- Nanorod polymer solar cell

  (Wendy Huynh, Janke Dittmer), Delia Milliron, Ilan Gur

  Collaboration with Prof. Jean Frechet

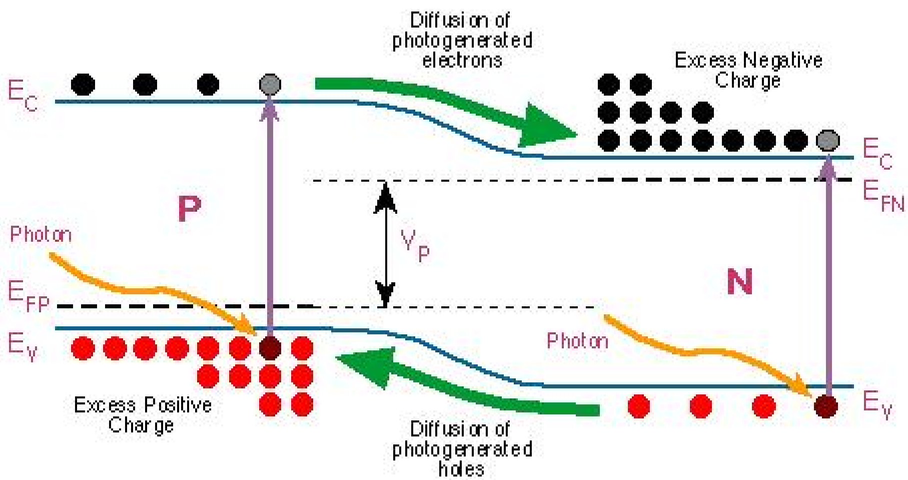
- Tetrapod Electrical Measurements

  Yi Cui, Prof. Uri Banin

Synthesis: Libero Manna, Erik Scher, Delia Milliron, Steven Hughes, Haitao Liu Antonis Kanaras

P. Alivisatos
Department of Chemistry, UC Berkeley
Molecular Foundry, Lawrence Berkeley National Lab

Conventional versus “Excitonic or Distibuted Junction” Solar Cells



•Small exciton binding energy

•High e-,h+ mobilities

•Directed paths

•“thick films”

•Rigid

•Must be made by vacuum deposition

•High exciton binding energy

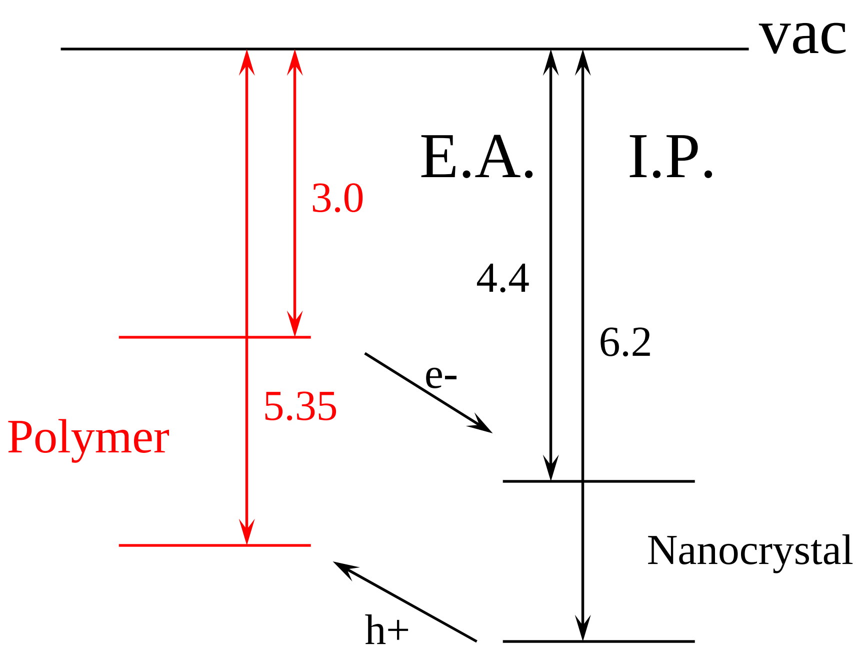
•Hopping conductivity/low mobility

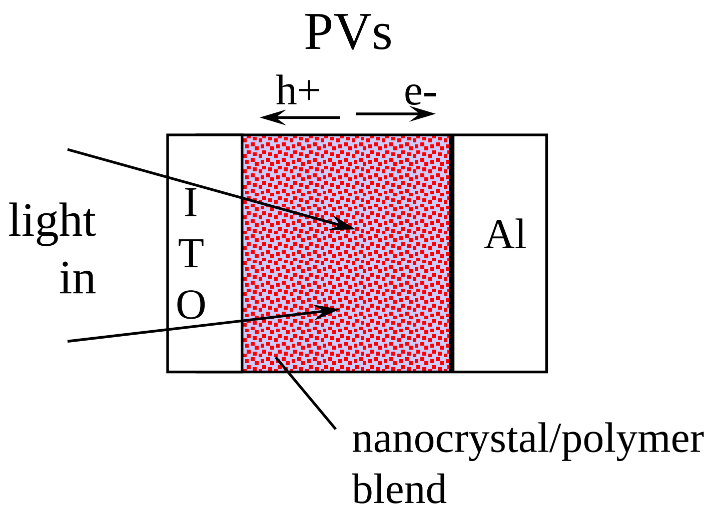
•Enhanced Oscillator strength
– thin films (~100 nm)

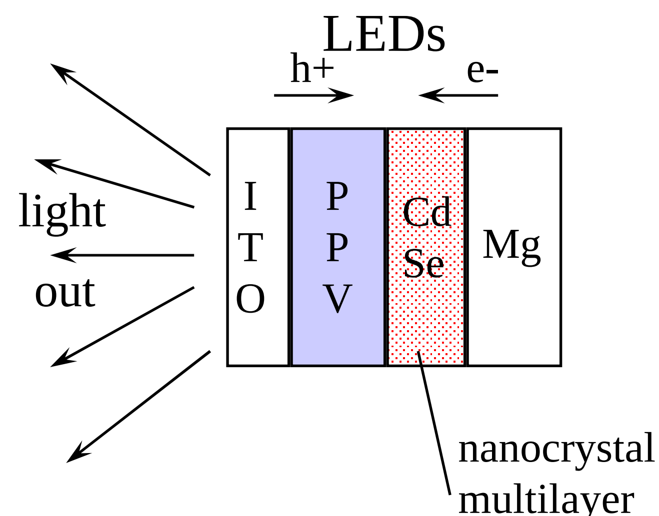
•Flexible (1 inch bend radius)

•All solution processing

Semiconductor Nanocrystals and Polymers
Band Offsets and Electrical Devices

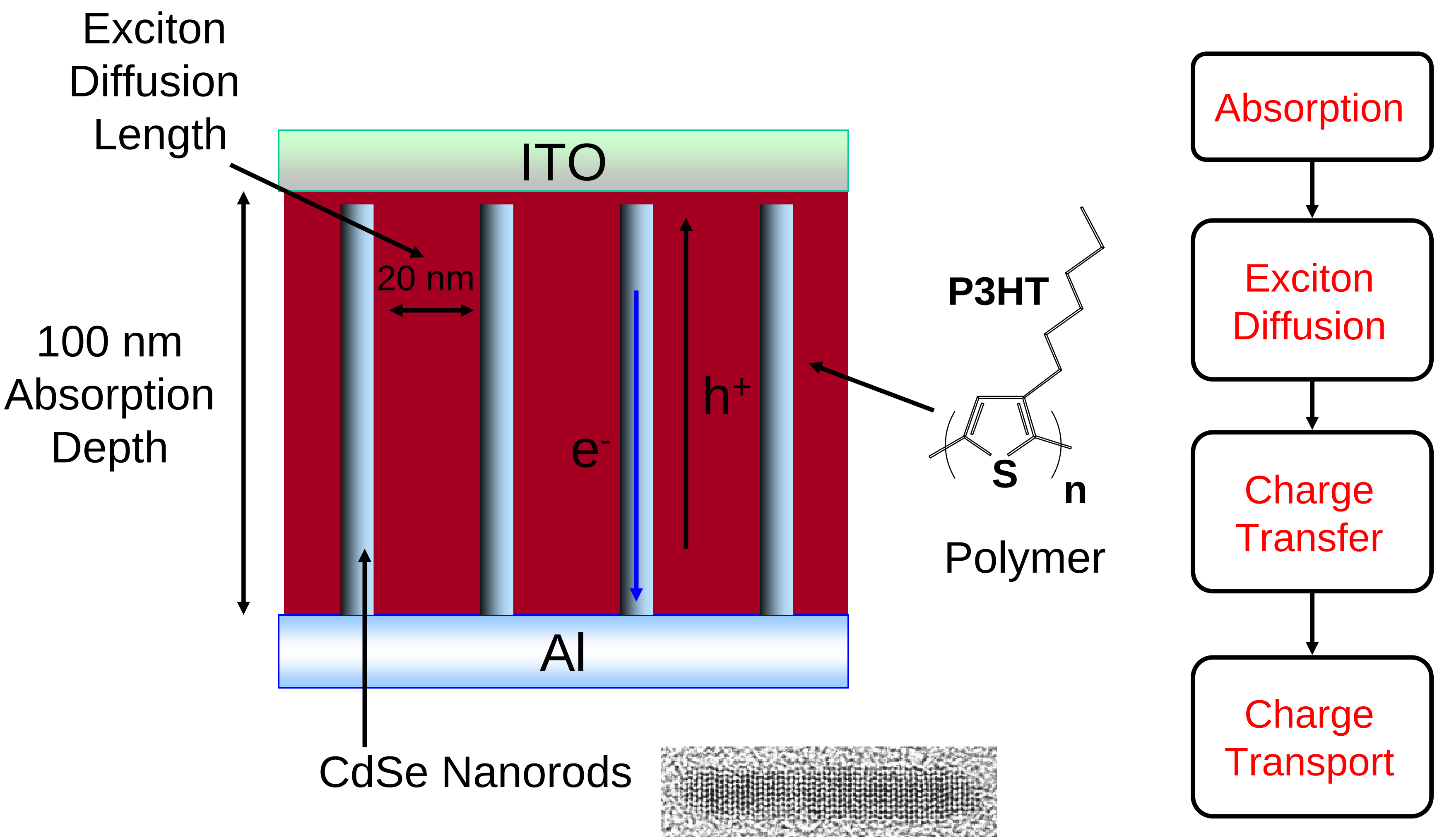






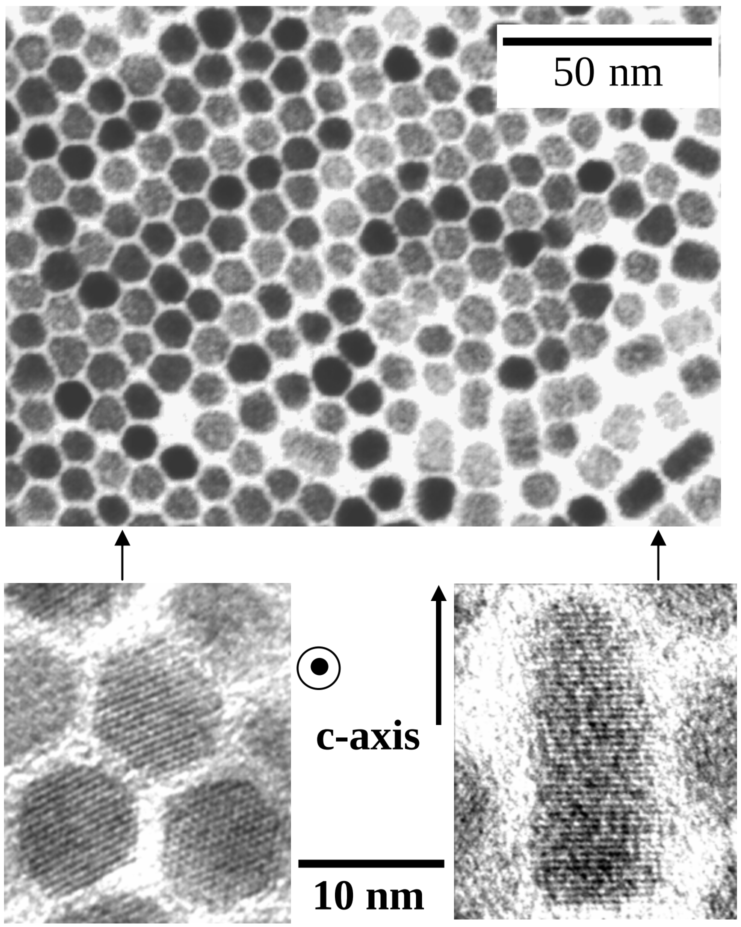
Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P., *Nature* **1994**, *370*, 354-357.
Schlamp, M. C.; Peng, X.; Alivisatos, A. P., *J. Appl. Phys.* **1997**, *82*, 5837-5842.

