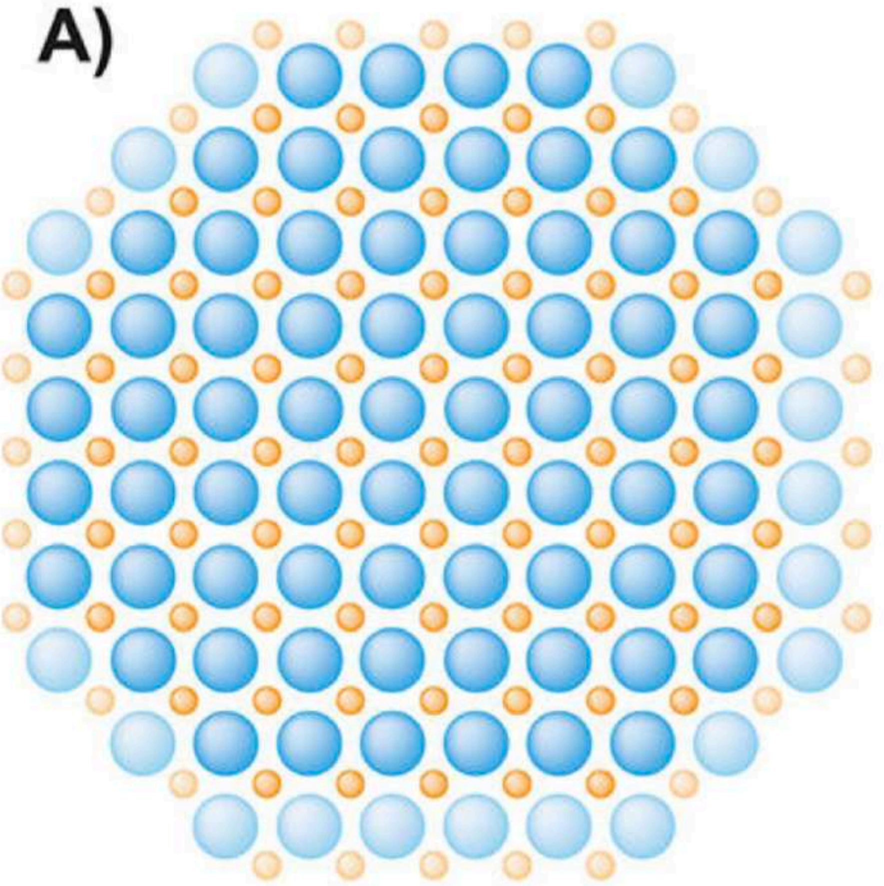




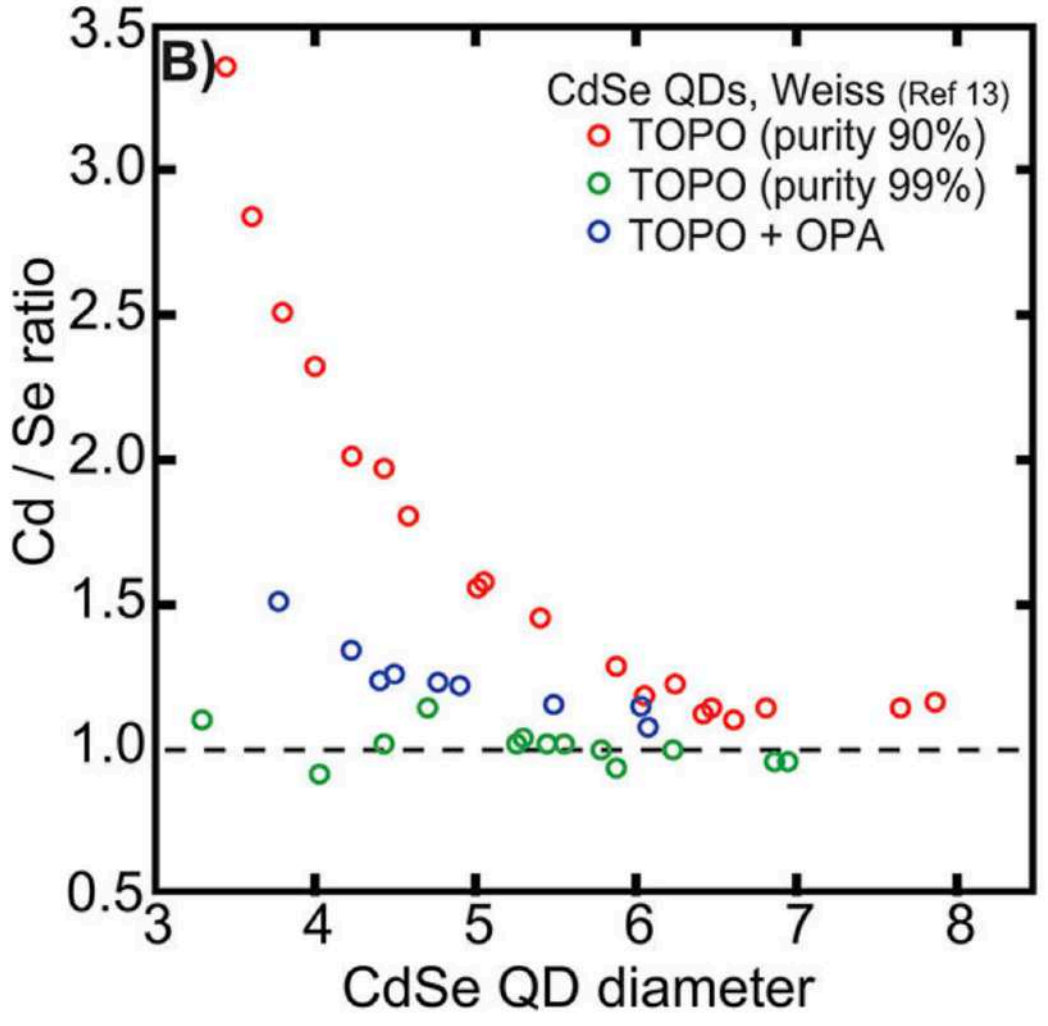
ELEMENTAL ANALYSIS

XPS, ICP

A)

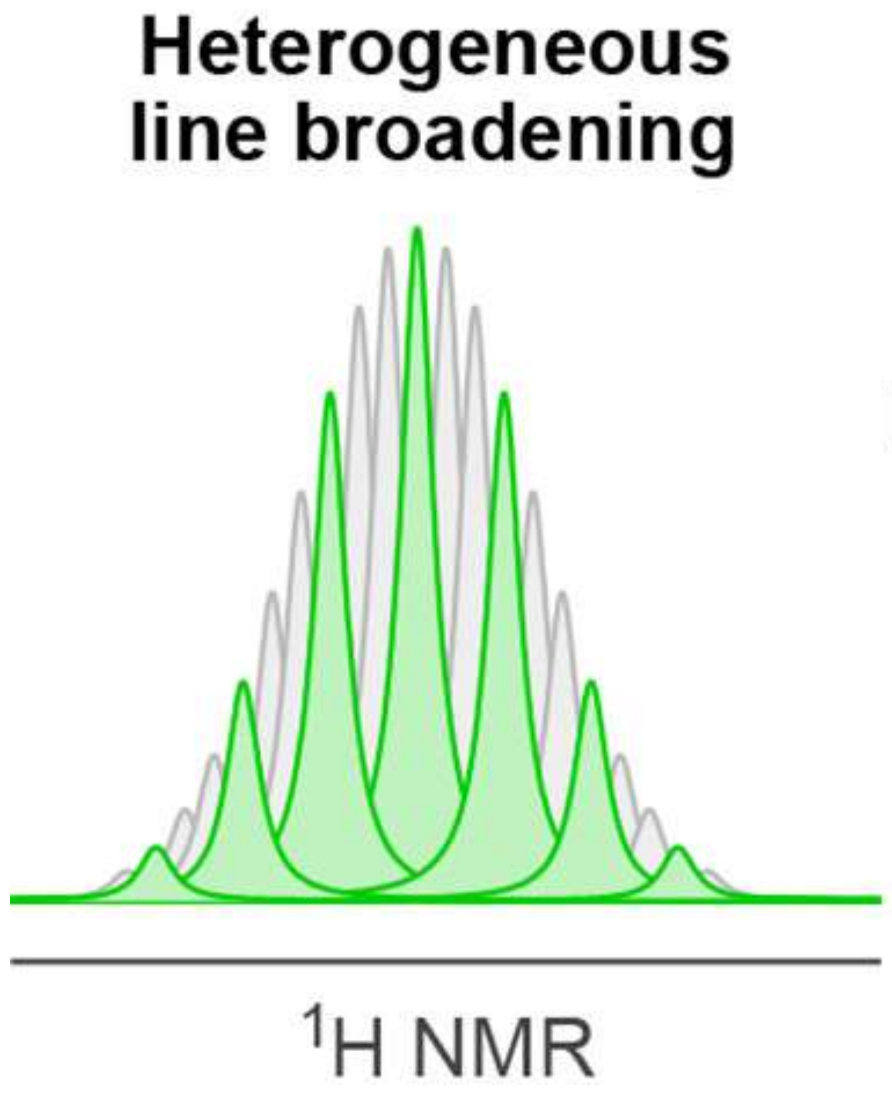


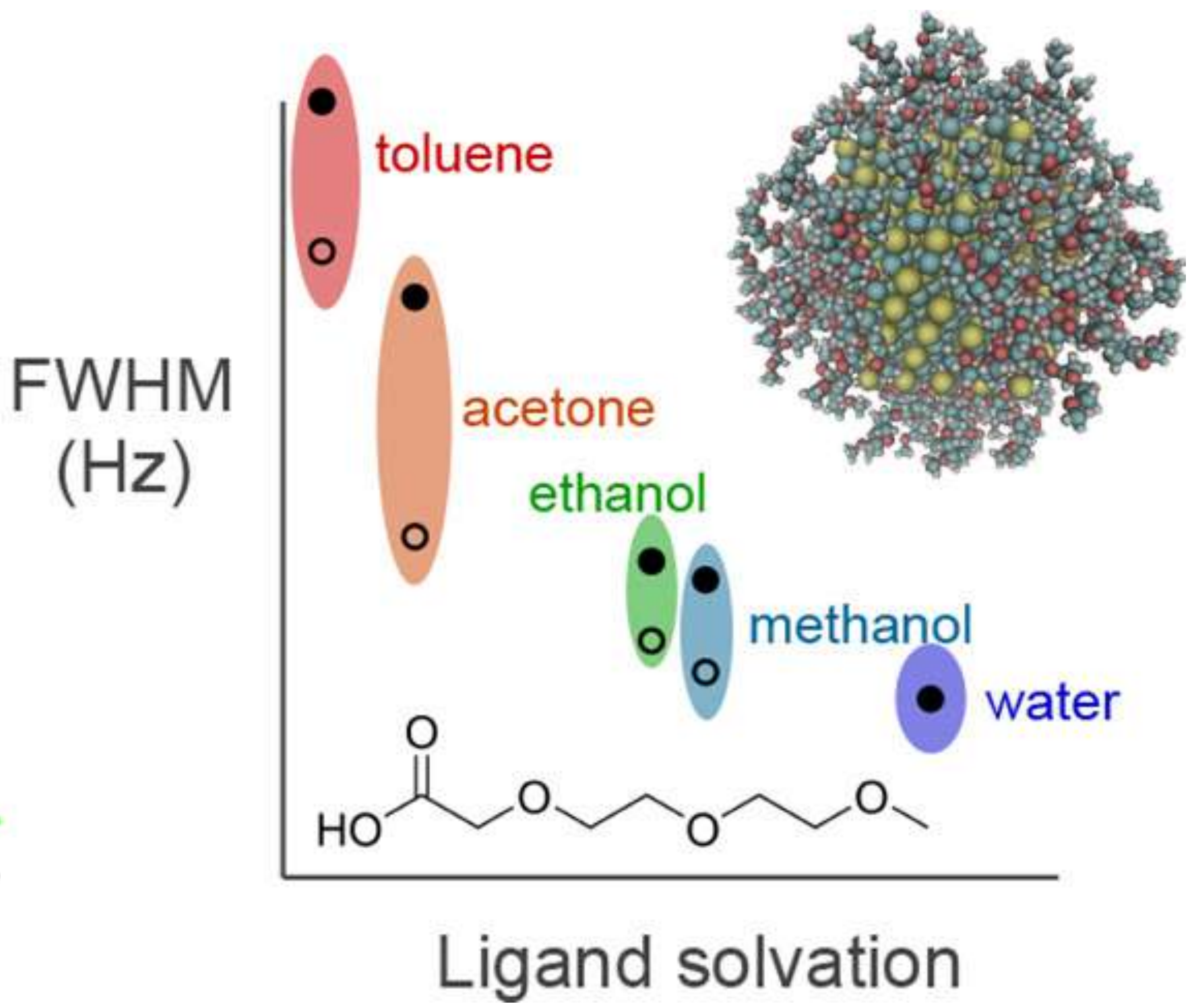
Stoichiometric core with
cation-rich shell model
metal cation
chalcogen



