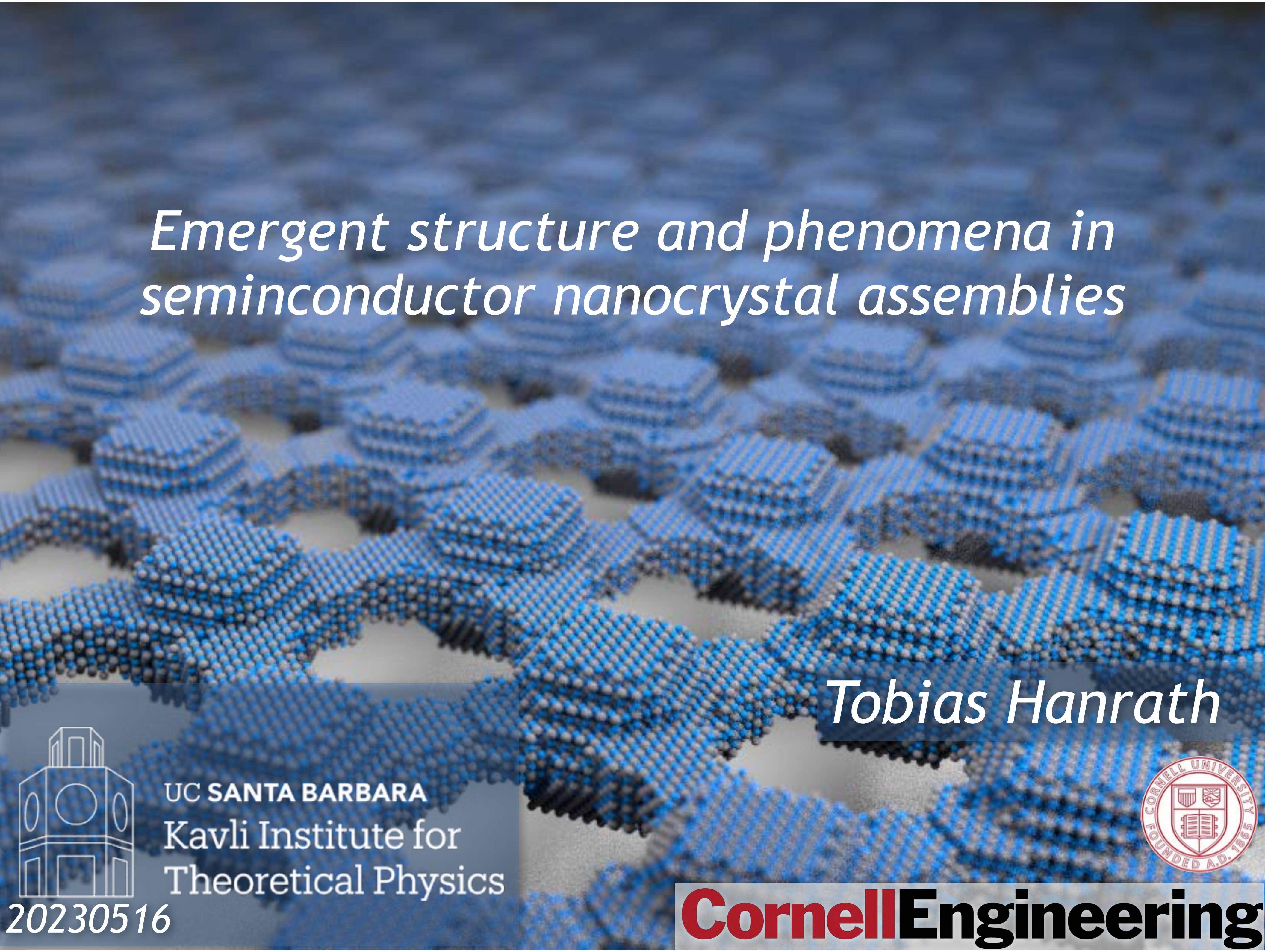


Emergent structure and phenomena in seminconductor nanocrystal assemblies

Tobias Hanrath

UC SANTA BARBARA
Kavli Institute for Theoretical Physics

Cornell Engineering

20230516

Credits:


F. Escobedo


L. Kourkoutis


P.Clancy


D. Smilgies


R. Robinson


F. Wise

Daniel Balazs
Jessica Cimada DaSilva
Tyler Dunbar
Alex Gonzalez
Jen-Yu Huang
Doug Nevers
Ben Savitsky
Michelle Smeaton
Kevin Whitham
Curtis Williamson
Yuanze Xu
Jun Yang

CornellEngineering

Cornell Engineering

colloidal nanocrystals as building blocks for programmable materials

BACK TO THE FUTURE

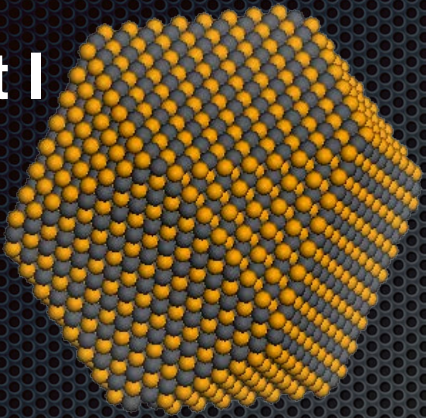
Cornell Engineering

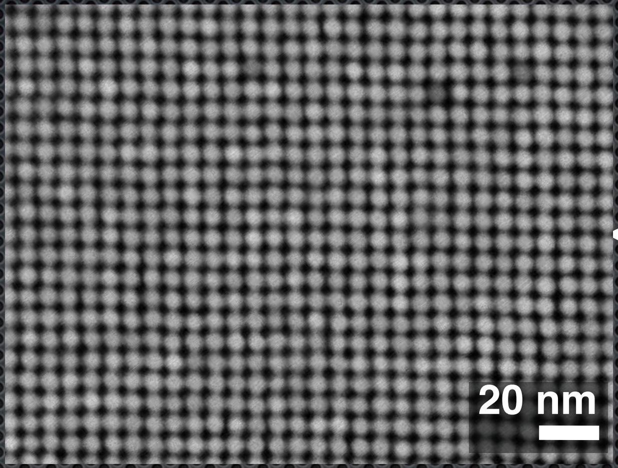
imagine the possibilities by 2040

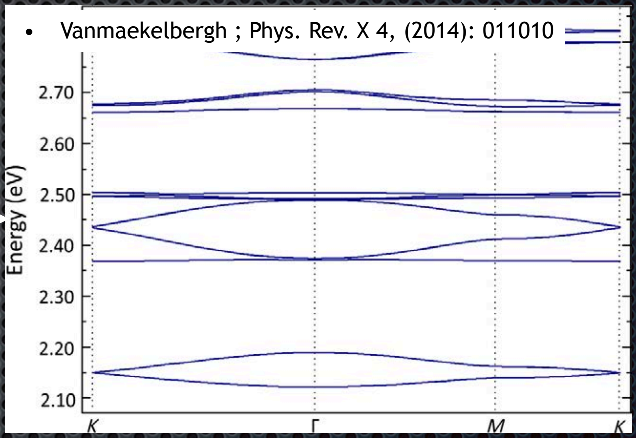
CornellEngineering

building blocks | emergent structure | emergent properties

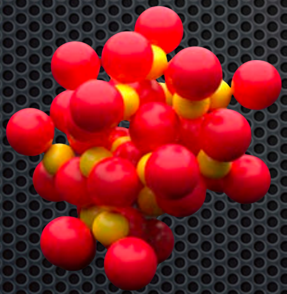
Part I

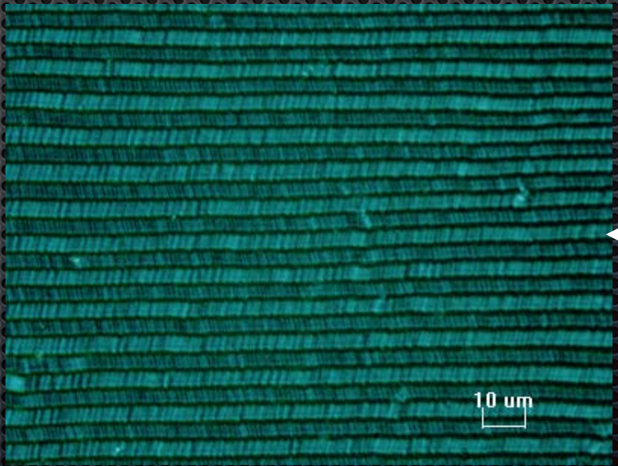


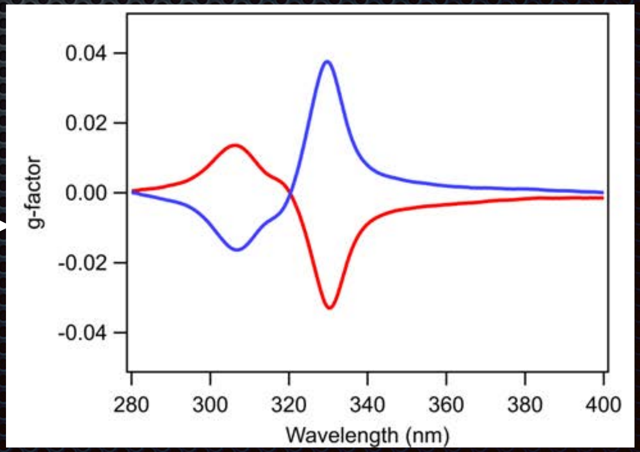




Part II



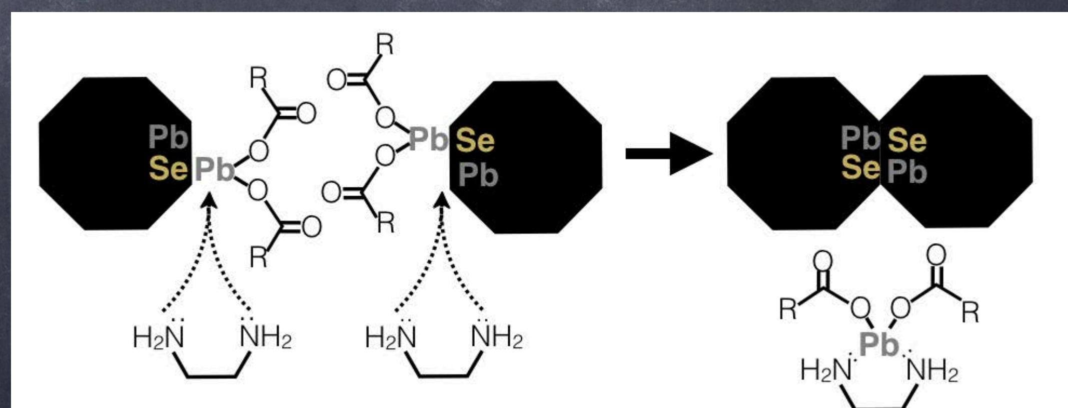




NC Assembly and Attachment at a Fluid Interface

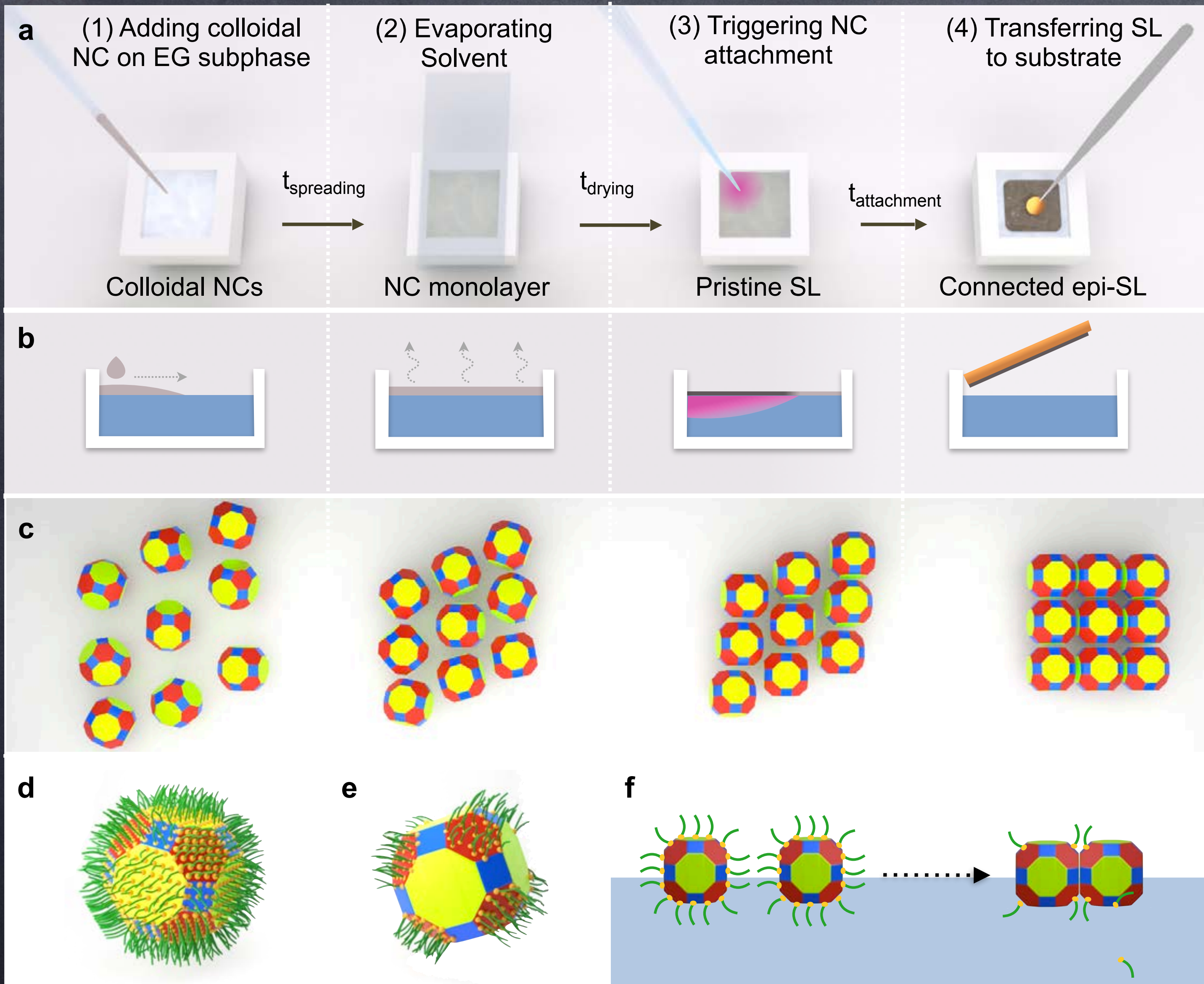
The interface between two immiscible fluids as a 2D reactive workbench

B. Franklin 1773

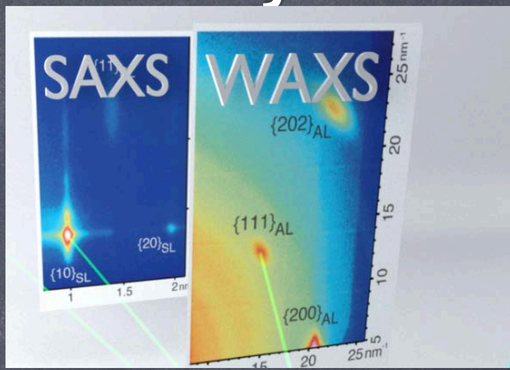


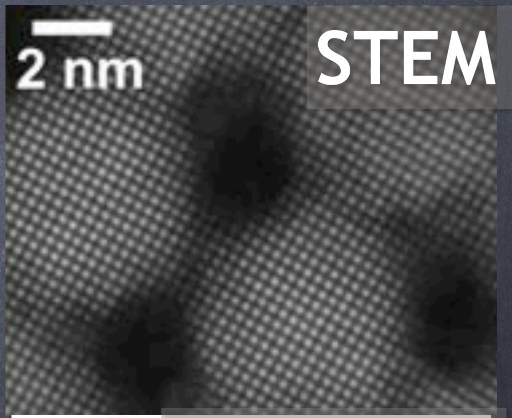
Whitham, Hanrath, *J.Phys. Chem. Letters* **2017,** 12, 2623
Cimada, Balazs, Dunbar, Hanrath Chem. Mater. 2021, 33, 24, 9457

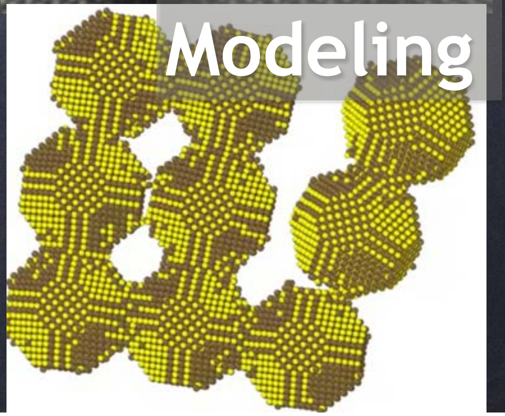
NC Assembly and Attachment at a Fluid Interface



Analysis



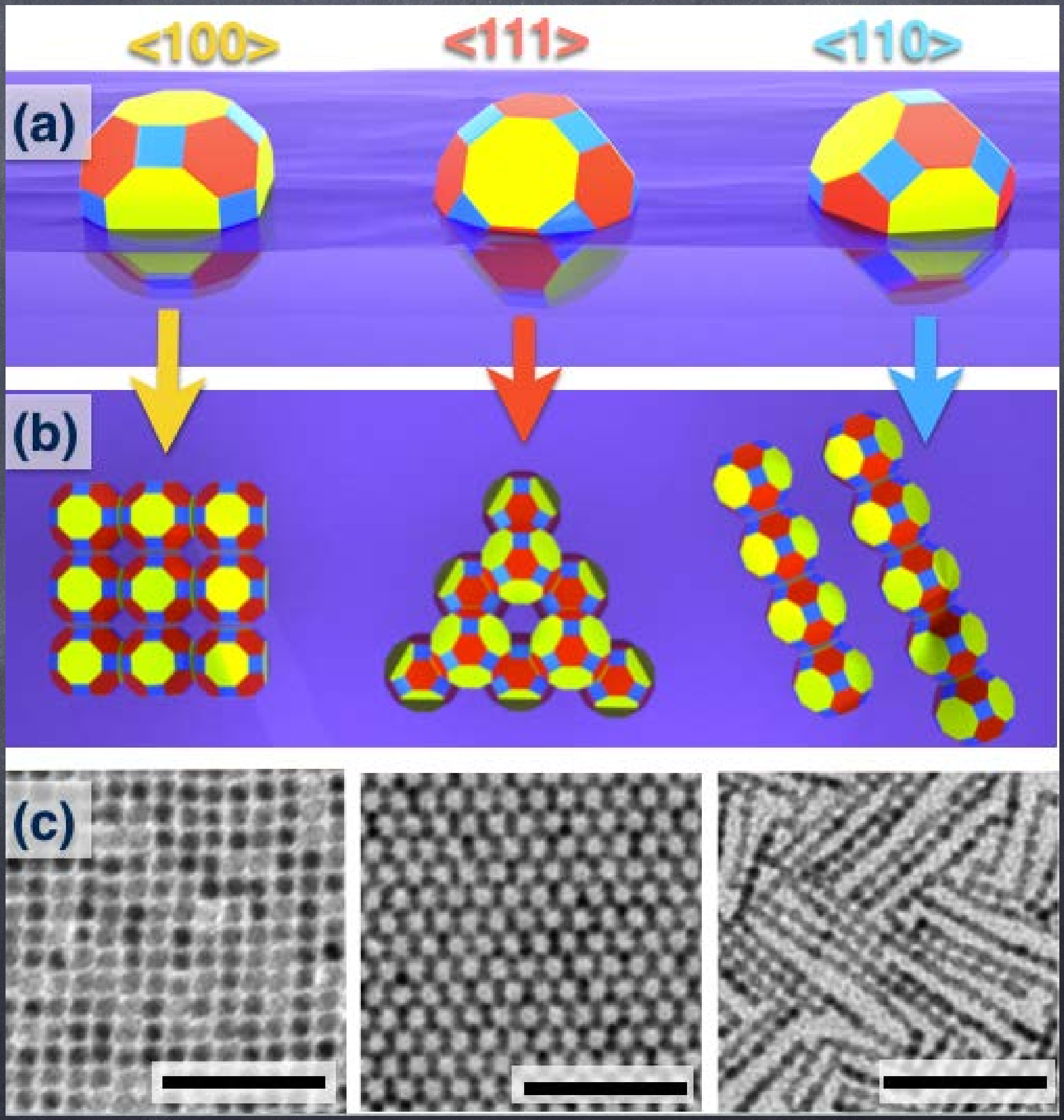




Cimada, Balazs, Dunbar, Hanrath Chem. Mater. 2021, 33
Whitham, Smilgies, Hanrath, Chemistry of Materials 2017, 30, 54
Whitham, Hanrath, J Phys Chem Lett 2017, 8, 2623

NC Superlattice Polytypes

Hypothesis:
Understanding and controlling the orientational alignment of particles at the interface is the key to direct the assembly of superlattices with specific symmetries.