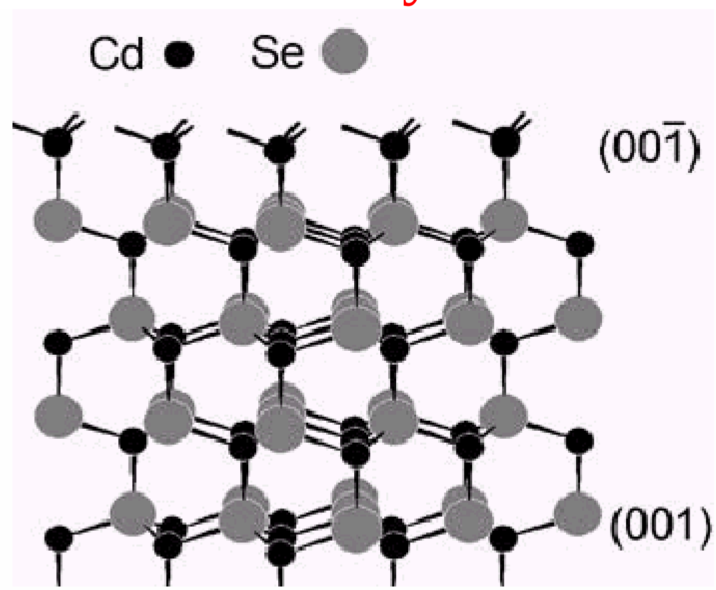
Self-assembled Nanorod-Polymer Photovoltaics



Transport: Bicontinuous Network

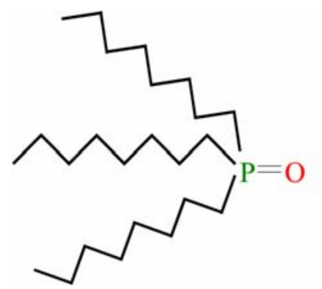
Faceting in Hexagonal CdSe Nanocrystals



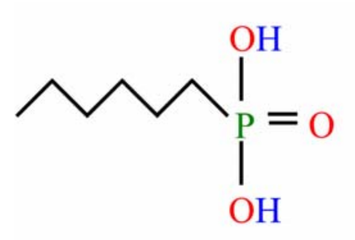


binary surfactant mixture

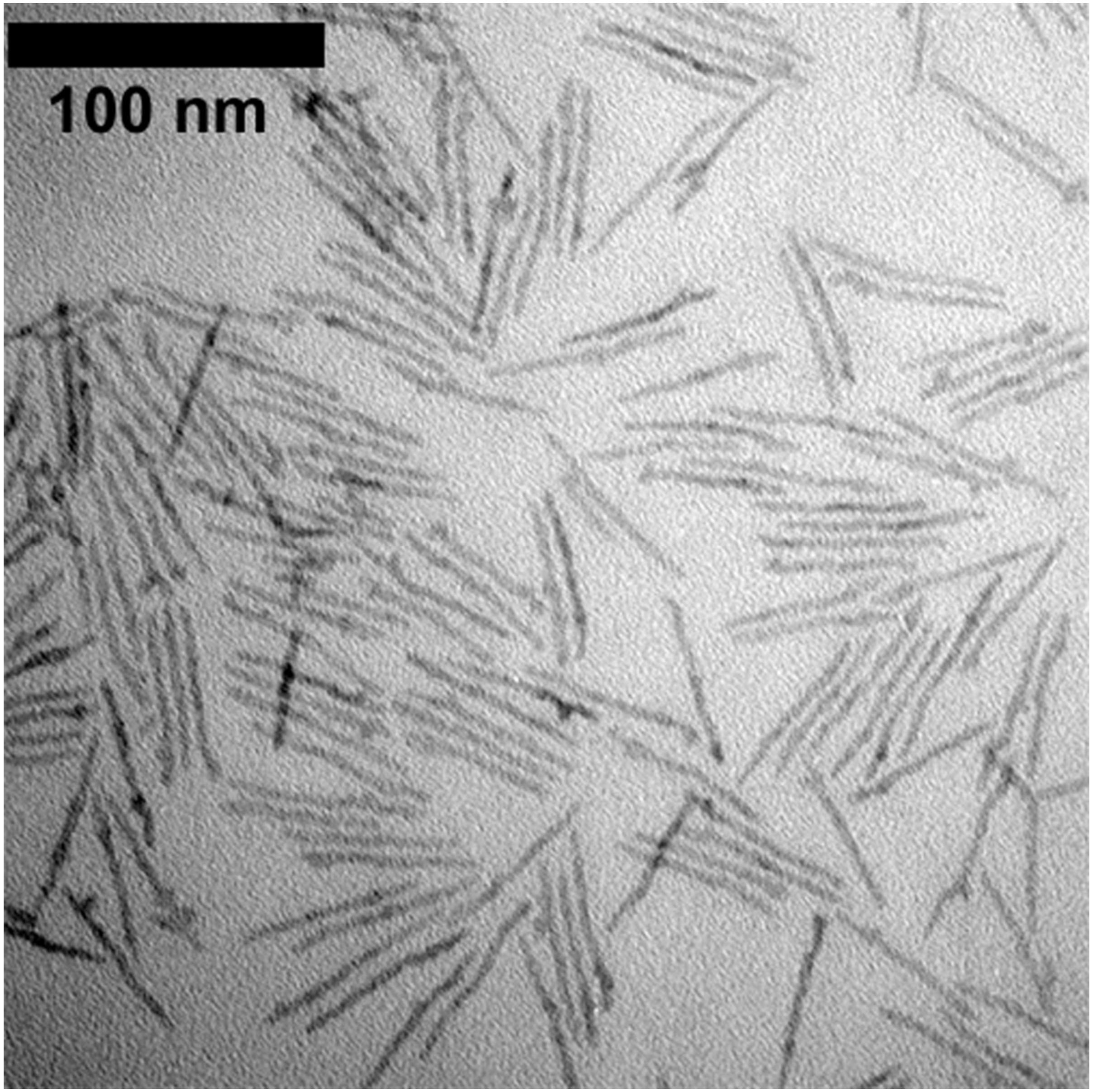
Tri-octyl
phosphine oxide
(TOPO)



Hexyl phosphonic acid
(HPA)



CdSe rods



Peng, X. G.; Manna, L.; Yang, W. D.; Wickham, J.; Scher, E. Kadavanich, A. P. Alivisatos, *Nature* **2000**, *404*, 59-61.

Simulations of Selective Adhesion

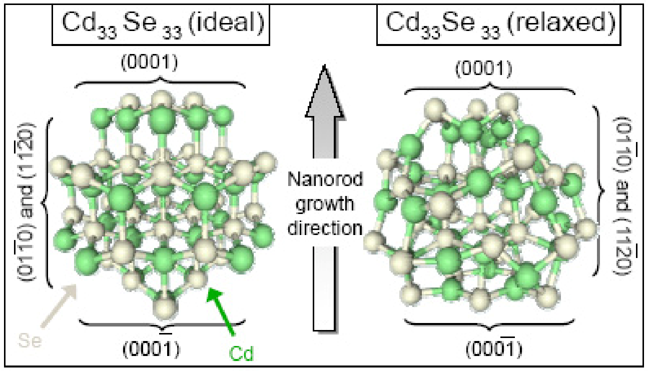
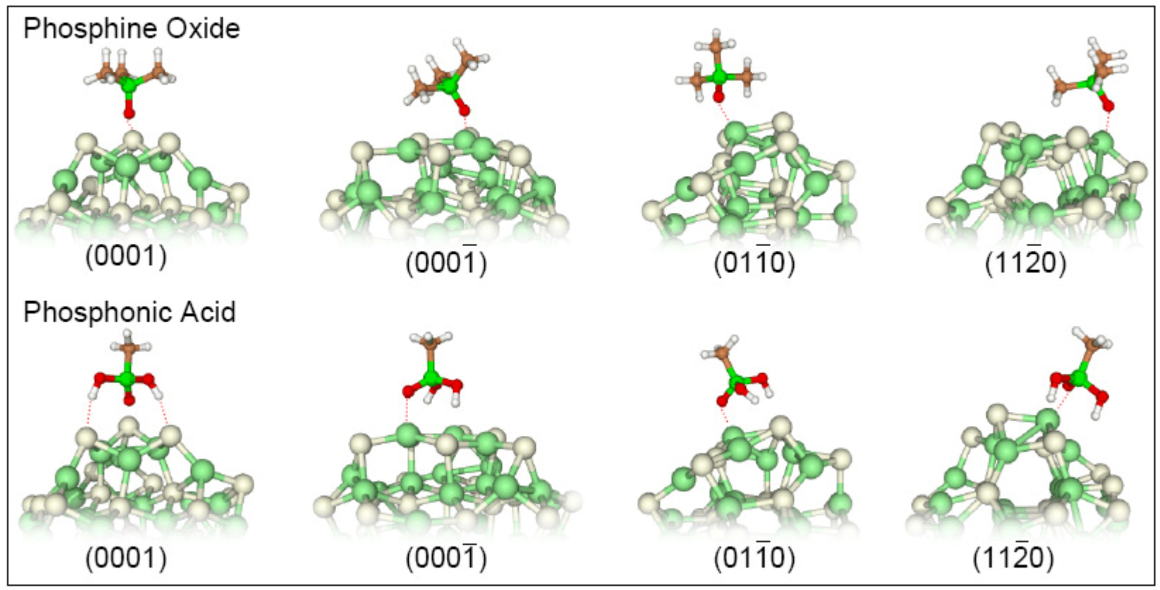


FIG. 1: Ideal wurtzite and relaxed structure of $Cd_{33}Se_{33}$ showing the (0001),$(000\bar{1})$, $(01\bar{1}0)$ and $(11\bar{2}0)$ facets to which ligands are attached. Cd (Se) atoms are shown in green (gray).