Cation excess compensated by Ligands

NMR



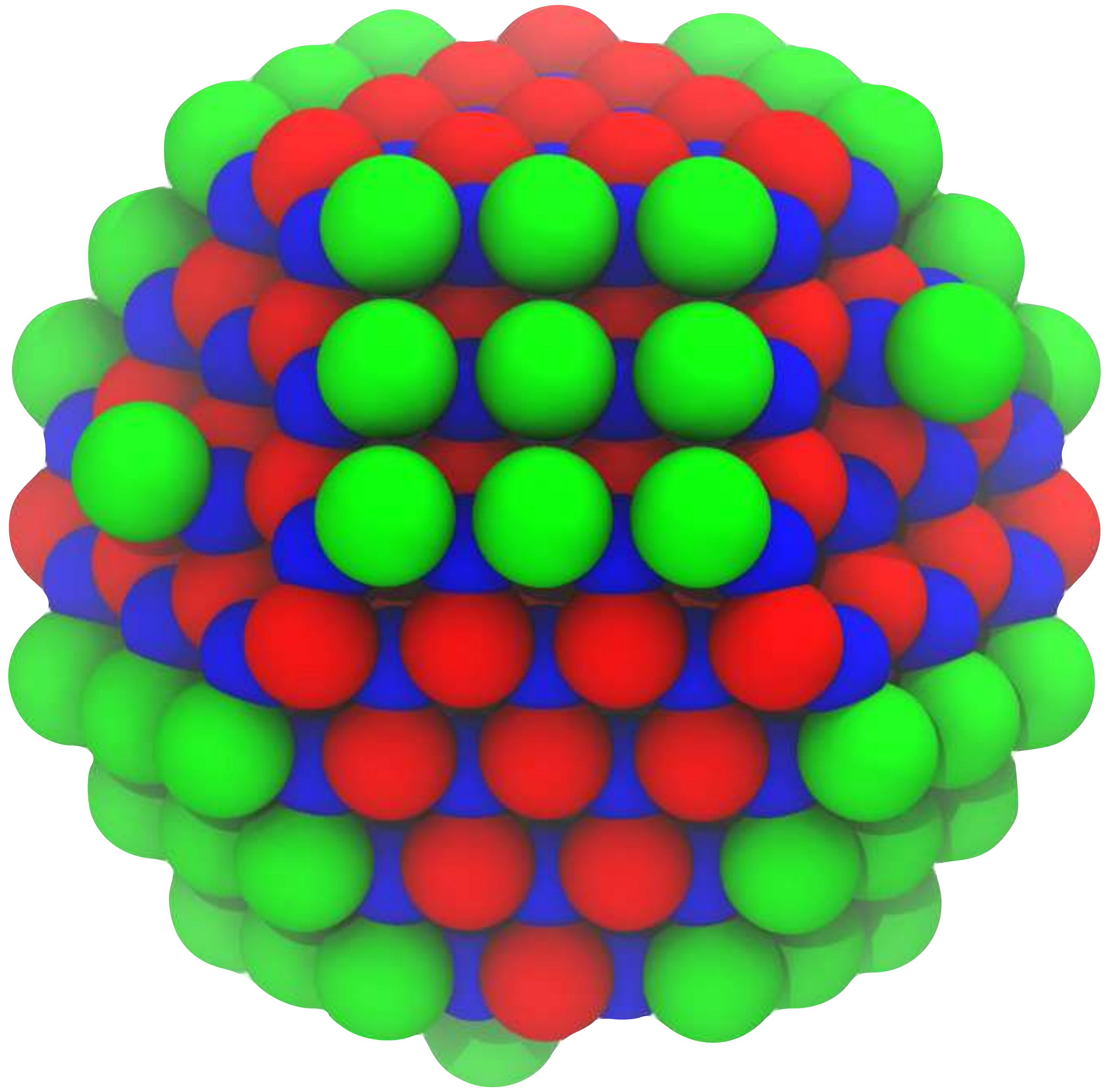


Ligands (Un)Bound to the Surface

Type of Ligands

Ligand Density at the Surface

CdSe

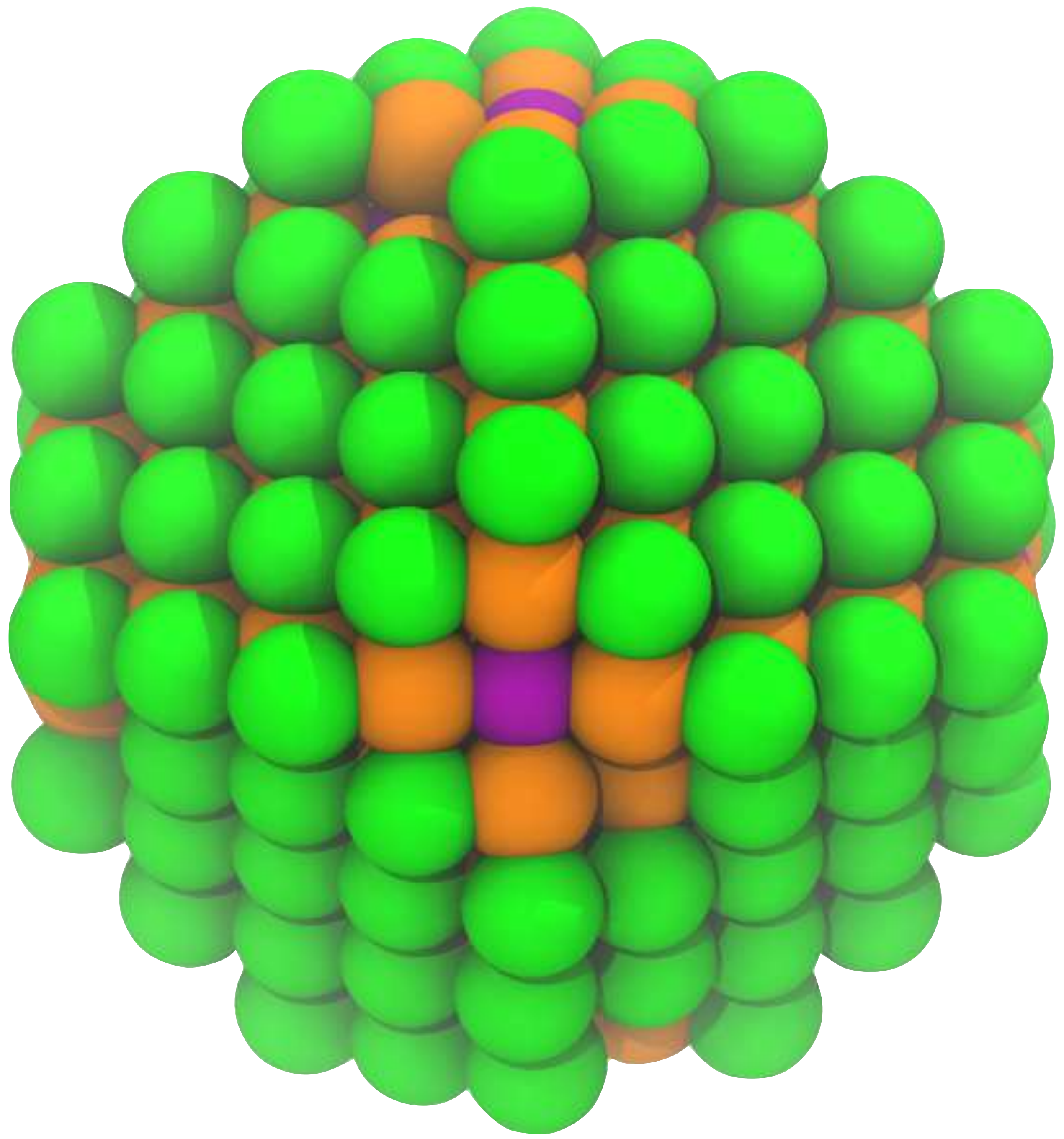


2.4 nm

Cd:Se = 1.2

Cd Se Br

PbS

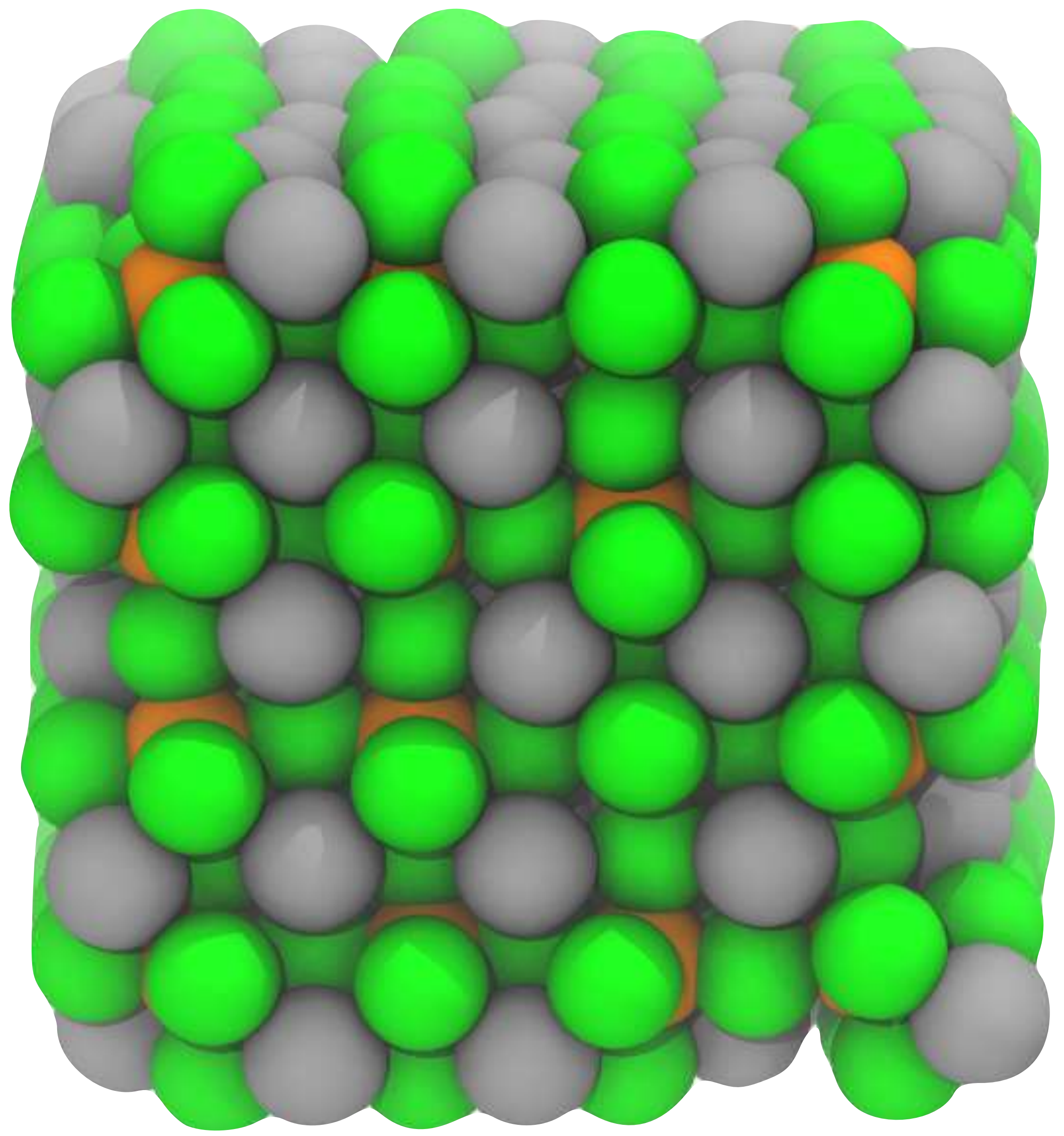


2.5 nm

Pb:S = 1.65

Pb S Br

$CsPbBr_3$

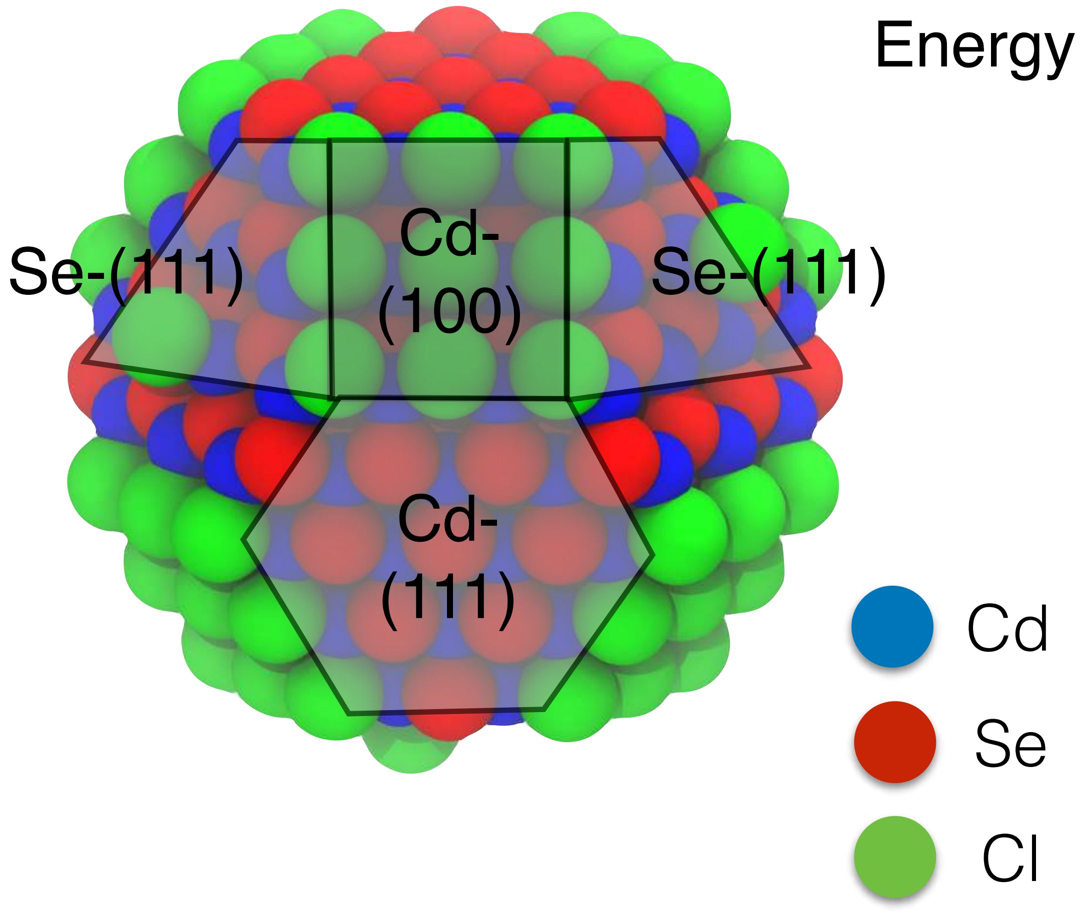


2.5 nm

Cs:Pb = 1.75

Br:Pb = 3.75

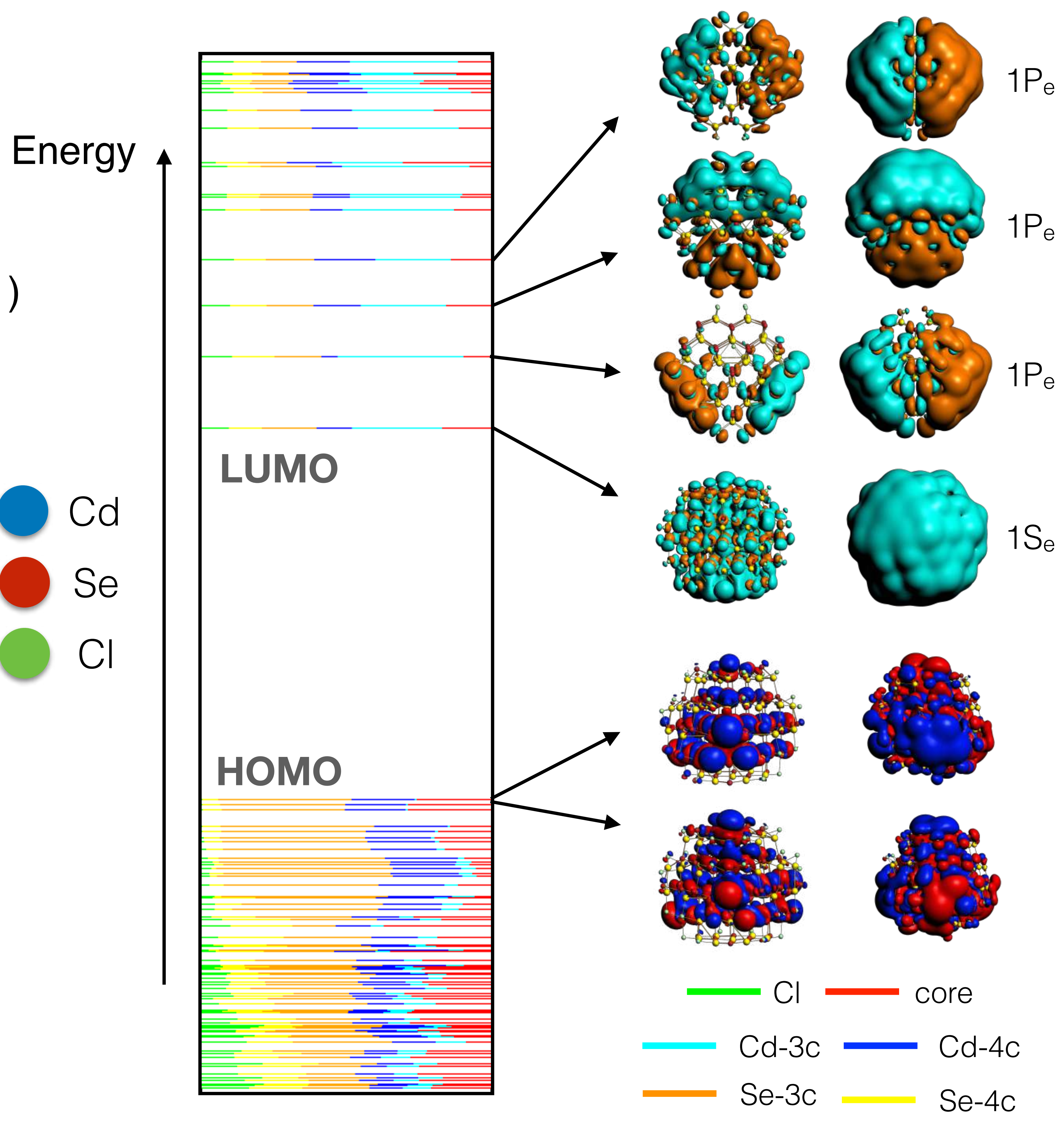
Cs Pb Br