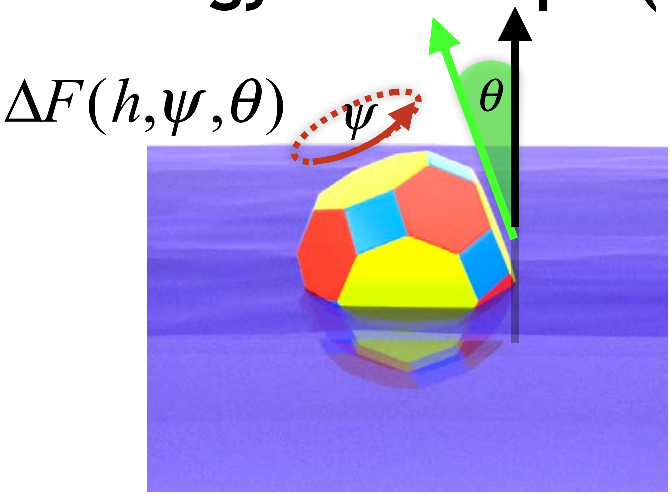


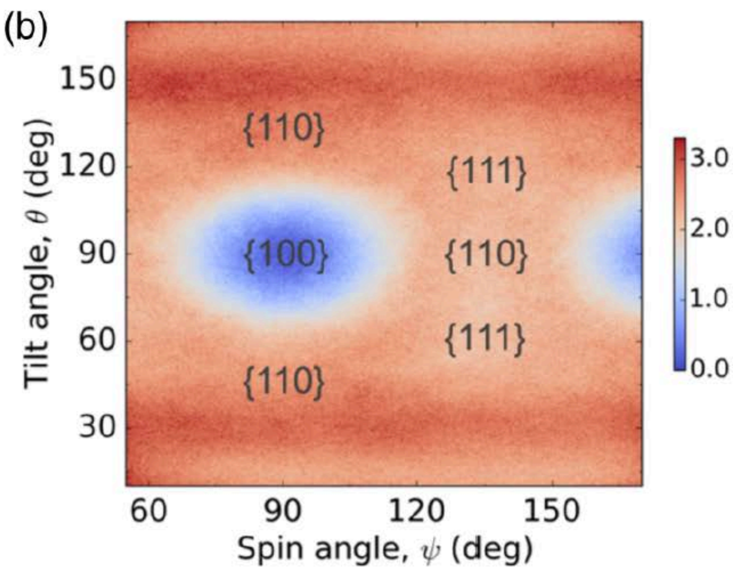
Critical question:
What thermodynamic and kinetic aspects of the assembly at the fluid interface determine the orientational alignment of the NC ?

Gupta, Hanrath, Escobedo *Physical Review Materials* **2017,** *1* (5), 055602

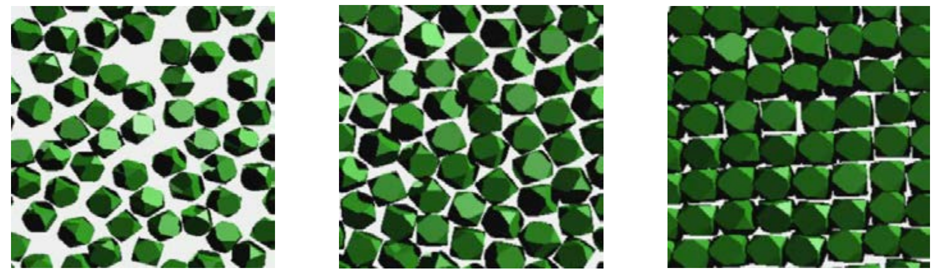
The role of thermodynamics and kinetics

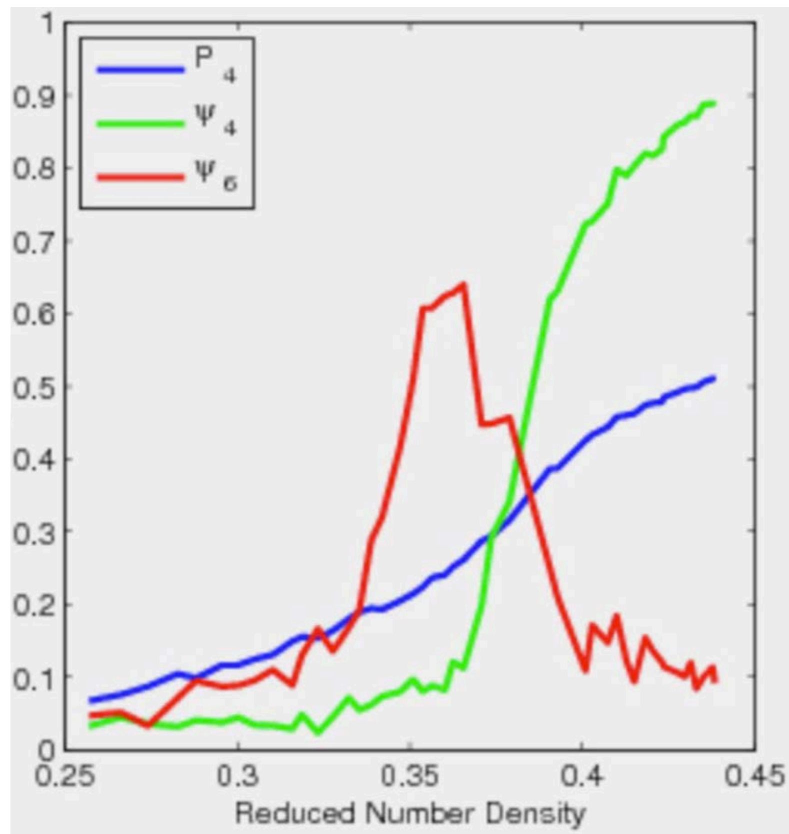
free energy landscape (MD)





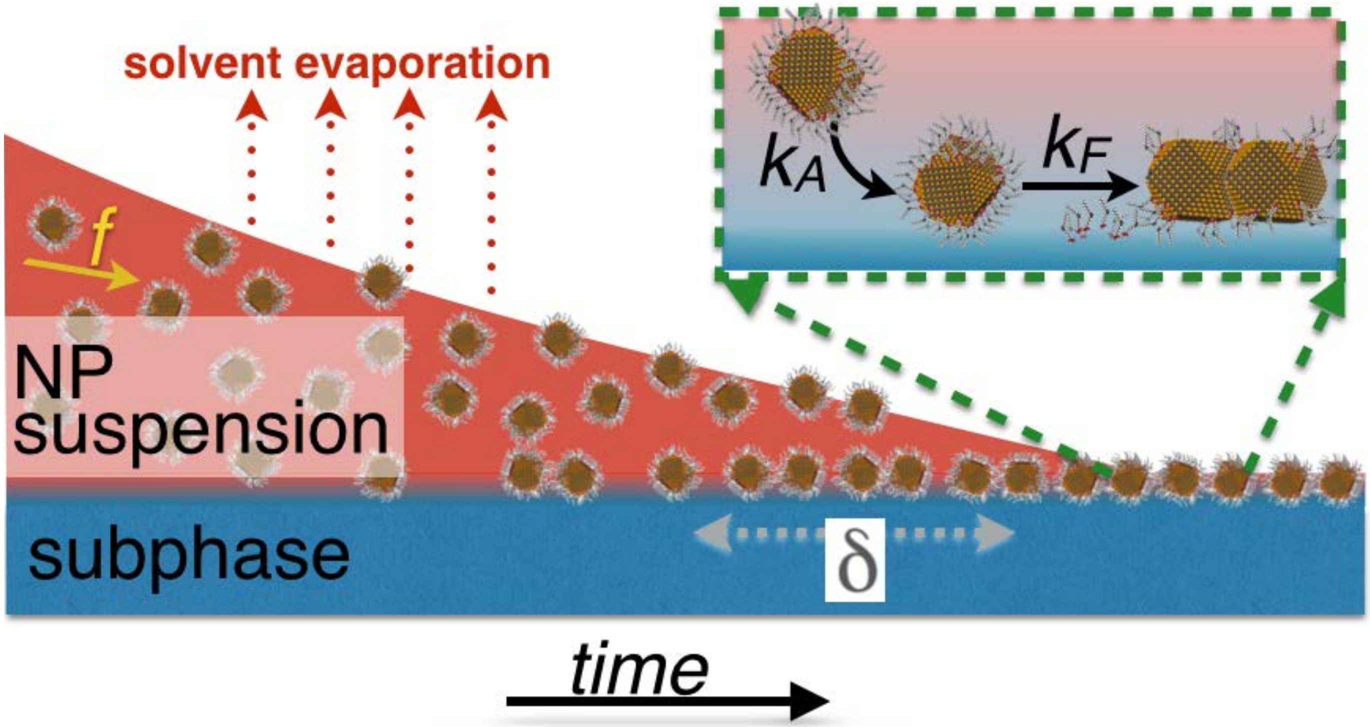
assembly kinetics (kMC)





Thapar, Hanrath, Escobedo, Soft Matter, 11 (**2015**), 1481.

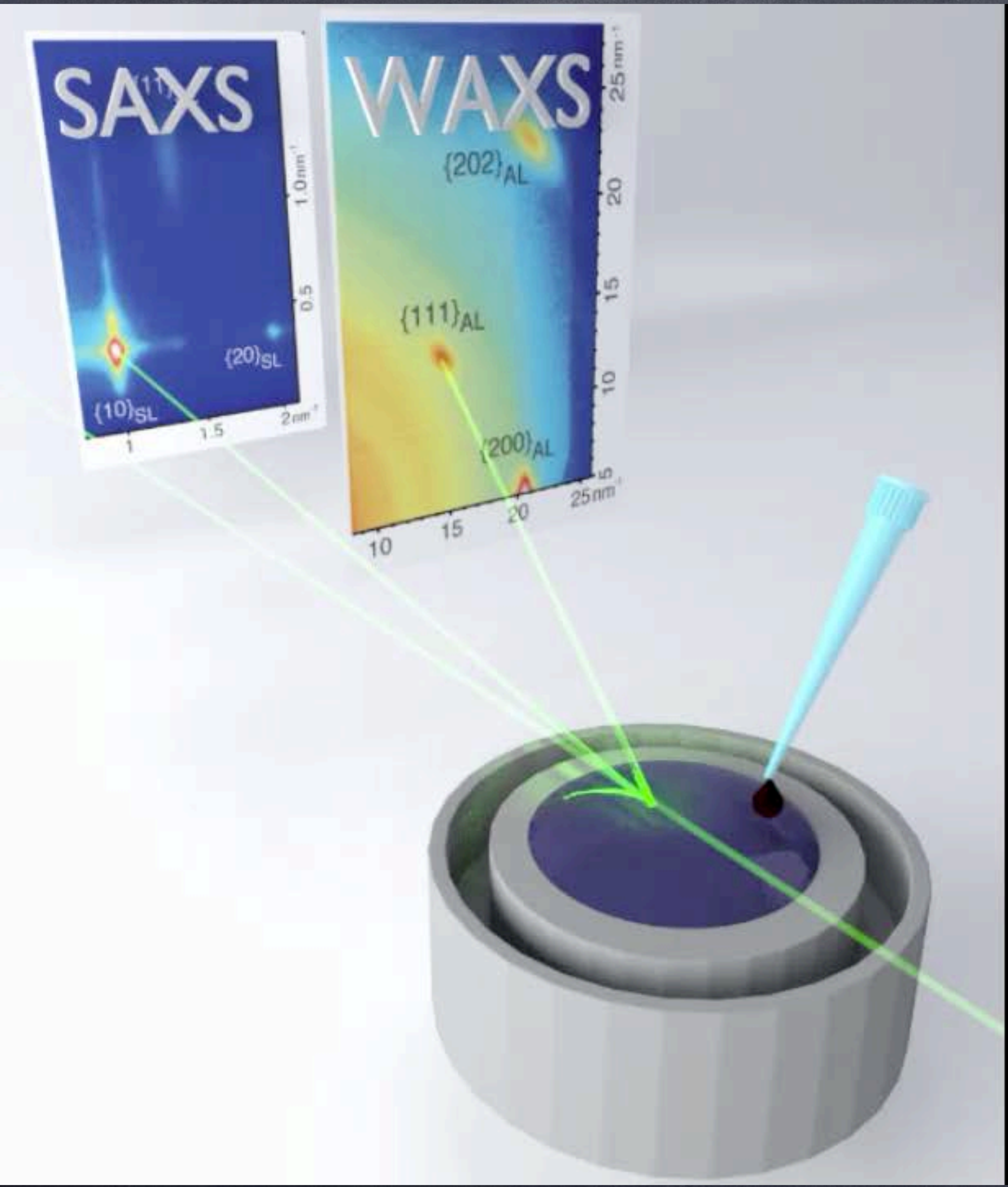
Physicochemical aspects of colloidal QD assembly at a fluid-fluid interface



competing dynamics of

- spreading / receeding fluid-fluid interface
- solvent evaporation
- particle assembly
- particle attachment
- ligand displacement

in-situ WAXS/SAXS analysis of interfacial assembly

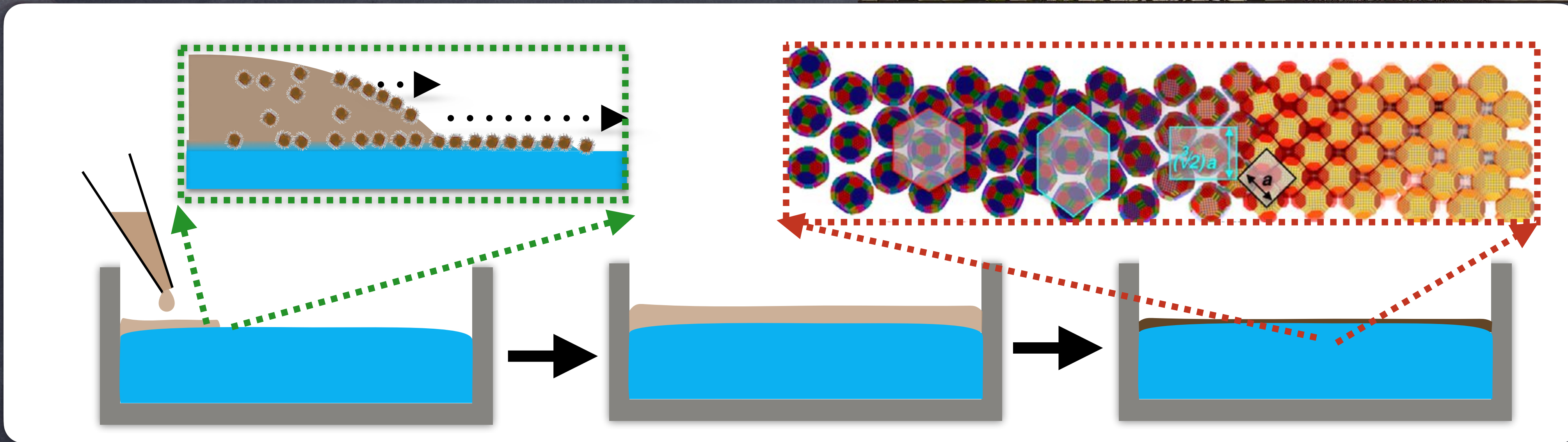


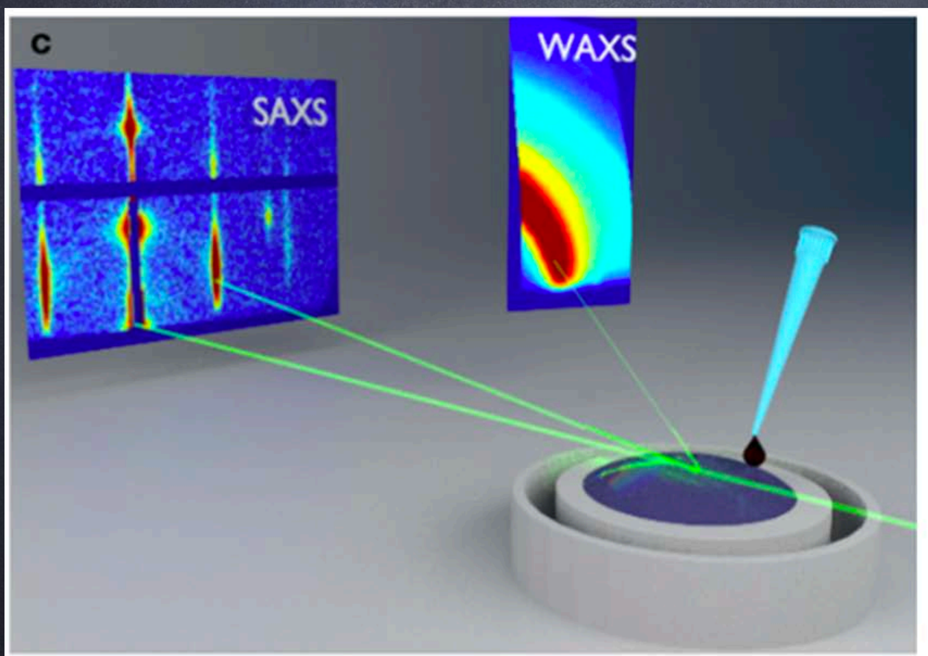
D. Balazs

T. Dunbar

Balazs, Dunbar, Smilgies, Hanrath, Langmuir 2020, 36, 6106

in-situ WAXS/SAXS





in- situ SAXS / WAXS with fast time resolution (200 ms) provided insights into the complex dynamic interplay between spreading and assembly subprocesses, including:

