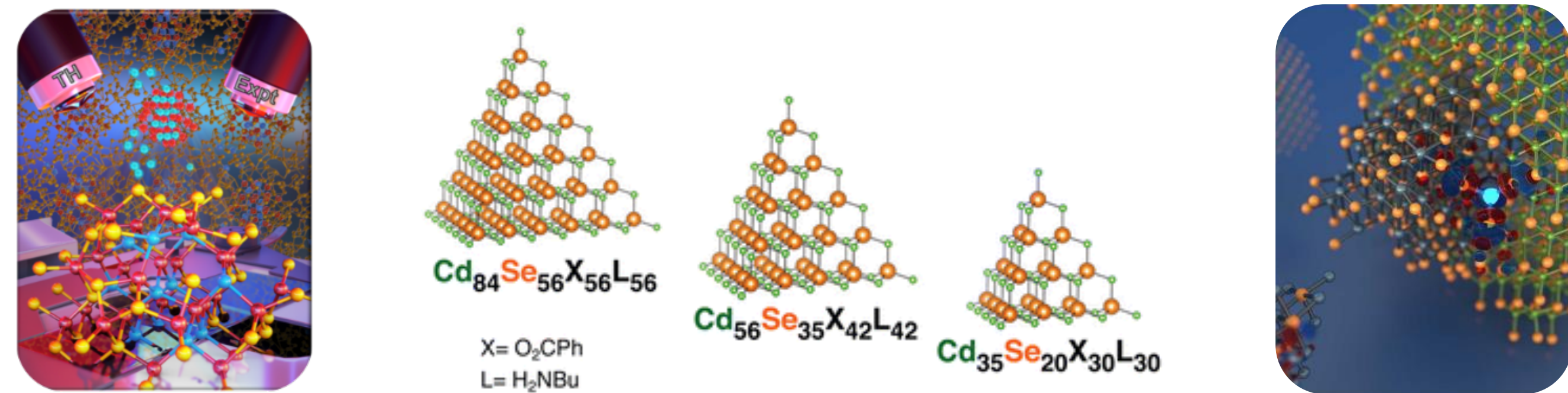


Introduction

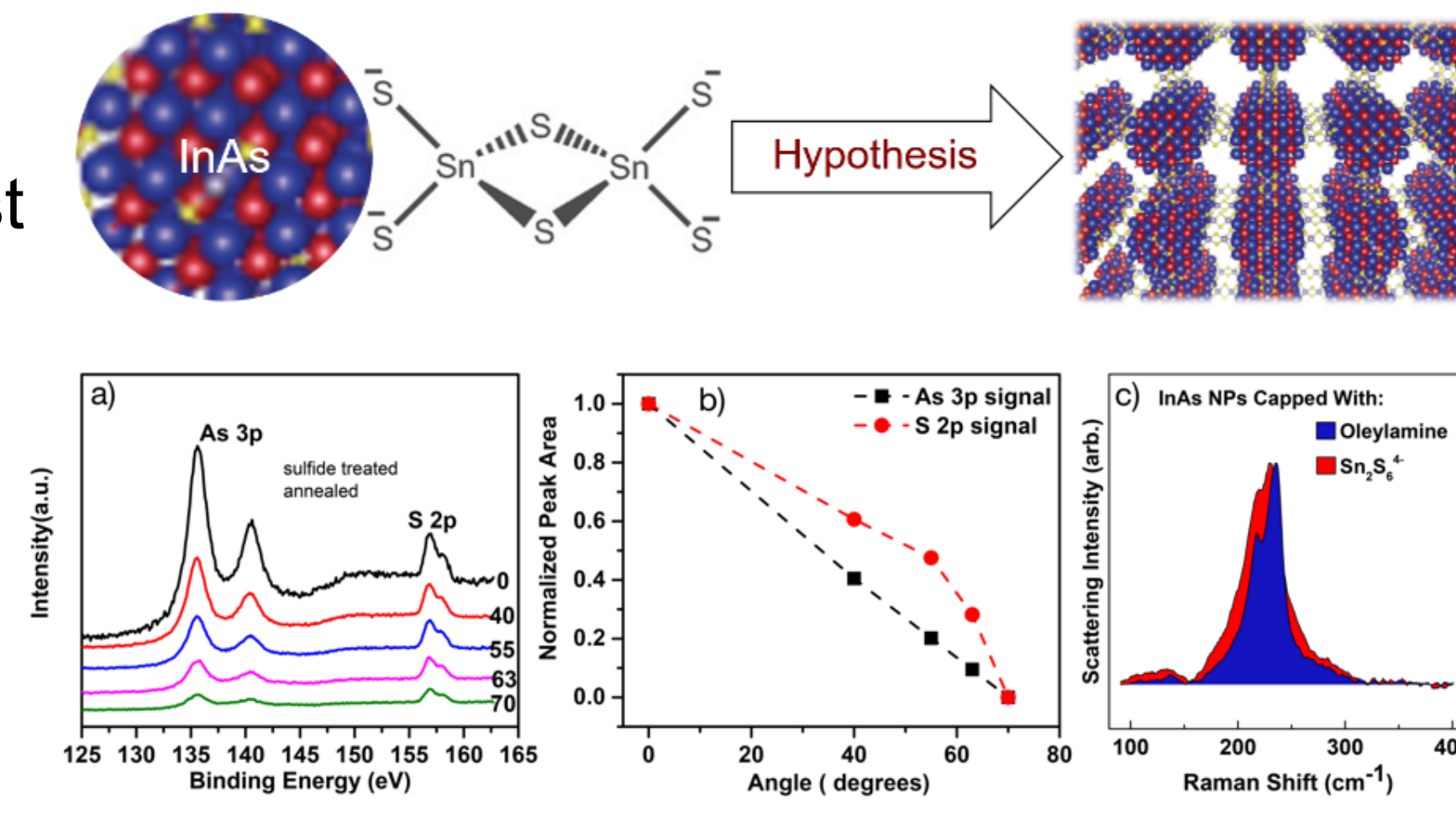


Semiconducting nanoparticles are building blocks of numerous materials with tunable electronic properties. Predicting the properties of these systems is challenging as the atomistic structure of nanoparticle-ligand interfaces is often unknown. We aim at validating structural models of nano-interfaces and at validating the **electronic properties of nanoparticles interfaced with organic and inorganic ligands**.

Ligand Engineering

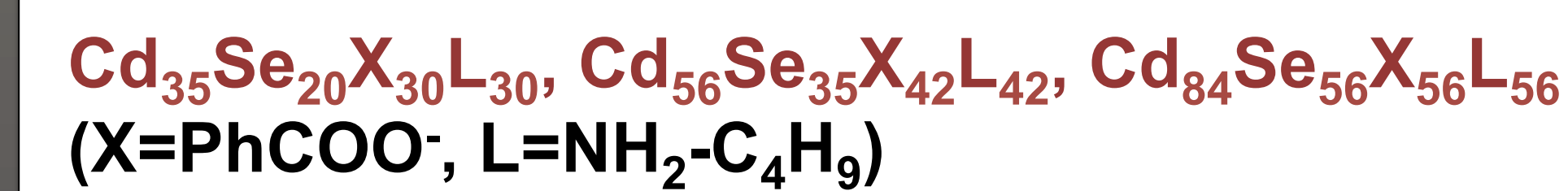
Inorganic ligands

- We investigated InAs NPs with Sn_xS_y ligands using first principles molecular dynamics (FPMD) and the Qbox code
- We validated interfacial structural models using a feedback loop between theory and experiment
- FPMD pointed at ligand decomposition for all initial configurations
 - we constructed DFT surface stability diagrams and predicted interfacial morphology & composition
- XPS and Raman experiments validated predictions



FPMD from “validated” interfacial configurations revealed complex inorganic matrix embedding the nanoparticles, with electronic structure resulting in negative photoconductivity, measured experimentally [1]