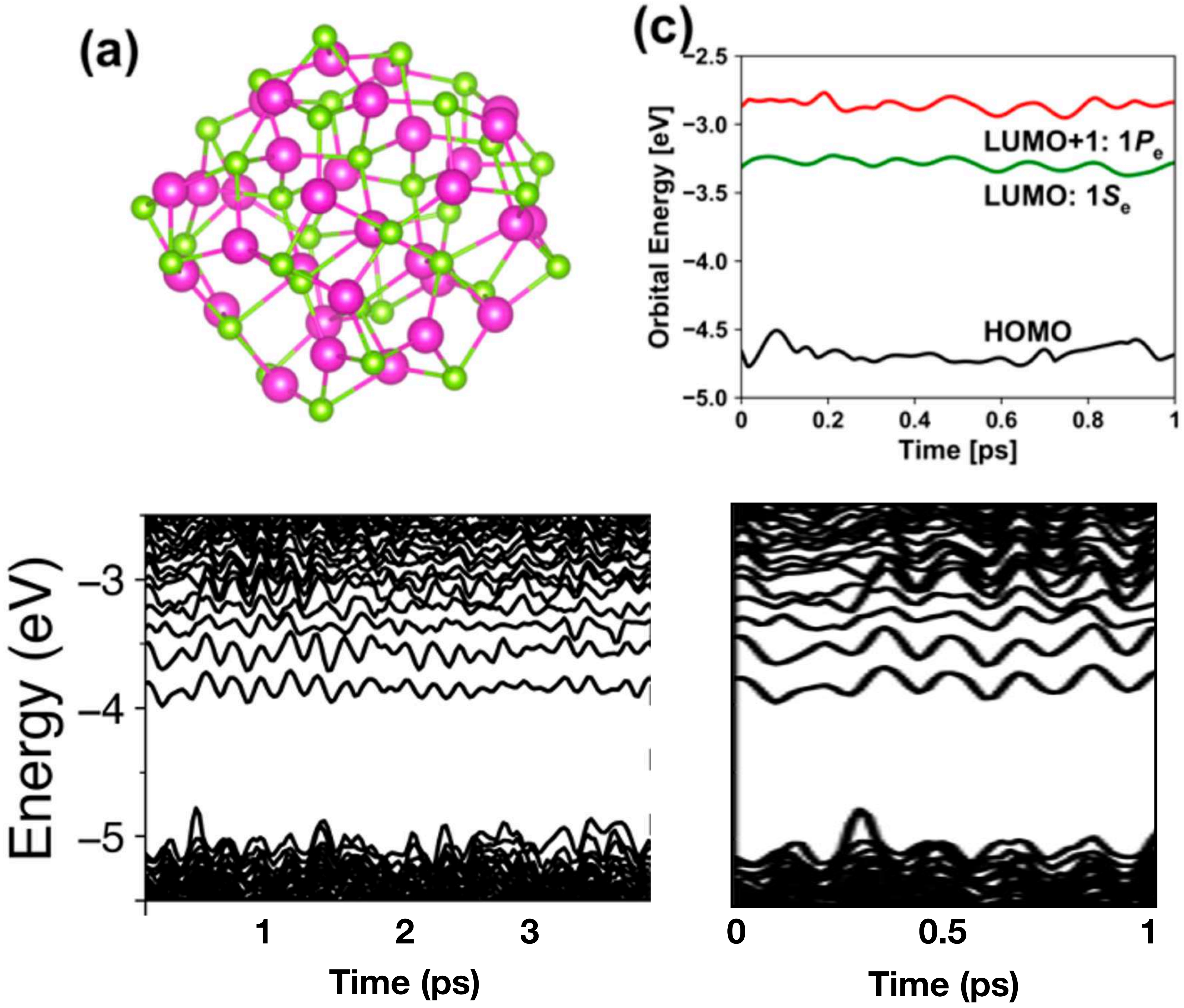


$Cd_{68}Se_{55}Cl_{26}$

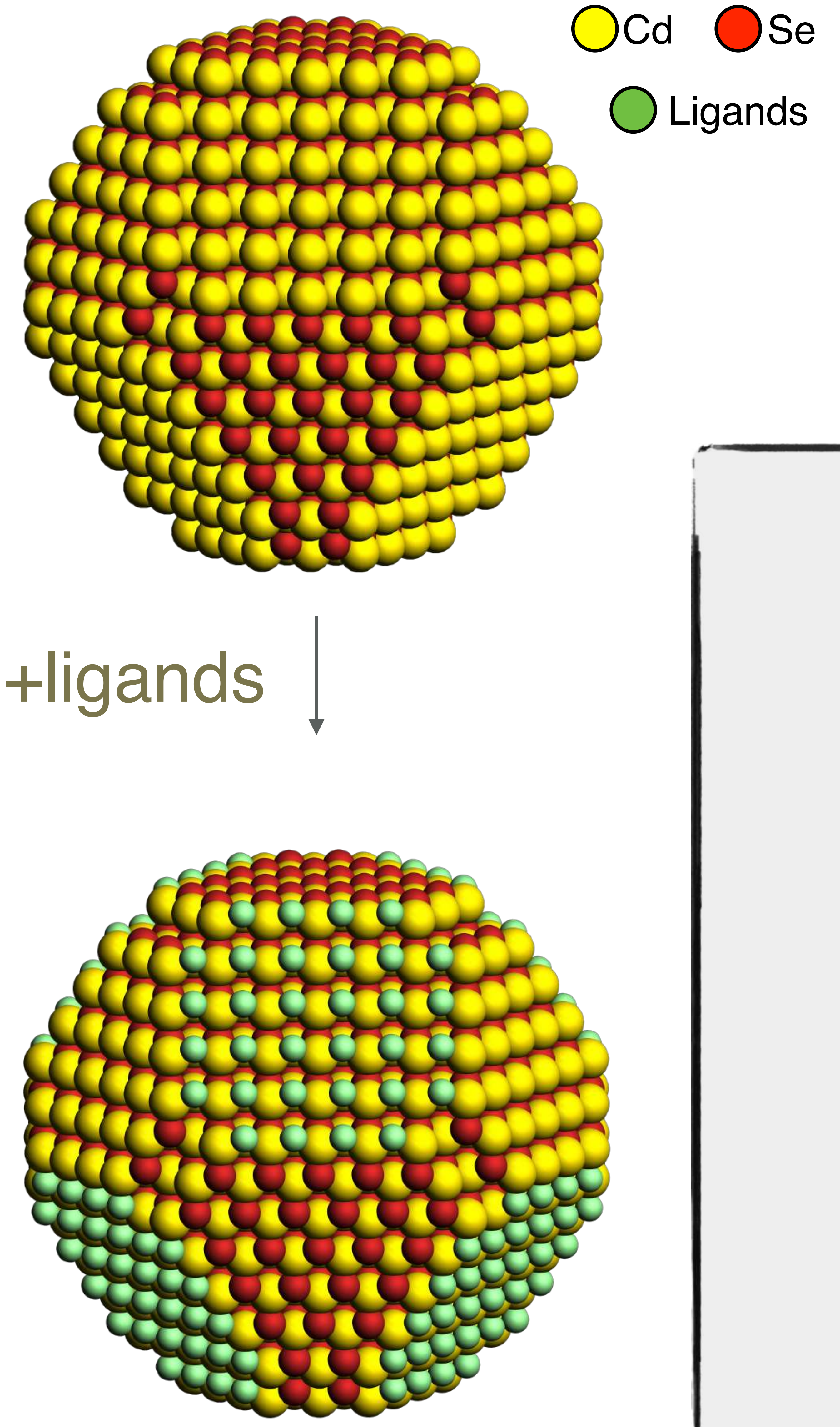
1.8 nm

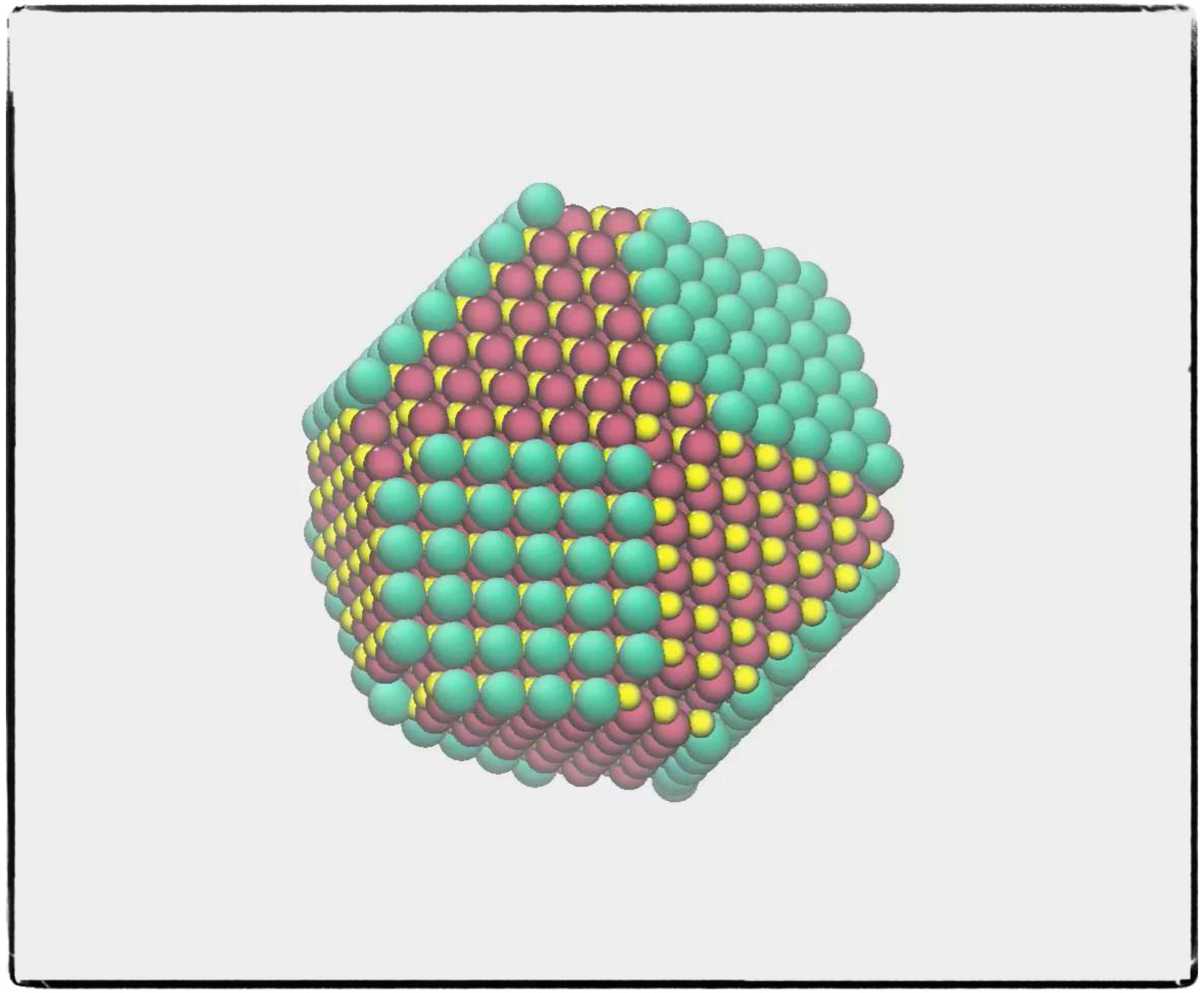
Cd:Se =1.2





Scaling to Large Sizes





Compound Attachment Tool (CAT)

GitHub: *https://github.com/nlesc-nano/CAT*

Core provided as input

Dummy positions

Ligands Attached as SMILES strings

Pre-optimization of ligands
with core frozen

Export : PDB, xyz, mol2, etc.

CP2K input for DFT and MM calculation

All automated !!