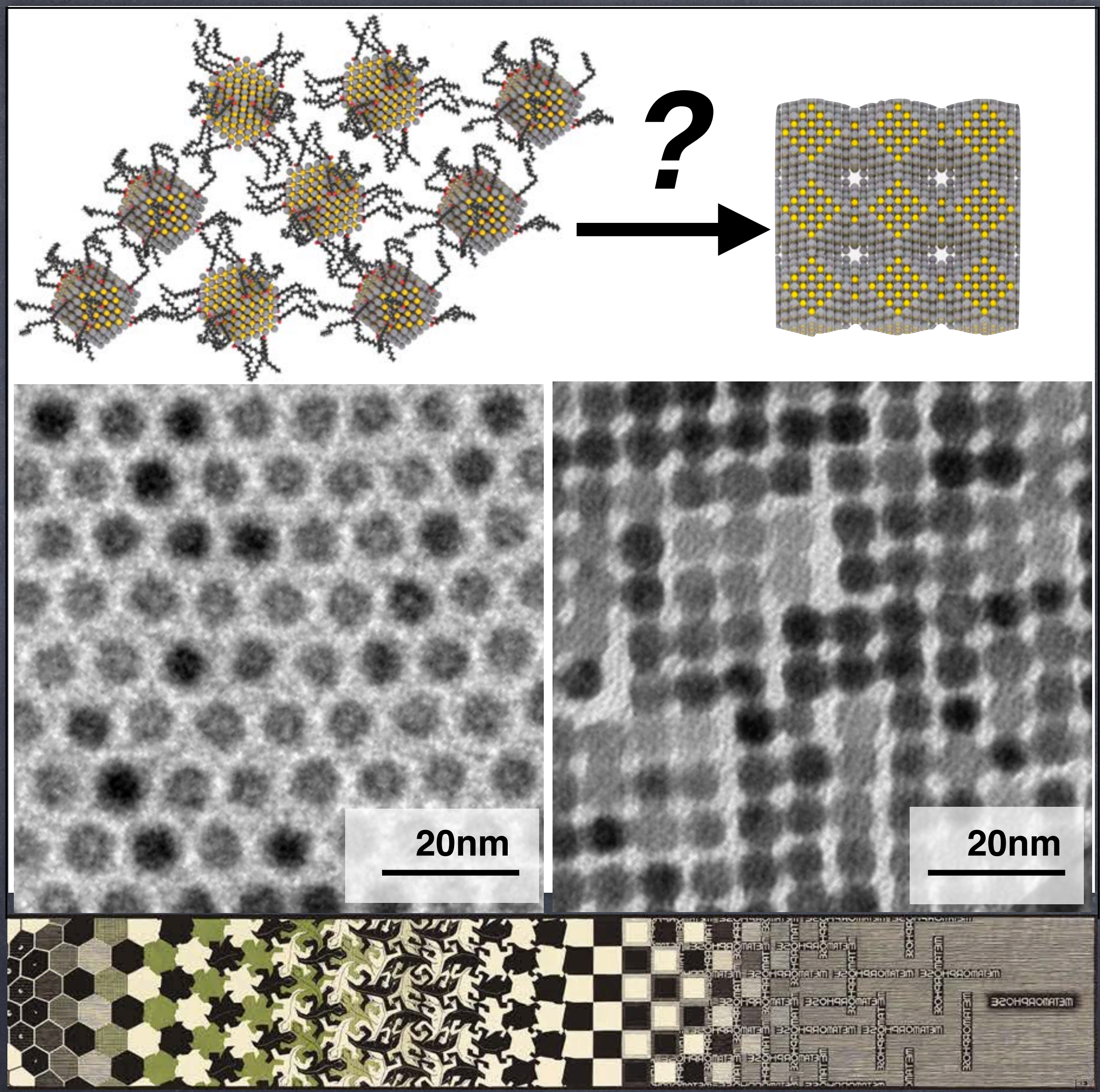
(i) the existence of a rapidly spreading monolayer colloidal QD film that preceeds the spreading of the bulk QD suspension,

(ii) transient signatures of QD superlattice nucleation at the liquid-liquid and liquid-gas interface, and

(iii) the correlation between solvent characteristics (QD solubility), the spreading behavior and the resulting film morphology.

Balazs, Dunbar, Smilgies, Hanrath, Langmuir 2020, 36, 6106

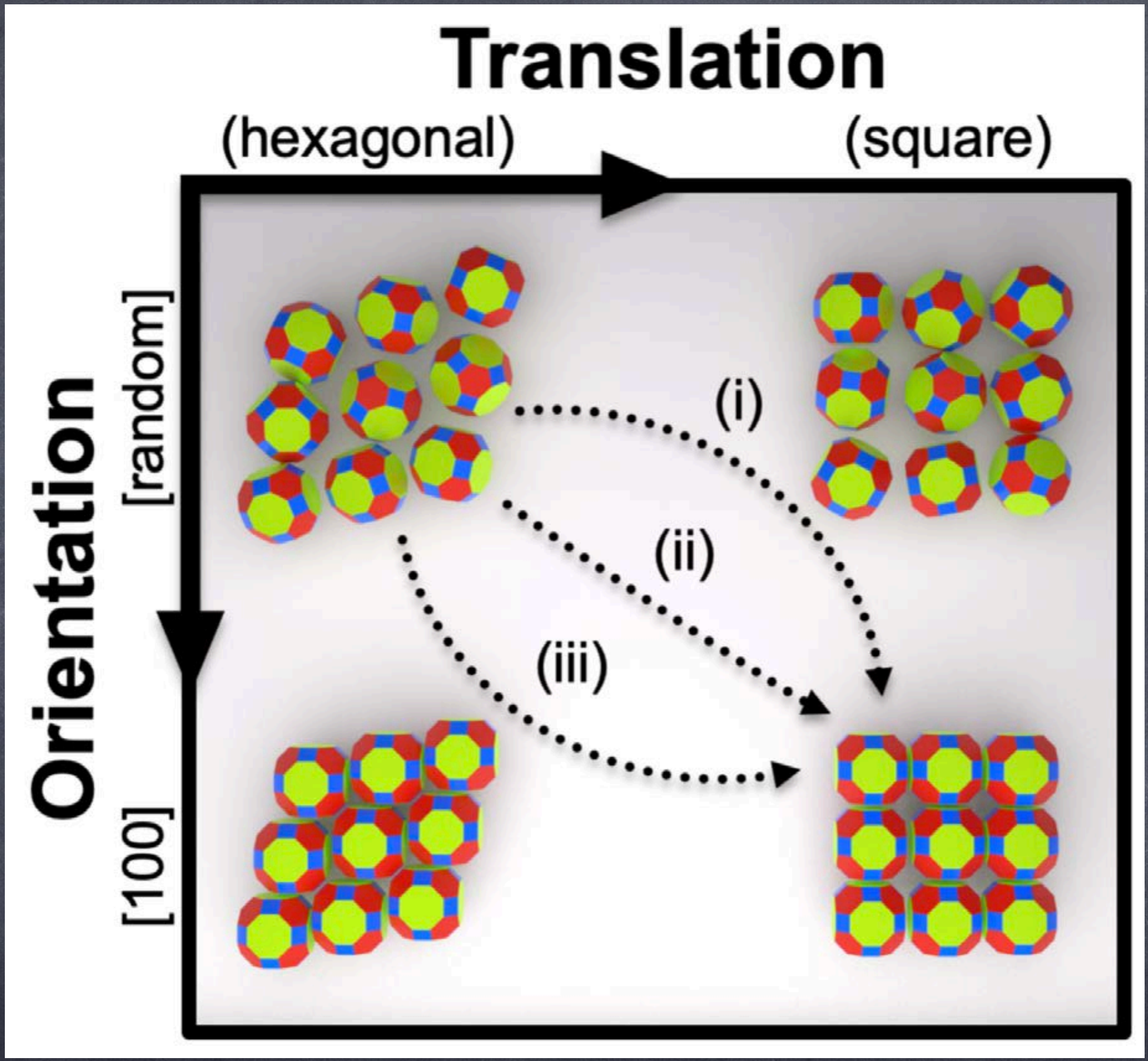
Superlattice Transformation Pathway



Note that this process involves $O(10^4)$ 'irreversible' attachments

Whitham, Hanrath, J Phys Chem Lett 2017, 8, 2623

Superlattice Transformation Pathway



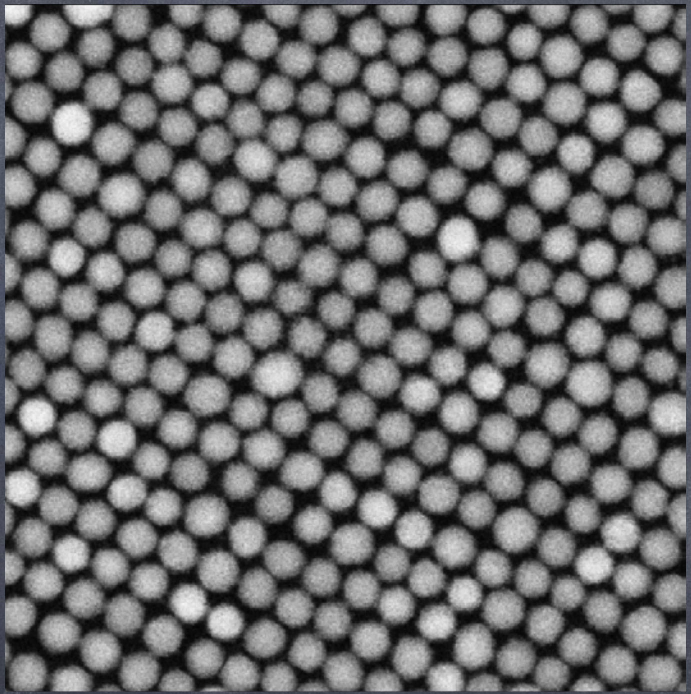
Superlattice structure transformation involves complex choreography of transformation and orientation

Cimada et al. Nano Lett. 2020, 20 (7), 5267-5274.
doi:10.1021/acs.nanolett.0c01579

Structure Analysis with the Pixel Array Detector

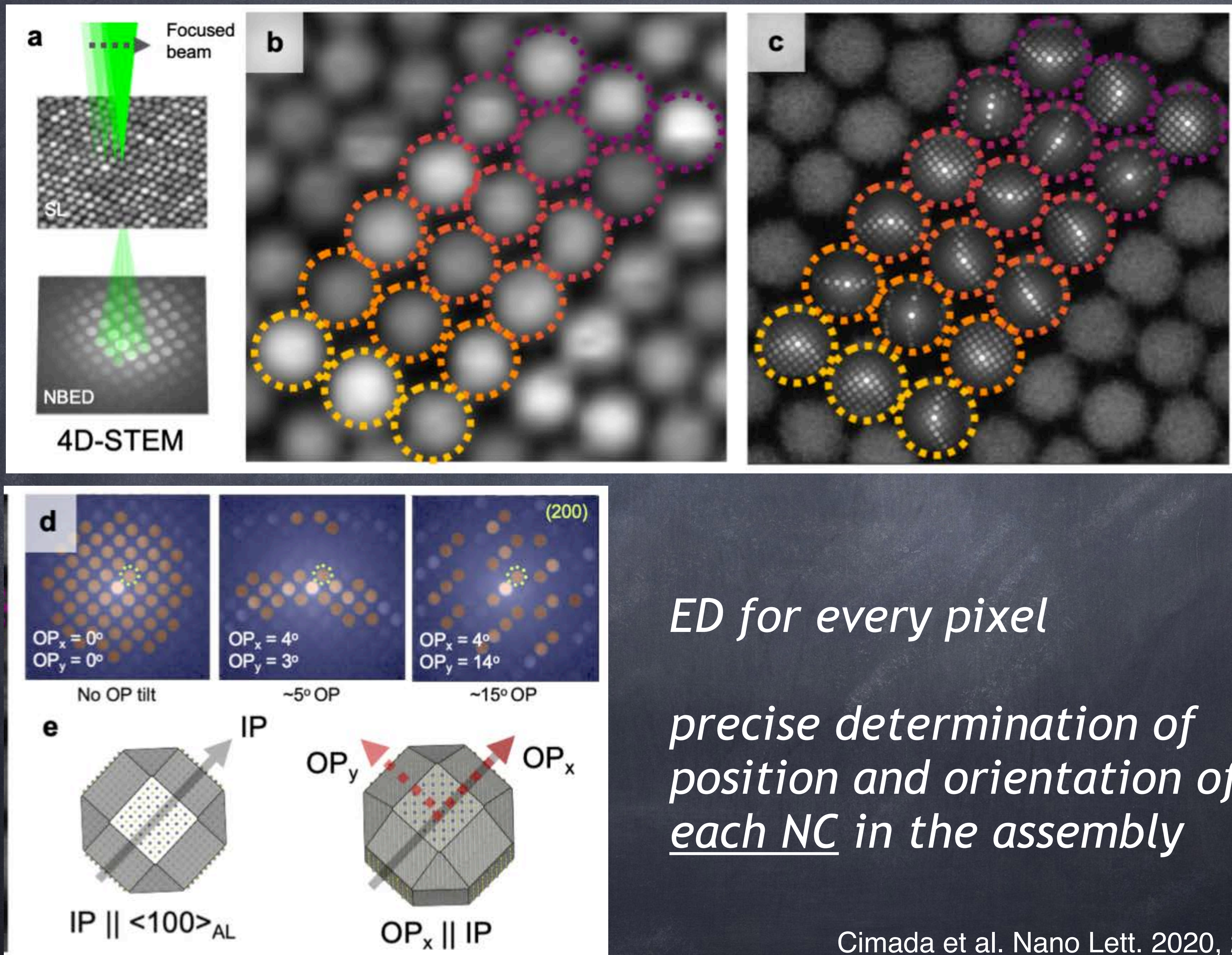
M. Smeaton

J. Cimada



Cimada et al. Nano Lett. 2020, 20, 5267

Structure Analysis with the Pixel Array Detector

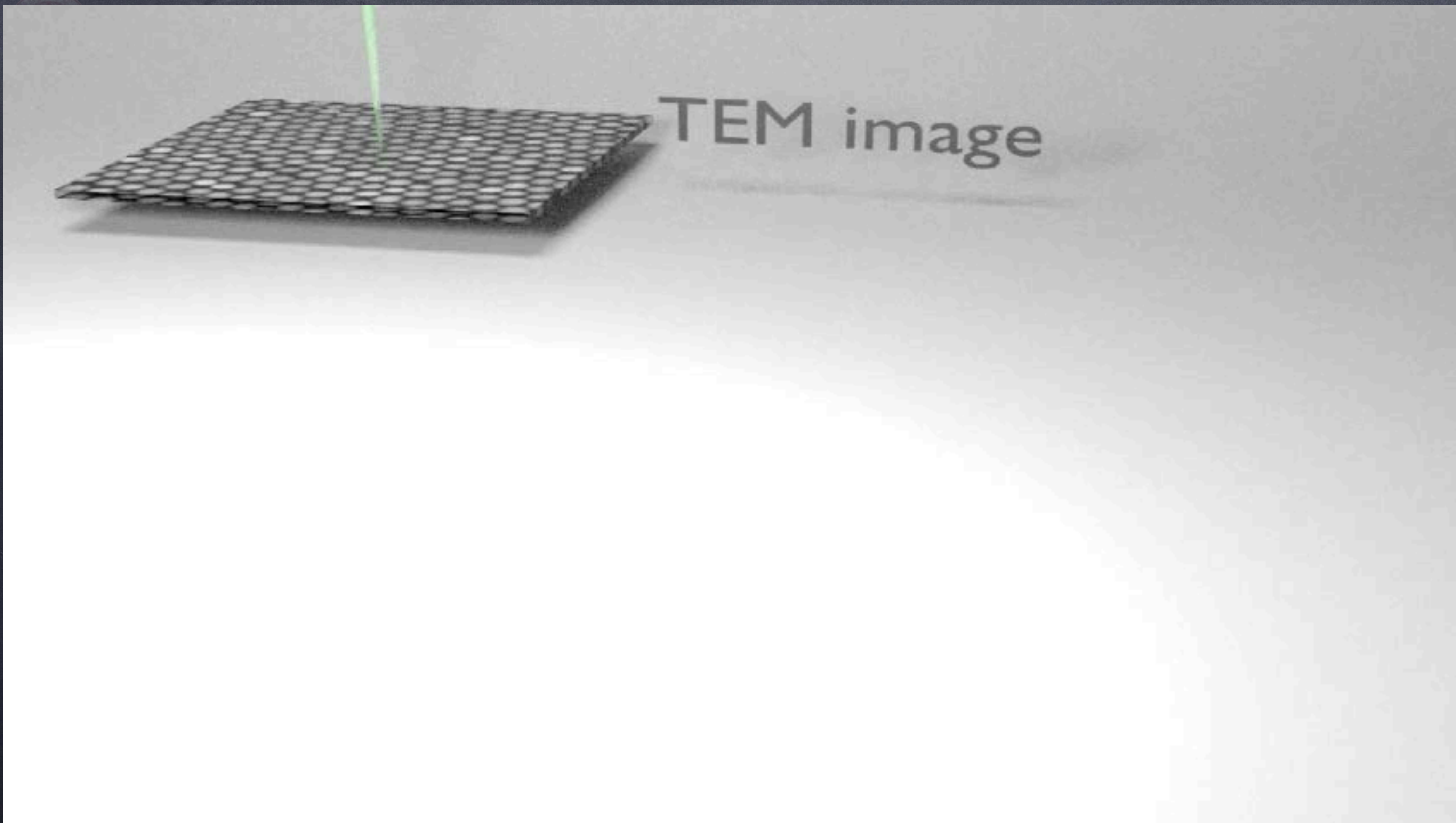


ED for every pixel

precise determination of position and orientation of <u>each NC</u> in the assembly

