Molecular Ligands Controls Superlattice Structure and Crystallite Orientation in Colloidal Quantum Dot Solids

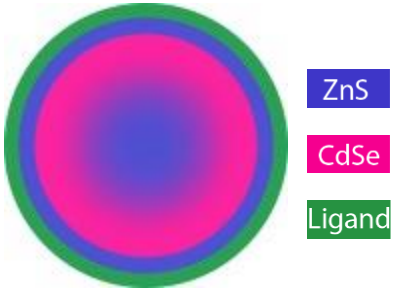
Pralay K. Santra

Centre for Nano and Soft Matter Sciences (CeNS), Bangalore

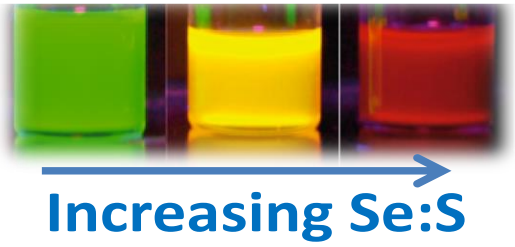
Quantum Dots

Semiconductor nanoparticles with quantum confinement

Heterostructure – controlling electronic properties

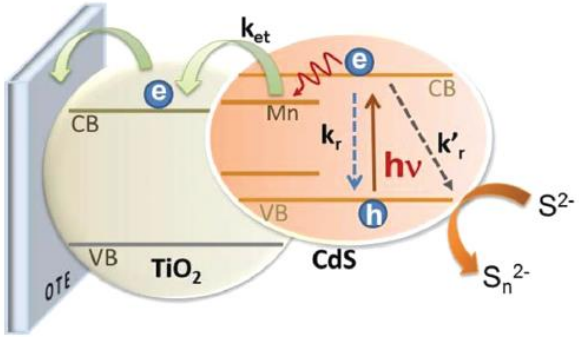


Santra et al. *J. Am. Chem. Soc.* **2009**, *131*, 470

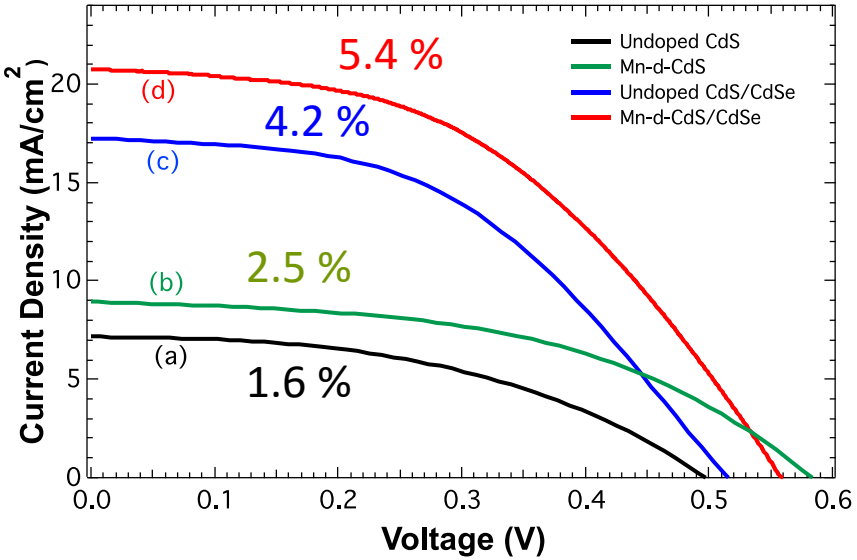


Santra et al. *J. Am. Chem. Soc.* **2013**, *135*, 877

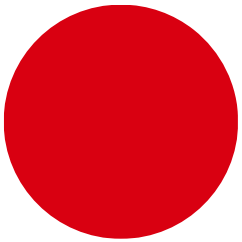
Doping



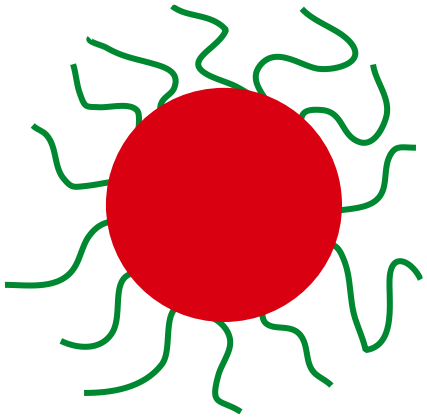
Santra et al. *J. Am. Chem. Soc.* **2012**, *134*, 2508



Quantum Dots



Inorganic core



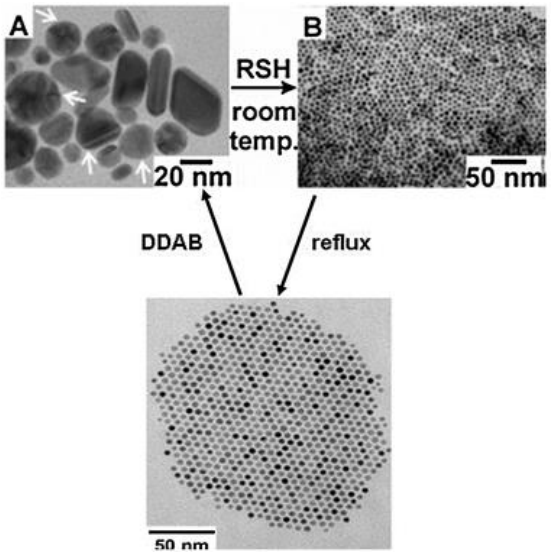
Inorganic core
+ organic passivating molecules

Passivating molecules play significant role:

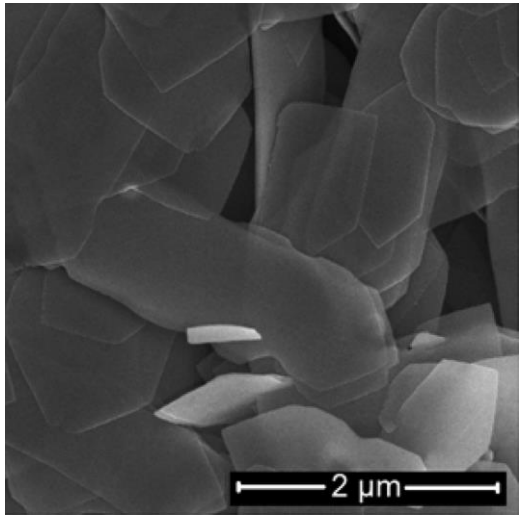
- Controlling size and size distribution
- Anisotropy
- Stabilization