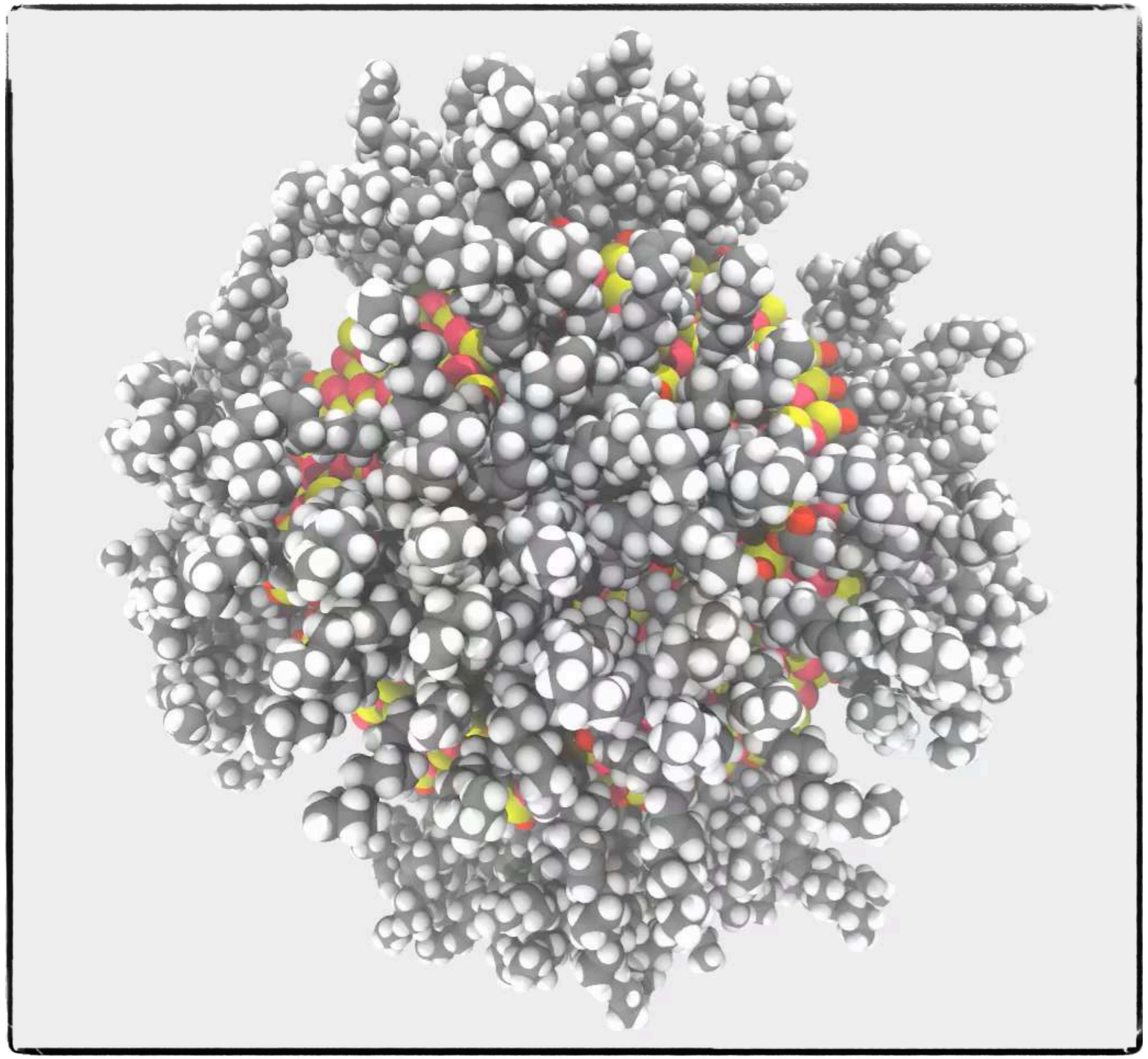
Classical Molecular Dynamics Simulations

Ensemble
NPT
P = 1atm ; T = 298K

Timescale
1 microsecond

Number of Atoms
20.000

Box size
(90 Å x 90 Å x 90 Å)

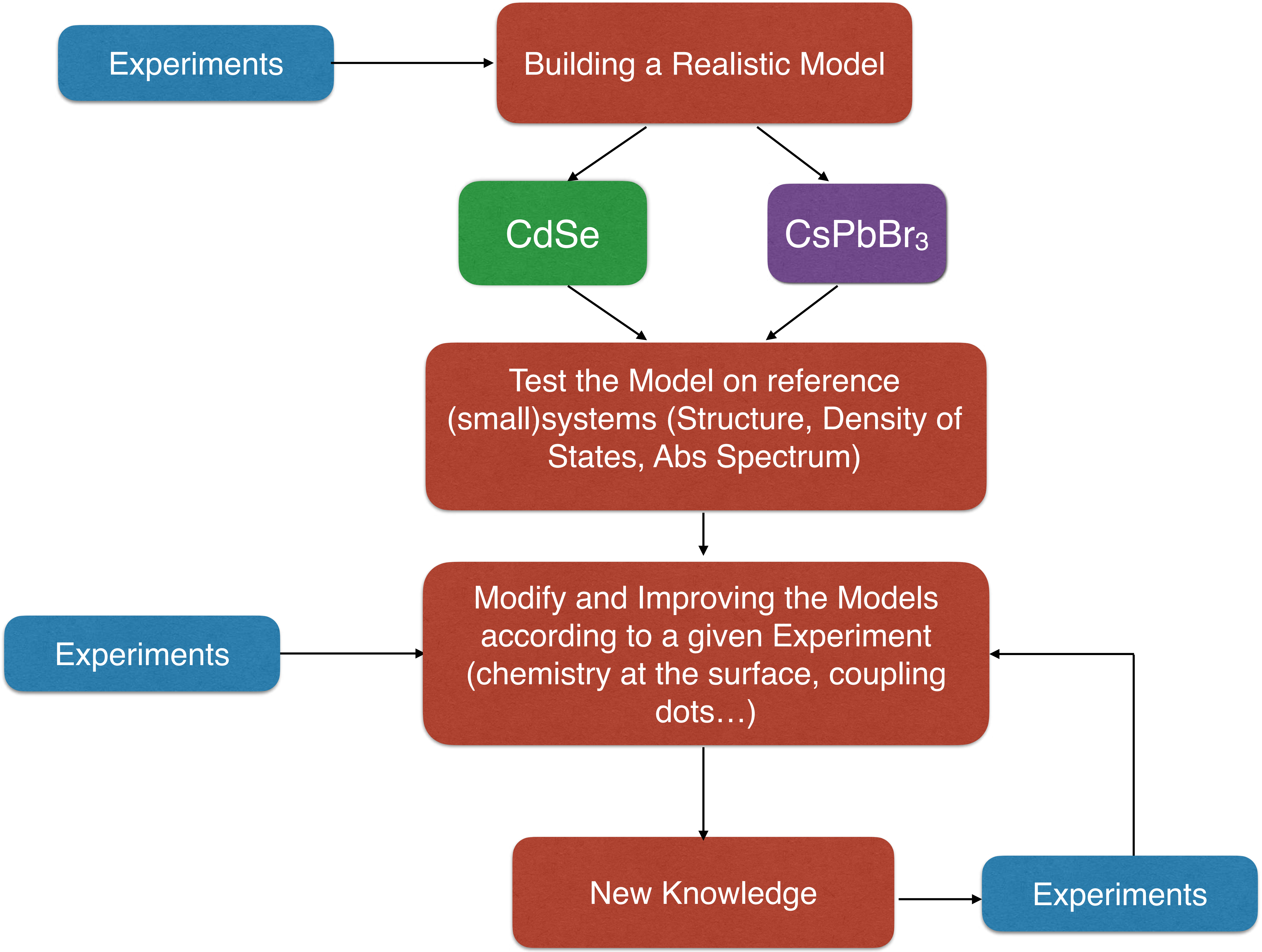


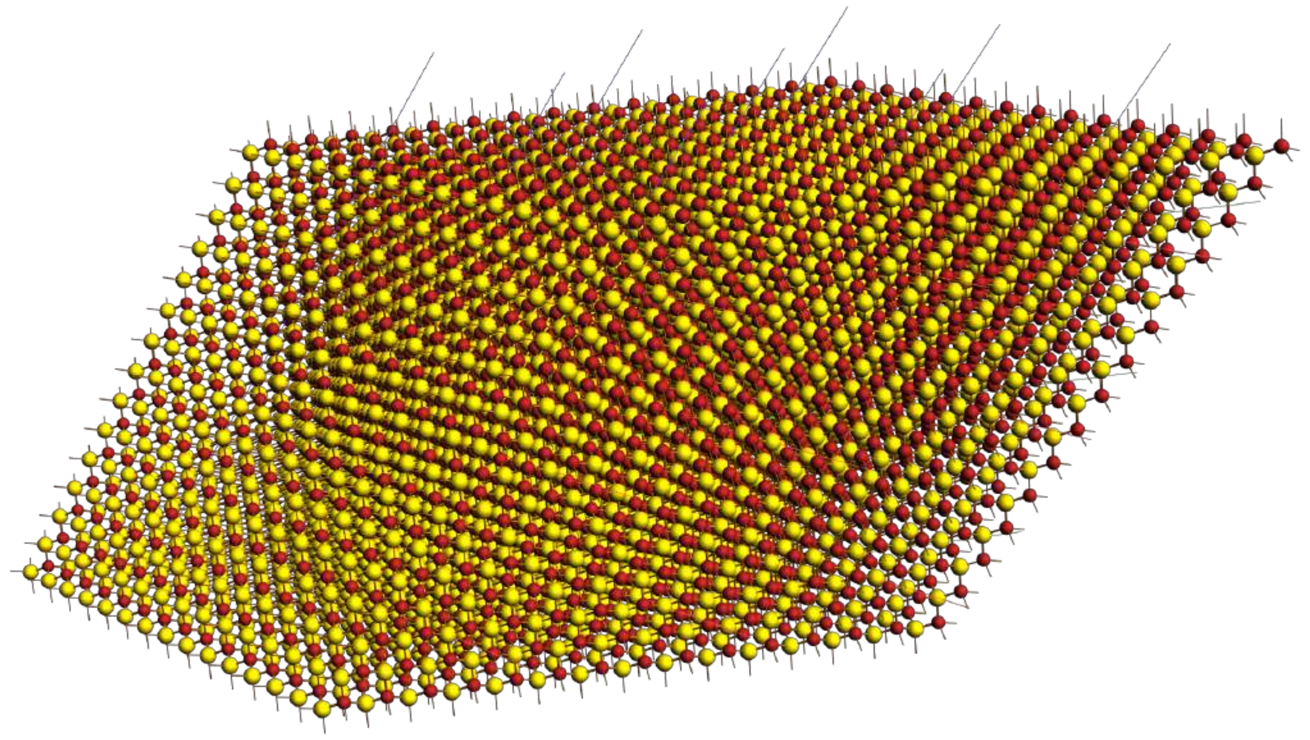
GitHub: *https://github.com/nlesc-nano/auto-FOX*

Interfaced to CP2K

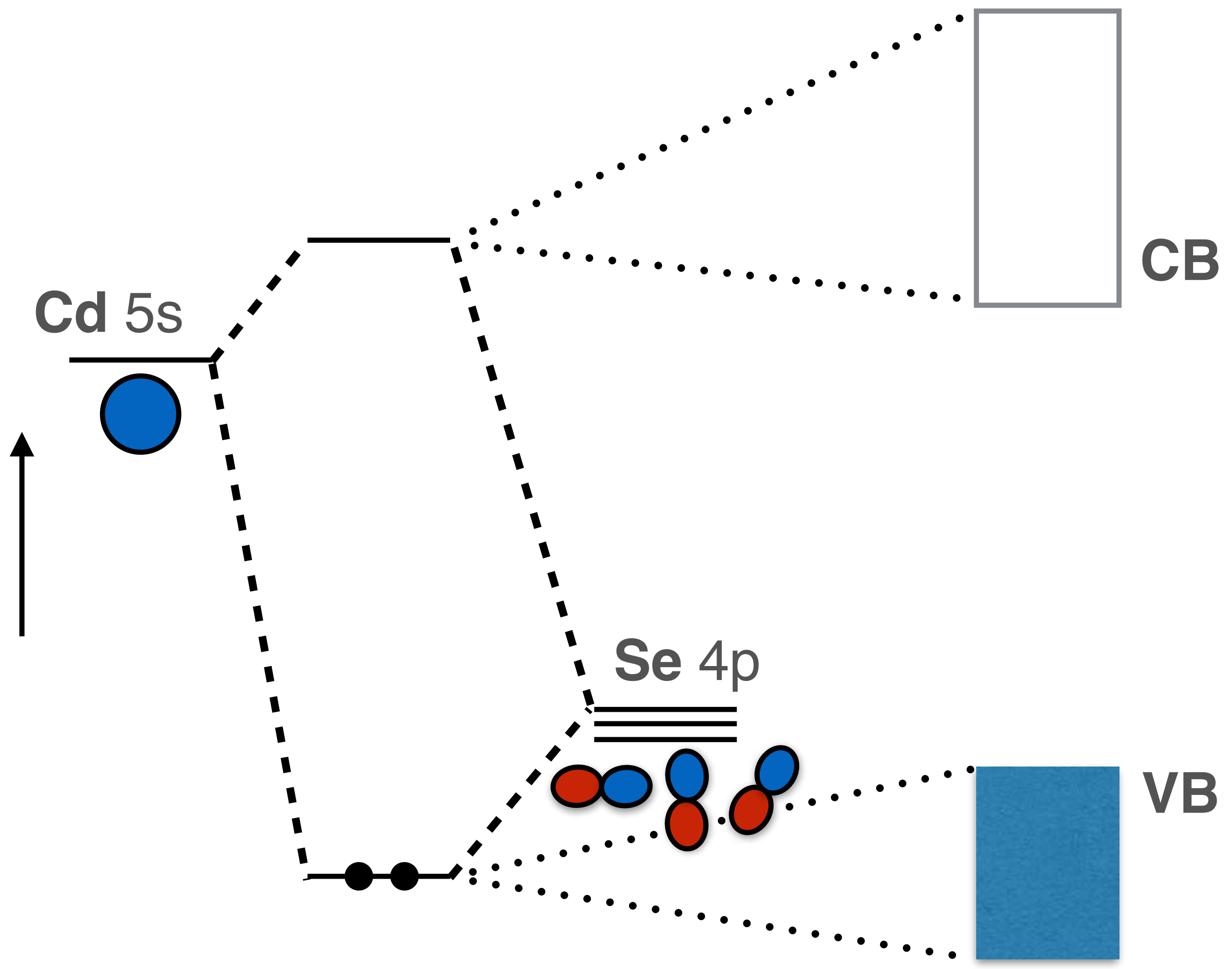
User-Friendly

Stable

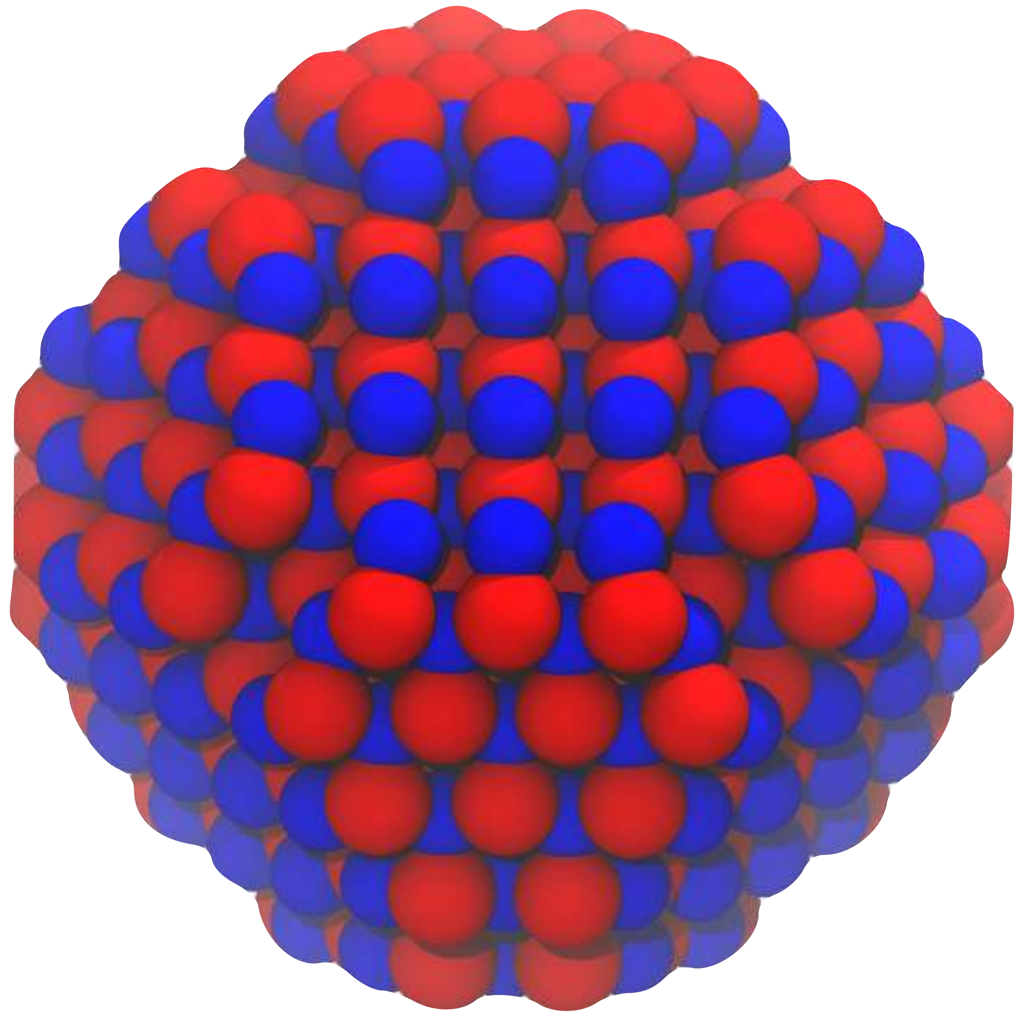

Experiments
Building a Realistic Model
CdSe
CsPbBr3
Test the Model on reference (small)systems (Structure, Density of States, Abs Spectrum)
Experiments
Modify and Improving the Models according to a given Experiment (chemistry at the surface, coupling dots…)
New Knowledge
Experiments