Cimada et al. Nano Lett. 2020, 20, 5267

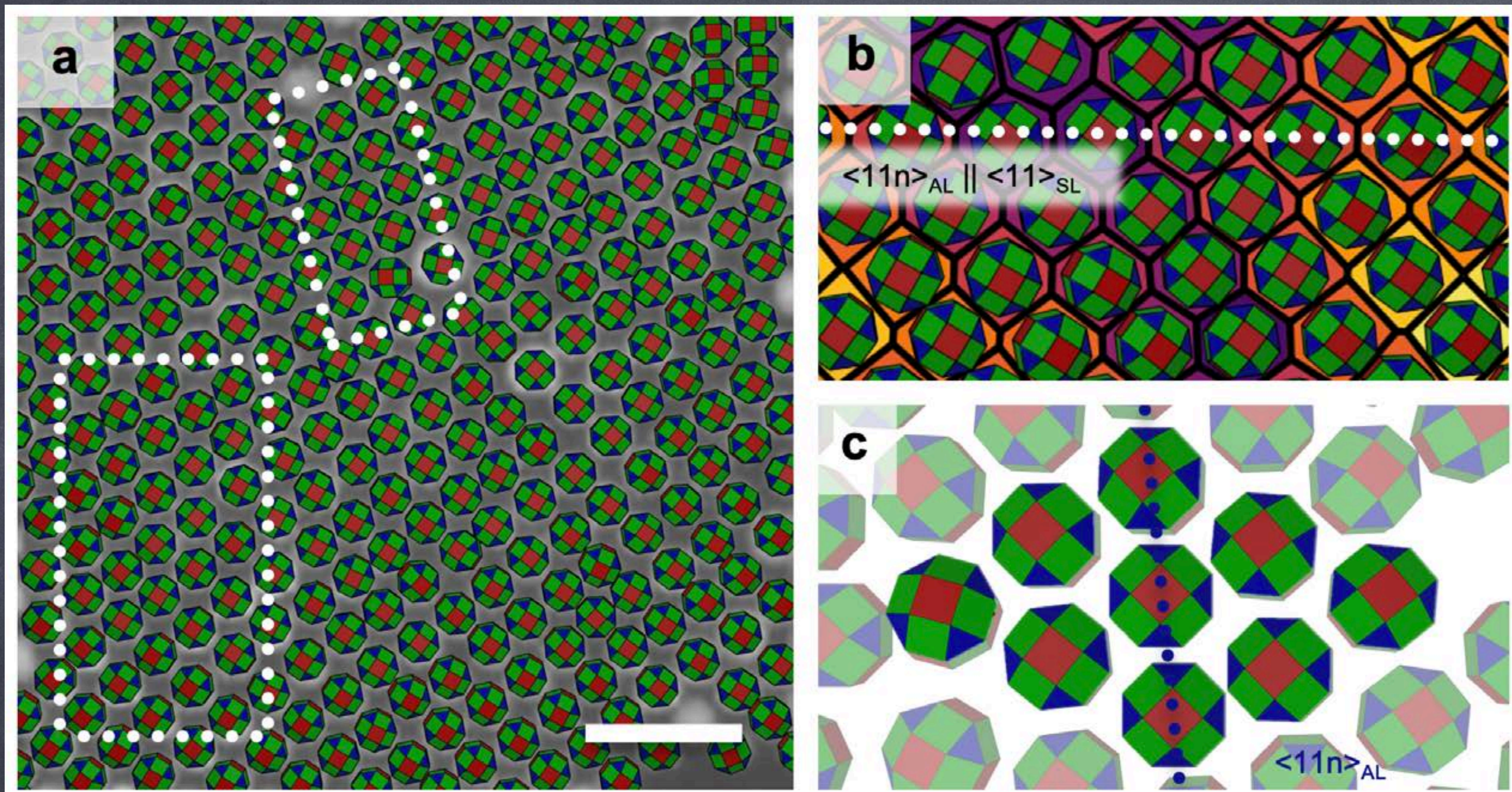
Structure Analysis with the Pixel Array Detector

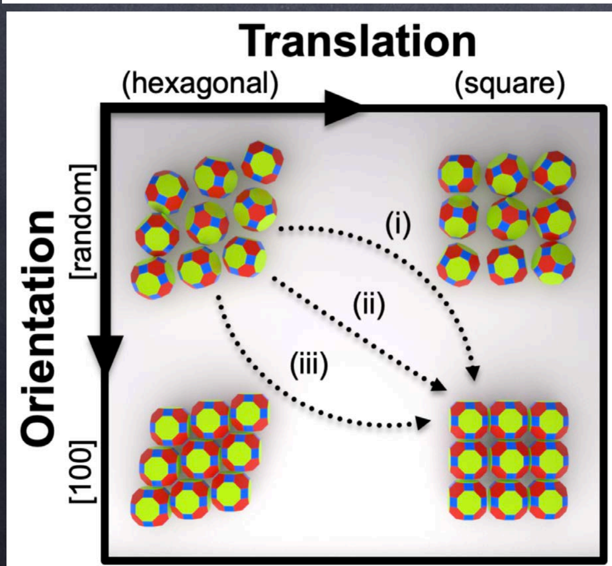


rich insights into superlattice structure and the interplay order of superlattice and constituent QDs.

Cimada et al. Nano Lett. 2020, 20, 5267

Structure Analysis with the Pixel Array Detector

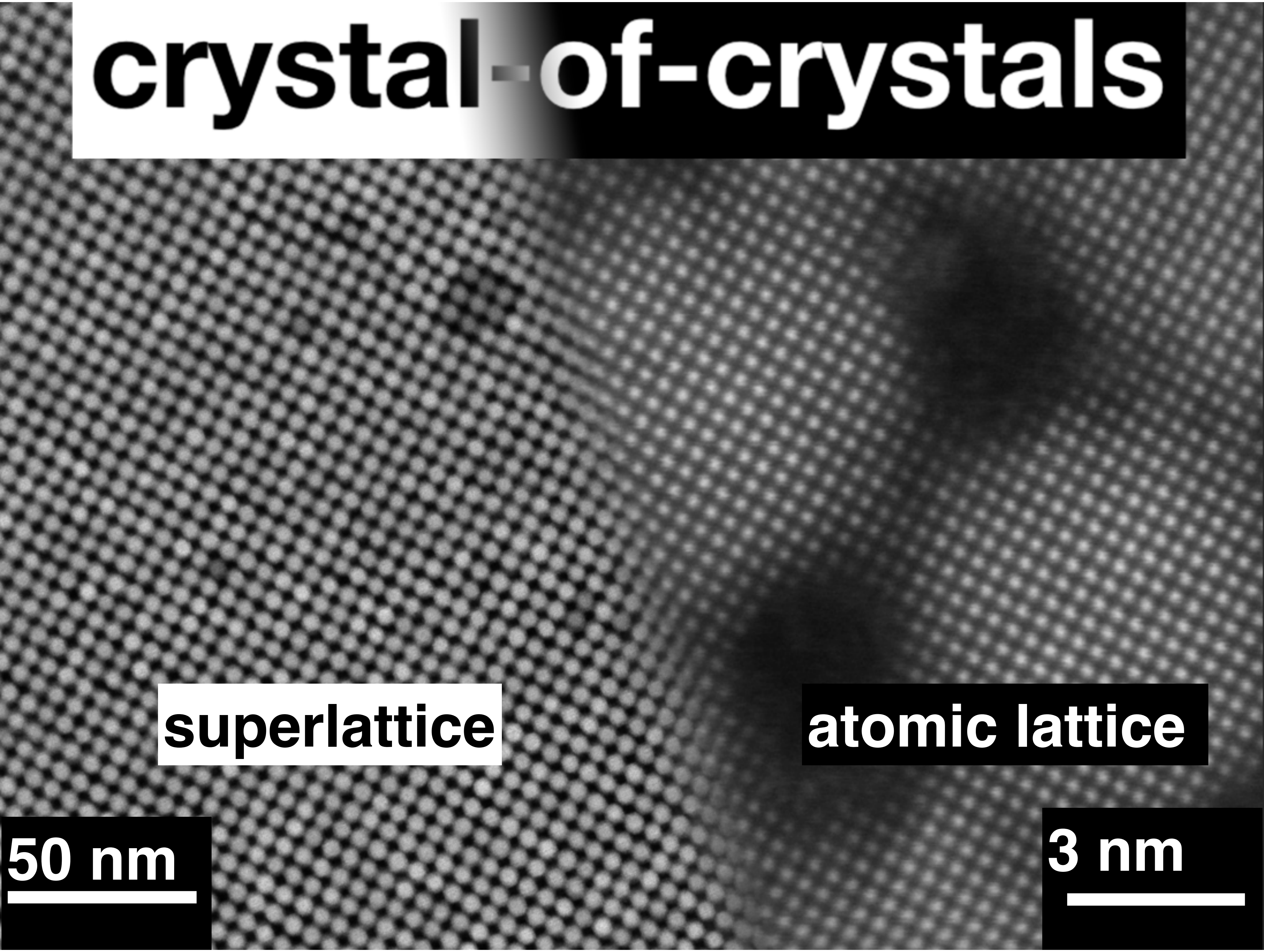




- superlattice structure transformation pathway (iii)

- alignment along <11n>; residual ligands as directing agents

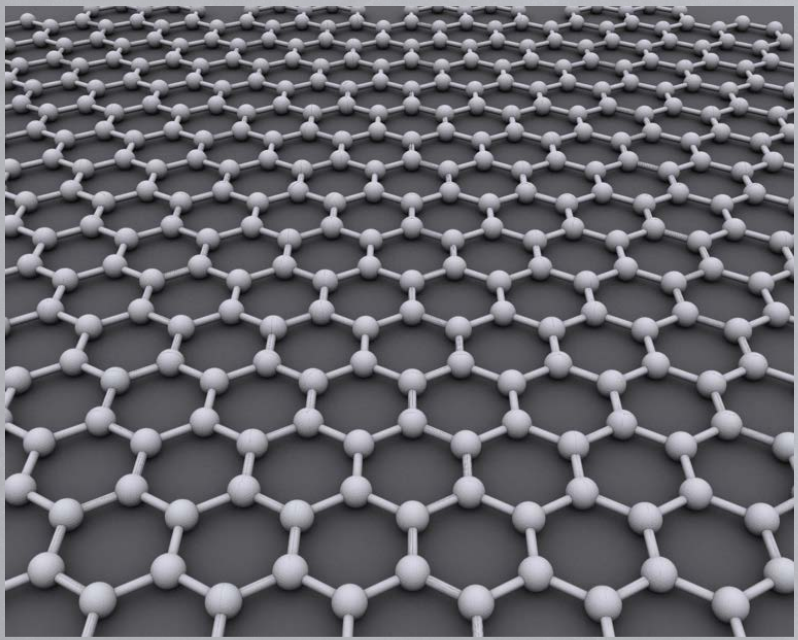
Cimada et al. Nano Lett. 2020, 20, 5267



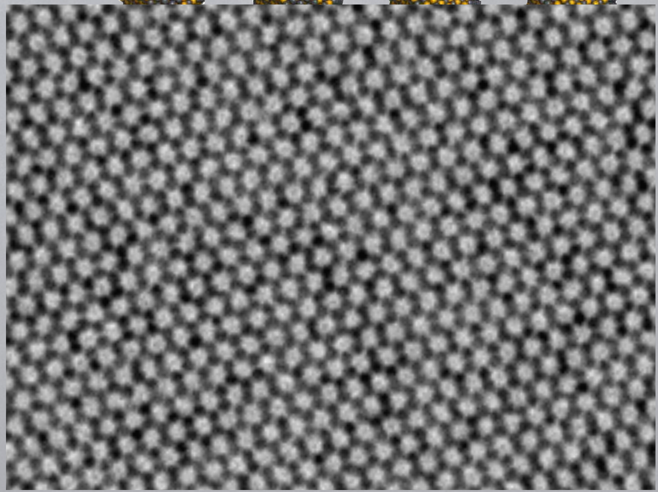
crystal-of-crystals
superlattice
atomic lattice
50 nm
3 nm

Analogous 2D systems
emergent properties

graphene

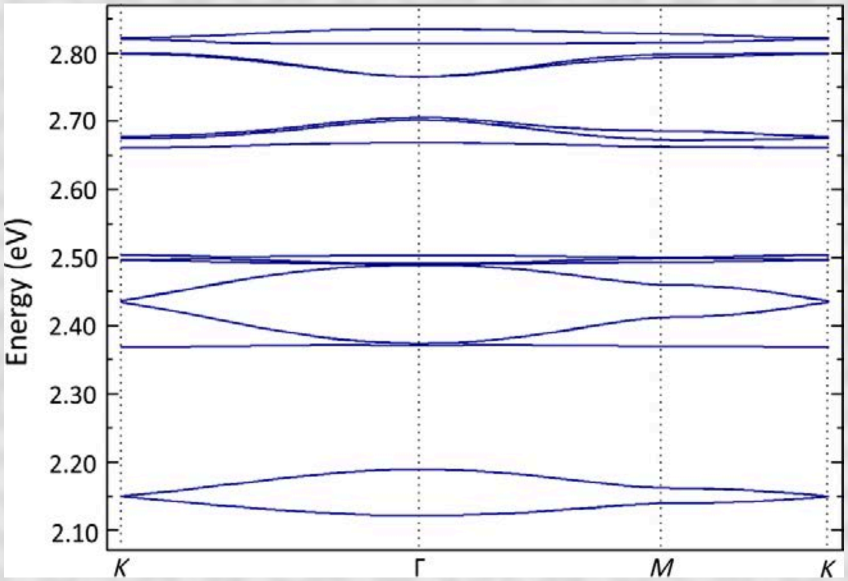


quasi-2D QD solids



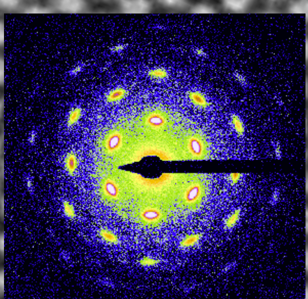
similar, yet different…

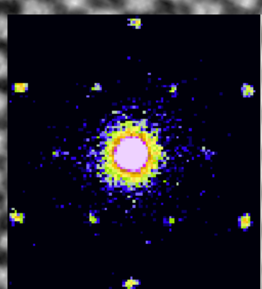
intriguing theoretical predictions about the electronic phases in quantum dot solids with dimensionality less than 2



<u>vanMaekelbergh *et al.*</u>

- 2D Materials 2, (2015): 034008
- Nature Communications 6, (2015): 6316
- Physical Review X 4, (2014): 011010
- Physical Review B 88,(2013): 115431.





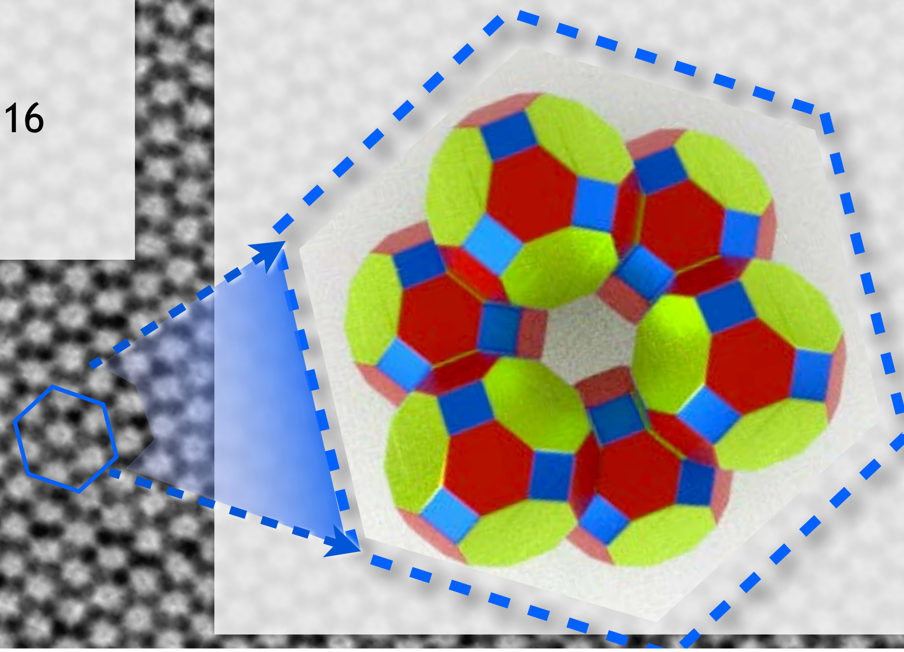
Combined control over

- the structure of the NQD building block,
- the geometry of the superlattice
- the nature of the interdot bond

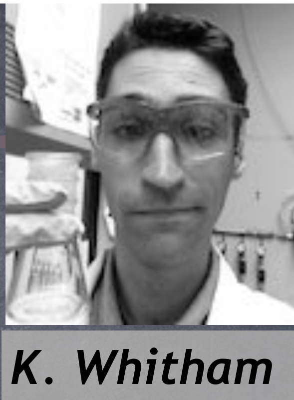
opens an exciting opportunity space for quantum dot solids as programmable optoelectronic materials

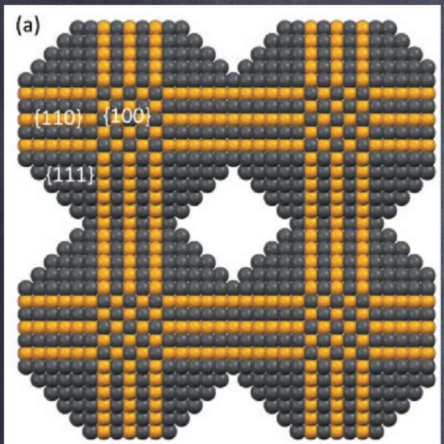
<u>theoretical predictions:</u>

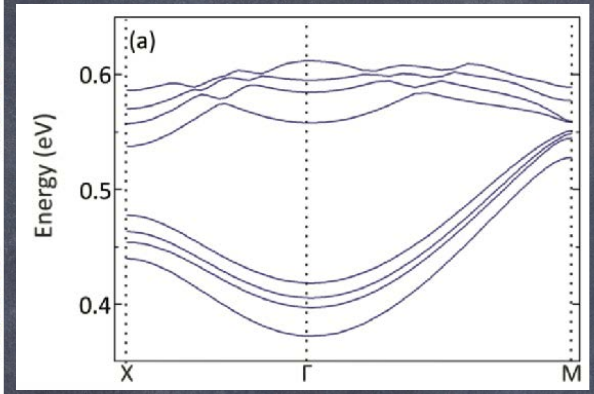
- minibands; coherent transport
- Dirac cones
- topological edge states