	$Cd_{15}Se_{15}$		$Cd_{33}Se_{33}$			
	$(000\bar{1})$	(0001)	$(000\bar{1})$	(0001)	$(01\bar{1}0)$	$(11\bar{2}0)$
Ligand	Cd	Se	Cd	Se	Cd/Se	Cd/Se
PO	1.06	0.66	0.85	0.63	1.23	1.37
PA	1.12	0.66	1.11	0.67	1.45	1.26
CA	0.68	0.42				
TMA	0.91	1.05				

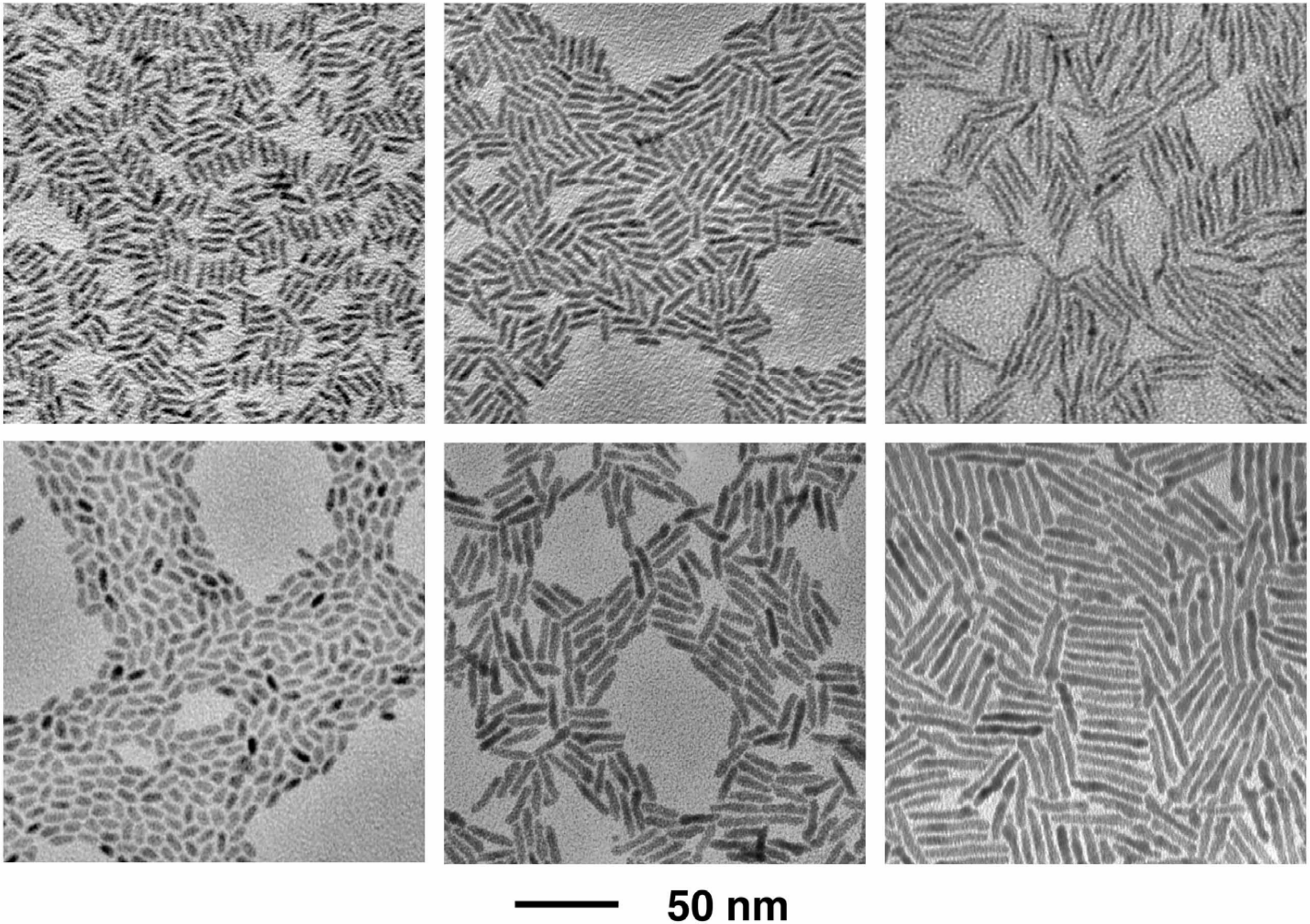
TABLE I: Calculated binding energies of phosphine oxide (PO), phosphonic acid (PA), carboxylic acid (CA) and trimethylamine (TMA) ligands to the (0001),$(000\bar{1})$, $(01\bar{1}0)$ and $(11\bar{2}0)$ facets of $Cd_{15}Se_{15}$ and $Cd_{33}Se_{33}$ quantum dots. All binding energies in eV.



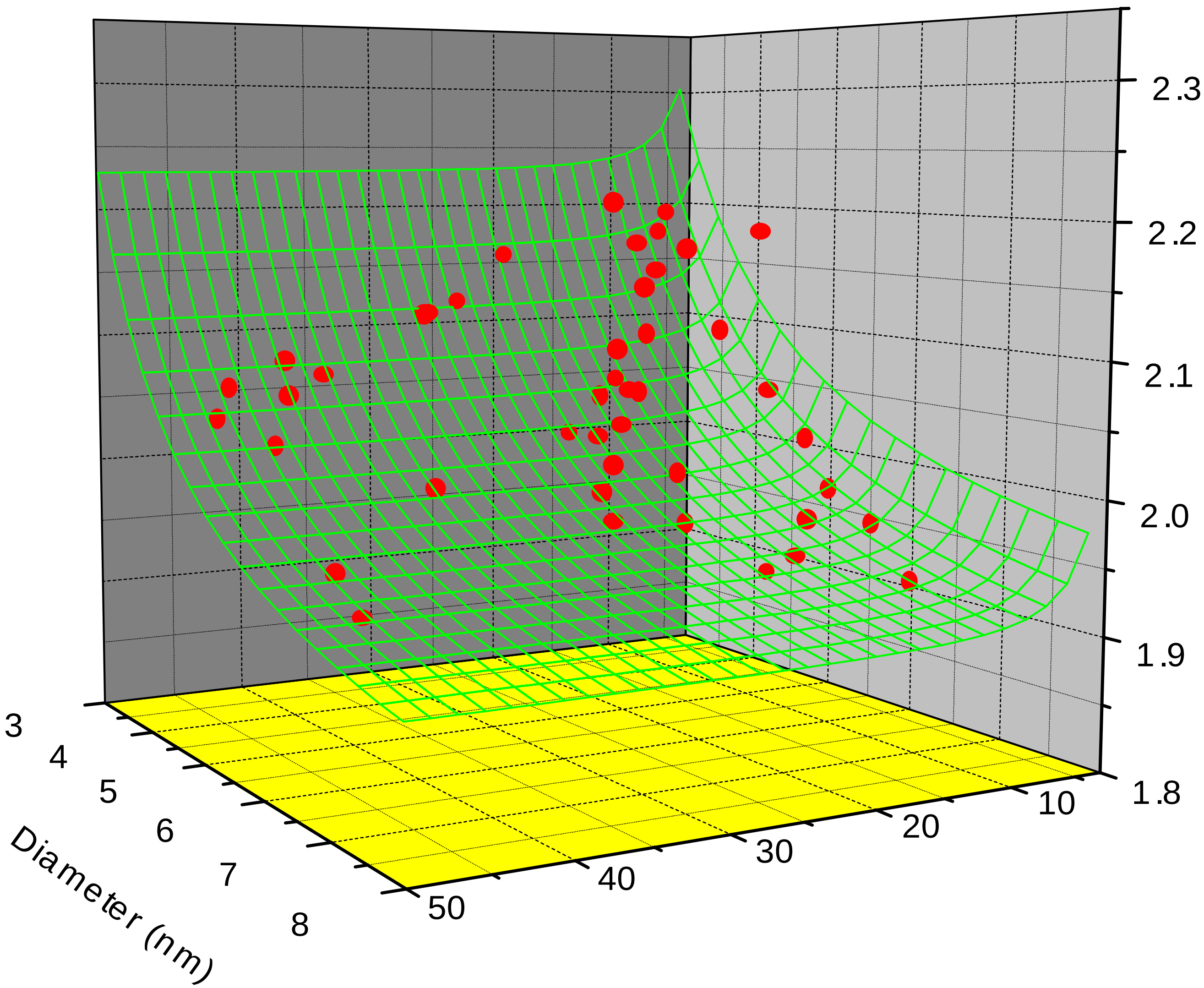
Aaron Puzder, Andrew J. Williamson, Natalia Zaitseva, and Giulia Galli
Lawrence Livermore National Laboratory

planewave implementation of density functional theory.

Independent control of length and diameter

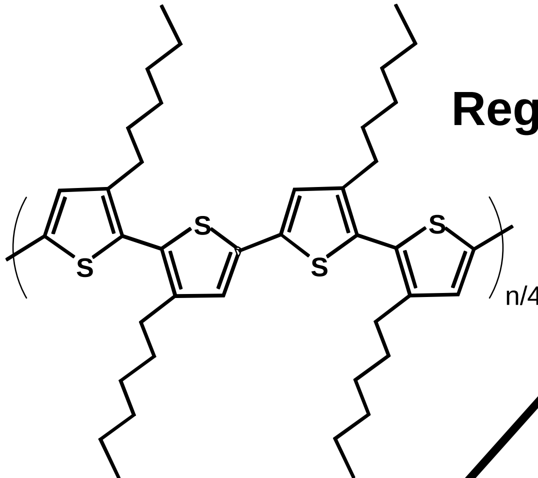


Bandgap vs. width and length

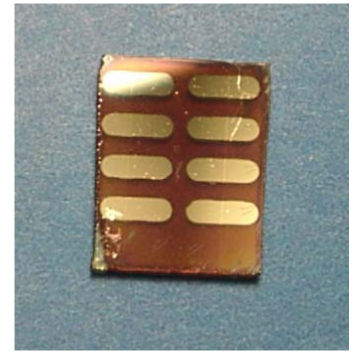


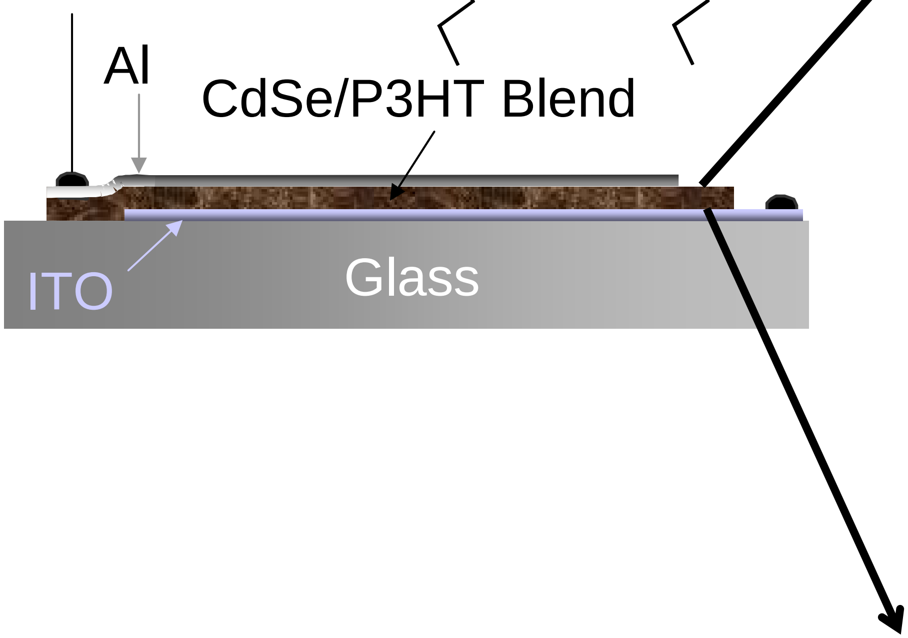
Li, L. S., J. T. Hu, W. D. Yang and A. P. Alivisatos (2001). "Band gap variation of size- and shape-controlled colloidal CdSe quantum rods." Nano Letters **1**(7): 349-351.