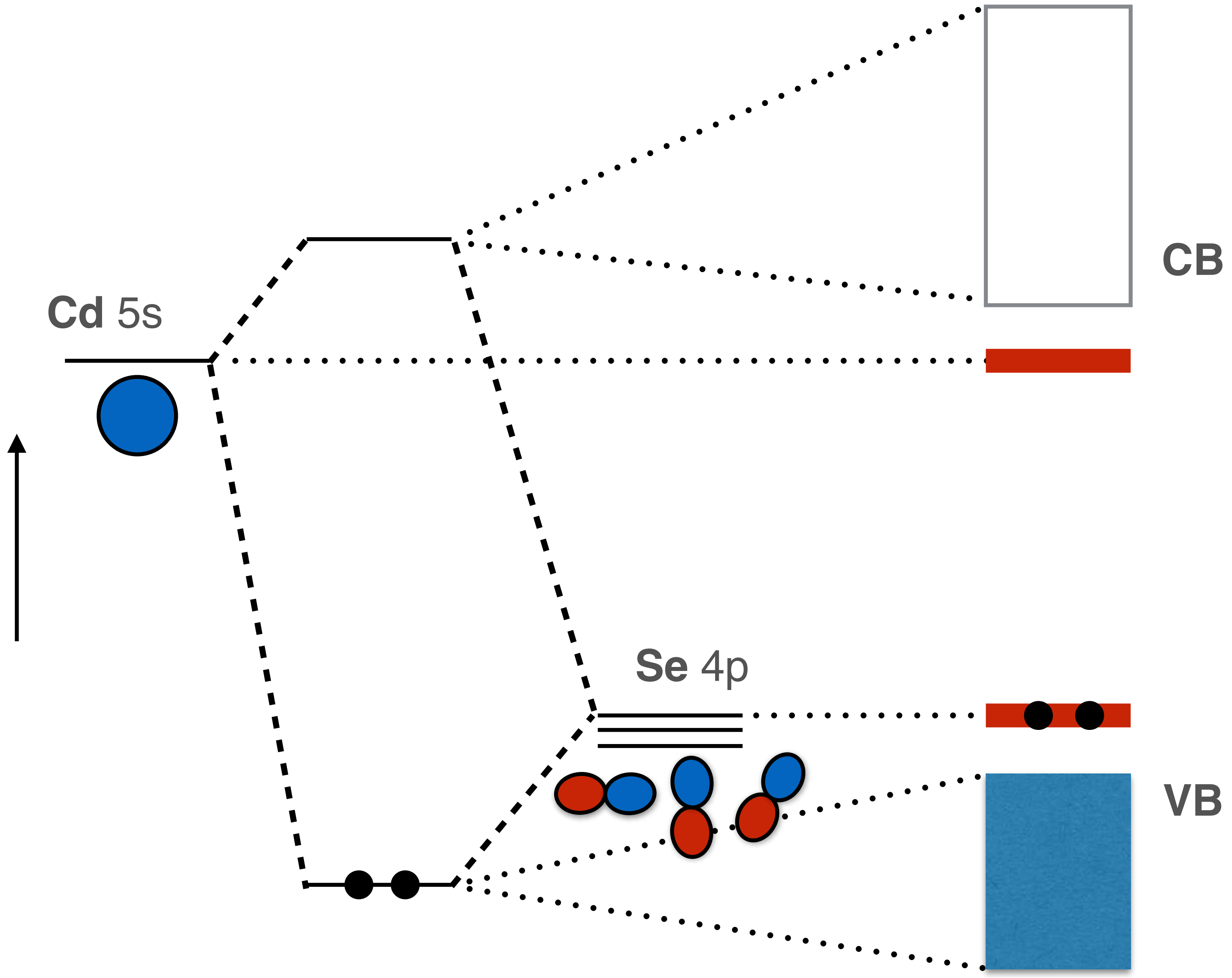


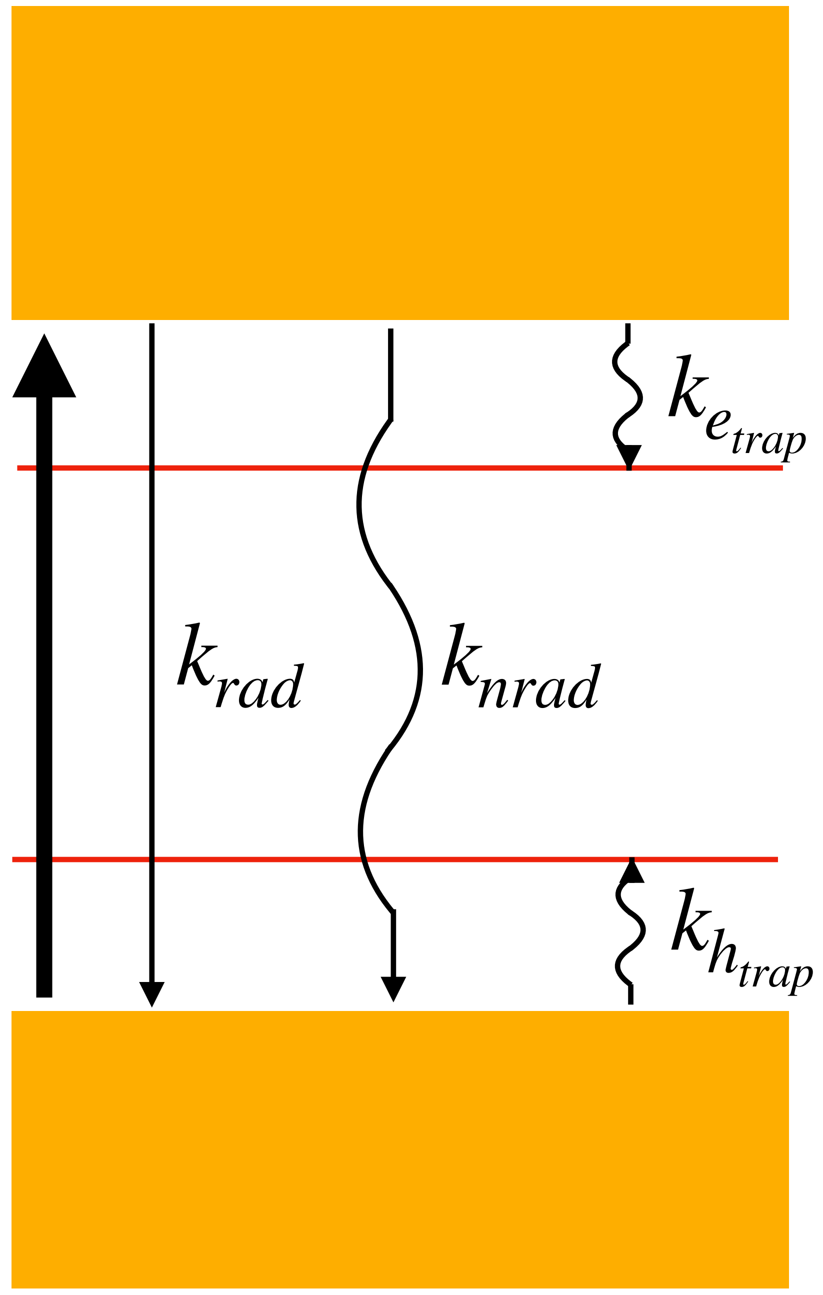
CdSe Zincblende



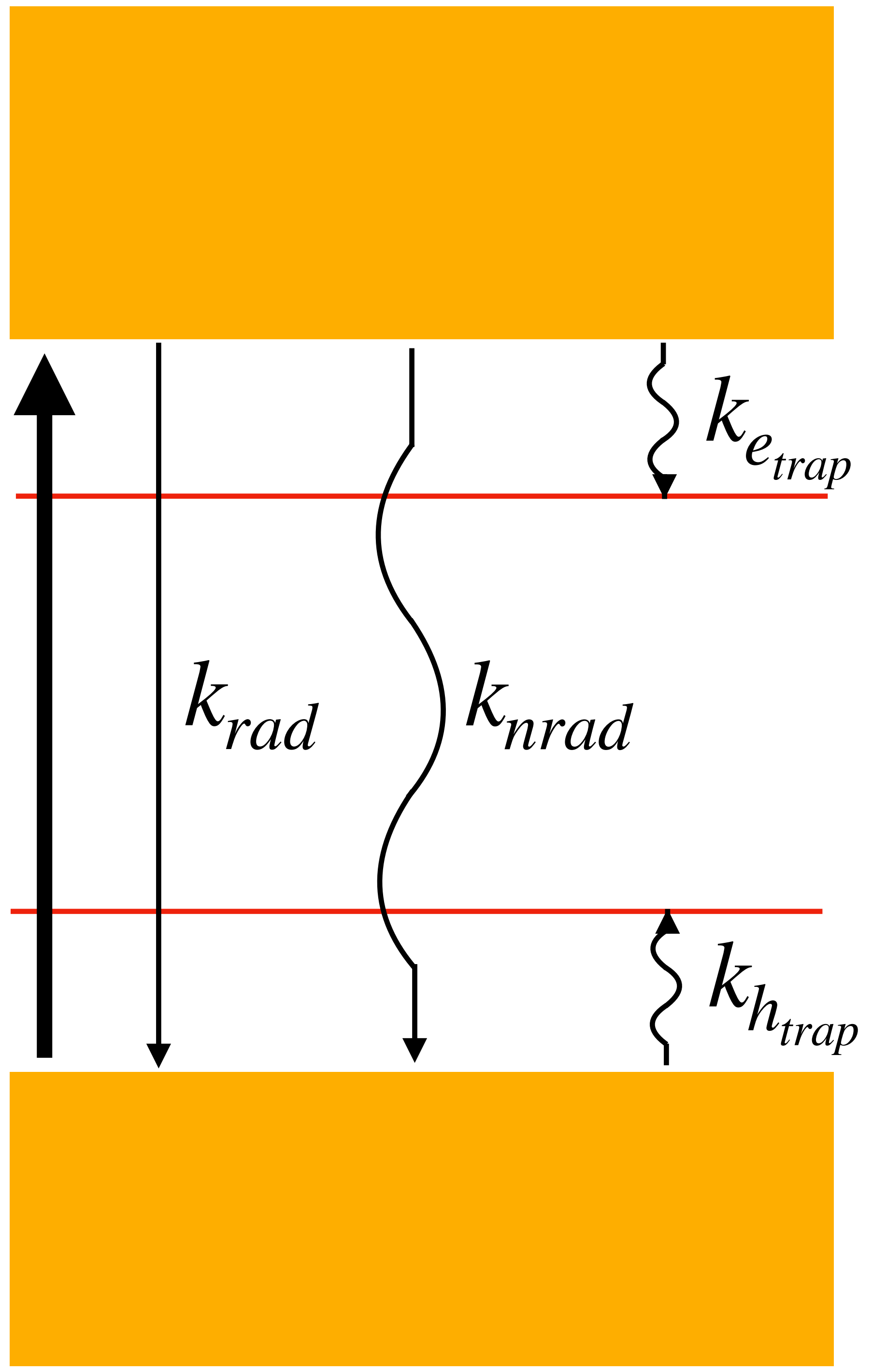
CdSe 3.0 nm





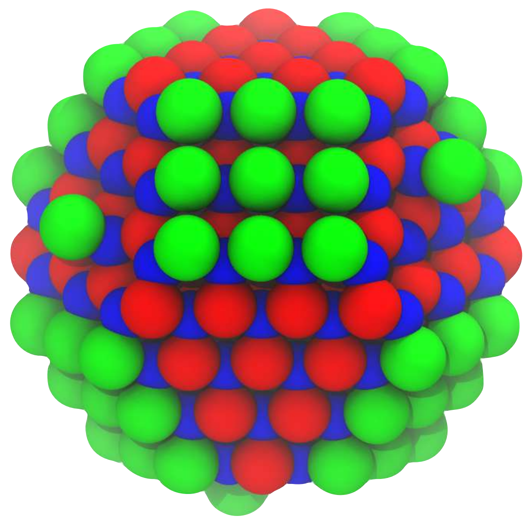


PLQY TYPICAL NCs



$$PLQY = \frac{k_{rad}}{k_{rad} + k_{nrad} + k_{e_{trap}} + k_{h_{trap}}}$$

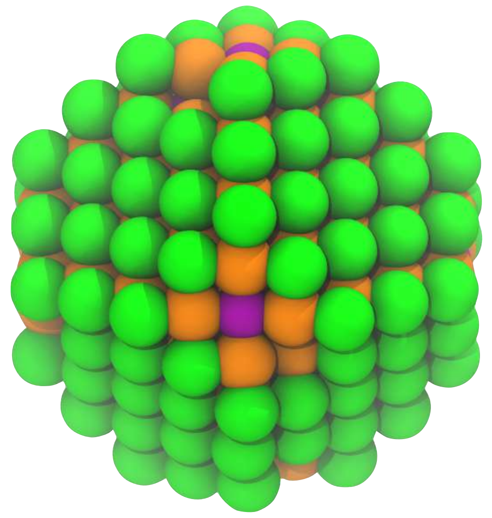
CdSe
CdTe



~ **10-50%**

Chakrabarty et al., J. Mat. Chem. C, **2015**, 3, 7561

PbS
PbSe



~ **50-60%**

Semonin et al., JPCL, **2010**, 1, 2445

What are the PL quenching mechanisms ?