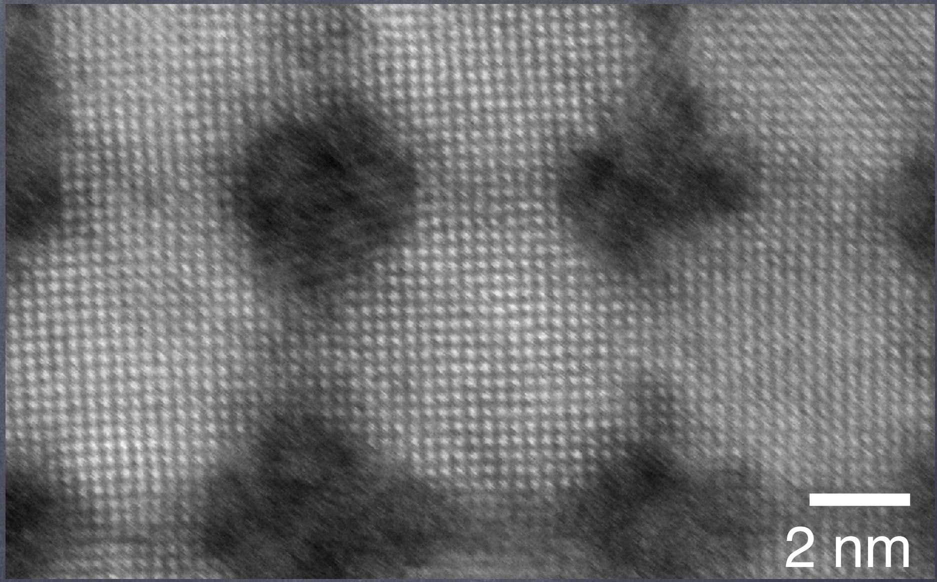
The Impact of Disorder on Quantum Confinement and Quantum Coupling



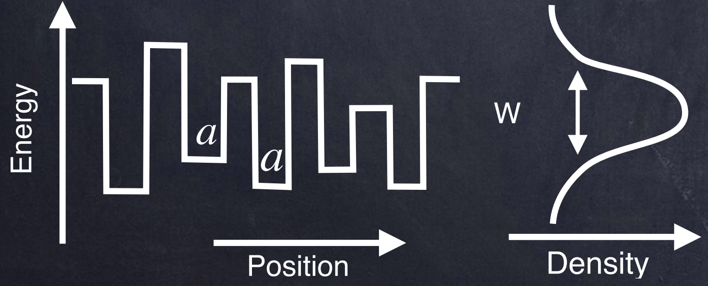




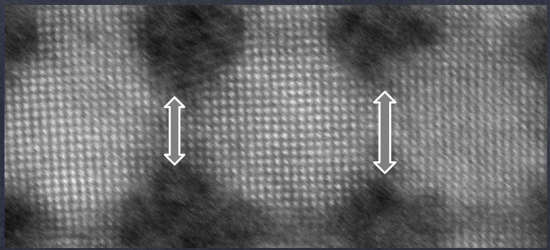
Kalesaki, E., Evers, W. H., Allan, G., Vanmaekelbergh, D., and Delerue, C., Phys. Rev. B, 88(11), 2013.



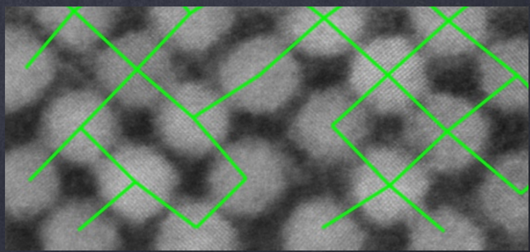
On-site Energy



Coupling



Connectivity



Whitham, et. al. Nature Materials, 15,557, 2016.

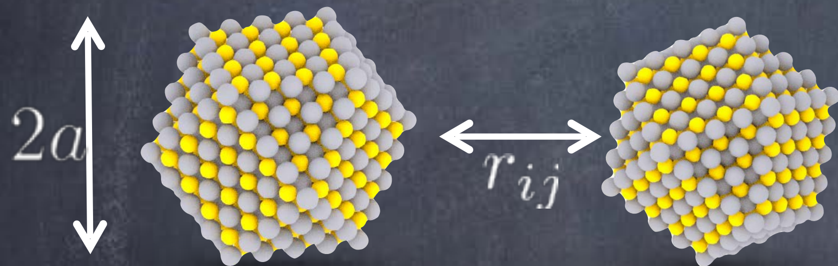
Charge transport in quantum dot solids

K. Whitham

Charge transfer rate

$$\gamma \propto e^{-\left(\frac{2r_{ij}}{a}+\frac{\epsilon_{ij}}{kT}\right)}$$

Distance



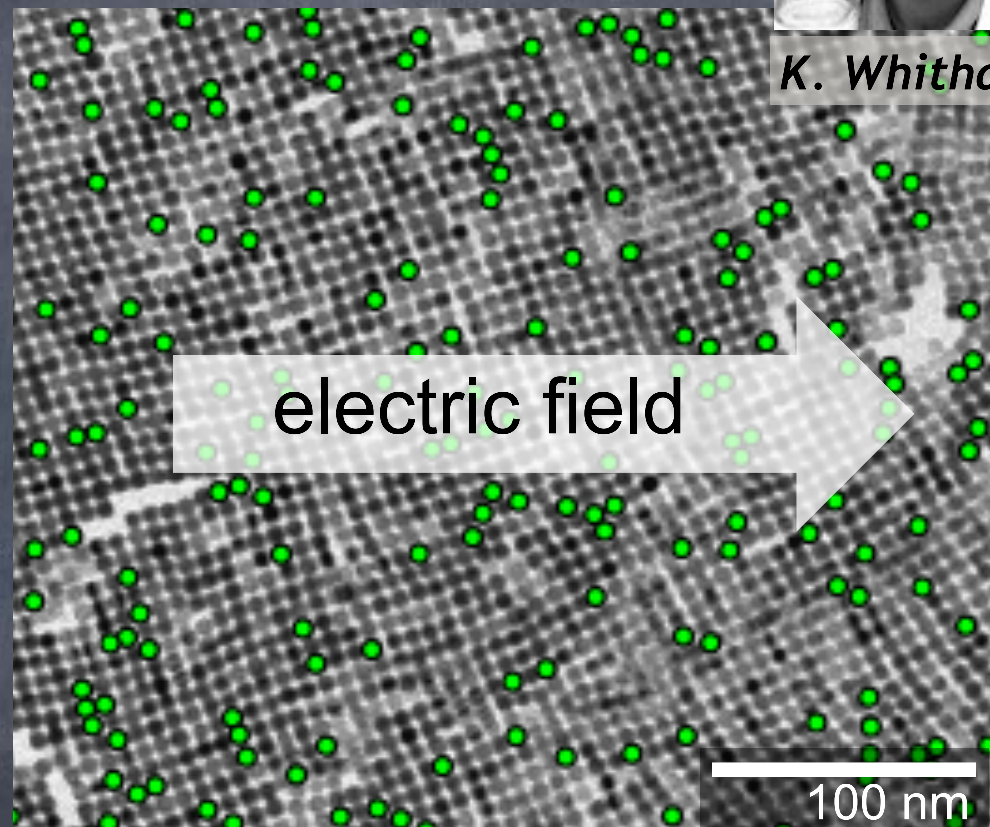
Energy

$$\psi \propto e^{(-r/a)}$$

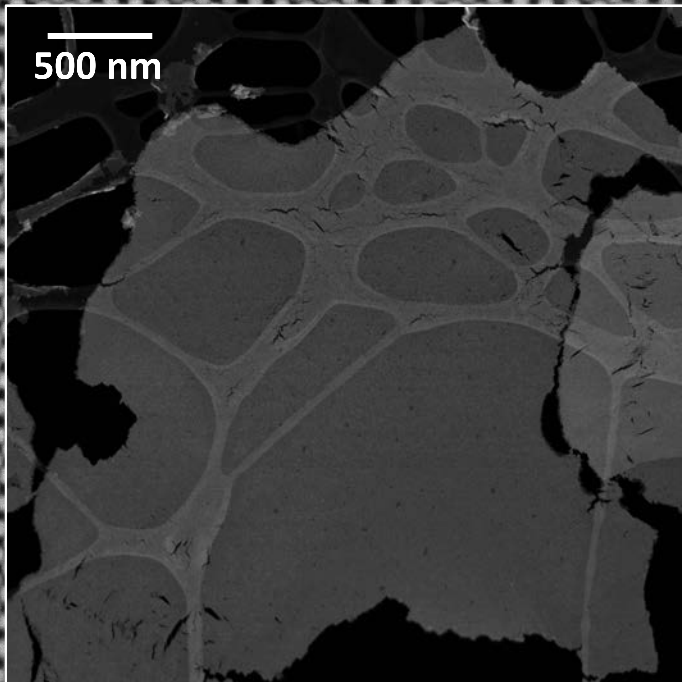
ϵ_{ij}

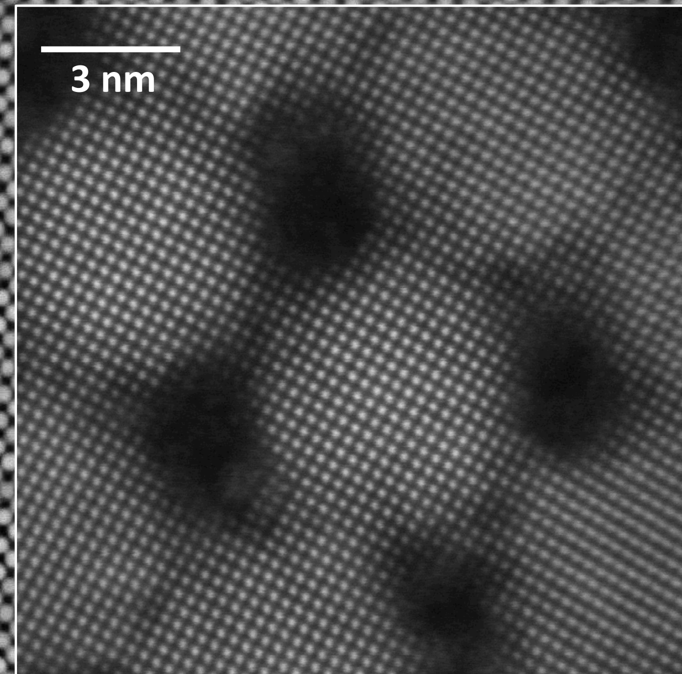
j

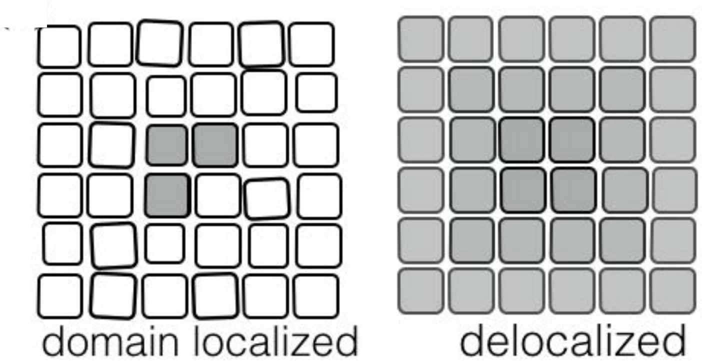
i

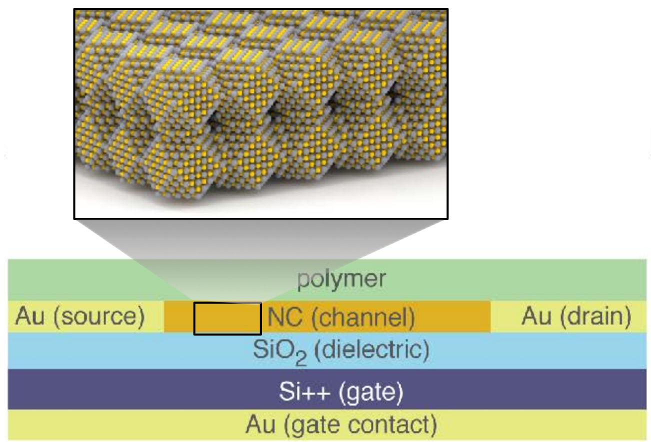


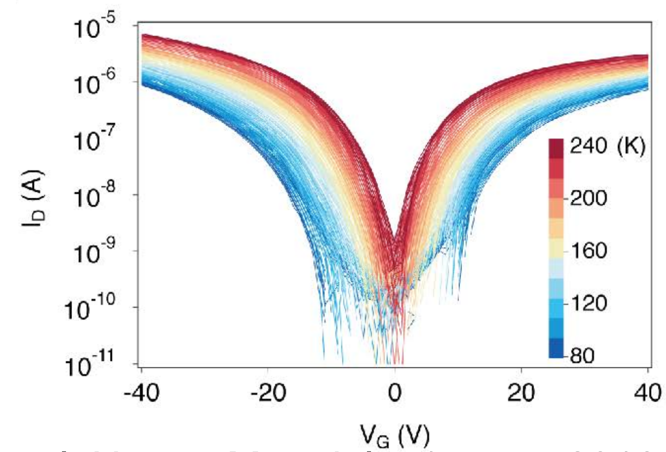
Disorder in ϵ_{ij}, r_{ij} causes incoherent transport











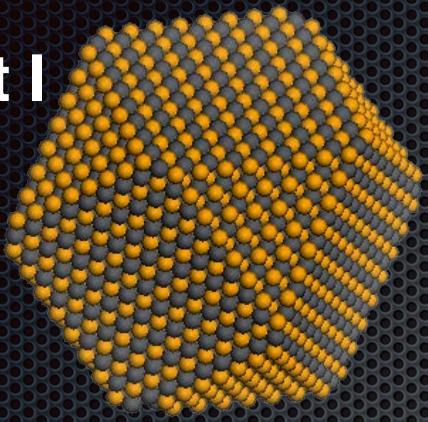
Whitham, et. al. Nature Materials, 15,557, 2016.

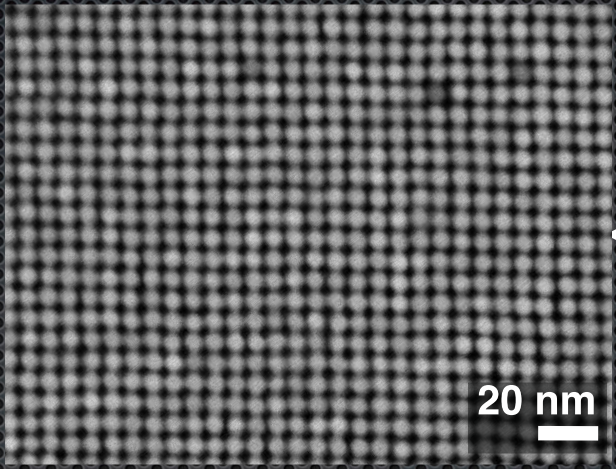
Despite strong dot-to-dot coupling and high-fidelity ordering, the charge delocalization is limited to ~4-5 dots.

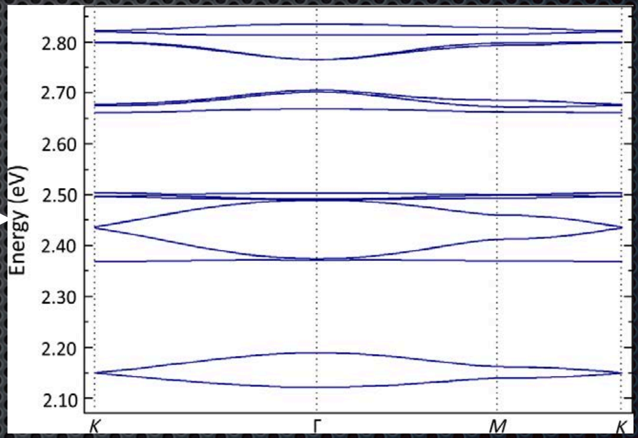
CornellEngineering

building blocks | **emergent structure** | **emergent properties**

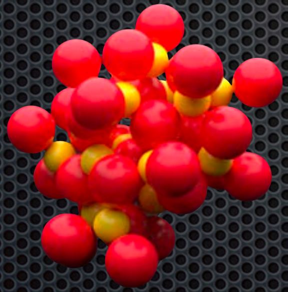
Part I

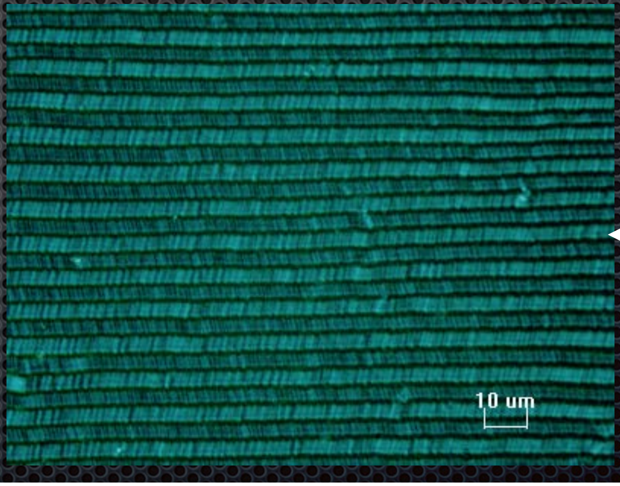


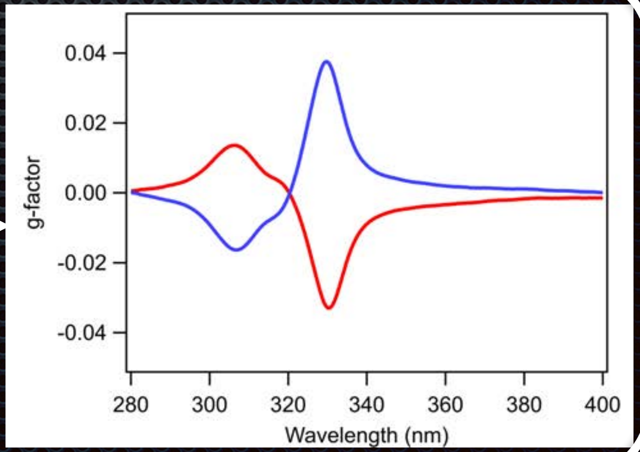




Part II







Bonus: emergent anisotropy

Cornell Engineering

Scale-up of colloidal NC synthesis

50 mL

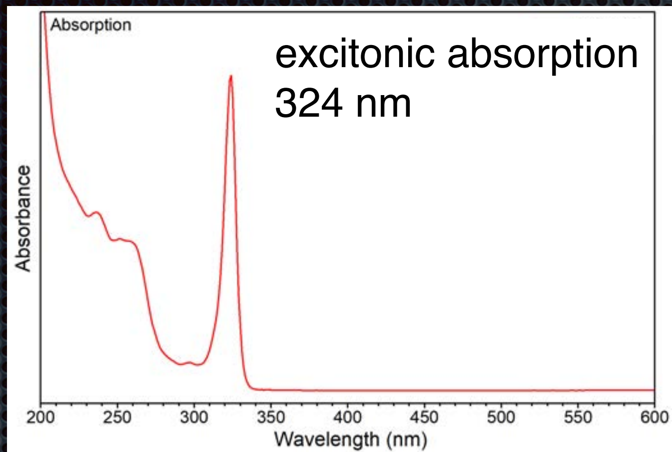
2000 mL

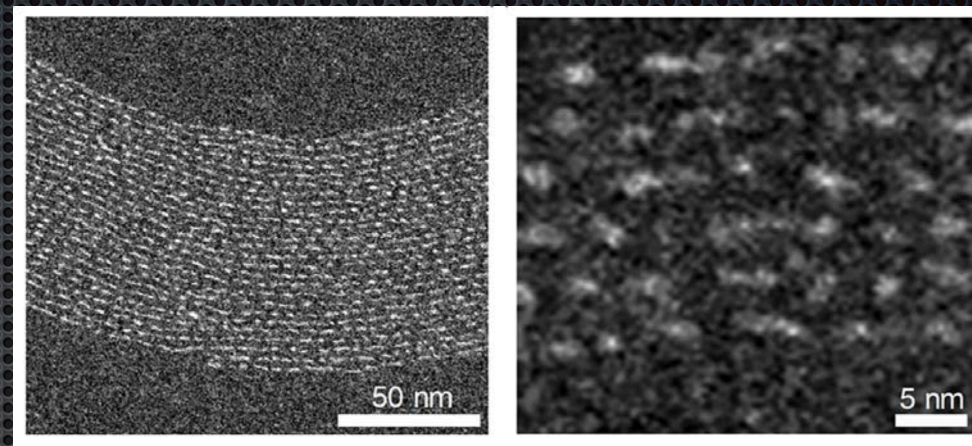
https://www.youtube.com/watch?v=kDPyjDrpW3c
Snupp UIV