……

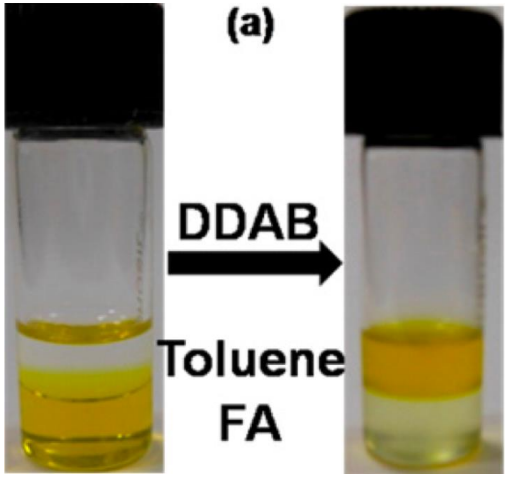
Ligand-**QD** interaction



B.L.V. Prasad et al *New J. Chem.*, **2011**,*35*, 755

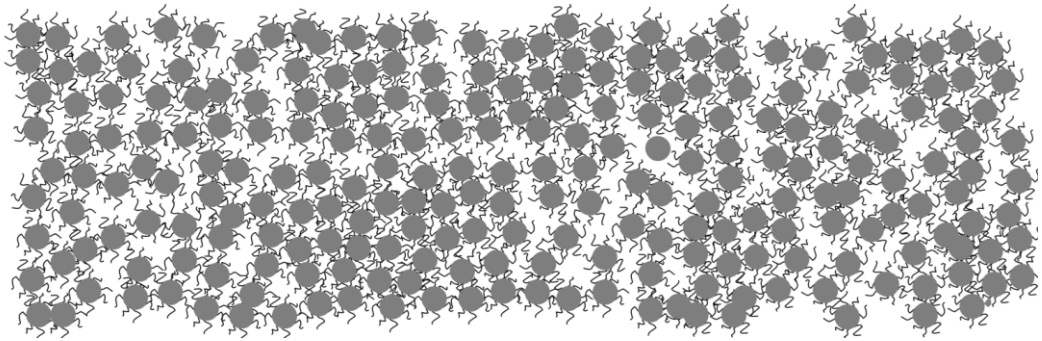


Herron et al *Chem. Mater.* **2014**, *26*, 7106

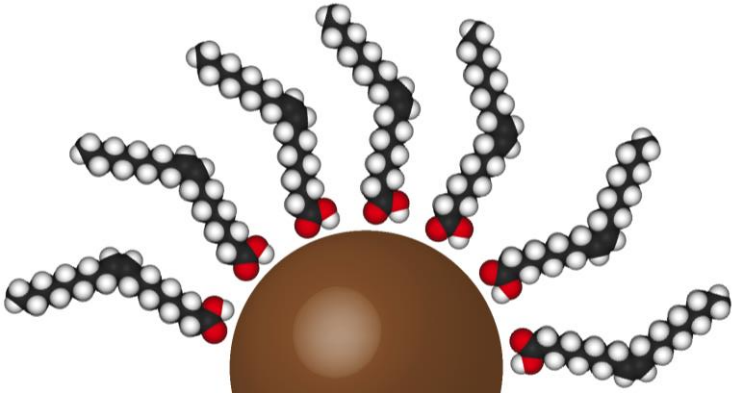


Nag et al *J. Phys. Chem. Lett.* **2013**, *4*, 1676

Issues with CQD Solids



- Individual quantum dots must be electronically coupled within the quantum dot solid

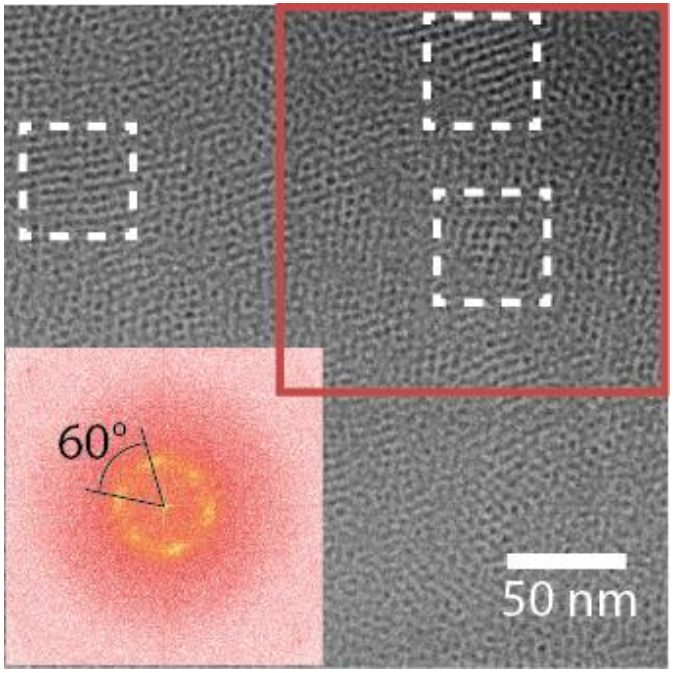


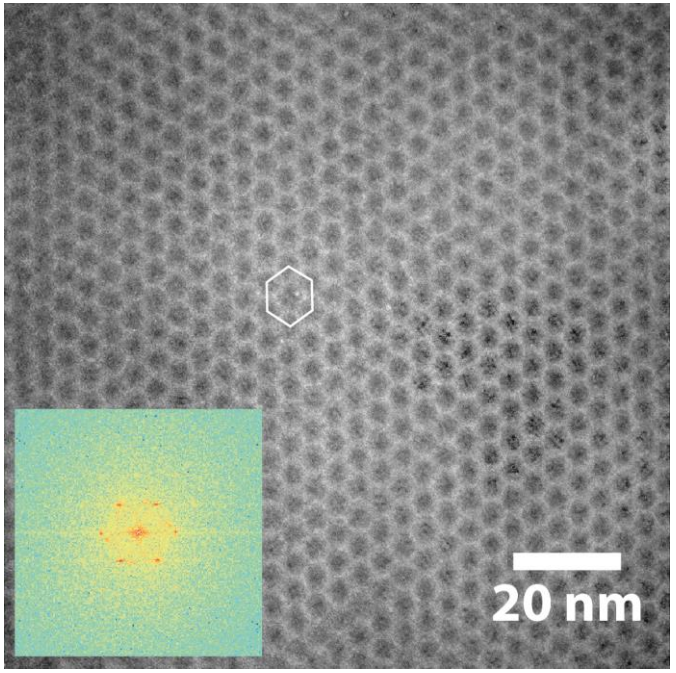
OA: long chain molecule
(18-carbon chain)
High boiling point

Charge transport important for any electronic devices

- Interparticle distance
- Size distribution
- Surface Chemistry
- Stoichiometry
- Morphological orders