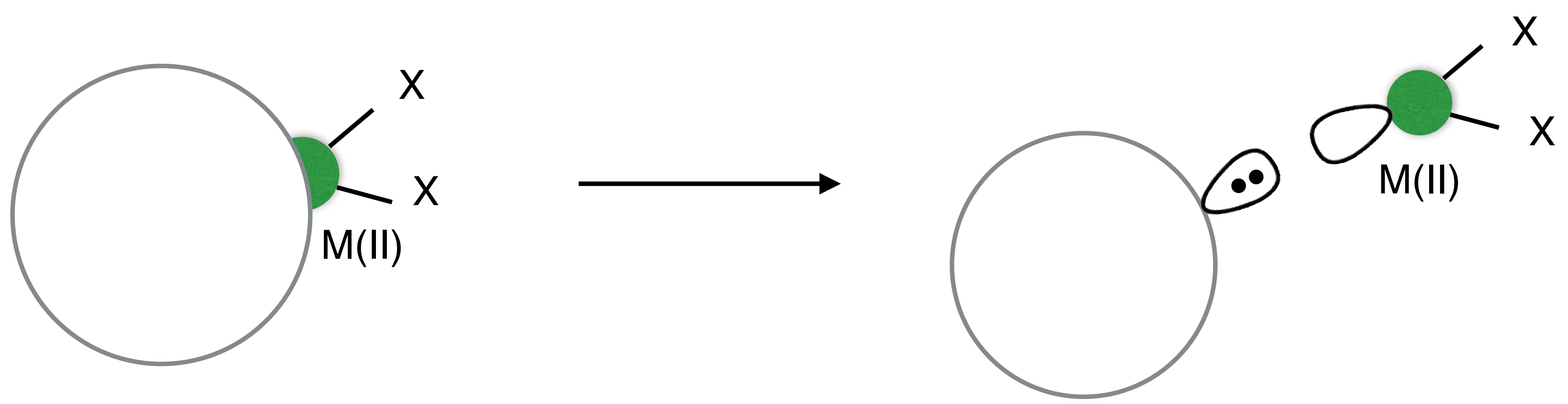
How do Trap States emerge in Colloidal Nanocrystals ?

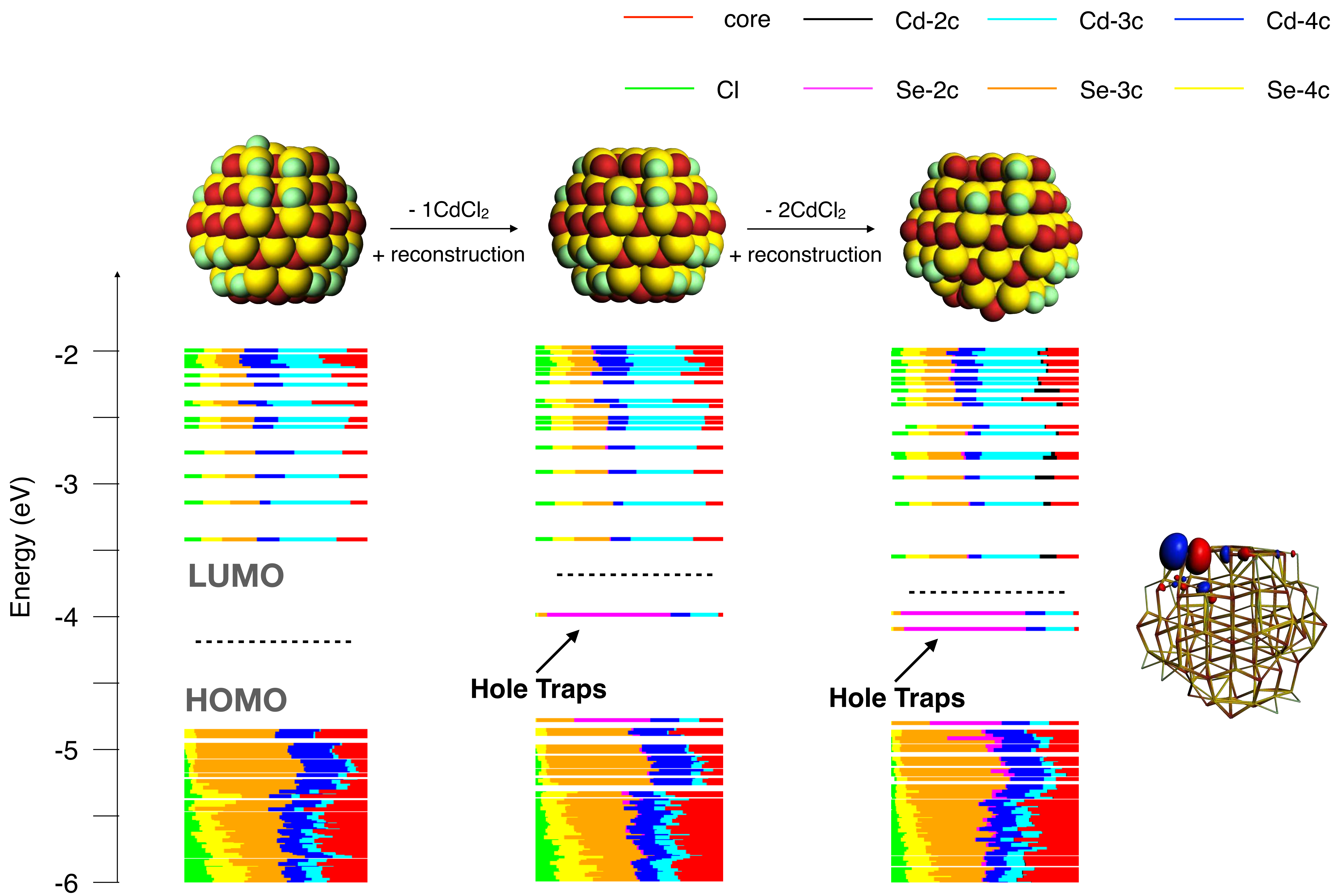
Understanding the Surface

Ligand Binding Types

Coordination Numbers

Surface Chemistry





J|A|C|S JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

Ligand Exchange and the Stoichiometry of Metal Chalcogenide Nanocrystals: Spectroscopic Observation of Facile Metal-Carboxylate Displacement and Binding

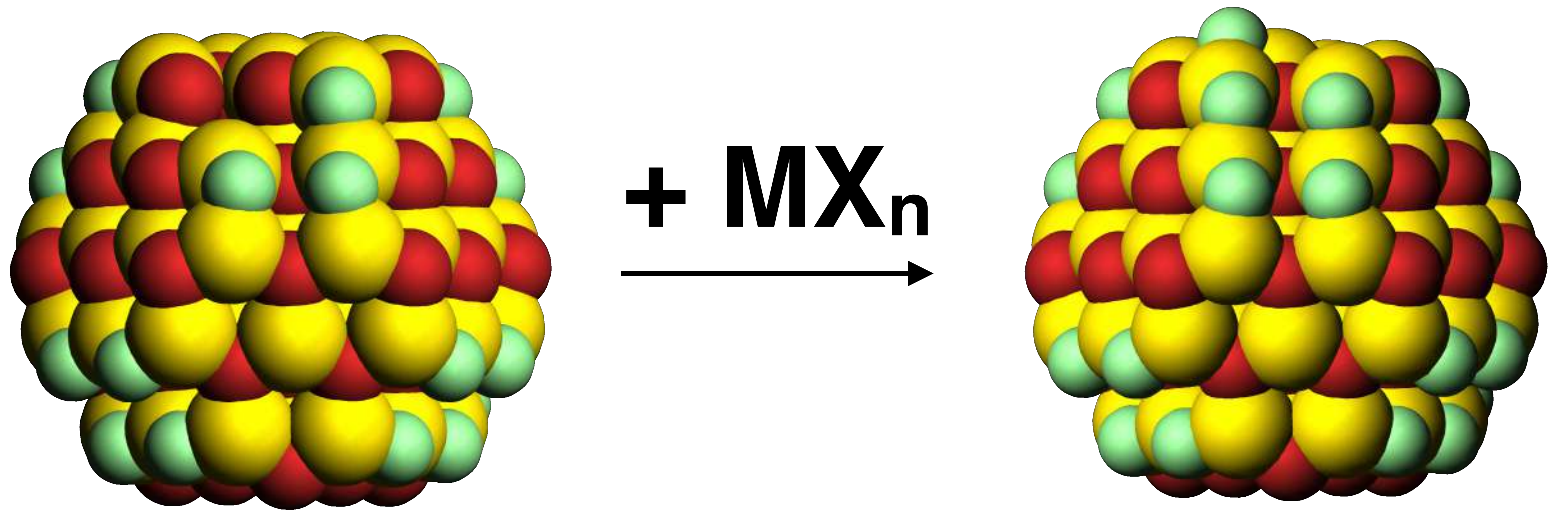
Nicholas C. Anderson, Mark P. Hendricks, Joshua J. Choi, and Jonathan S. Owen*

cm CHEMISTRY OF MATERIALS
Article
pubs.acs.org/cm

On the Origin of Surface Traps in Colloidal II–VI Semiconductor Nanocrystals

Arjan J. Houtepen,[†] Zeger Hens,[‡,§] Jonathan S. Owen,[⊥] and Ivan Infante[*,¶]

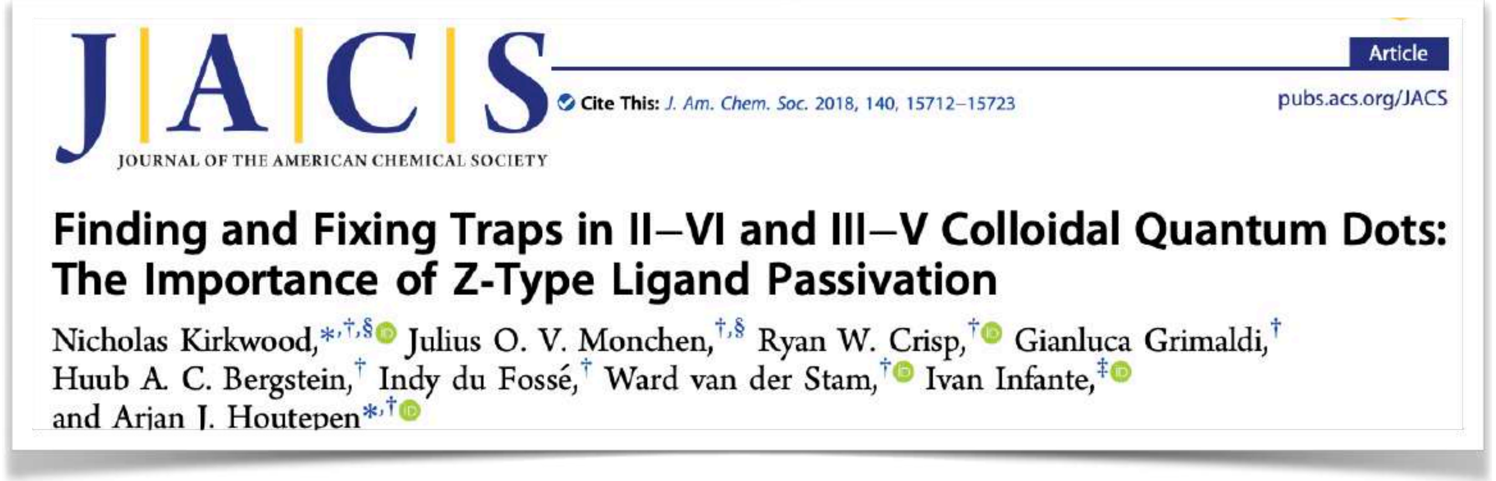
CdTe CdTe



Quantum Dots + MX_n

M = In^{3+}, Cd^{2+}, Zn^{2+}, Li^{+},...

X = Cl^{-}, RCO_2^{-},...



JACS Journal of the American Chemical Society

Cite This: J. Am. Chem. Soc. 2018, 140, 15712−15723

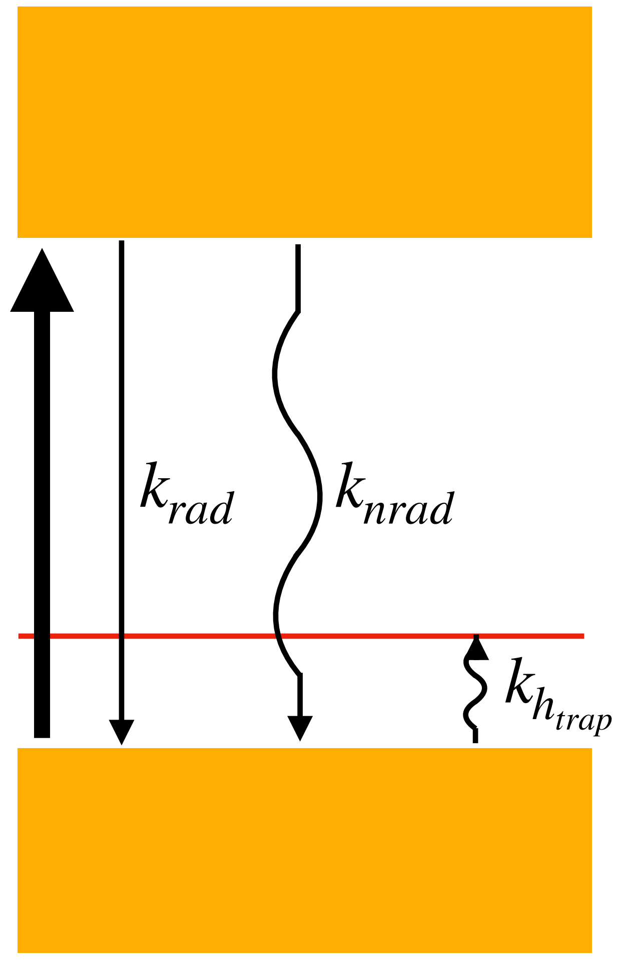
pubs.acs.org/JACS

Article

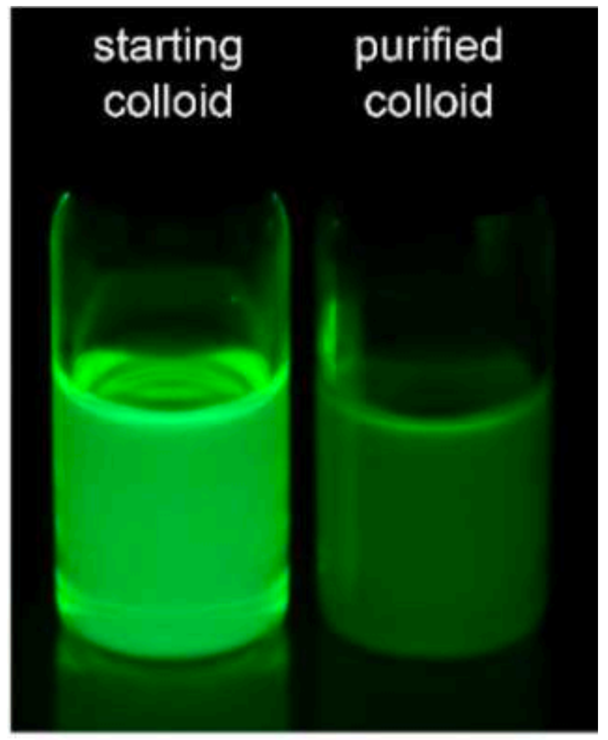
Finding and Fixing Traps in II−VI and III−V Colloidal Quantum Dots: The Importance of Z-Type Ligand Passivation