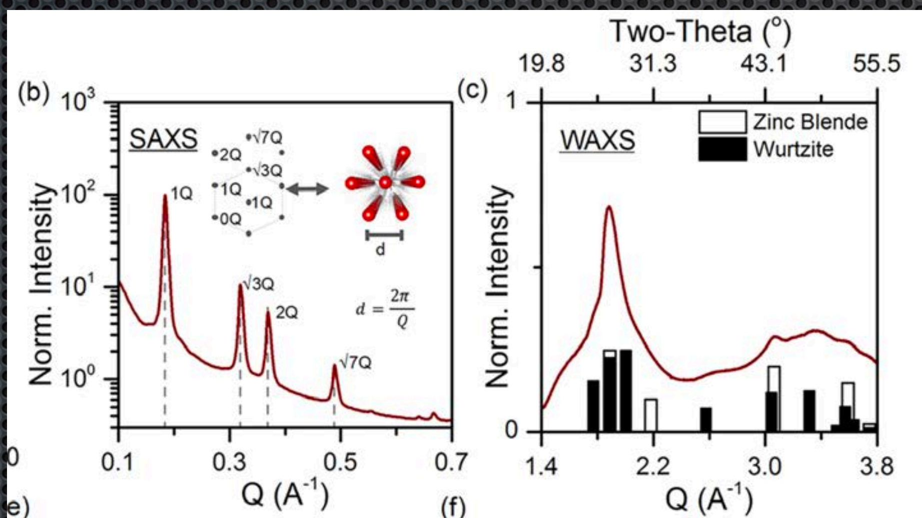
Williamson, Nevers, Hanrath, Robinson, *JACS* **2015,** *137* 15843

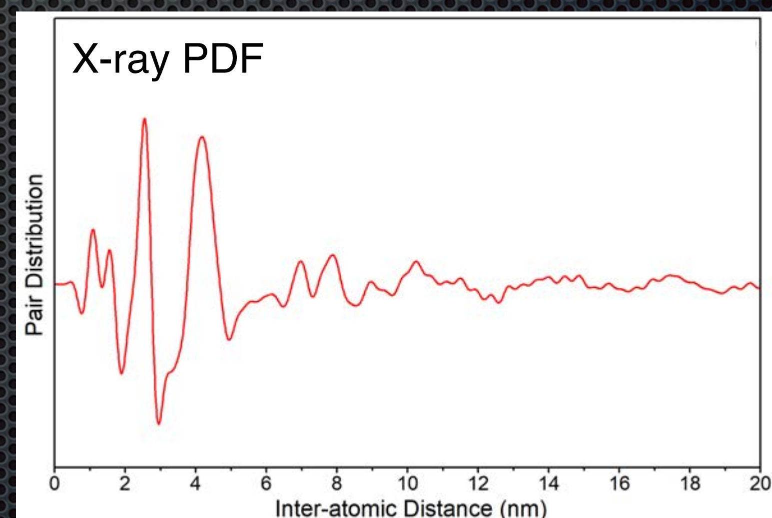
High Concentration Synthesis of colloidal ‘magic-sized’ CdS nanocrystals

CornellEngineering





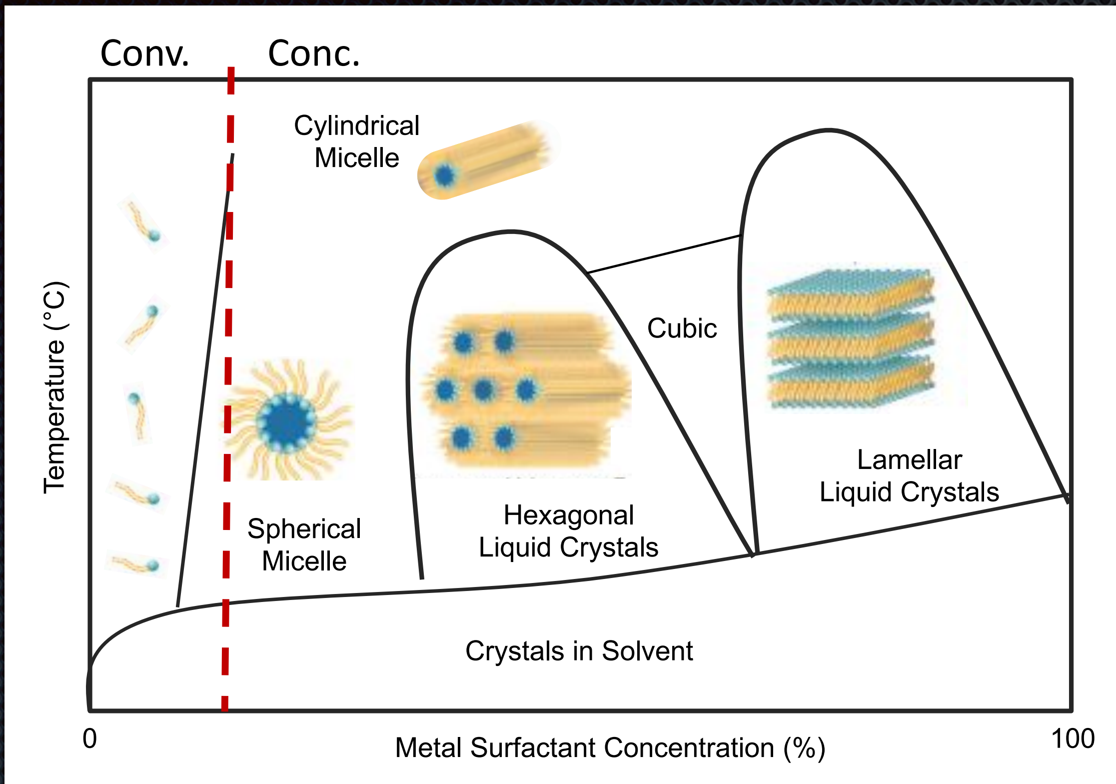


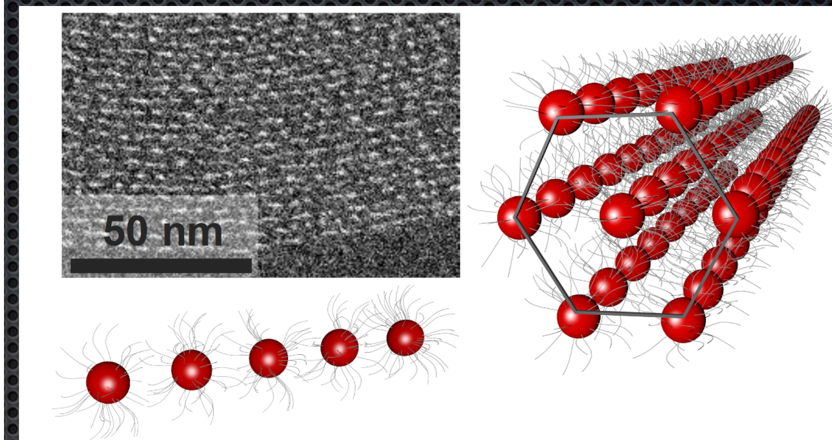


Williamson, Nevers, Hanrath, Robinson, *JACS* **2015,** *137* 15843

Nevers, Williamson, Savitzky,Hadar, Banin, Kourkoutis, Hanrath, Robinson, JACS **2018,** *140,* 3652

Mesophase stabilization of ‘magic-sized’ CdS nanocrystals



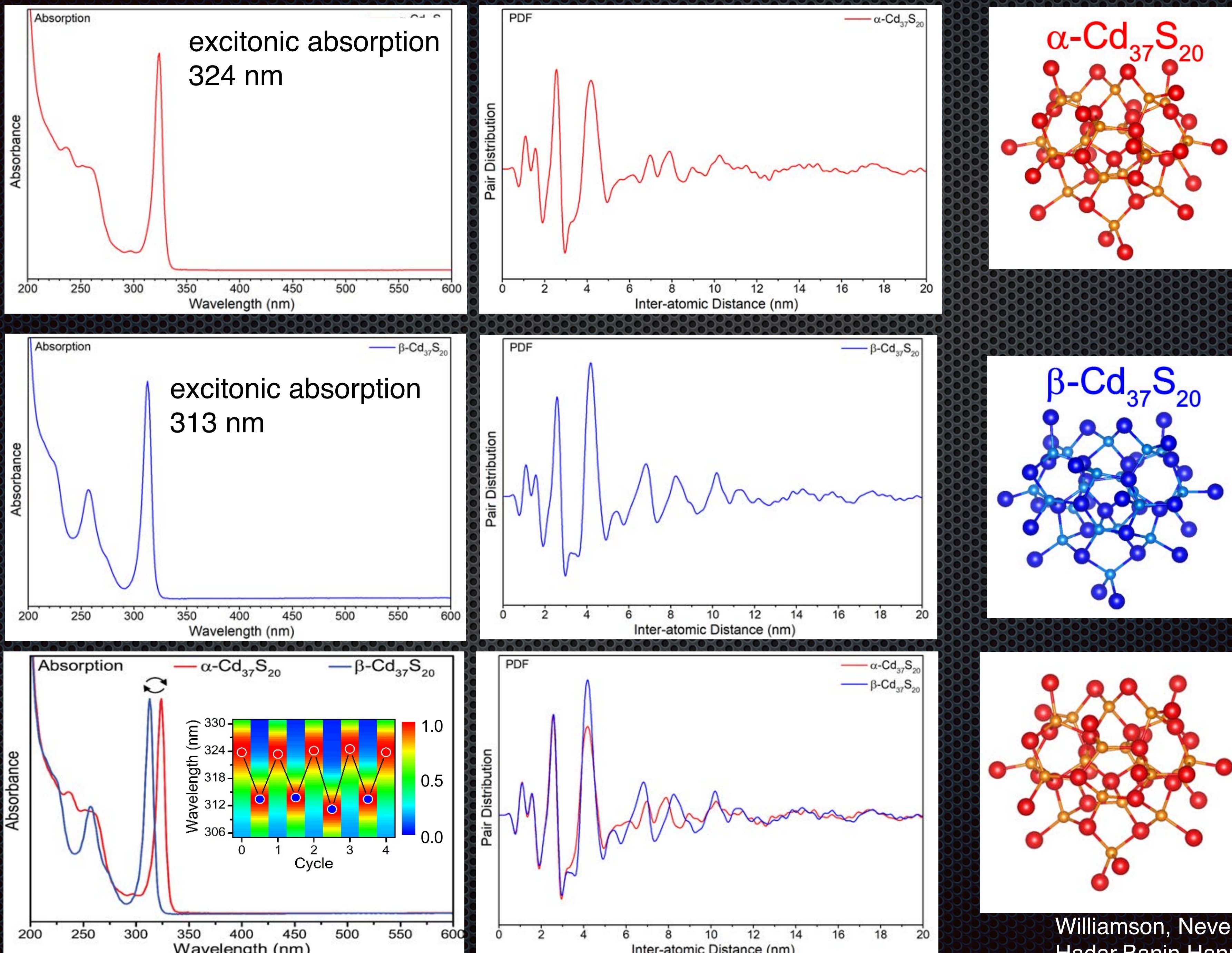


lyotropic phase behavior stabilizes magic size clusters

analogies to liquid crystals enable other emergent properties…

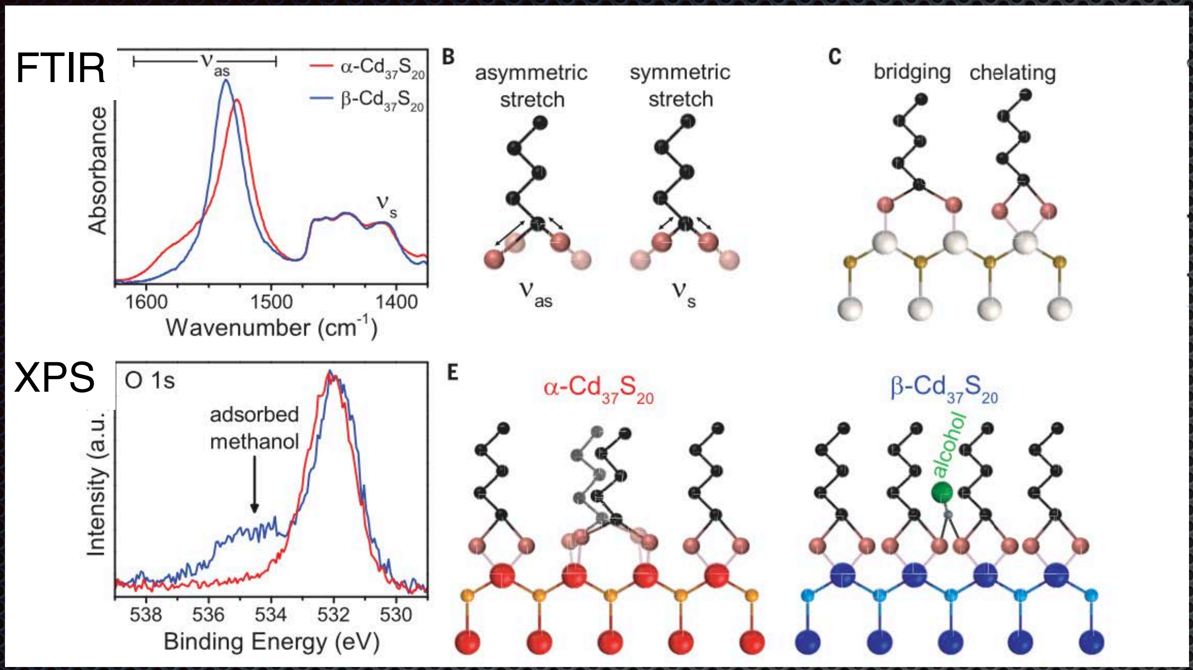
Nevers, Williamson, Savitzky,Hadar, Banin, Kourkoutis, Hanrath, Robinson, JACS **2018,** *140,* 3652

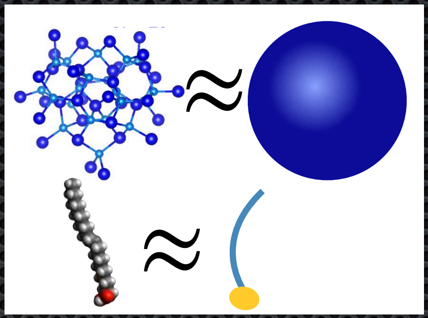
Isomerization of CdS magic-sized clusters



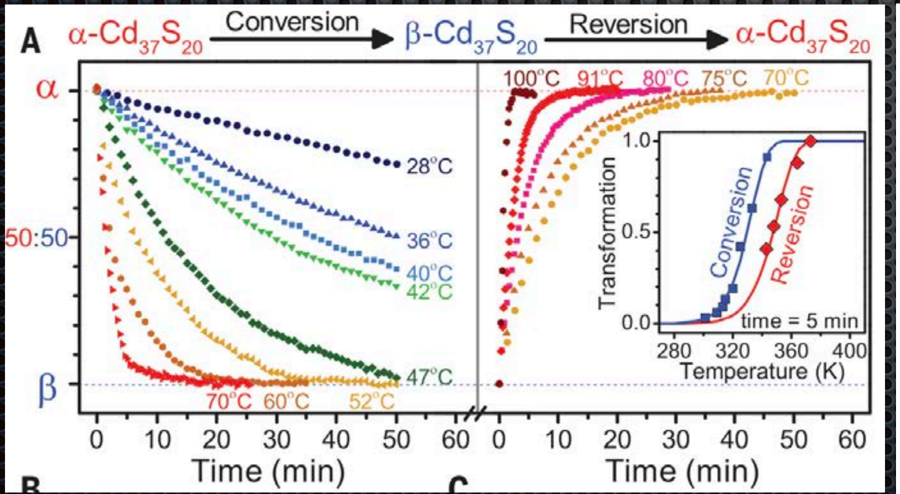
Williamson, Nevers, Nelson, Hadar,Banin,Hanrath, Robinson, Science 363, 731 (2019)

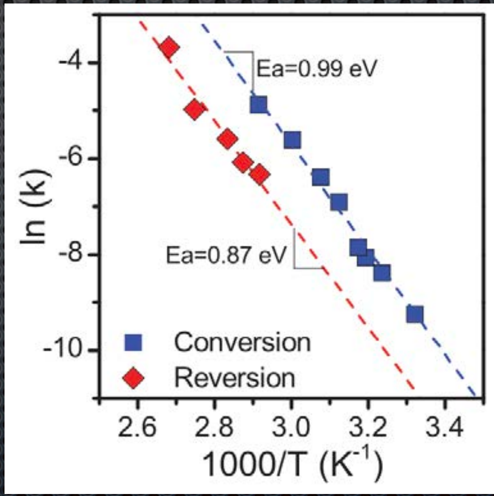
Isomerization of CdS magic-sized clusters





- distortion of the ligand-binding motifs & hydroxyl species changes the surface energy via physisorption.