Oleic acid passivated PbS QD: TEM Analysis

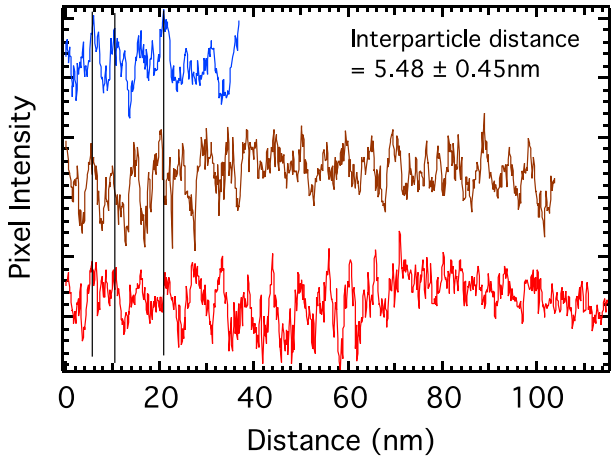




Particle size (d_{QD}) = 3.21 ± 0.23 nm

d_{QD} (from FFT) = 3.18 nm

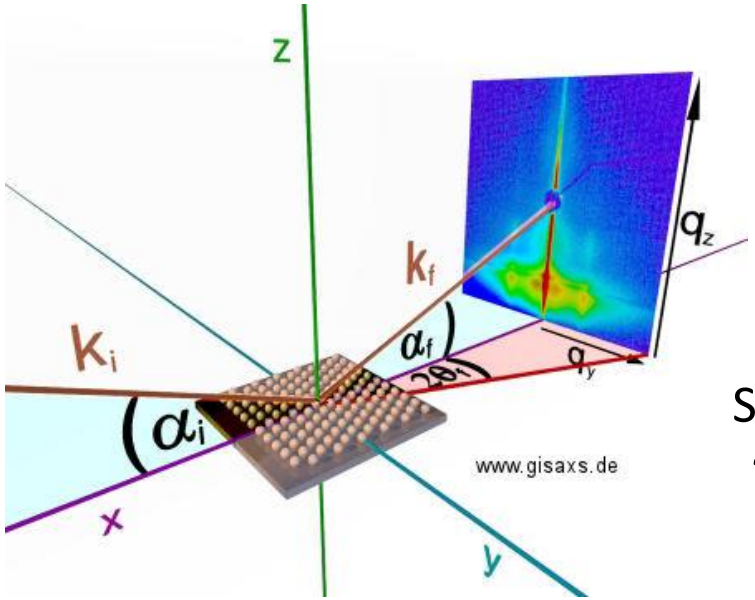
Interparticle distance (L_{IP}) = 5.48 ± 0.45 nm



Santra et al. *Chem. Mater.* **2016**, *28*, 7072

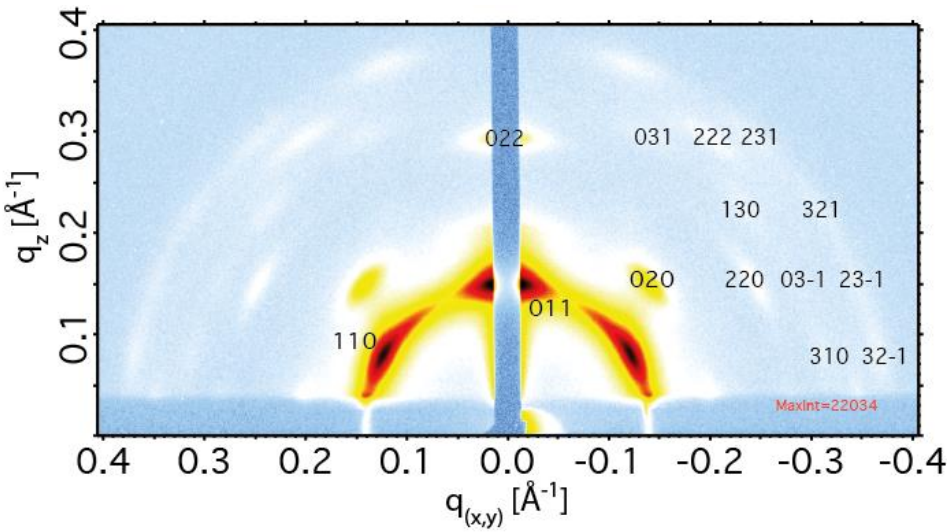
Grazing Incidence Small Angle Scattering (GISAXS)

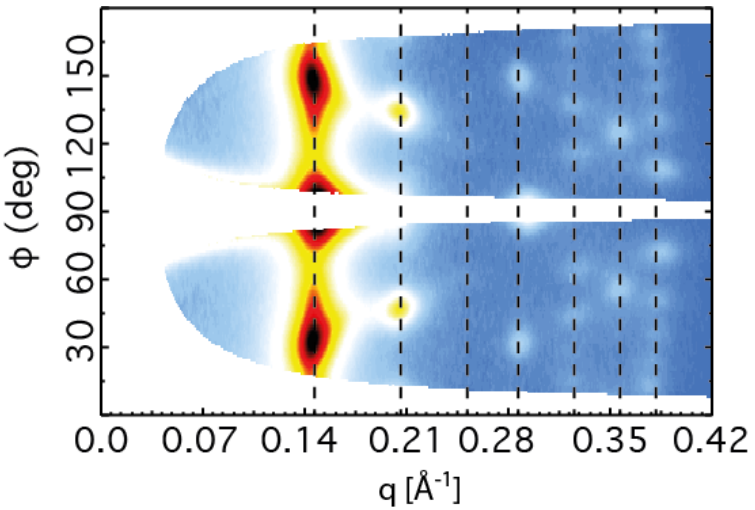
- No structural analysis can be performed from TEM image analysis



Spot Size:
~ 1 mm^2

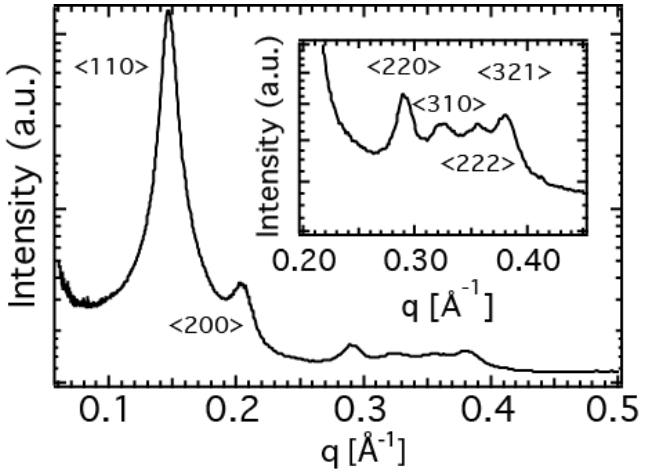
Oleic Acid Passivated PbS QDs - Superlattice