Organic ligands

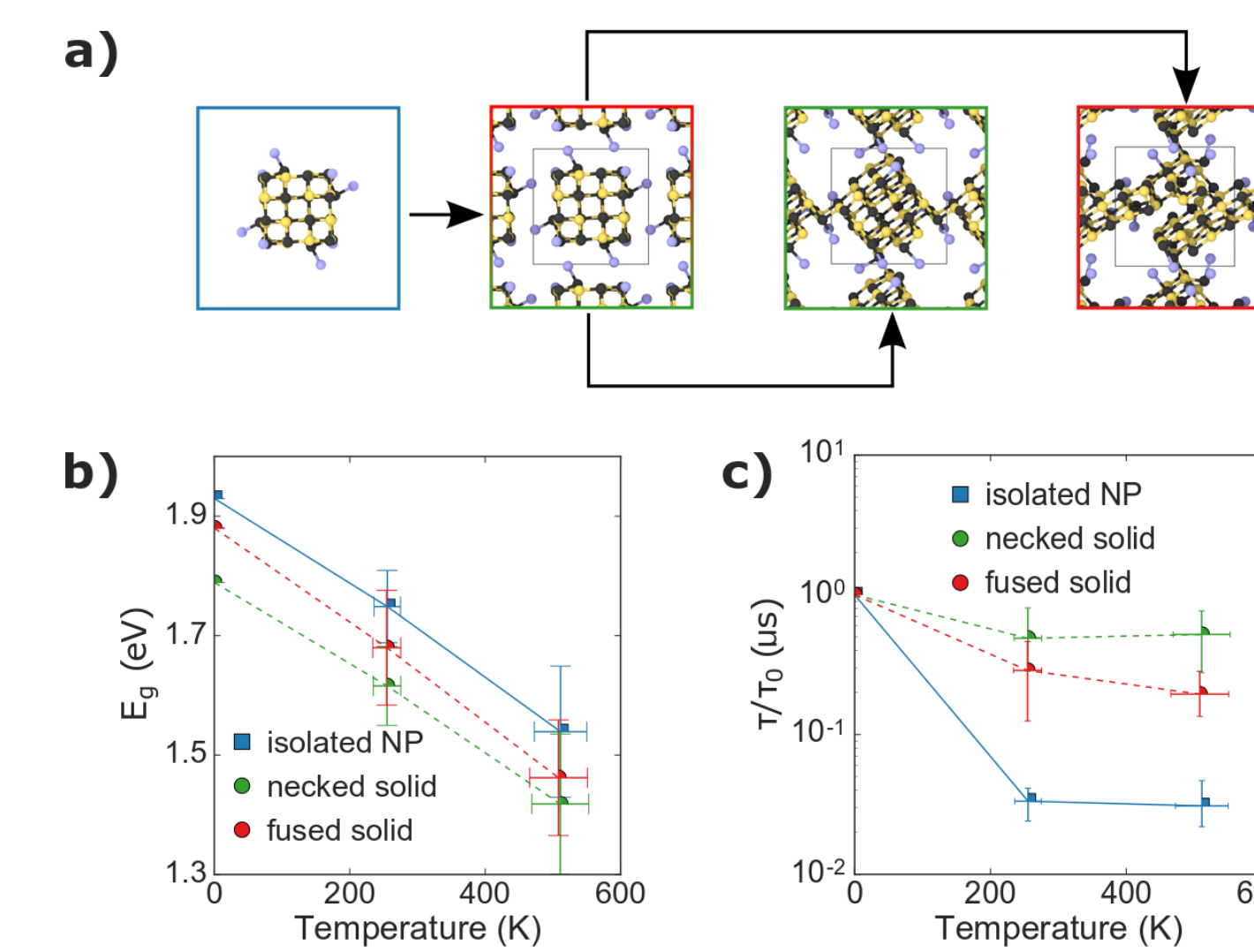
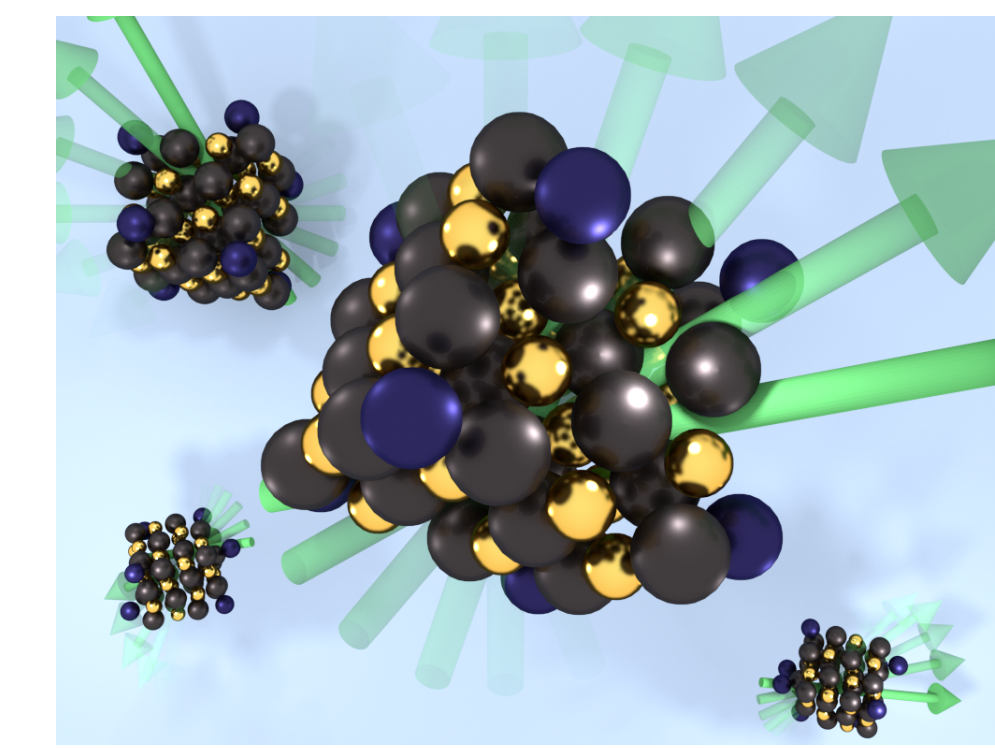


We chose NPs of known structure and stoichiometry and we investigated the atomistic and electronic structure of the interface with ligands. FPMD simulations (Qbox code) indicated the crucial role of hydrogen bonded amine in the stabilization of the cluster; GW calculations (WEST code) of electronic states for comparison with experiments are ongoing.

Interacting Nanoparticles at Finite Temperature

We used FPMD (Qbox code) to generate realistic models of interacting PbSe NPs, with the goal of comparing computed and measured dipole moments.