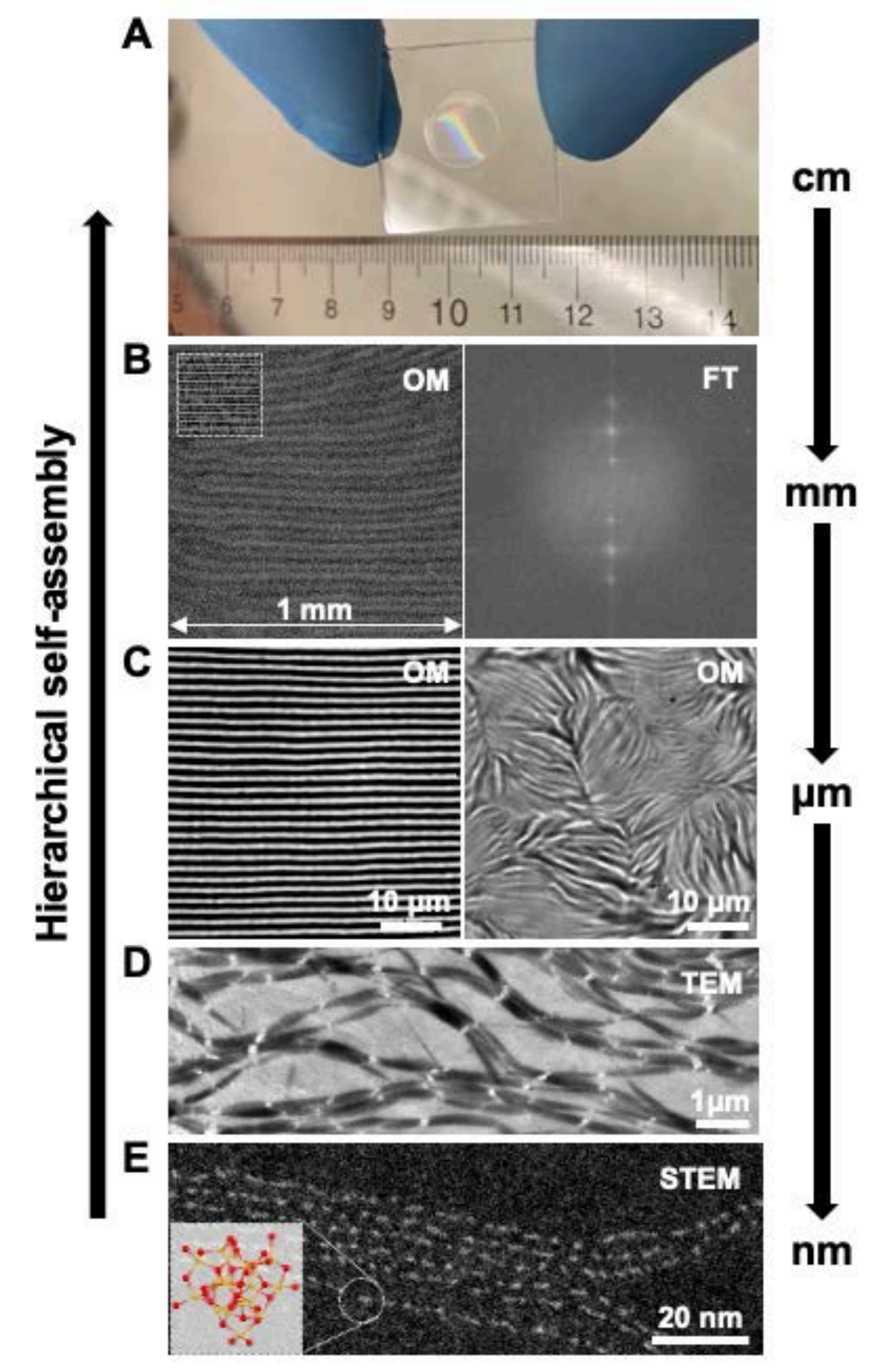




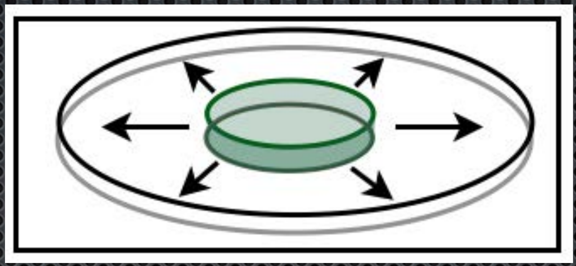
isomerization kinetics and thermodynamics

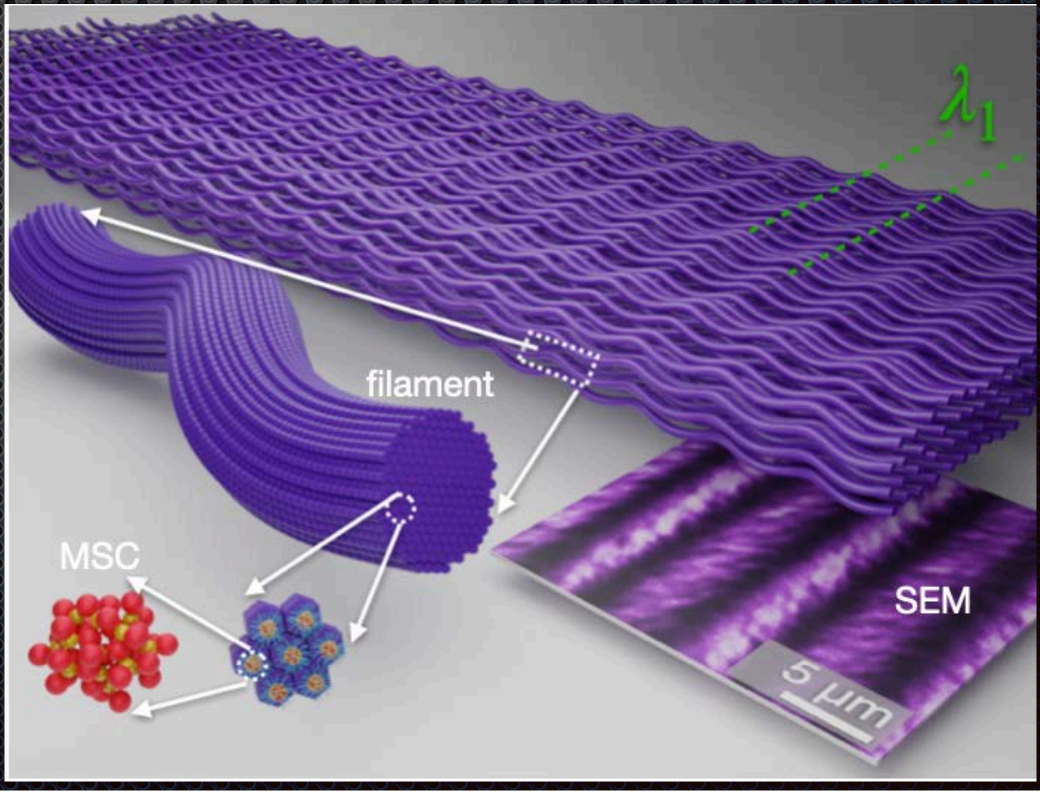
Williamson, Nevers, Nelson, Hadar, Banin, Hanrath, Robinson, Science 363, 731 (2019)

Hierarchical Assemblies of CdS magic-sized clusters



controlled evaporation-driven assembly in a 'Hele-Shaw' type cell

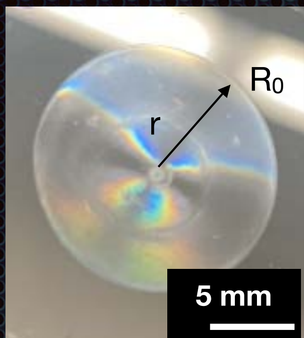


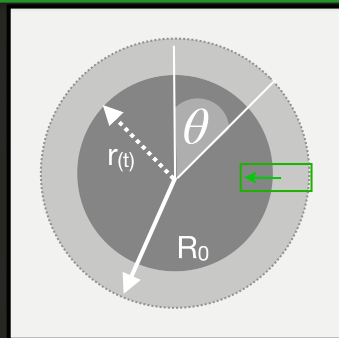


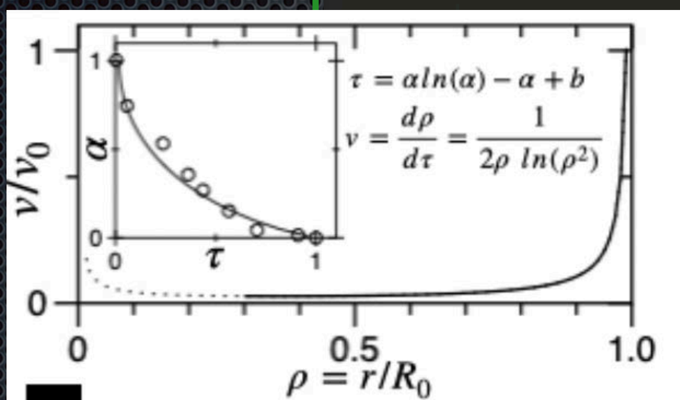
Han, …, Hanrath, Robinson,
Nature Materials, 2022, 21, 518

Hierarchical Assemblies of CdS magic-sized clusters

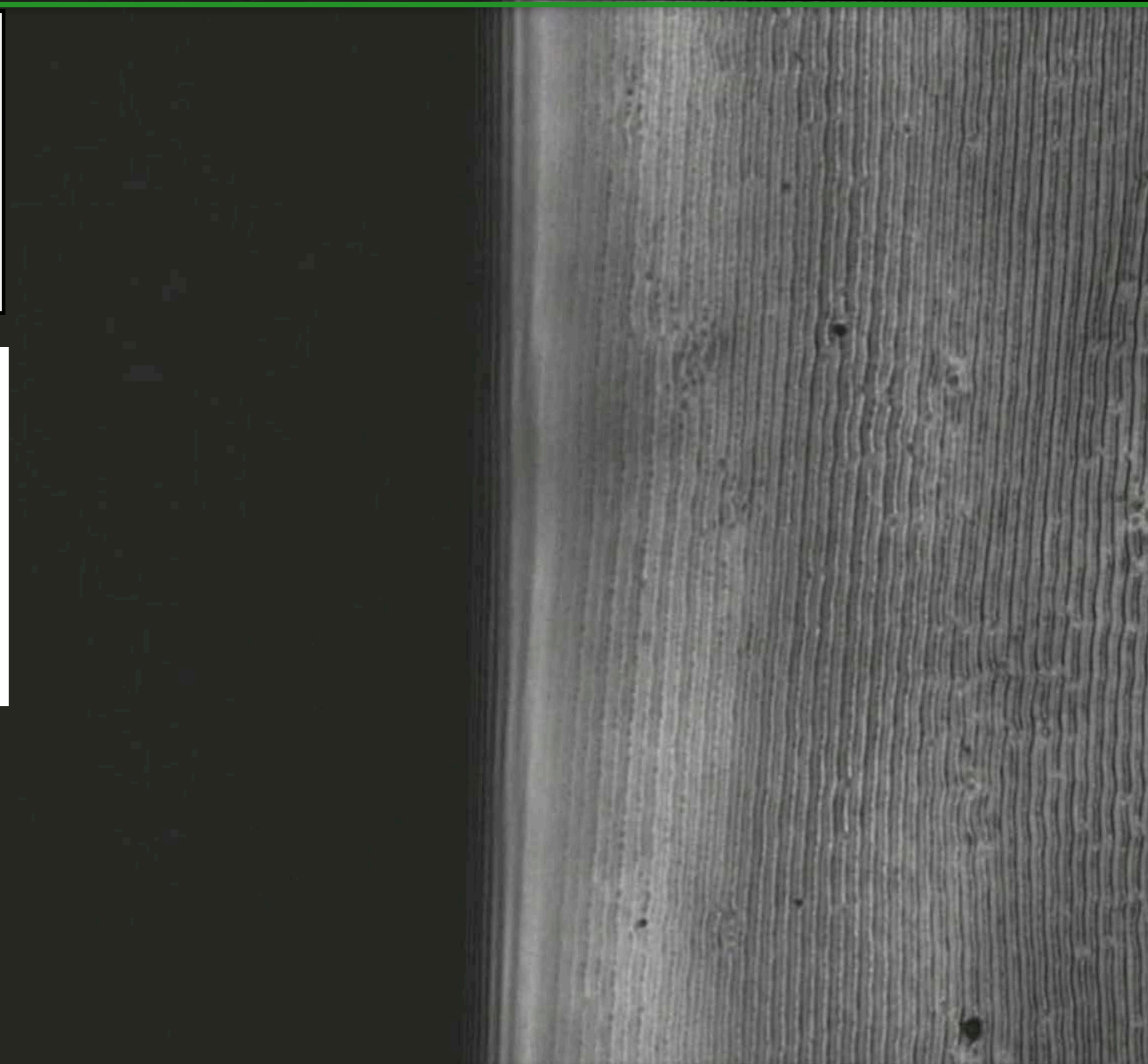
in-situ microscopy







$$Pe = \frac{R_0^2}{D_0 \tau_d}$$

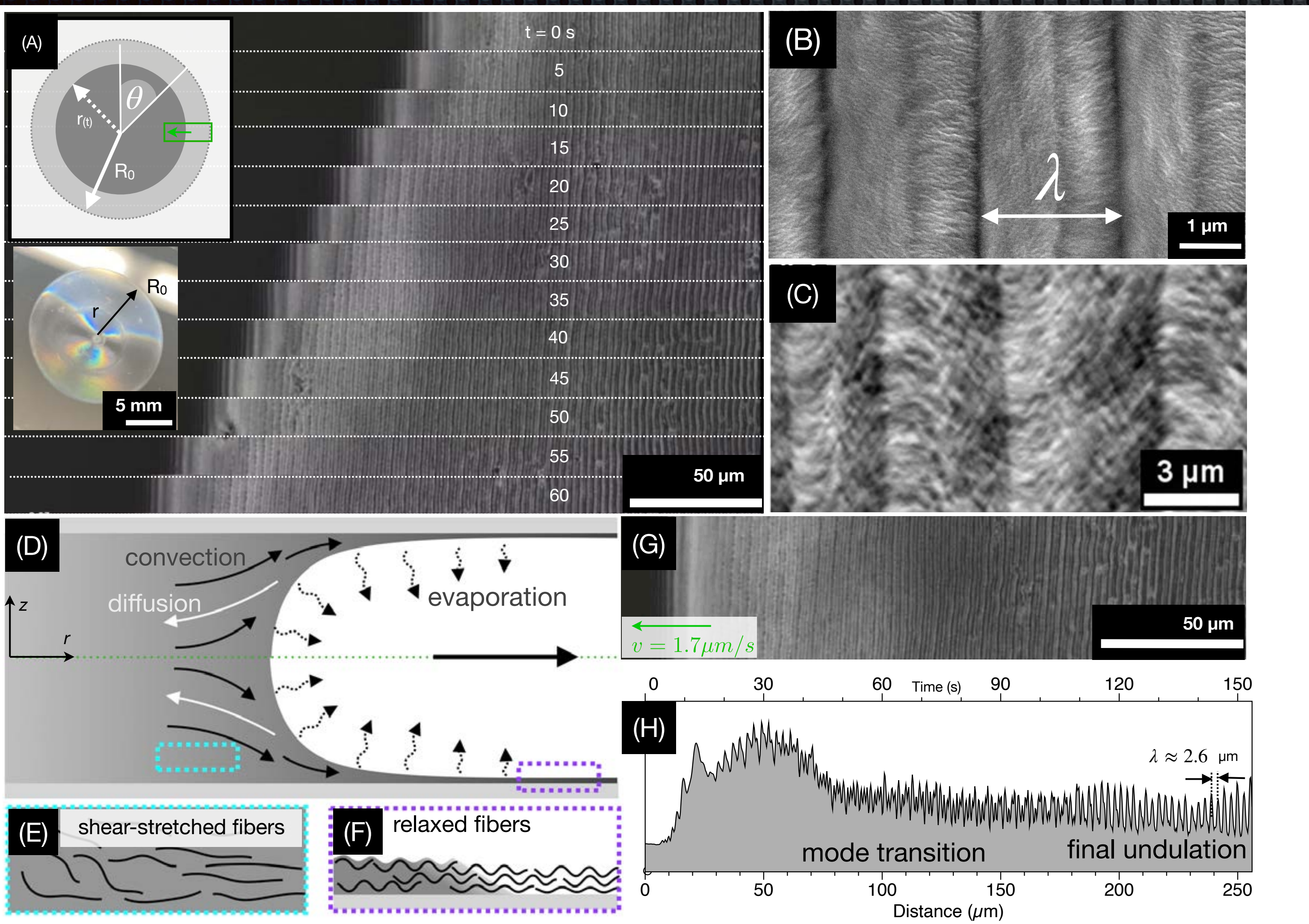


(under review)

Hierarchical Assemblies of CdS magic-sized clusters

Cornell Engineering

evolution of film structure analogies to liquid crystals



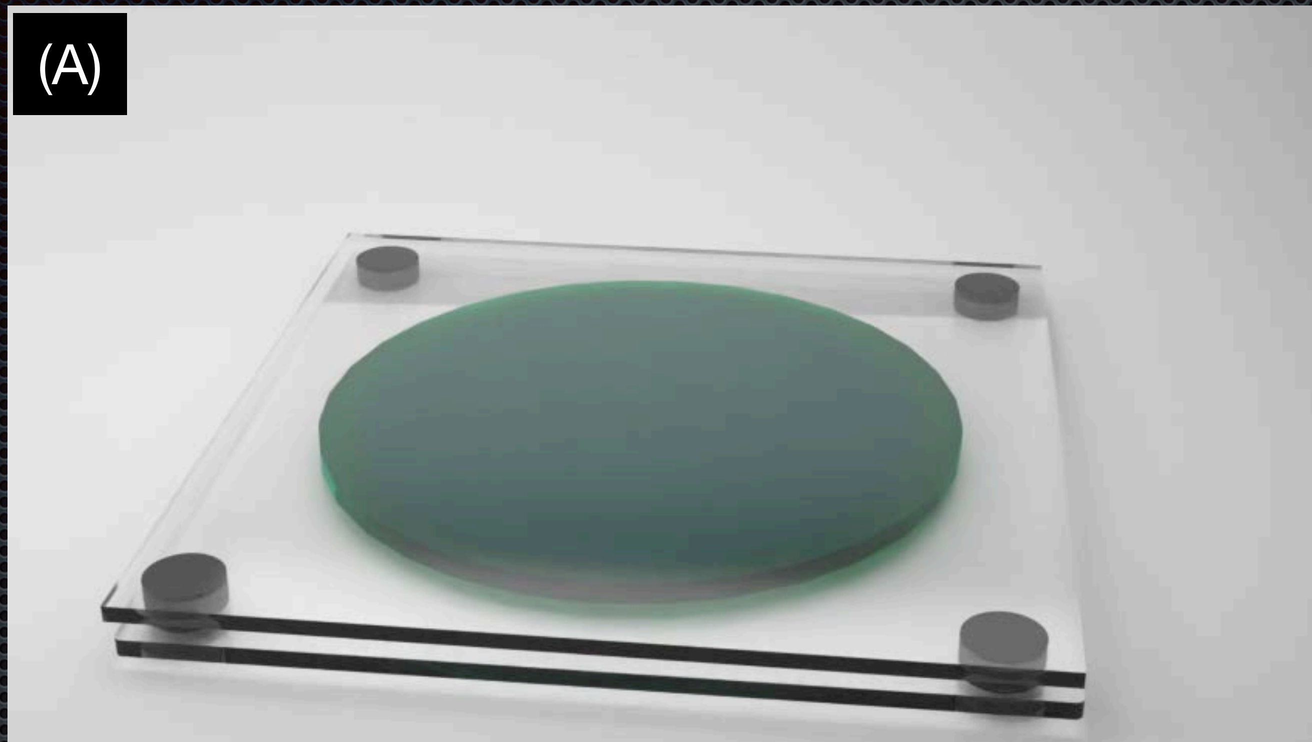
nanofiber alingment in hydrodynamic shear