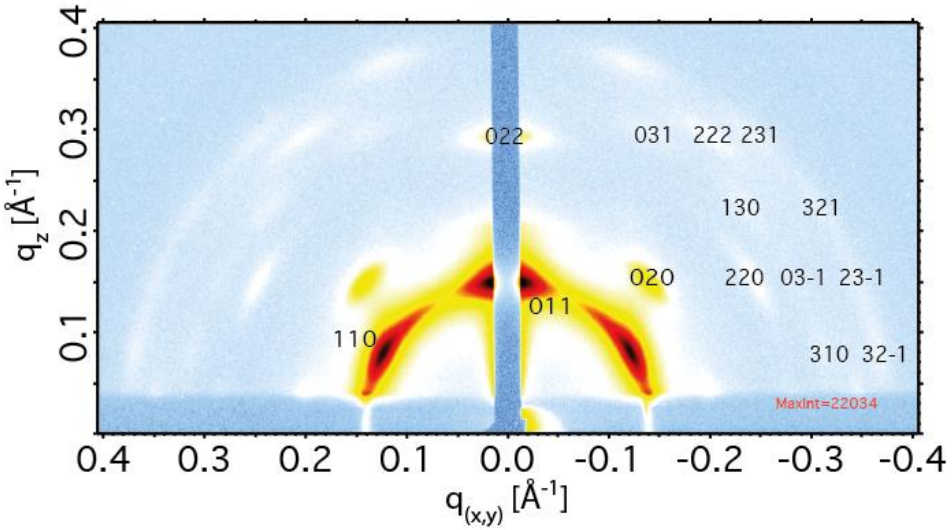
Body Centered Cubic
(Space group #229)

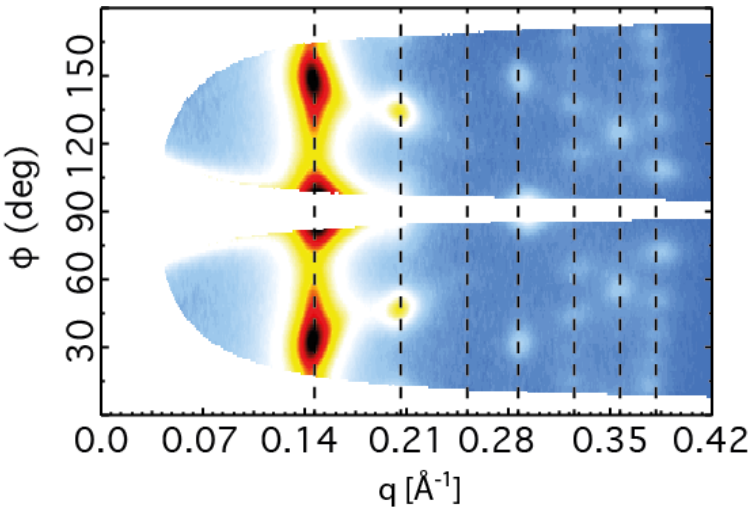
$\mathrm{Im}\bar{3}m$



Santra et al. *Chem. Mater.* **2016**, *28,* 7072

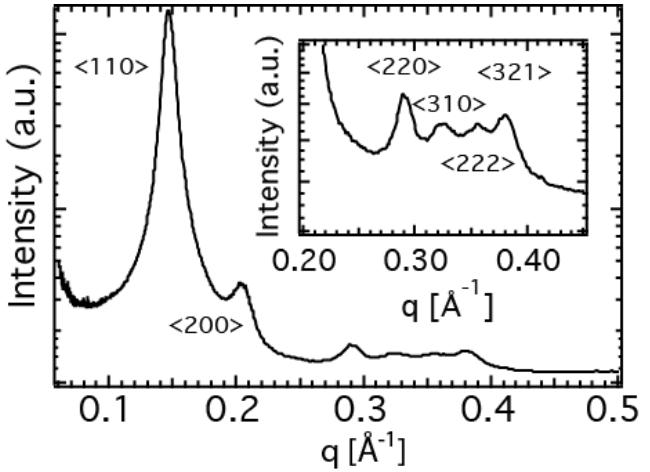
Oleic Acid Passivated PbS QDs - Superlattice





Body Centered Cubic (Space group #229) $\mathrm{Im}\bar{3}m$

Lattice Constant (a_{SL}) = 6.31 ± 0.09 nm



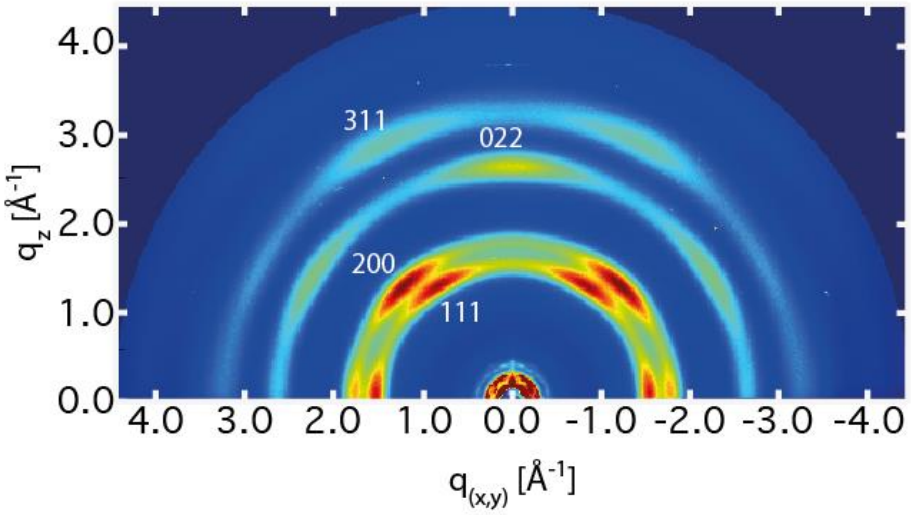
Interparticle distance (L_{IP}) = $\frac{\sqrt{3}a}{2}$