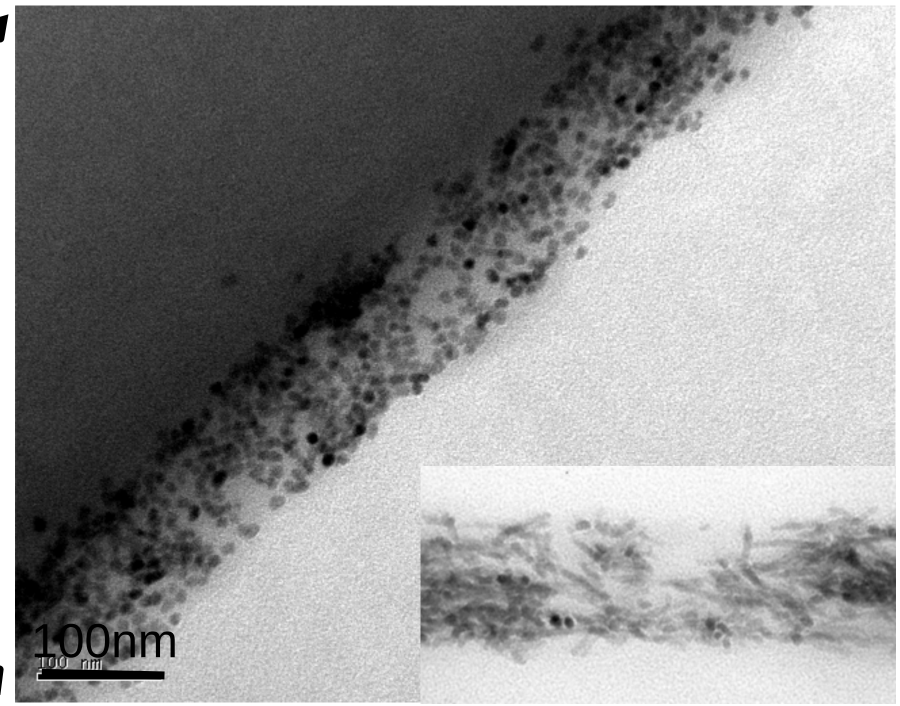
Nanocrystal/Polymer Solar Cells



Regioregular P3HT

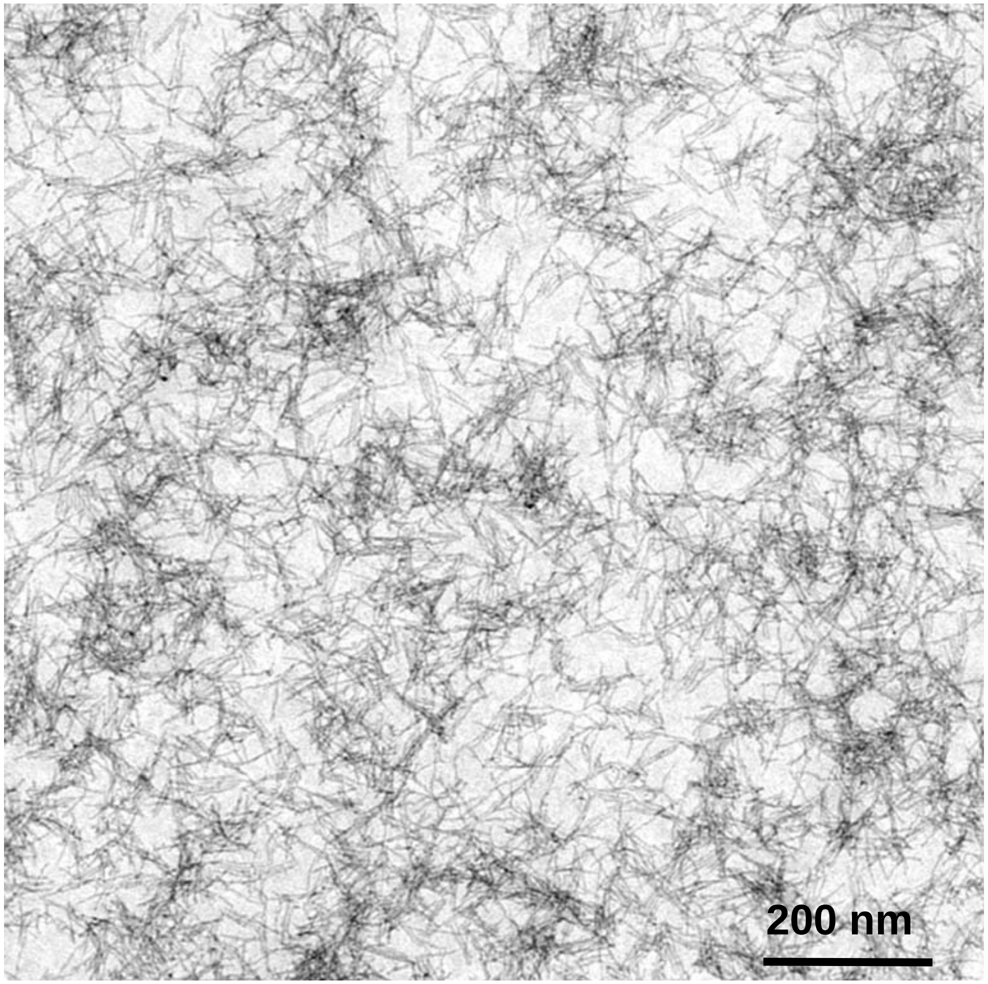






Huynh, W. U., J. J. Dittmer, Alivisatos (2002). "Hybrid nanorod-polymer solar cells." Science **295**(5564): 2425-2427.

CdSe nanorod/P3HT films

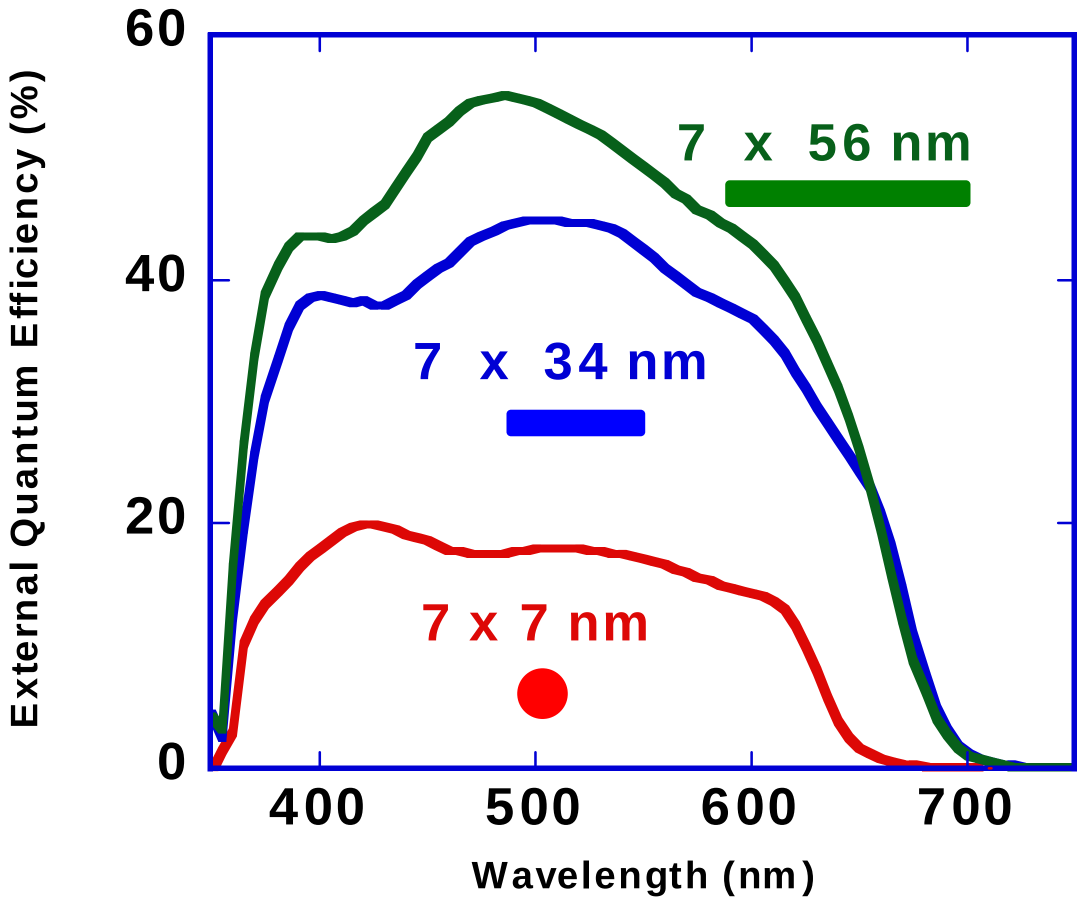


spin cast from 8% pyridine 92% chloroform solvent mixture

Huynh, W. U., J. J. Dittmer, W. C. Libby, G. L. Whiting and A. P. Alivisatos (2003).

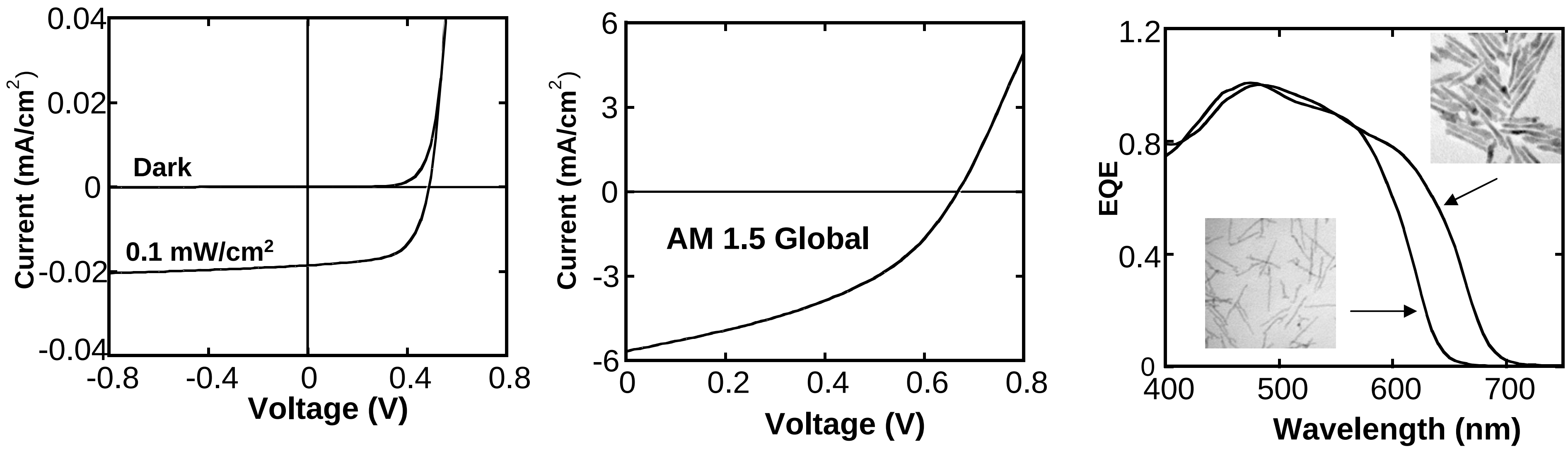
"Controlling the morphology of nanocrystal-polymer composites for solar cells." Advanced Functional Materials **13**(1): 73-79.