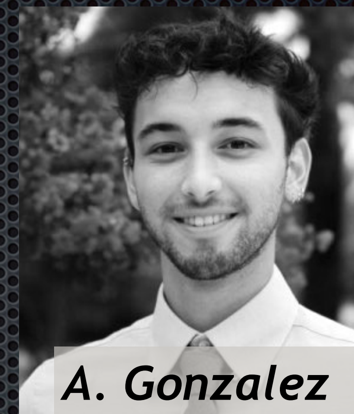
mechanical relaxation of stress

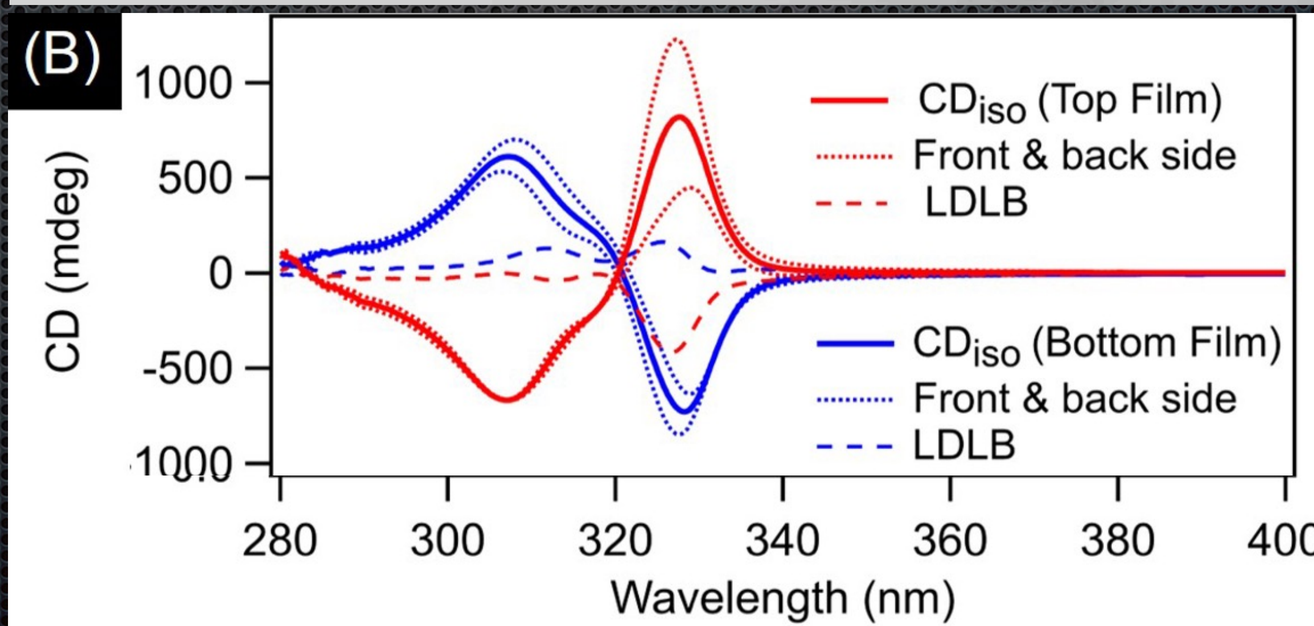
(under review)

Emergence and Inversion of Chiraliry

Cornell Engineering

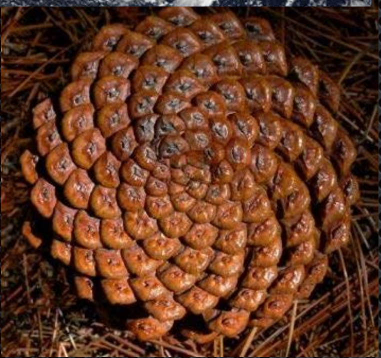


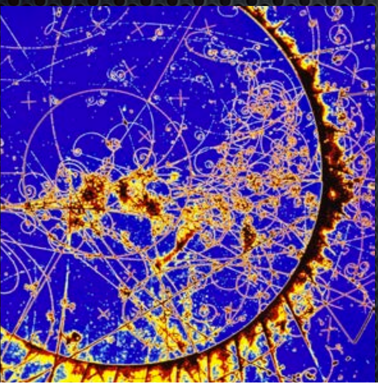


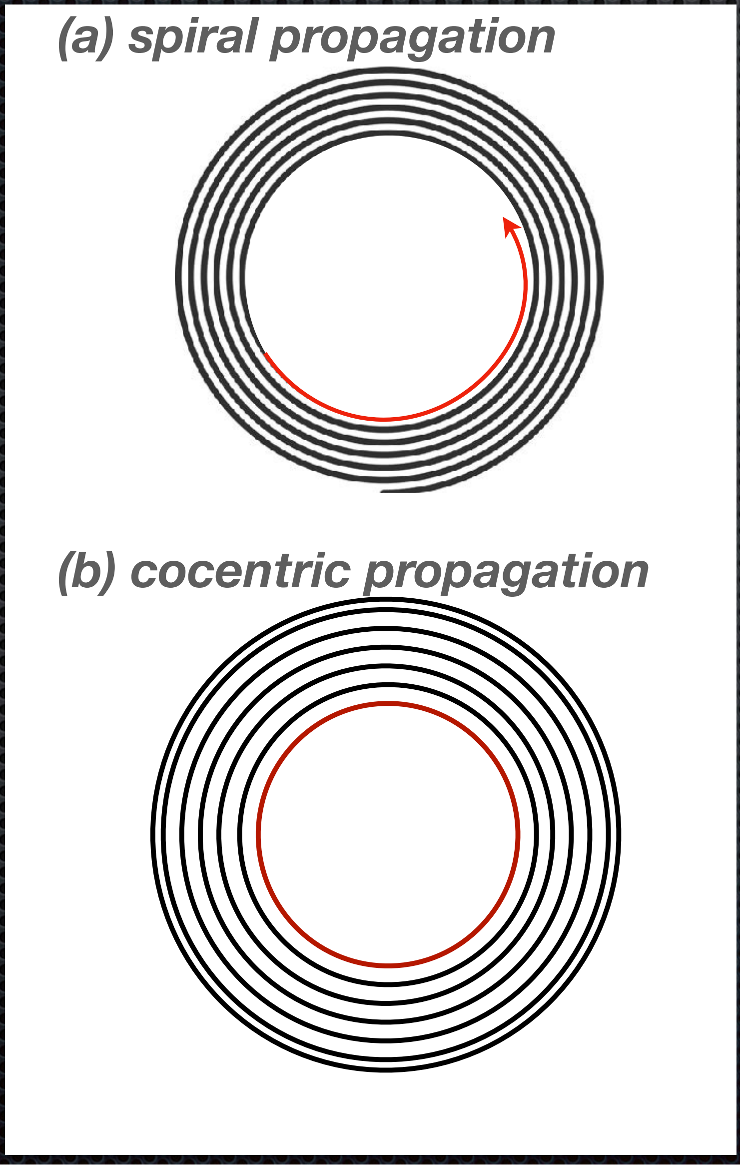


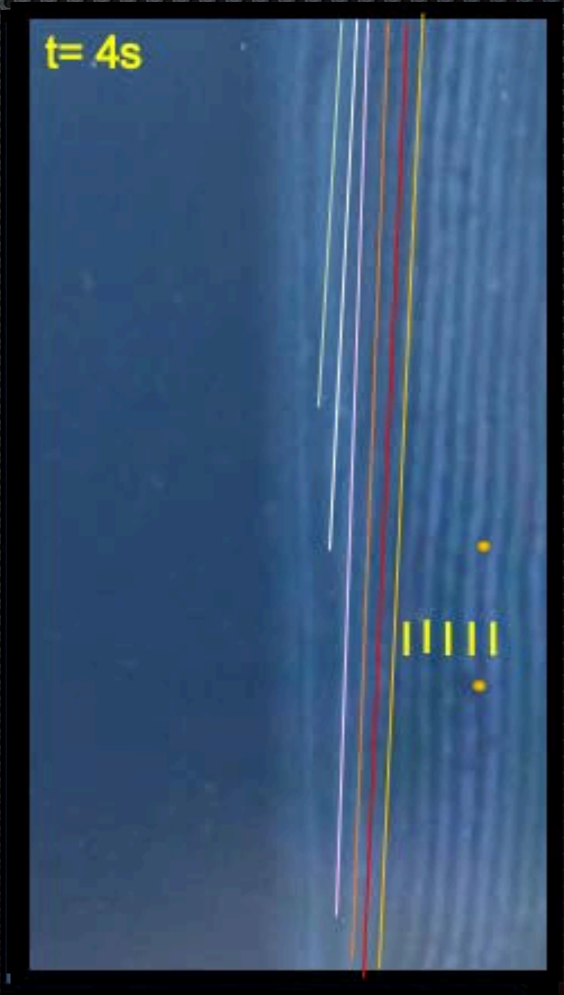
(under review)

Symmetry Breaking and Spiral Propagation



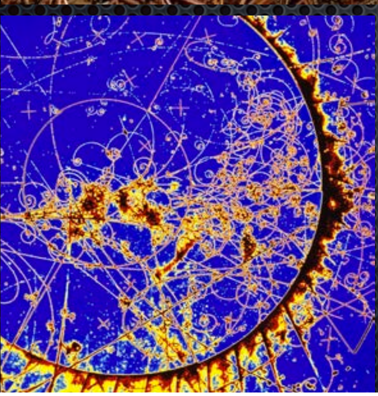




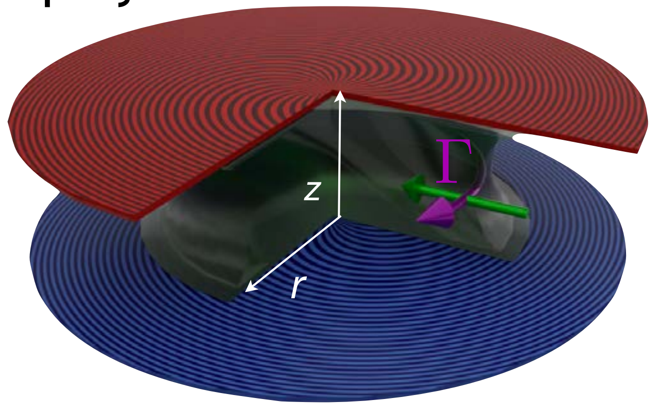


(under review)

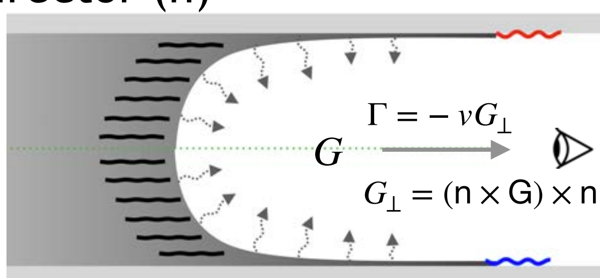
Symmetry Breaking and Spiral Propagation

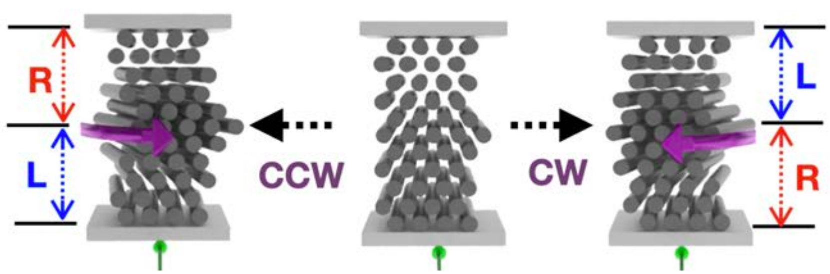


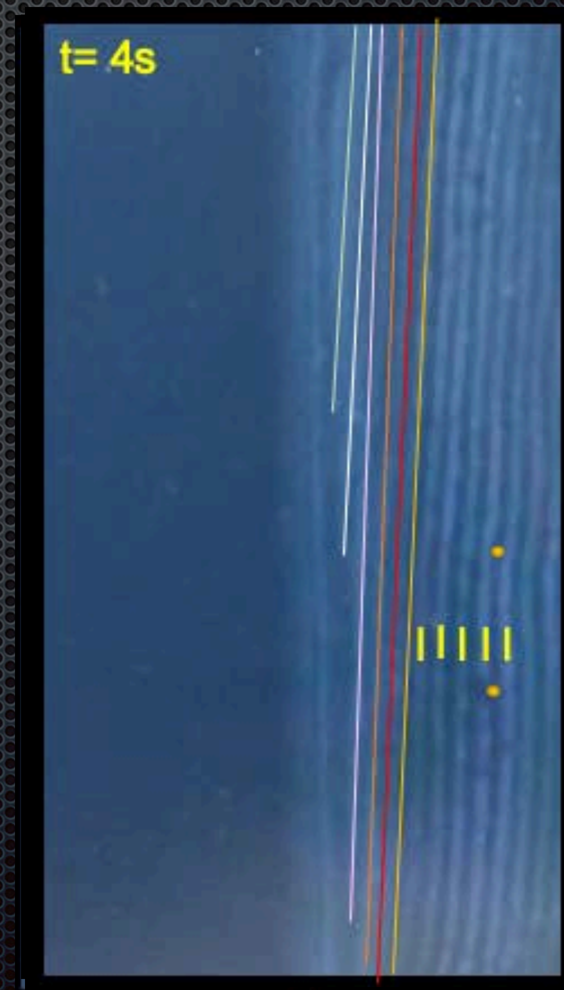
interplay of shear and torsion



Chemical Lehmann effect: coupling between chemical potential gradient (G) and director (n)

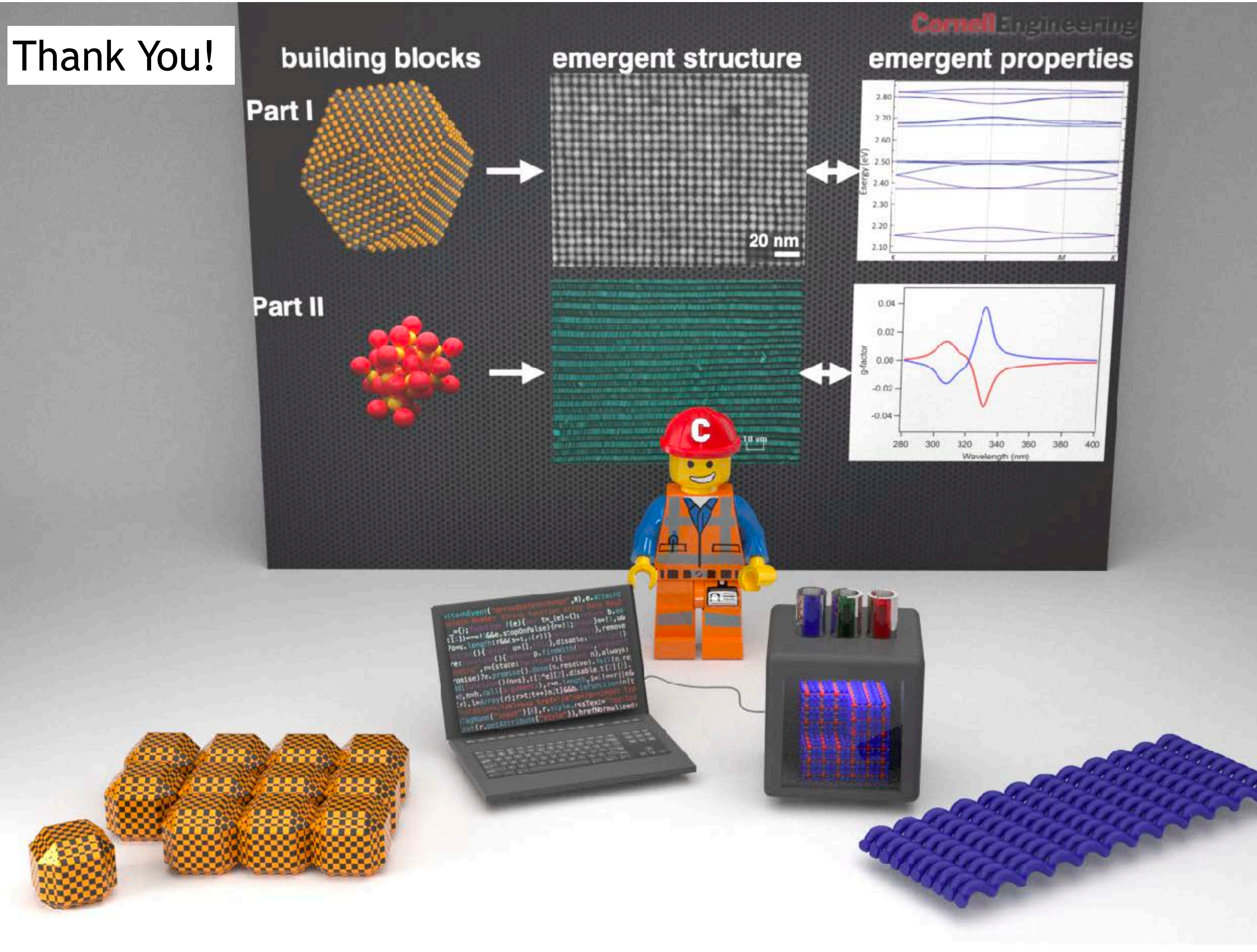






(under review)

Thank You!



Cornell Engineering
building blocks
emergent structure
emergent properties
Part I
20 nm
2.80
2.70
2.60
2.50
2.40
2.30
2.20
2.10
Energy (eV)
Part II
0.04
0.02
0.00
-0.02
-0.04
g-factor
280
300
320
340
360
380
400
Wavelength (nm)