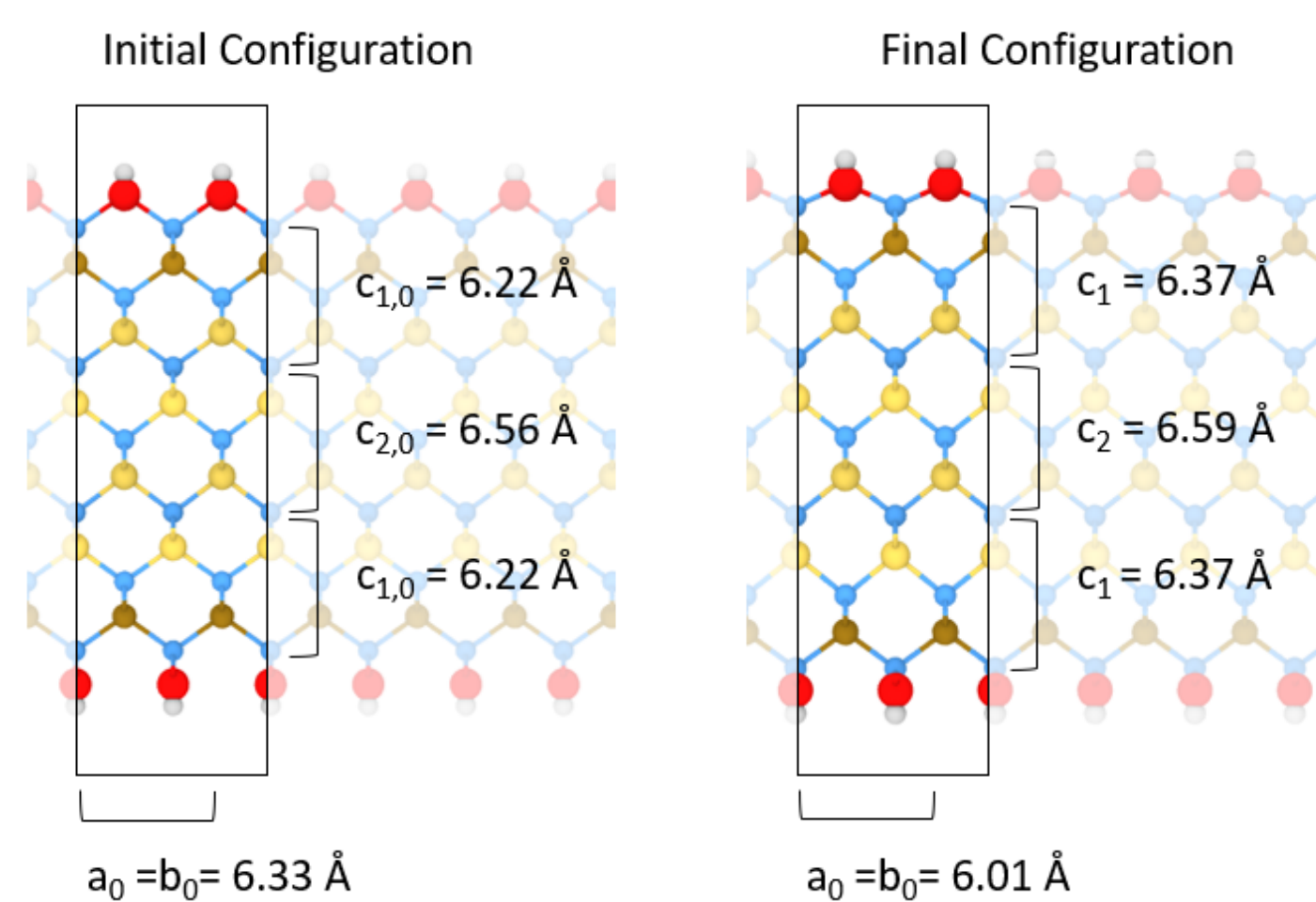
- We found that at finite temperature, interacting NPs act as dynamical dipolar systems – average dipole moments/ polarizabilities are increased compared to the isolated NPs, with large dipolar fluctuations.
- We also found that interacting NPs have smaller fundamental gaps than isolated ones, which decrease as a function of T, and radiative lifetimes that are greatly reduced at finite T.



Our results were used to interpret a variety of experimental results on dipole moments of chalcogenide NPs [2]