Shape and Performance



Measured at low intensity ~ 0.1 mW/cm^2

Plastic/Nanorod Solar Cell Power Efficiency



AM 1.5 Efficiency

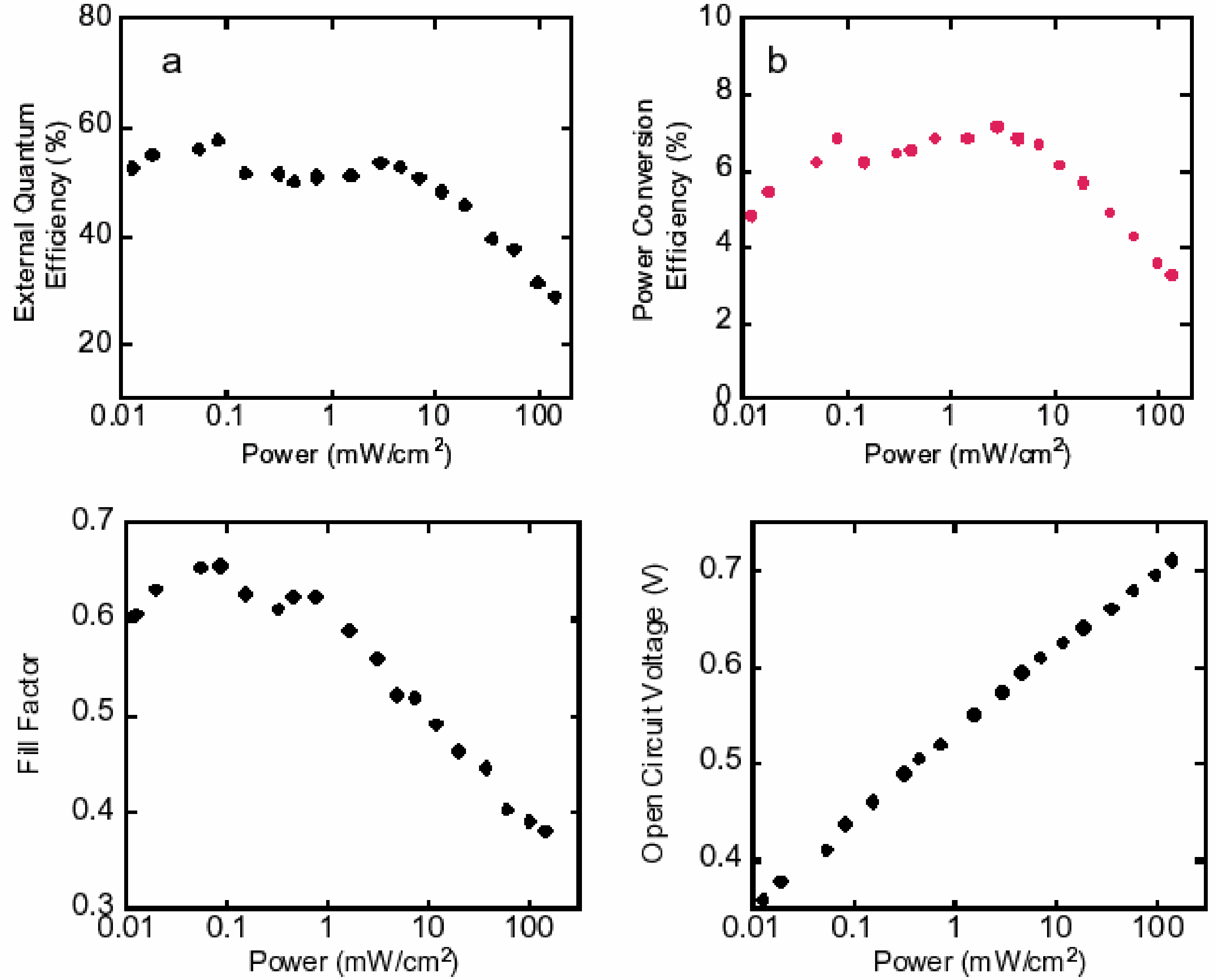
Power Conversion: **1.7%**

Short Circuit Current: 5.8 mA/cm^2

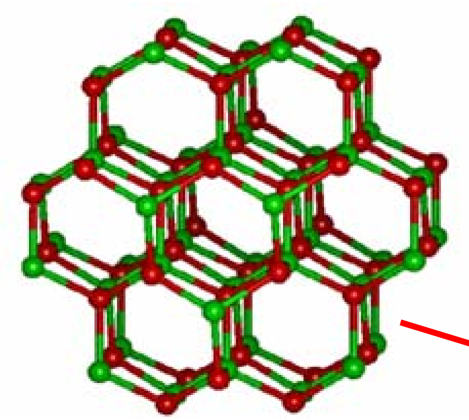
Fill Factor: 0.42

Voc : 0.67 V

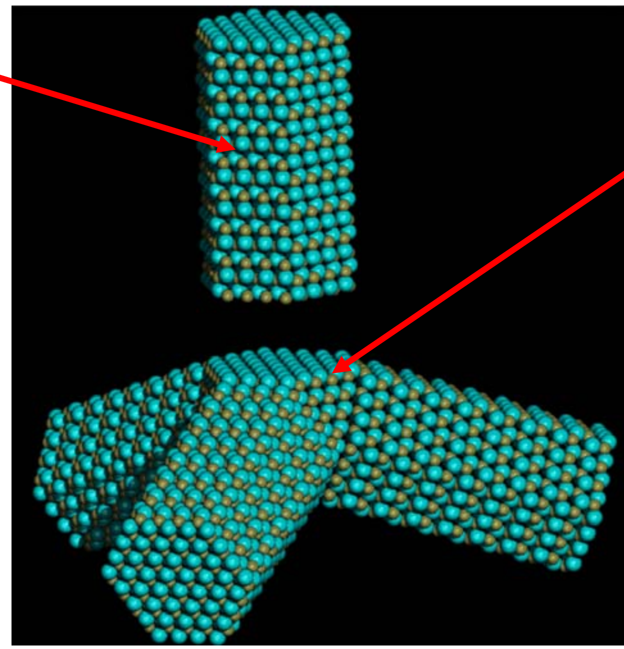
Intensity Dependence

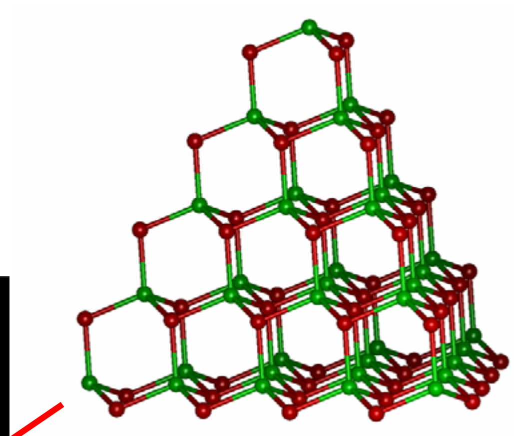


Wurtzite and Zinc Blende polytypism
a mechanism for branching II-VI nanocrystals



WZ
Stabilized by surfactant
Growth in WZ



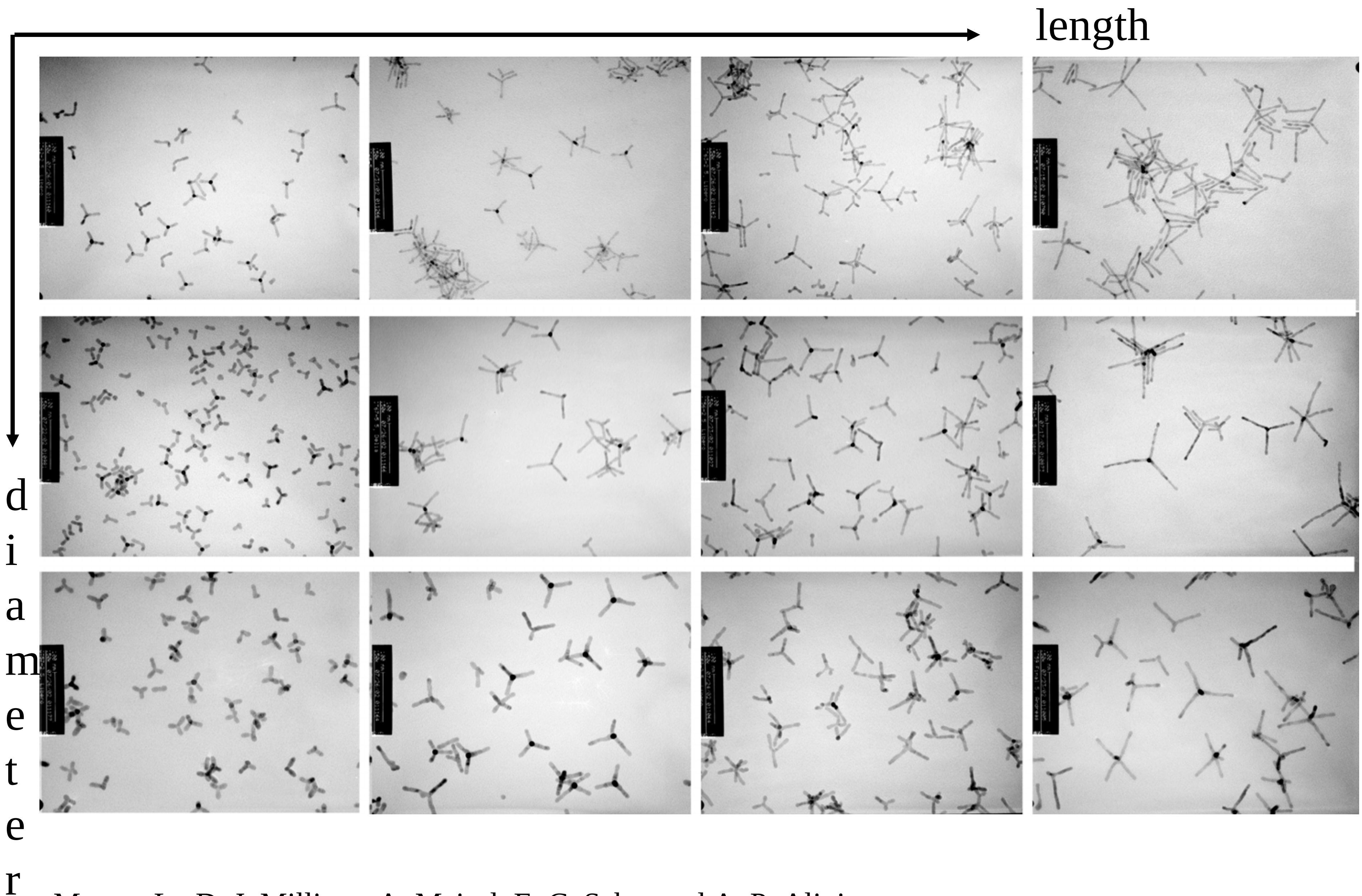


ZB
More stable by 7meV/unit cell
nucleation in ZB

Manna, L., E. C. Scher, et al. (2000). "Synthesis of soluble and processable rod-, arrow-, teardrop-, and tetrapod-shaped CdSe nanocrystals." Journal of the American Chemical Society **122**(51): 12700-12706.