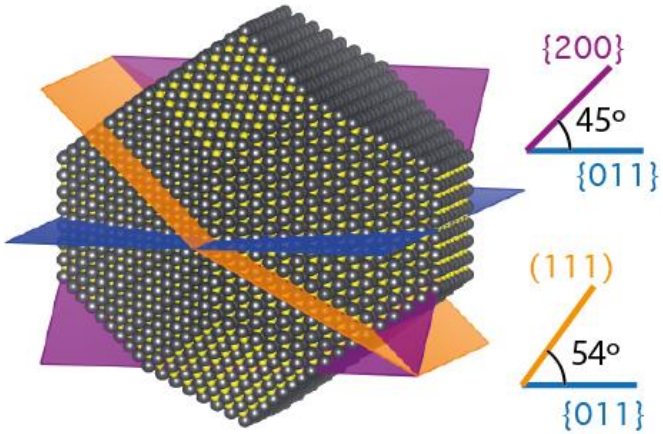
= 5.46 ± 0.08 nm

From TEM (L_{IP}) = 5.48 ± 0.45 nm

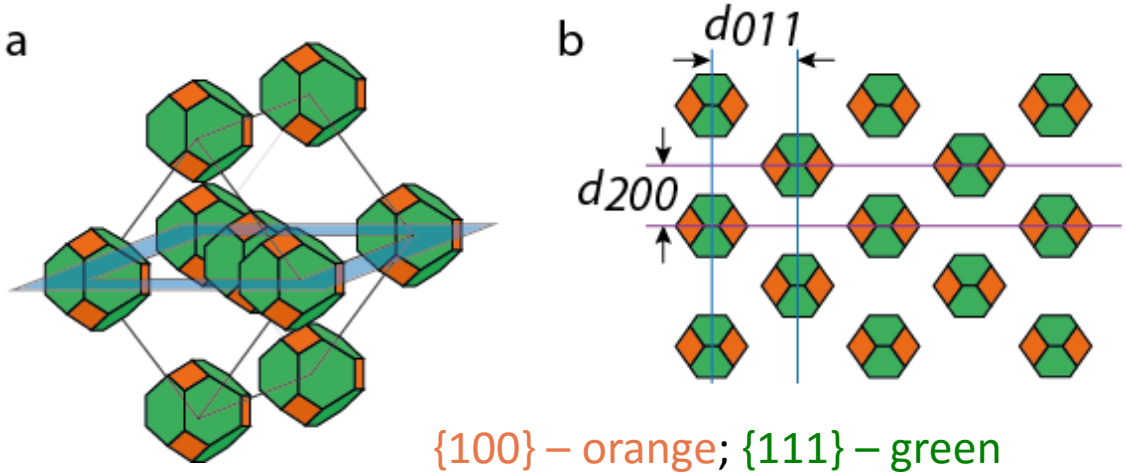
Santra et al. *Chem. Mater.* **2016**, *28,* 7072

Oleic Acid Passivated PbS QDs – Atomic Planes





- $\{011\}_{QD}$ and $\{022\}_{QD}$ planes are parallel



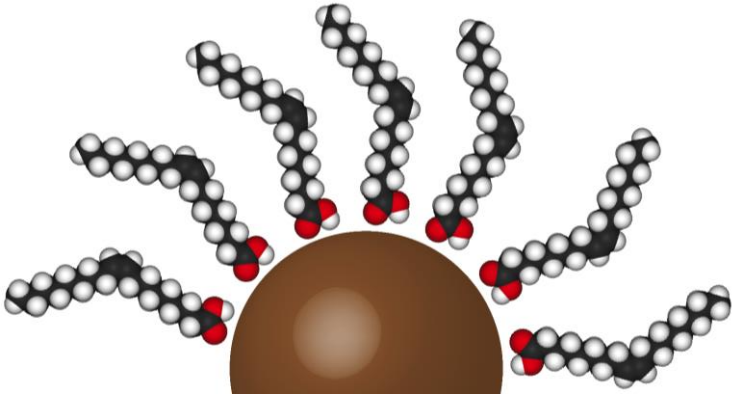
- QDs have specific arrangement within the SL
- $<011>_{QD}$ plane perpendicular to substrate

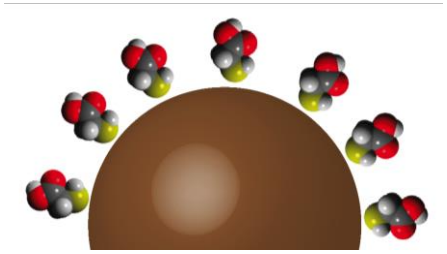
{100} – orange; {111} – green

Santra et al. *Chem. Mater.* **2016**, *28,* 7072

Effect of MPA Treatment on Superlattice

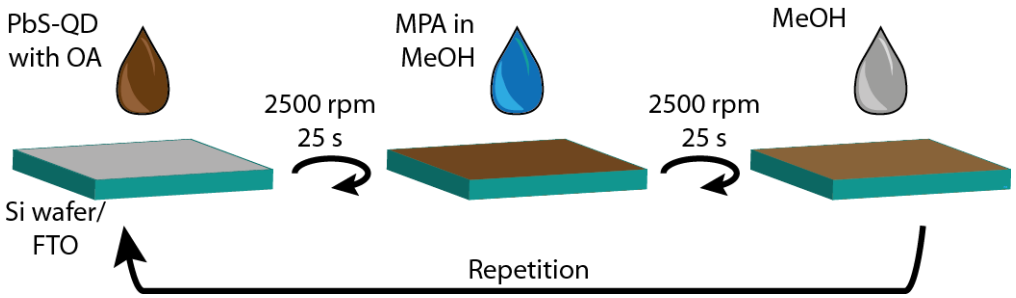
Decrease interparticle distance





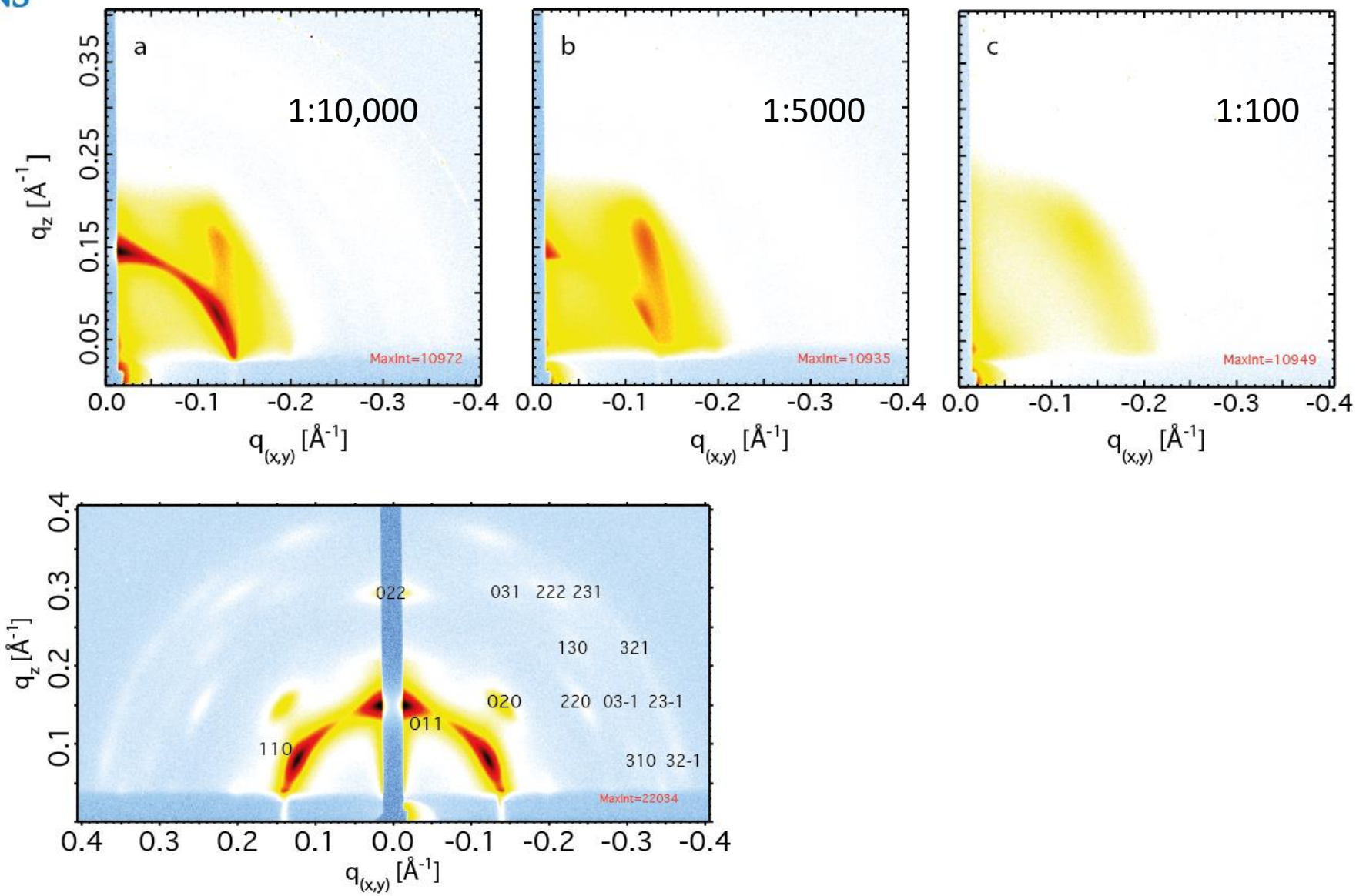
OA: long chain molecule
(18-carbon chain)
Highly insulating