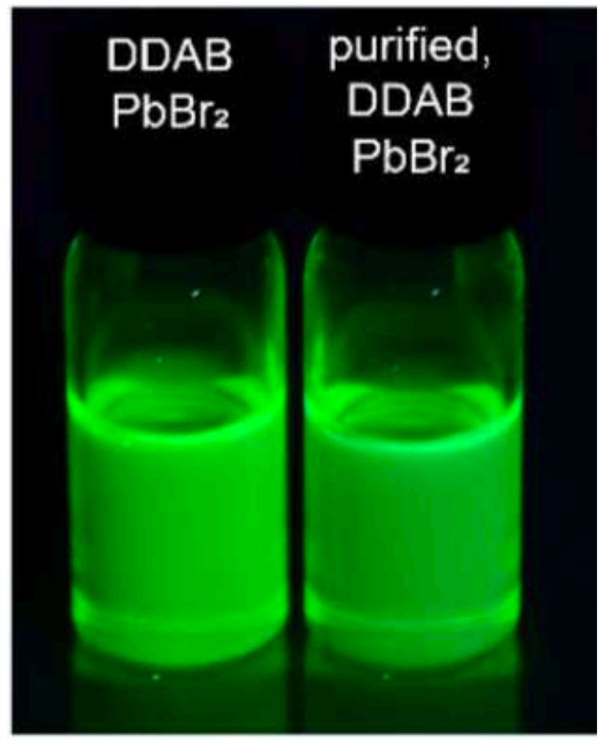
Nicholas Kirkwood, Julius O. V. Monchen, Ryan W. Crisp, Gianluca Grimaldi, Huub A. C. Bergstein, Indy du Fossé, Ward van der Stam, Ivan Infante, and Arjan J. Houtepen

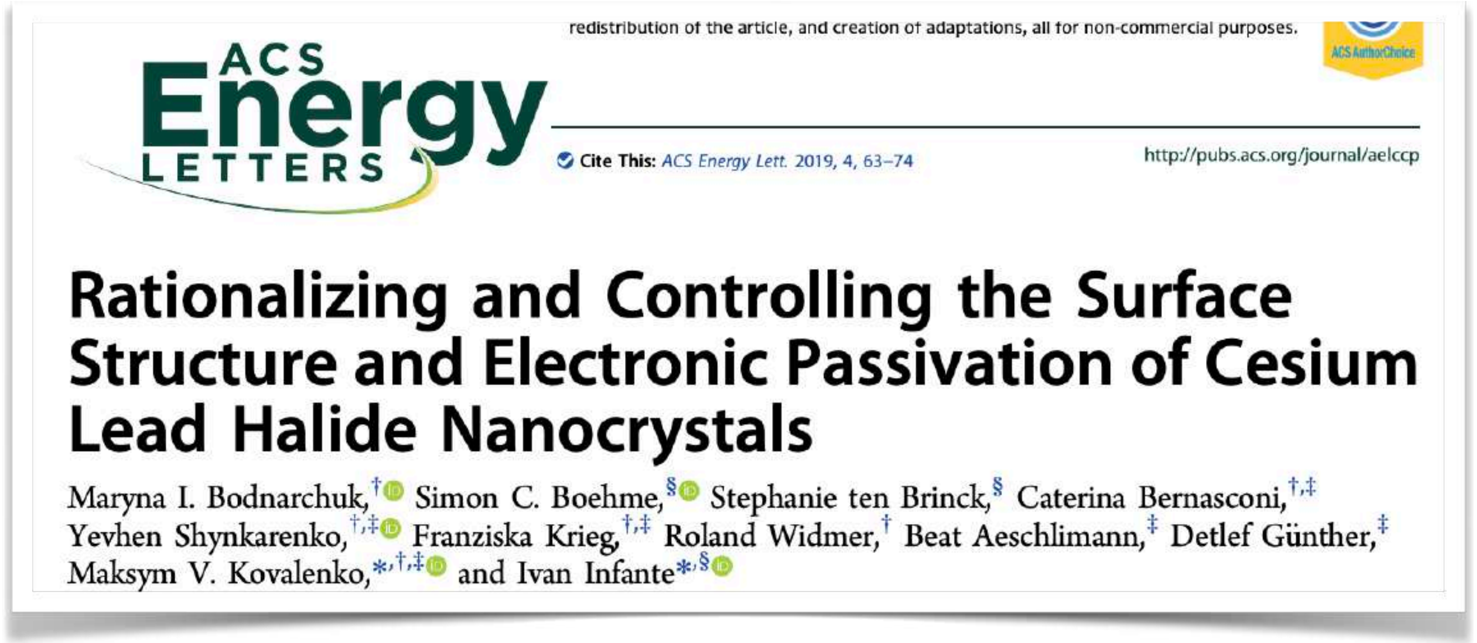
Fixing Hole Traps



$CsPbBr_3$







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ACS Energy Letters

Cite This: ACS Energy Lett. 2019, 4, 63−74

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Rationalizing and Controlling the Surface Structure and Electronic Passivation of Cesium Lead Halide Nanocrystals

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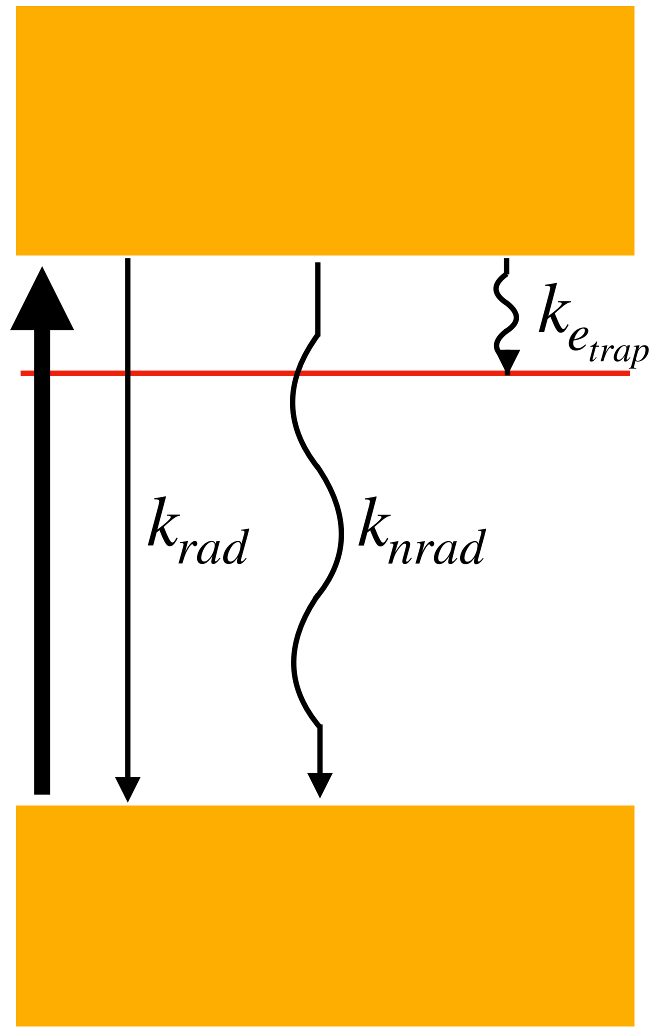
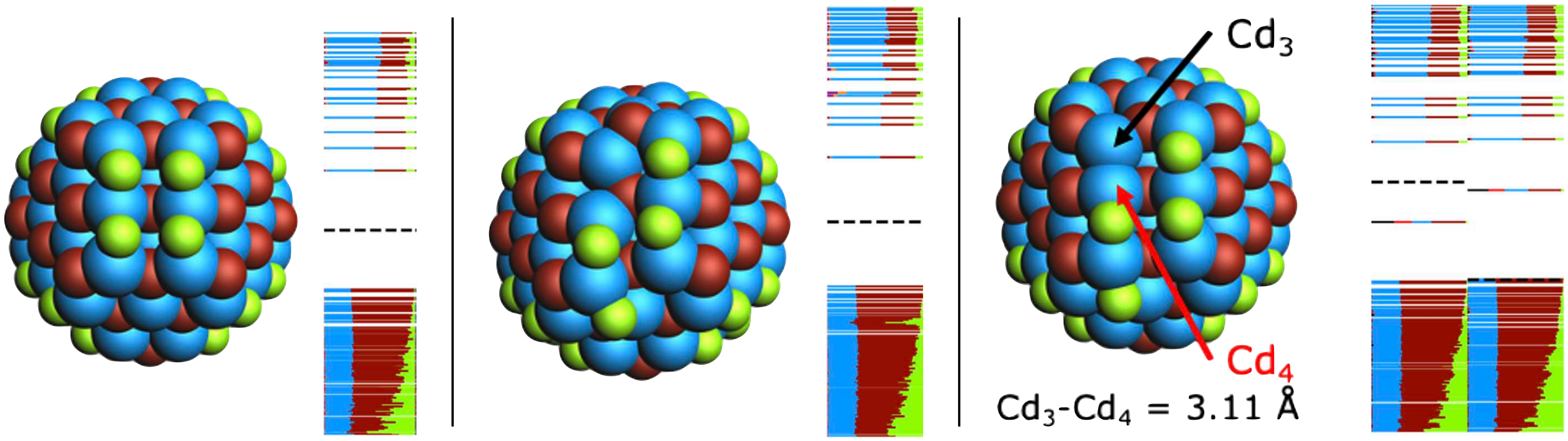
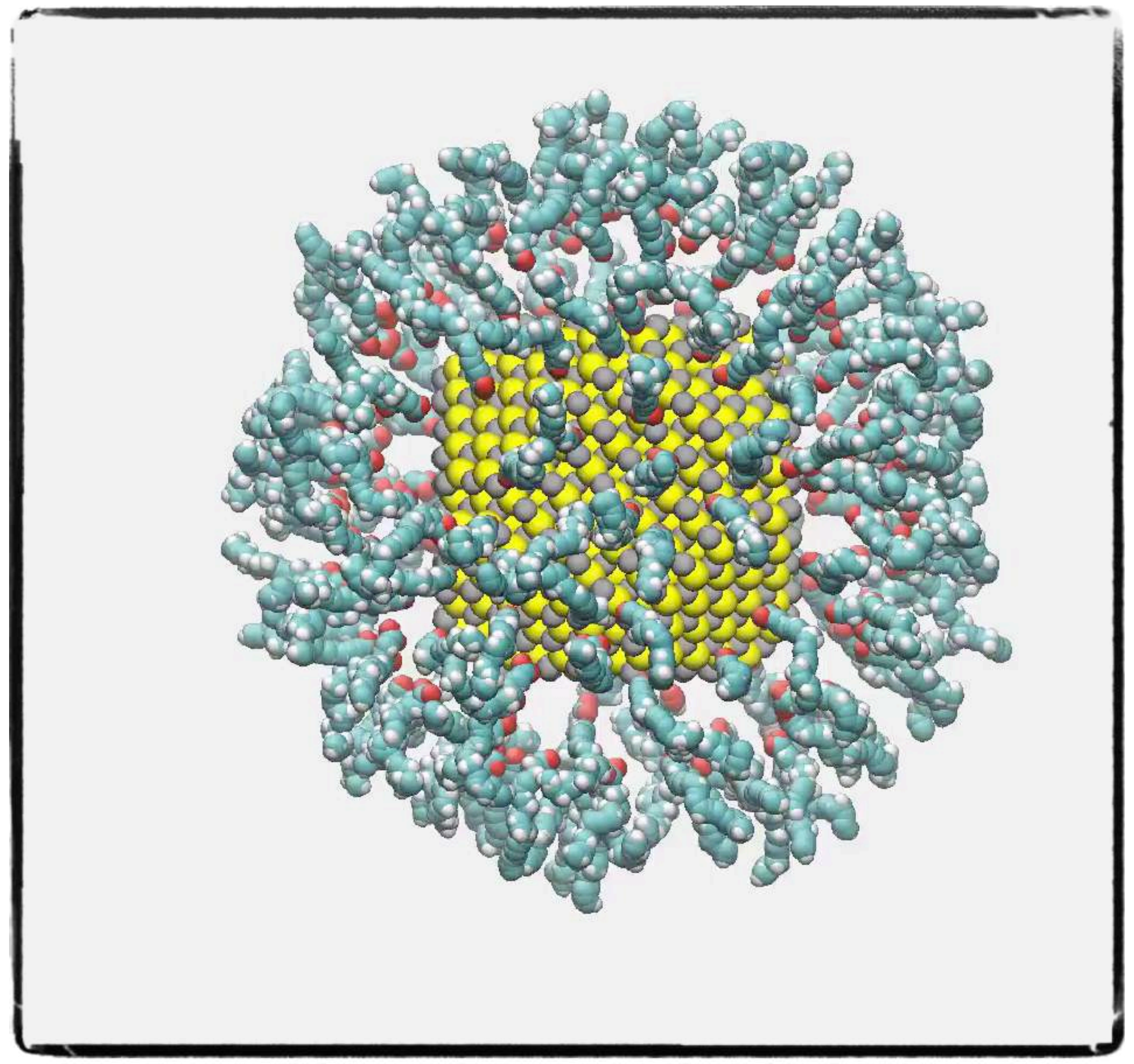
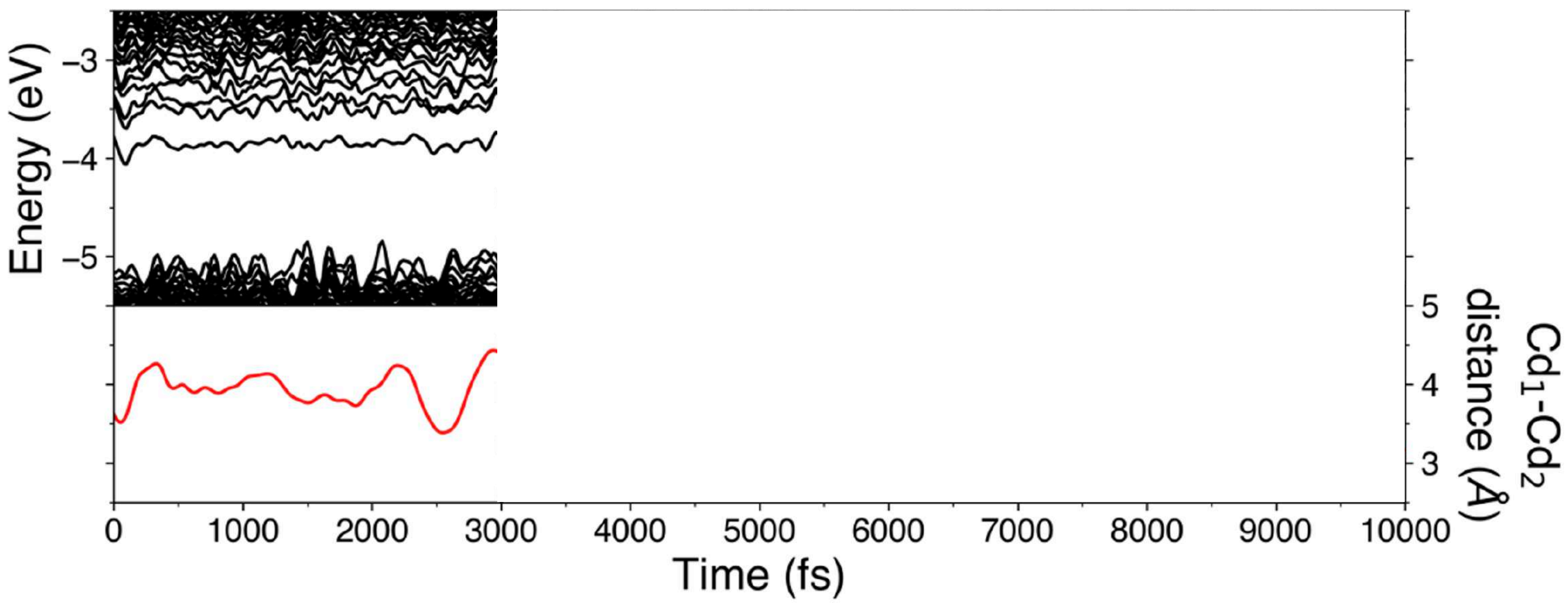
Electron Traps   DFT/PBE   AIMD NVT 10ps