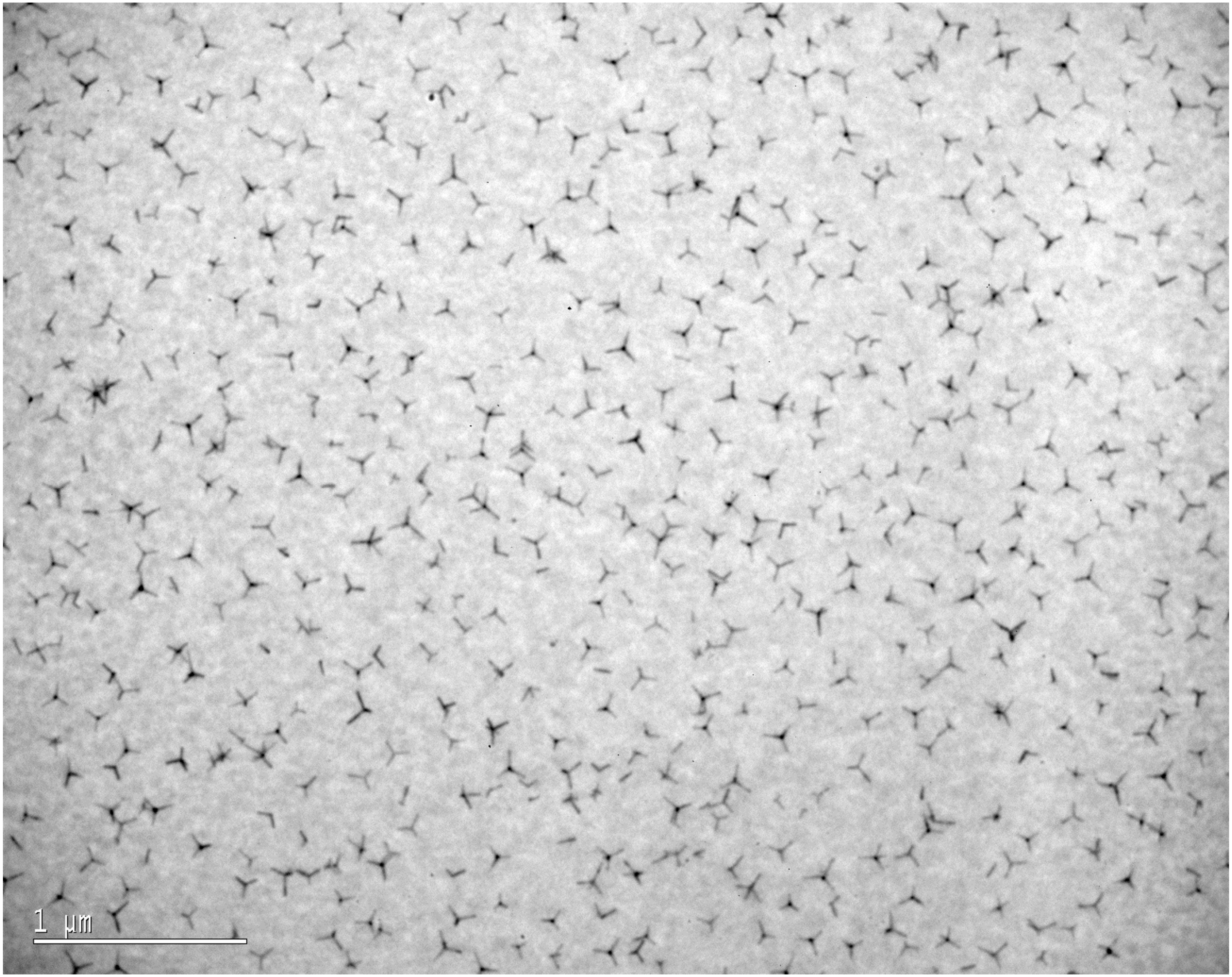
Manna, L., D. J. Milliron, et al. (2003). "Controlled growth of tetrapod-branched inorganic nanocrystals." Nature Materials **2**(6): 382-385.

CdTe Tetrapods

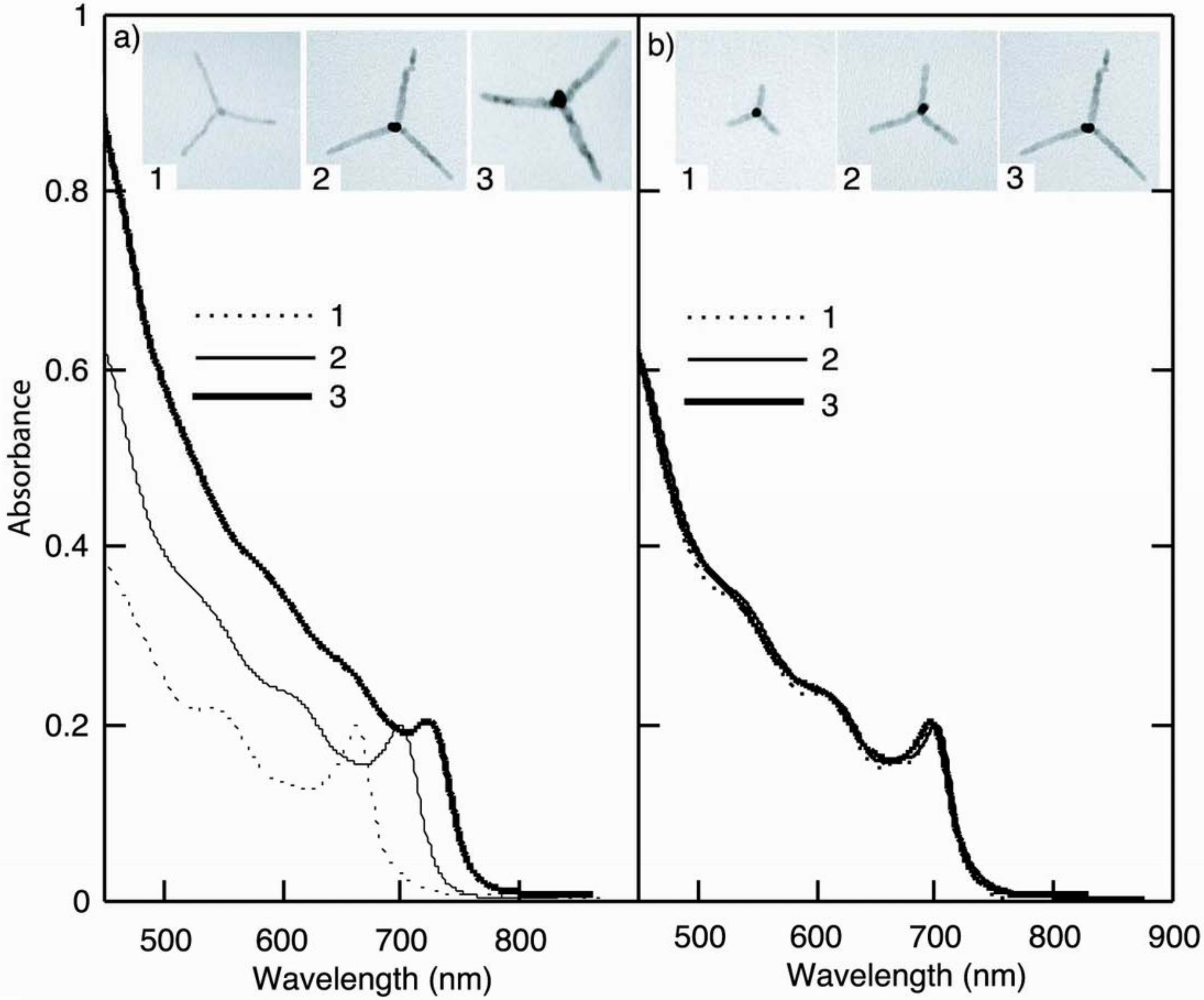


Manna, L., D. J. Milliron, A. Meisel, E. C. Scher and A. P. Alivisatos
"Controlled growth of tetrapod-branched inorganic nanocrystals." Nature Materials 2(6): 382-385. (2003).