MPA: 3-mercaptopropionic acid
(3-carbon chain)
bidendate



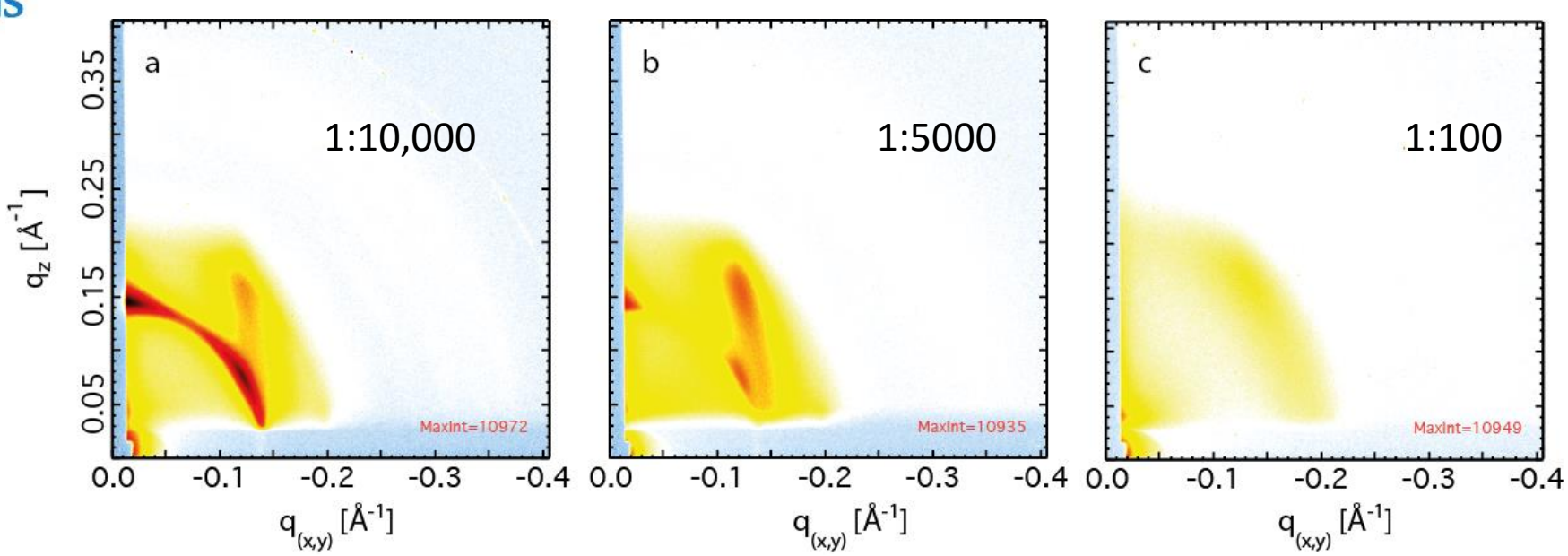
Santra et al. *Chem. Mater.* **2016**, *28,* 7072