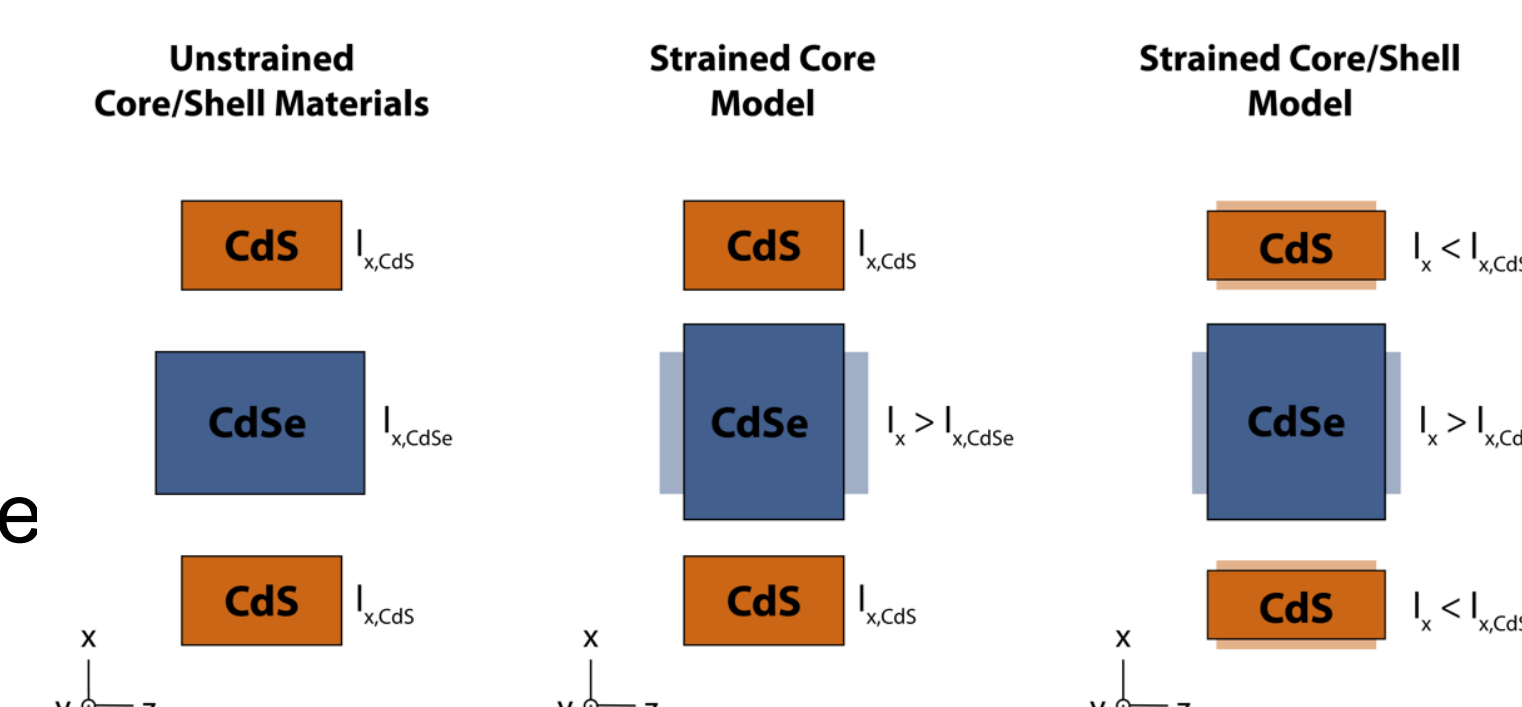
Atomically-Precise II-VI Semiconducting Nanoplatelets

The synthesis of atomically-precise nanoplatelets eliminates heterogeneities often present in nanoparticles, and hence offers the opportunity of validating theory and simulations for nanomaterials of known atomistic structure.