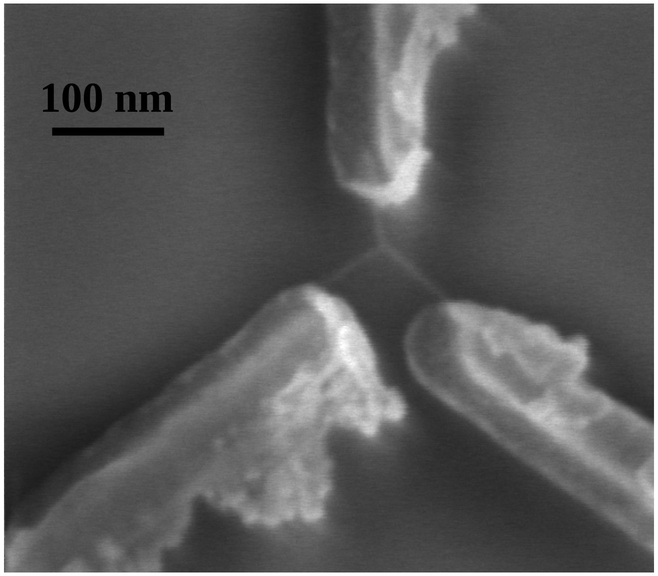
Field of Tetrapods

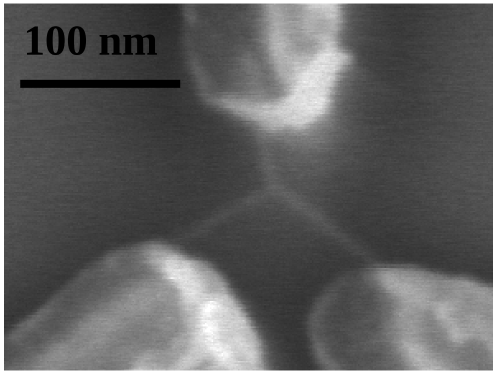


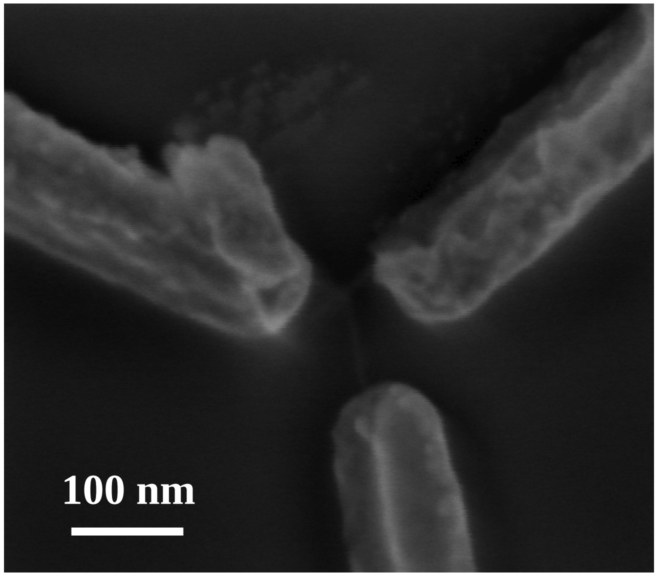
Quantum Confinement in Tetrapods

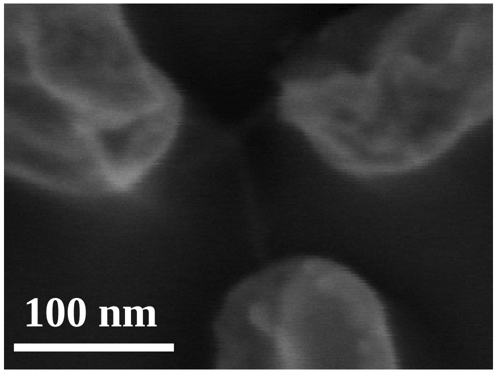


Electrical contact to tetrapods



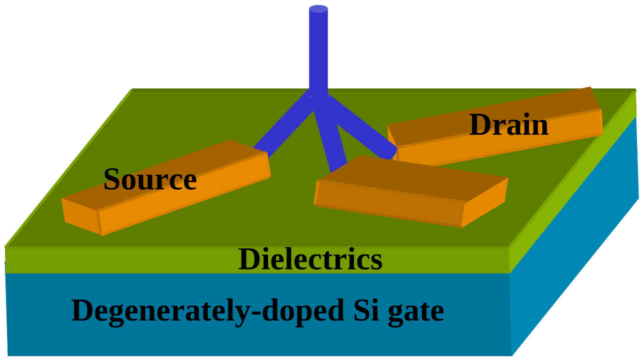


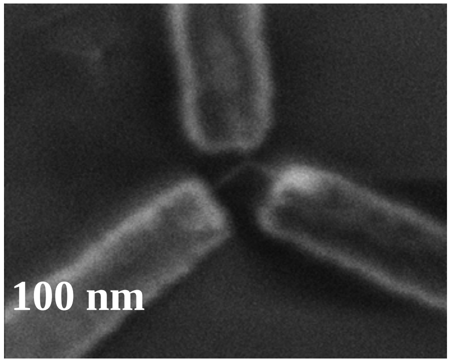


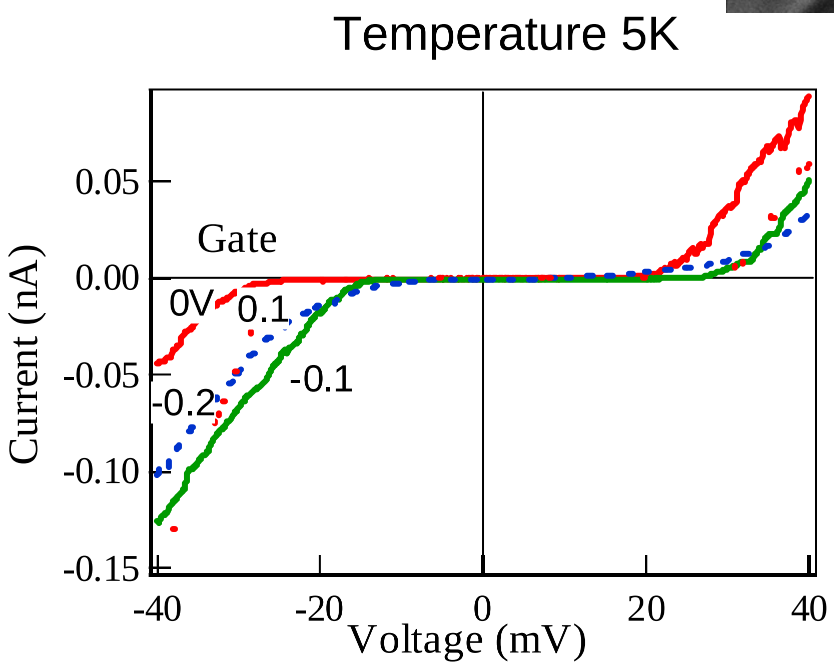


Yi Cui and Michael Bjork

Single electron charging







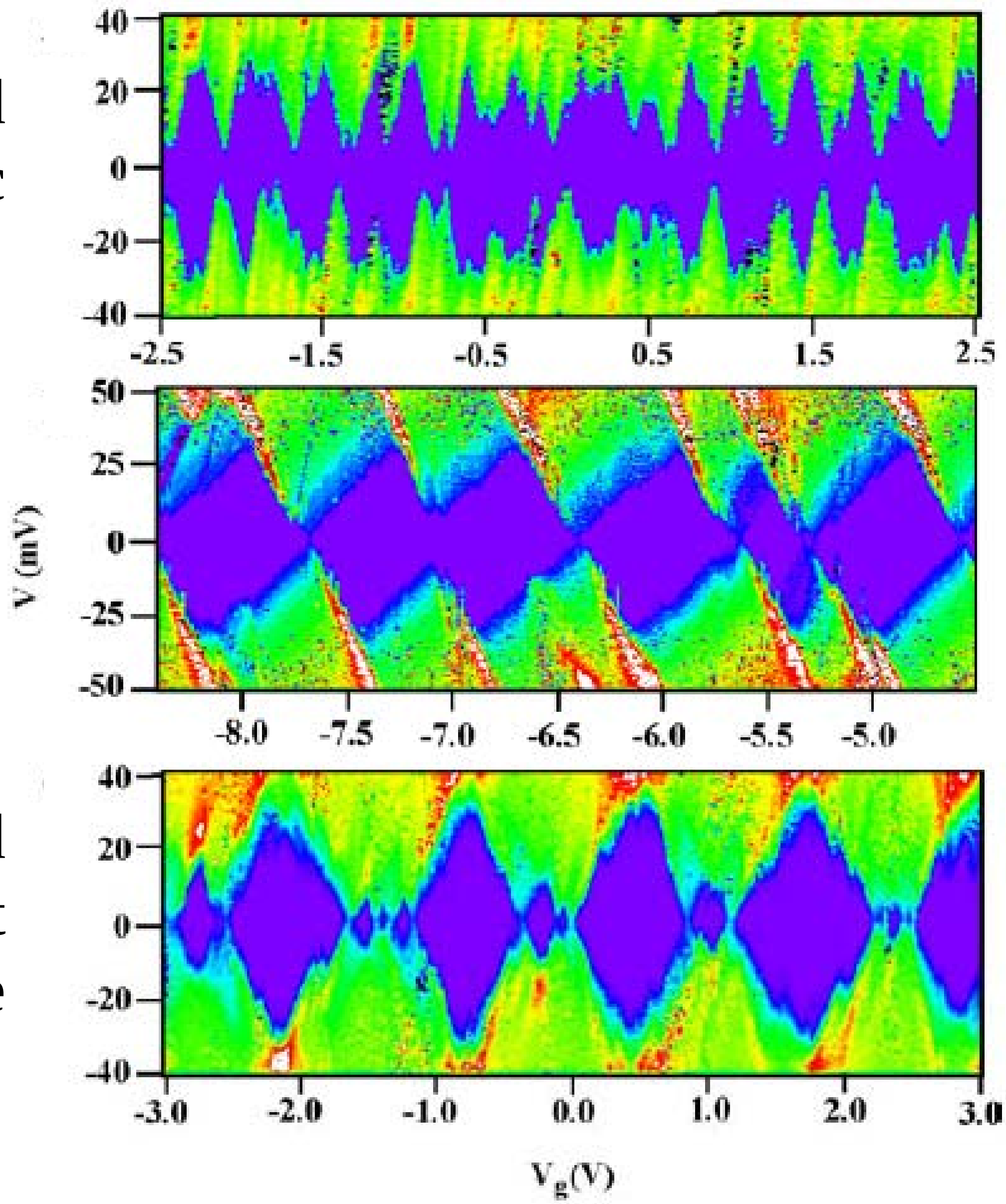
zero-conductance gap changeable by the gate voltage - the signature of single electron charging.

3D Conductance plots –Summary

Tetrapod
ionic
case

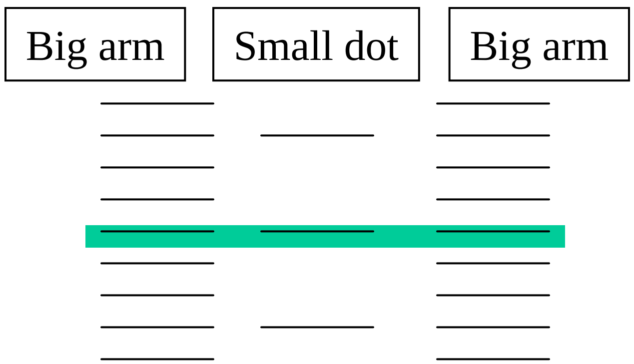
Nanorod
-“single dot”

Tetrapod
covalent
case



Types of coupling

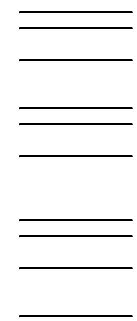
Ionic-bonding



Current can flow only if the charging energy levels of **three energy ladders** line up within bias or temperature window.

High coupling resistance

Covalent bonding

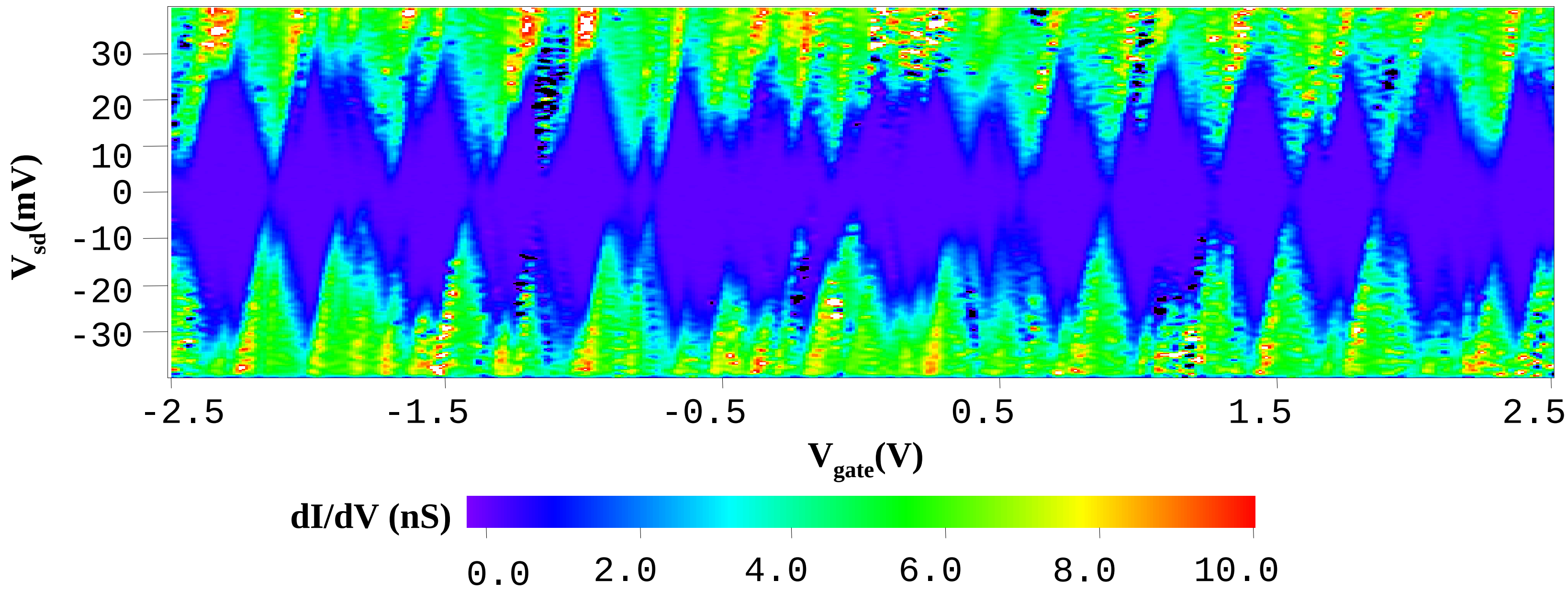


Three dots merge into single big quantum dot with distinct polarization energy. There is only one **energy ladder**