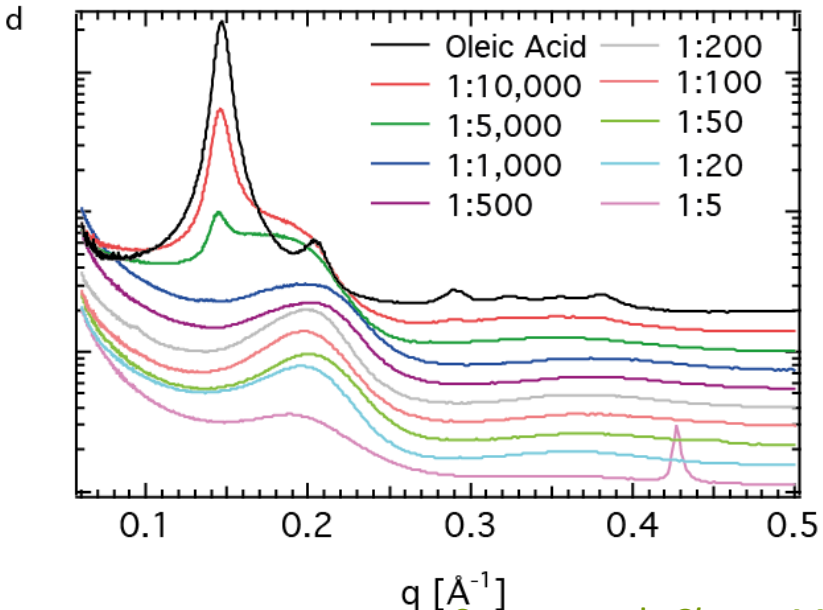
Effect of MPA Treatment on Superlattice



Santra et al. *Chem. Mater.* **2016**, *28,* 7072

Effect of MPA Treatment on Superlattice

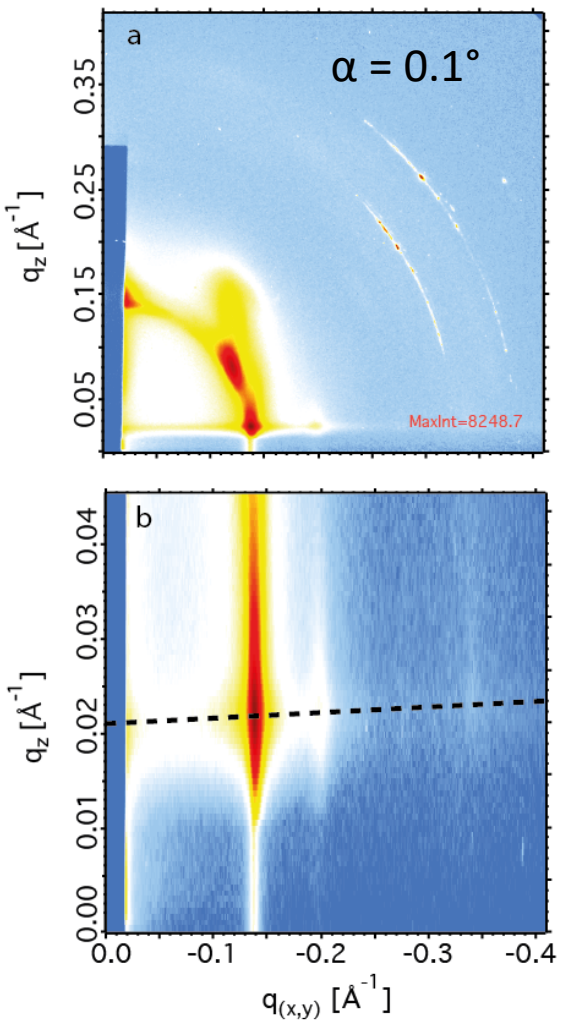


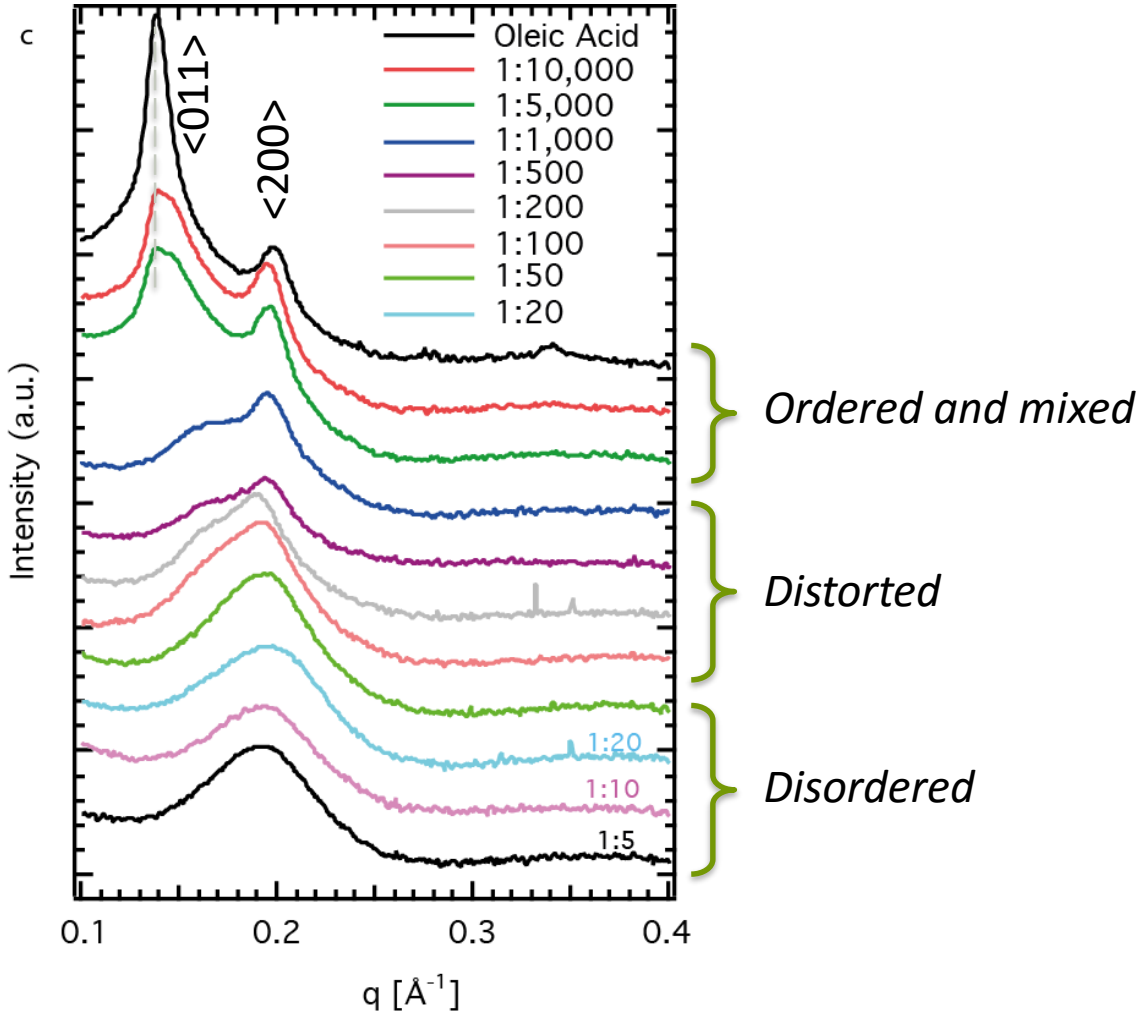


- Not a direct phase transition
- Final state is isotropic (L_{IP} = 3.17 ± 0.39 nm)
- Not possible to decipher the superlattice from standard GISAXS

Santra et al. *Chem. Mater.* **2016**, *28*, 7072

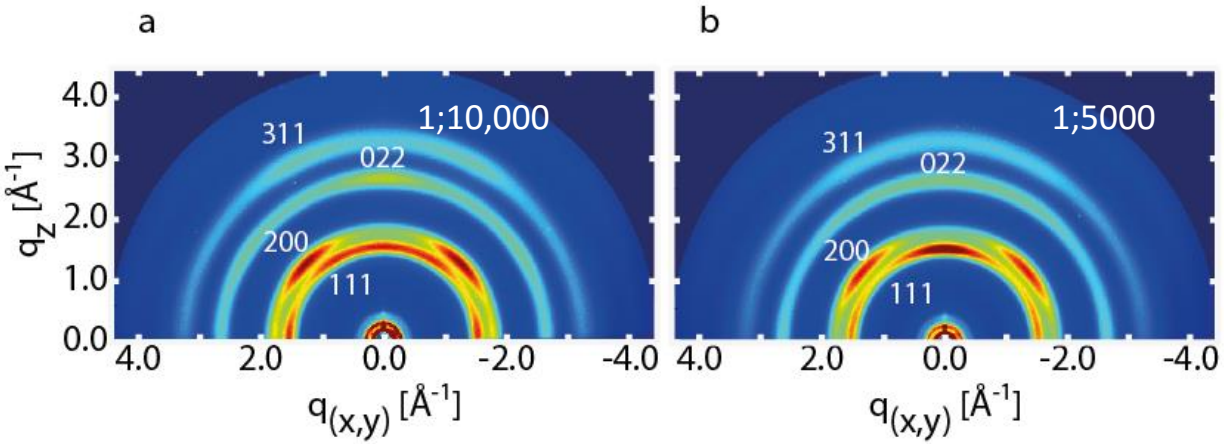
Elucidating the Superlattice after MPA Treatment