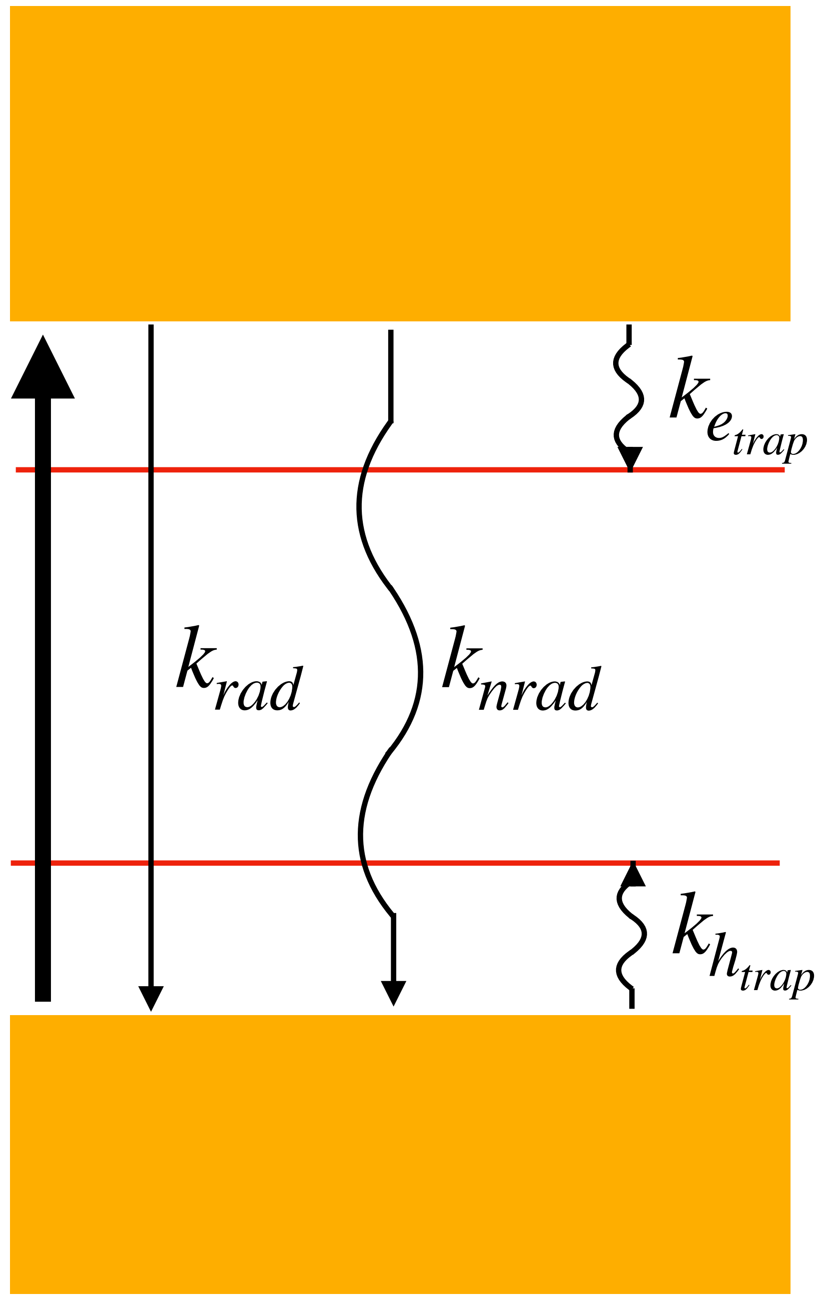








What about NAMD ?



Temperature Dependence

Role of Ligands

Role of Surface

Size Effect

Type of material

nano-QMflows

GitHub: https://github.com/SCM-NV/nano-qmflows

Interface between CP2k and PYXAID

Tully surface hopping

$$i\hbar \frac{dc_i}{dt} = \sum_{j=0}^{N_b-1} (\varepsilon_i \delta_{ij} - i\hbar d_{ij}) c_j$$

Energies | **Coupling Vectors**

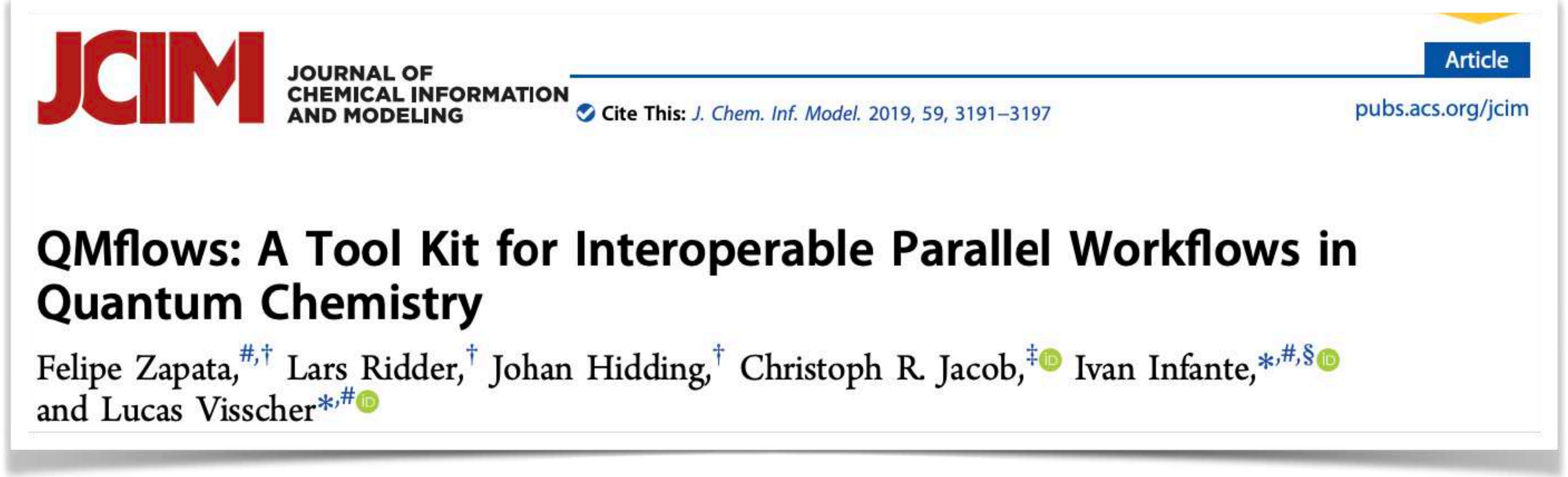
$$\varepsilon_i$$

Internal Engine to Compute Overlaps

LibInt Library

$$d_{ij} = \left\langle \Phi_i \middle| \frac{\partial \Phi_j}{\partial t} \right\rangle = \vec{d}_{ij}^{(1)} \frac{\vec{P}}{M}$$

Numerically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Article

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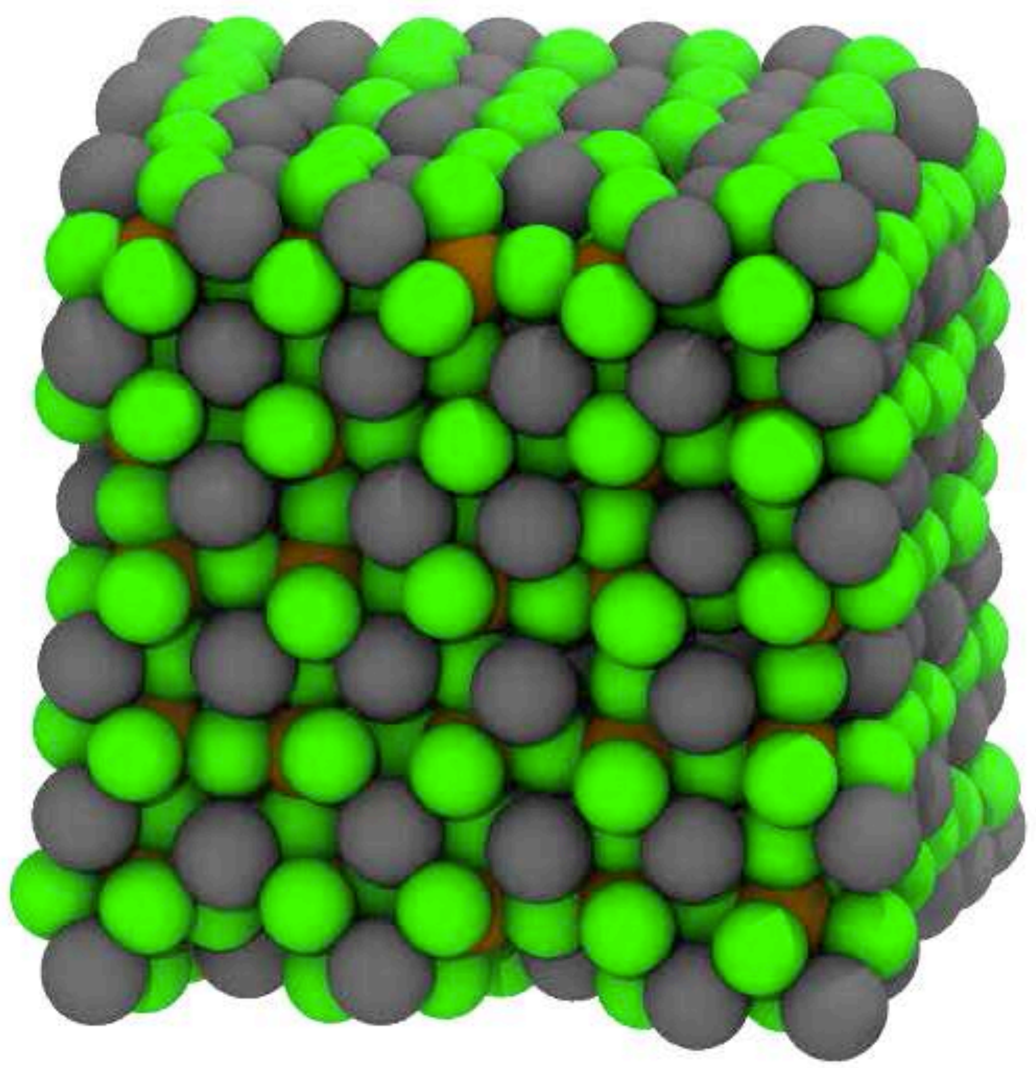
QMflows: A Tool Kit for Interoperable Parallel Workflows in Quantum Chemistry

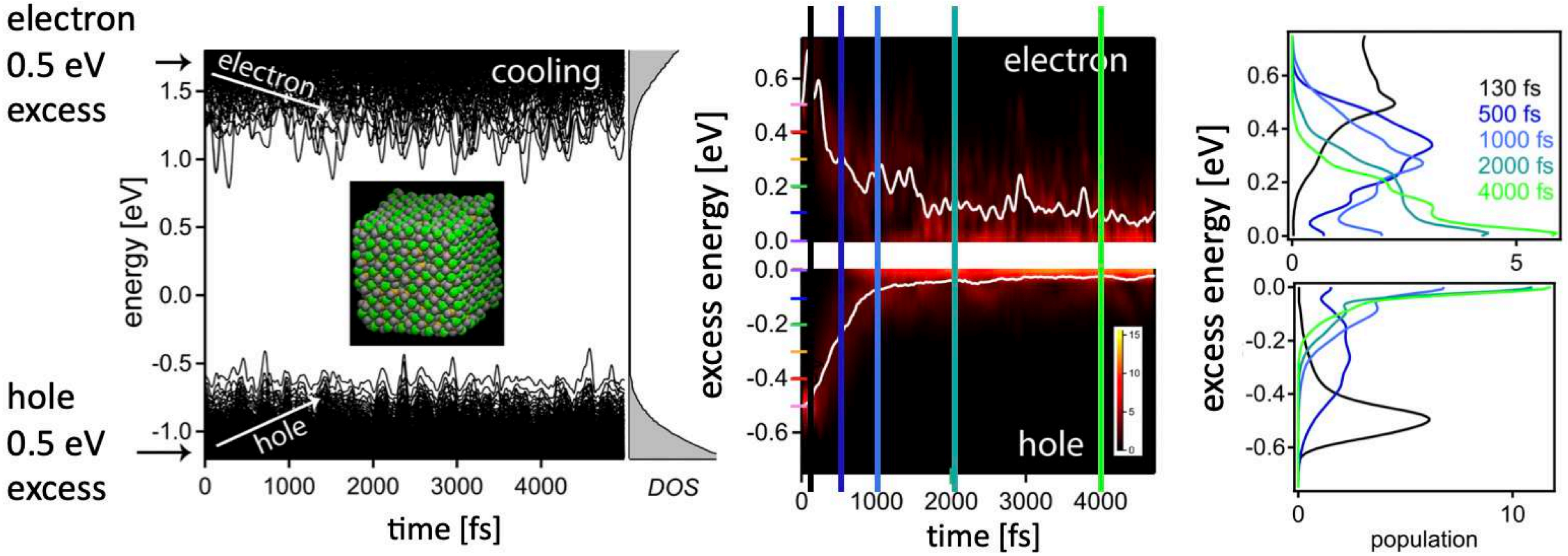
Felipe Zapata,[#,†] Lars Ridder,[†] Johan Hidding,[†] Christoph R. Jacob,[‡] Ivan Infante,[*,#,§] and Lucas Visscher[*,#]

$$t_{cool} = \left(\frac{a_g}{a_g + a_e}\right) t_g + \left(\frac{a_e}{a_g + a_e}\right) t_e$$

Electron and hole cooling



2.9 nm $CsPbBr_3$ NC



Cooling in PbS faster:
By factor 3 (electron) and 10 (hole)

electron: 0.57 eV/ps

hole: 0.67 eV/ps

NVE T = 300K

DFT/PBE

3.0 nm / 1000 atoms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Phonon-Mediated and Weakly Size-Dependent Electron and Hole Cooling in $CsPbBr_3$ Nanocrystals Revealed by Atomistic Simulations and Ultrafast Spectroscopy

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