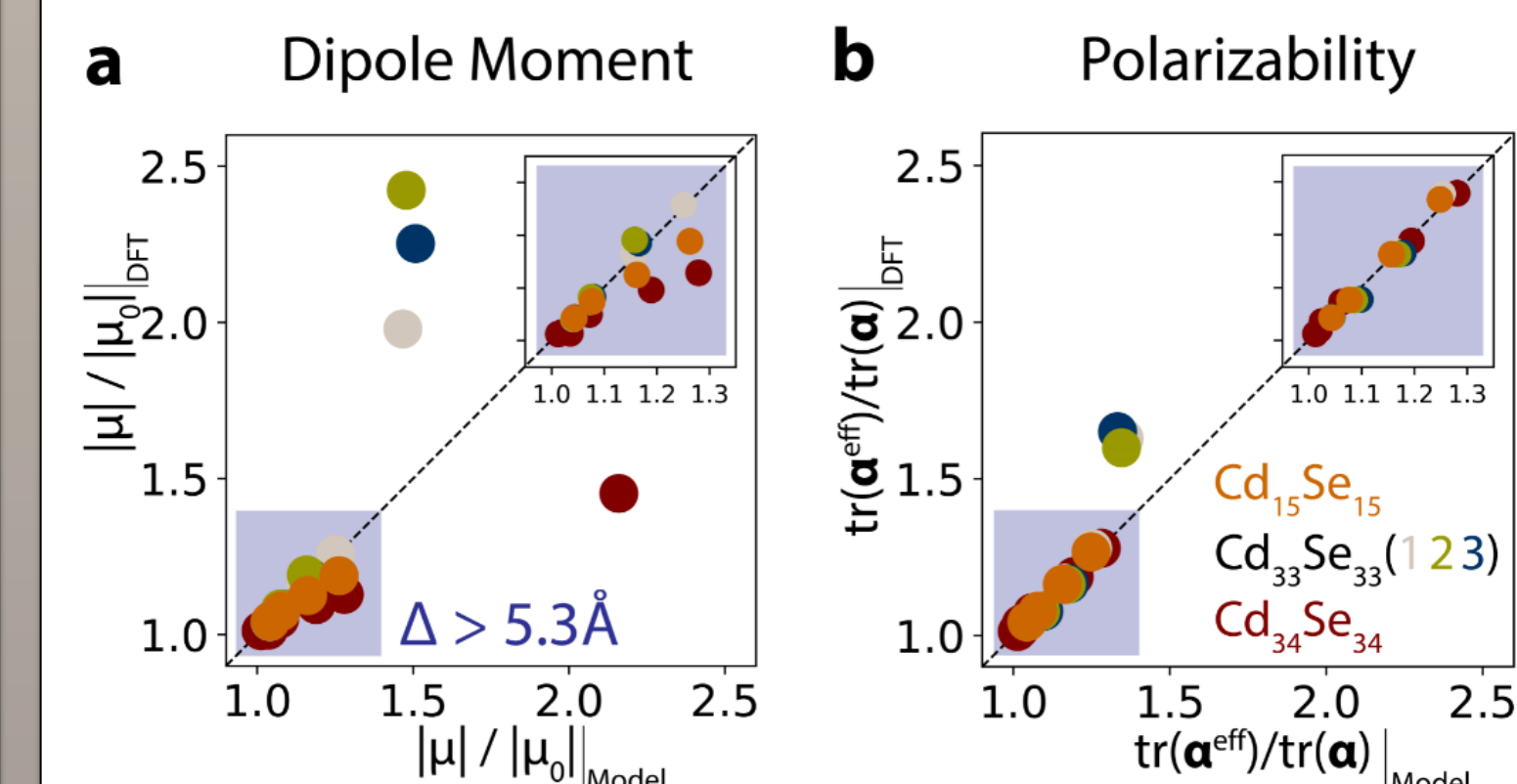
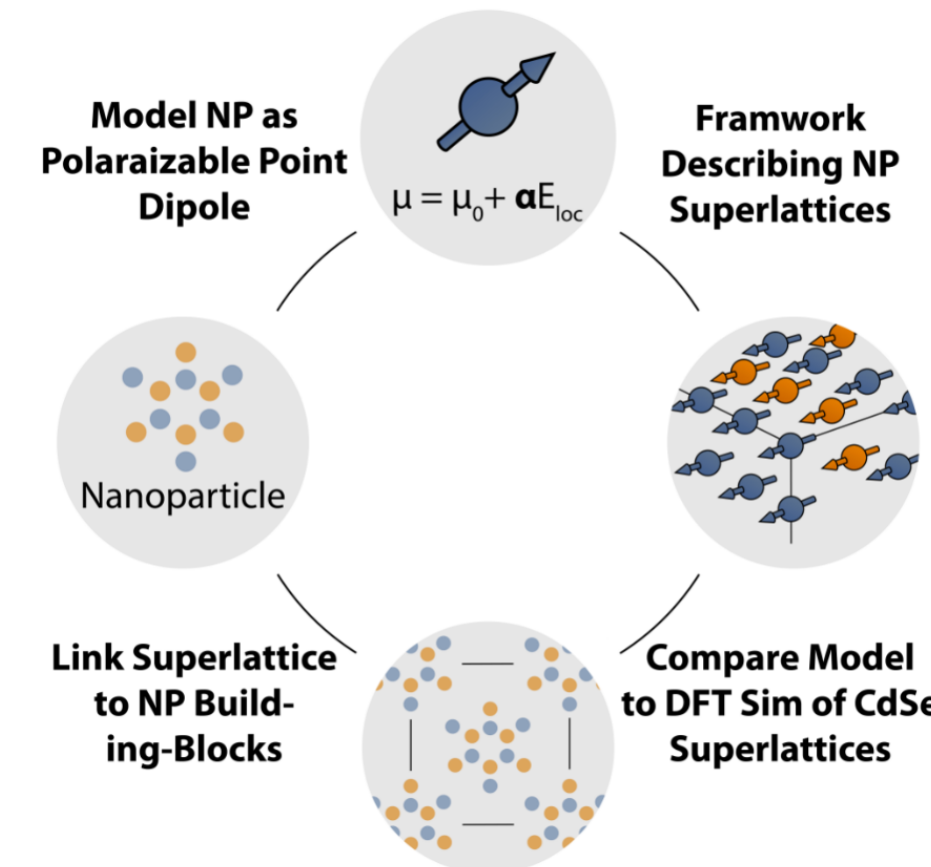
We used DFT calculations to compute the properties of nanoplatelet heterostructures of CdSe and CdS. Compared to CdSe NPLs, in agreement with experiment for CdS/4CdSe/CdS we found:

- A decrease in band gap
 - An expanded lattice (axial) with layer-dependent lattice constant
- We validated our theoretical approach and interpreted experiments by carrying out an analysis of the interplay between stress and quantum confinement in determining the electronic and dielectric properties of shell/core/shell nanoplatelets. In addition we built a model based on elasticity theory.