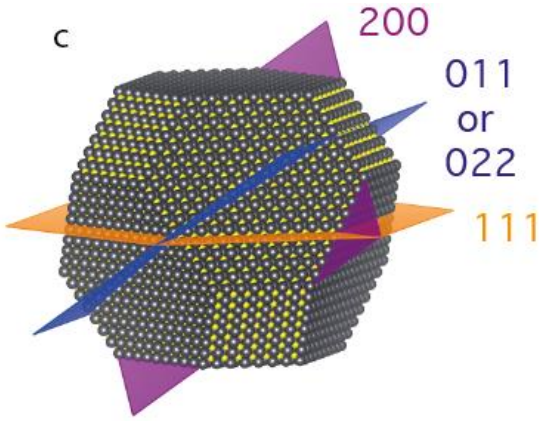




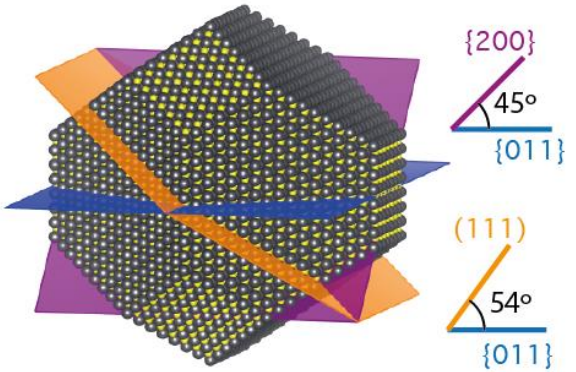
Santra et al. *Chem. Mater.* **2016**, *28*, 7072

Effect of MPA Treatment on Individual QDs - GIXRD



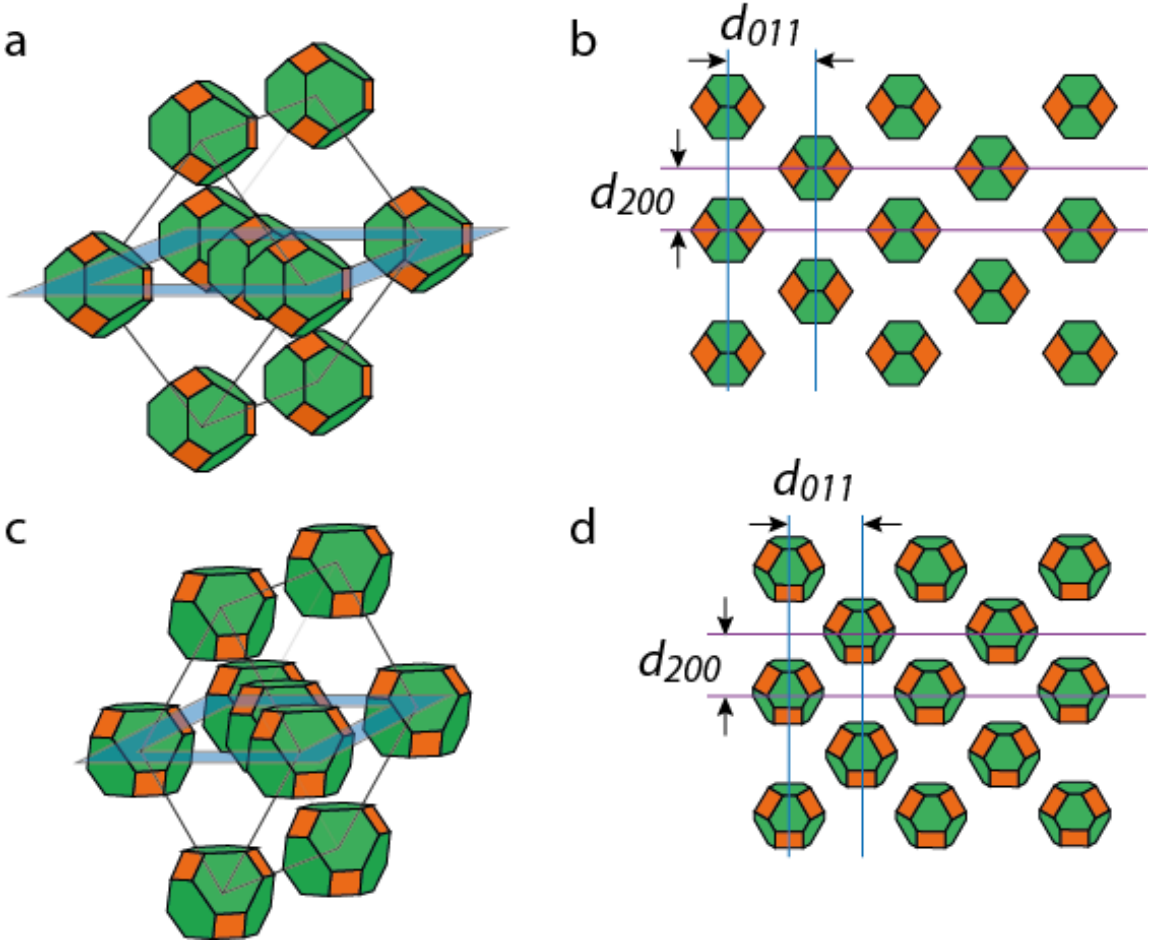


Untreated PbS



Santra et al. *Chem. Mater.* **2016**, *28,* 7072

Overall Picture



- Oleic binds weaker on {100} compared to {111} facets
- MPA replaces oleic acid first from {100} surface
- Rotation of QDs allow the d_{011} to decrease

{100} – orange; {111} – green

Santra et al. *Chem. Mater.* **2016**, *28,* 7072

Conclusion

What have we learned?

- Long chain oleic acid passivated QD makes the superlattice in BCC with <011>QD plane oriented perpendicular to substrate
- Concentration of MPA molecules strongly affects the superlattice (BCT or disordered) with <011> planes oriented perpendicular to the substrate
- Different interaction between the –SH and –COOH with the facets of the QD lead to a structural change in the superlattice

What are the "take home" messages?

- Ligand-QD interaction and ligand length plays main role in superlattice

What are the implications of this study?

- Role of concentration of the passivating molecules
- Charge transport can be controlled via orientation of the QDs in the QD solid

Acknowledgement

Stanford University

- Axel Palmstrom
- Stacey Bent

SSRL

- Christopher Tassone

Thank you for your attention!

nature materials

ARTICLES

PUBLISHED ONLINE: 22 FEBRUARY 2016 | DOI: 10.1038/NMAT4576

Charge transport and localization in atomically coherent quantum dot solids

Kevin Whitham[1], Jun Yang[2], Benjamin H. Savitzky[3], Lena F. Kourkoutis[2,4], Frank Wise[2] and Tobias Hanrath[5]*