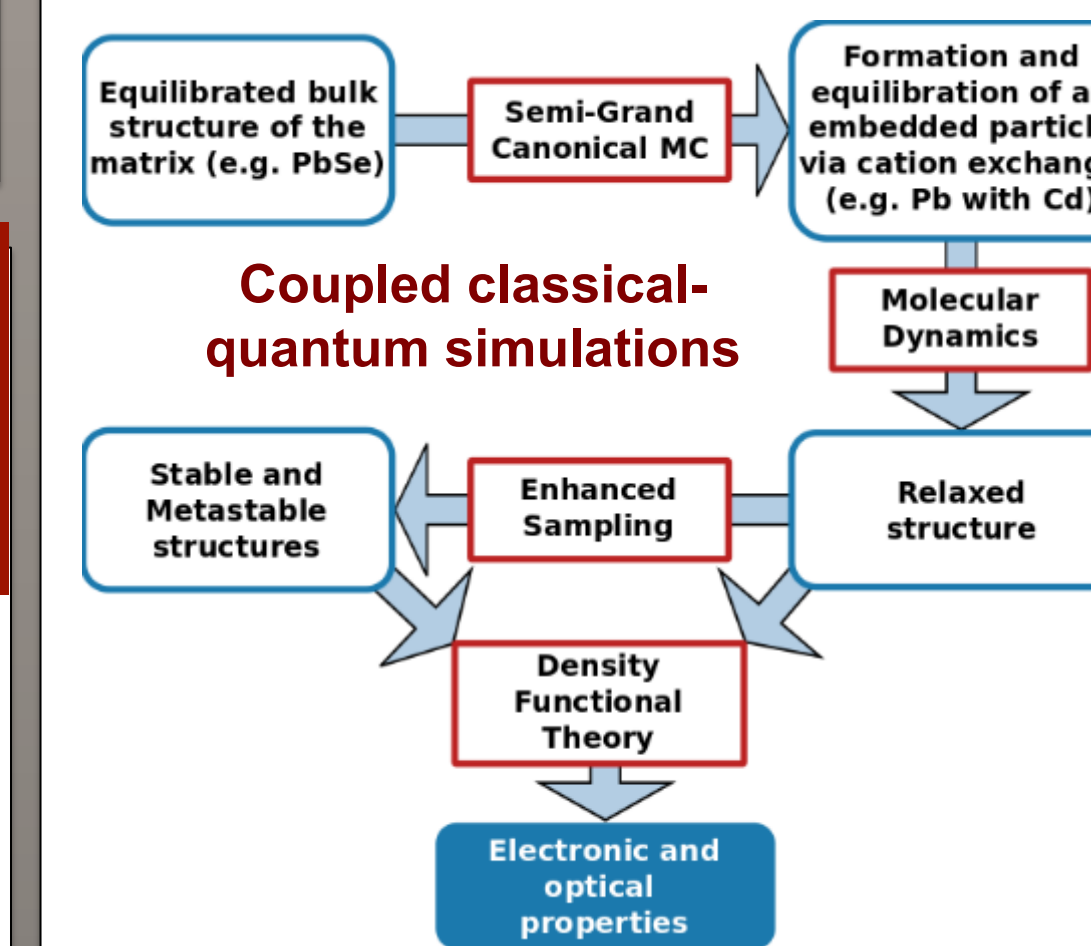
Dipoles and Polarizabilities of Nanoparticle Superlattices

We developed a modelling framework that links the collective behavior of nanoparticle superlattices to the properties of the underlying building blocks using an analytical expression of the interaction energy, with parameters derived from DFT.

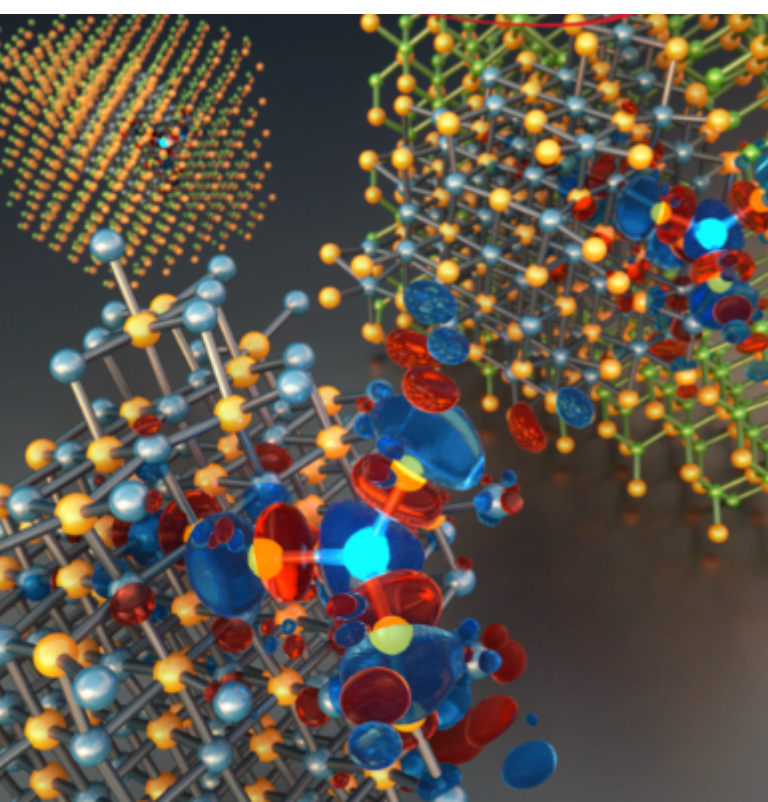


We verified the model using DFT simulations of CdSe NP superlattices, and investigated the interplay between dipoles and polarizabilities in determining the structural properties of the superlattices. [5]

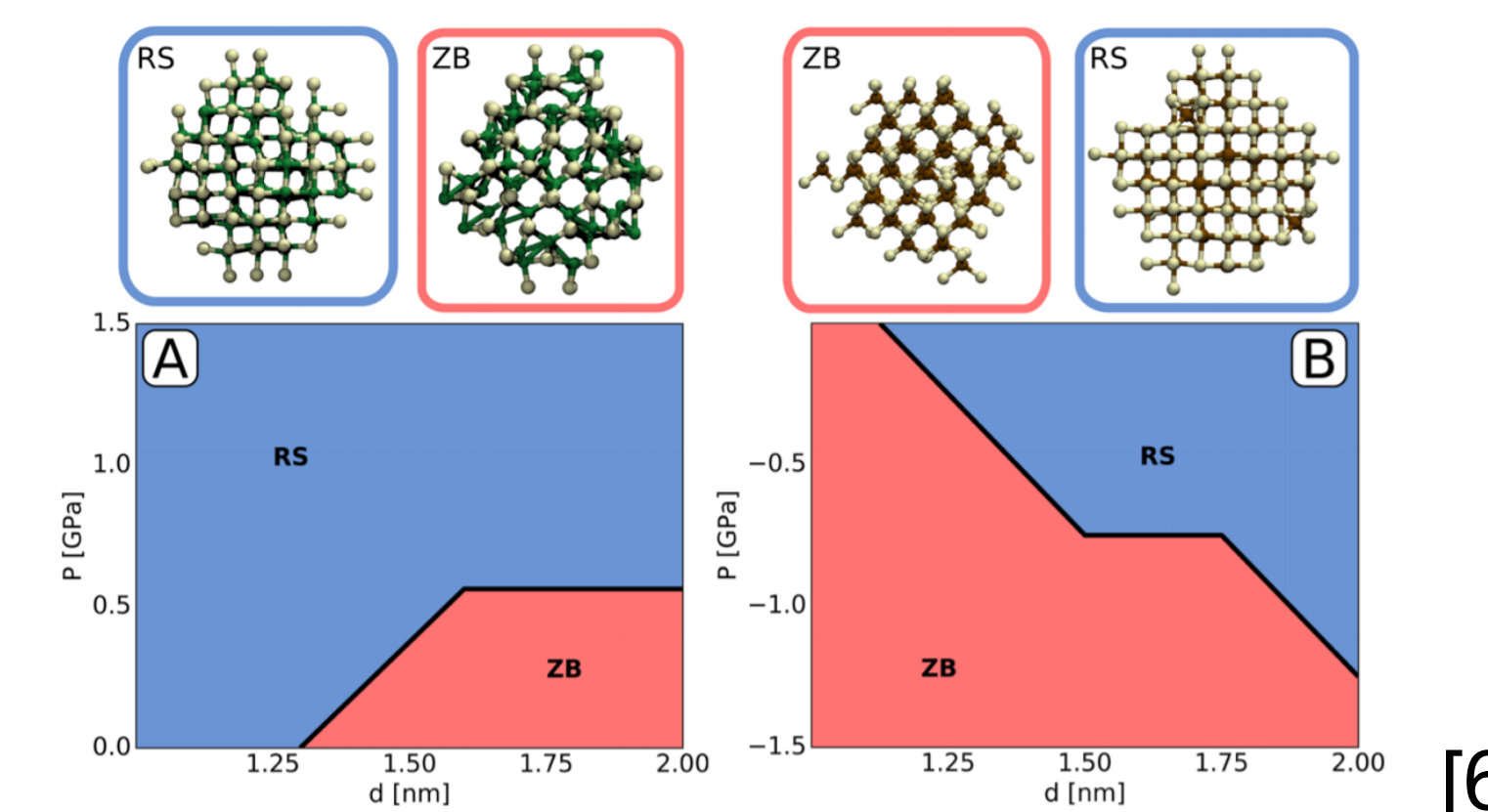
Embedded Nanoparticles



We initially sought to validate interfacial states observed experimentally. The end results was the identification of interfacial defects and trap states detrimental to charge carriers in PbSe/CdSe embedded NP systems



We predicted that the structure and band gap of embedded CdSe NPs can be tuned by applying pressure to the matrix, eliminating trap states and improving electronic properties (experimental validation is ongoing)



References and Acknowledgements

- Scalise, E., Srivastava, V., Janke, E. M., Talapin, D., Galli, G., and Wipperman, S. *Nature Nanotechnology*, Accepted. (2018)
- Greenwood, A. R., Vörös, M., Giberti, F., and Galli, G. *Nano Lett.* 18(1), 255-261 (2018)
- Hazarika, A., Fedin, I., Hong, L., Guo, J., Srivastava, V., Cho, W., Coropceanu, I., Portner, J., Diroll, B. T., Greenwood, A. R., Galli, G., Klie, R., and Talapin, D. *Submitted*.
- Greenwood, A. R., Mazzotti, S., Norris, D., and Galli, G. *In Preparation*.
- Mazzotti, S., Giberti, F. and Galli, G. *In Preparation*.
- Giberti, F., Vörös, M., and Galli, G. *Nano Lett.* 17(4), 2547-2553 (2017)

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