Low coupling resistance ~ quantum resistance

Signatures of a coupled system –|ionic case

Temperature 5K



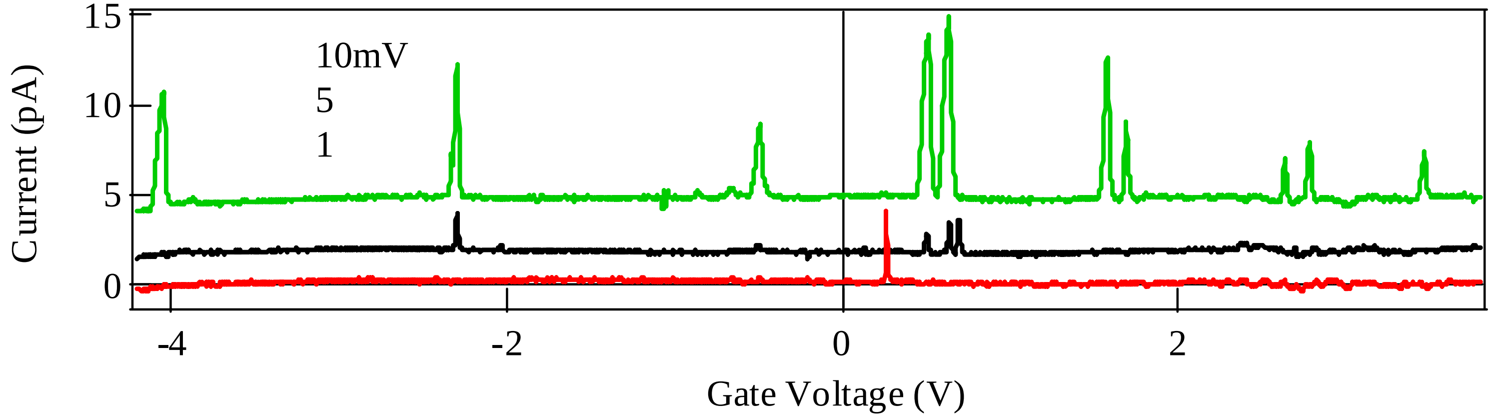
1) **the Coulomb diamonds do not close at zero bias voltage.**
2) **Saw-tooth shapes of the diamonds.**

(Yi Cui, Uri Banin and Paul Alivisatos, unpublished results)

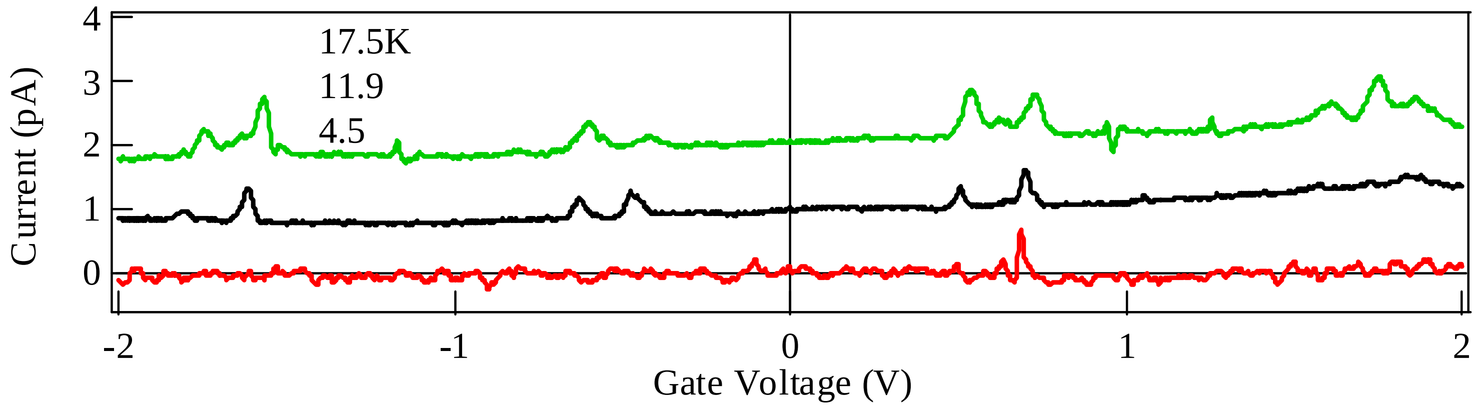
Additional evidence for ionic coupling

The number of current peaks in a gate scan increases with bias.

Dependence on source-drain bias

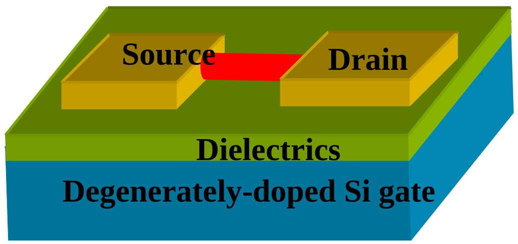


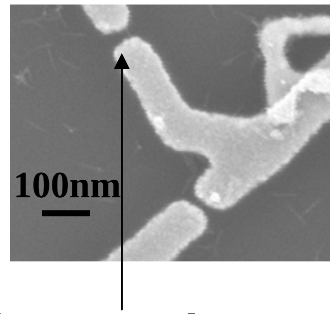
Dependence on temperature



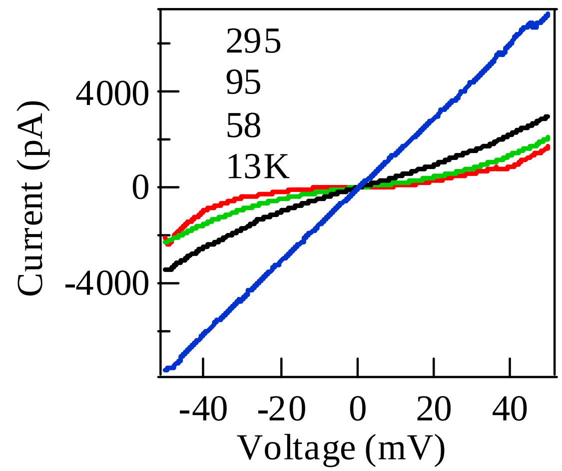
The number of current peaks in a gate scan increases with temperature.

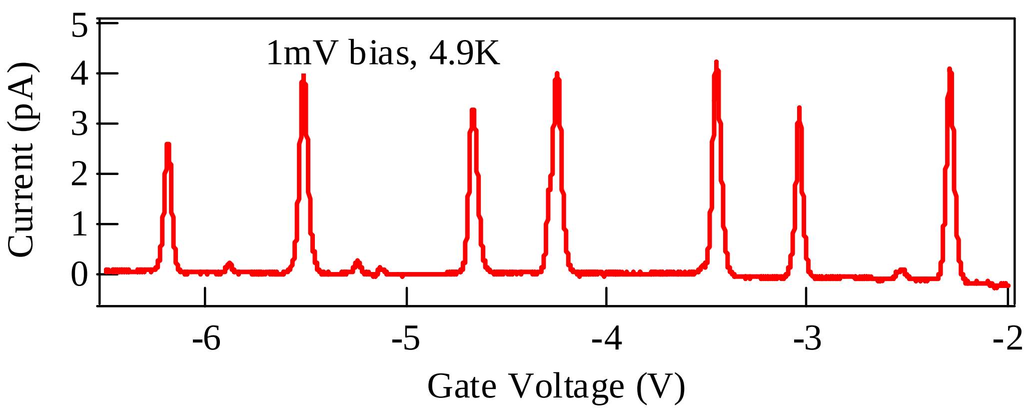
Single nanorod transport

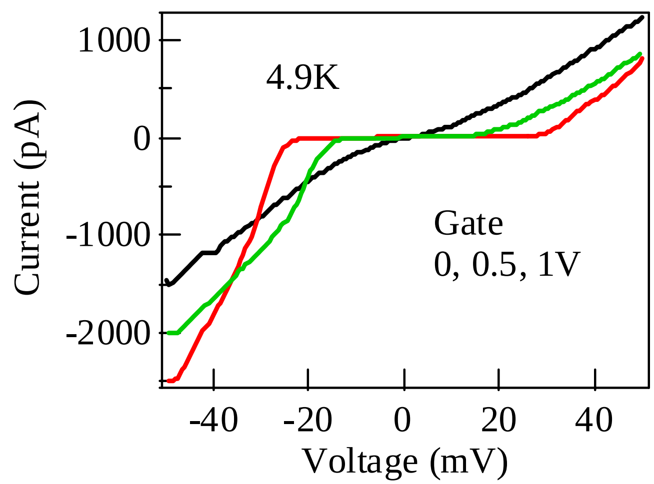




4 by 80 nm CdSe nanorod







Evidence of single electron charging:

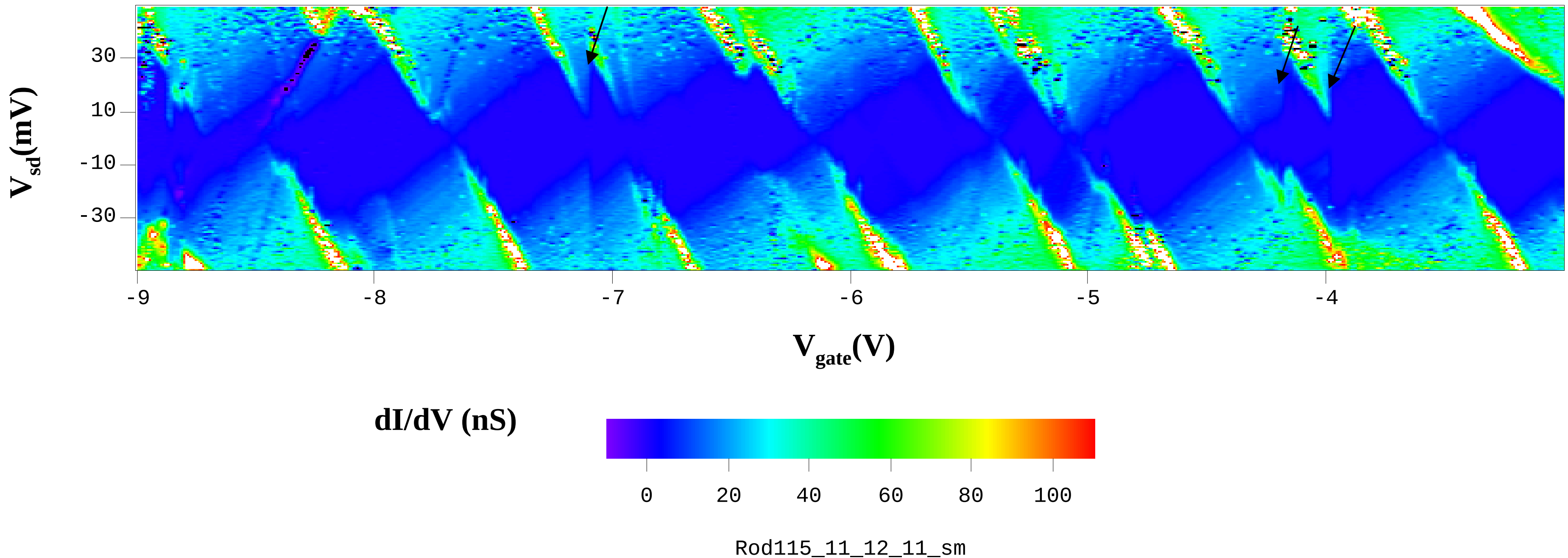
1). Voltage gap in I-V scan, gap size modulated by gate voltage.

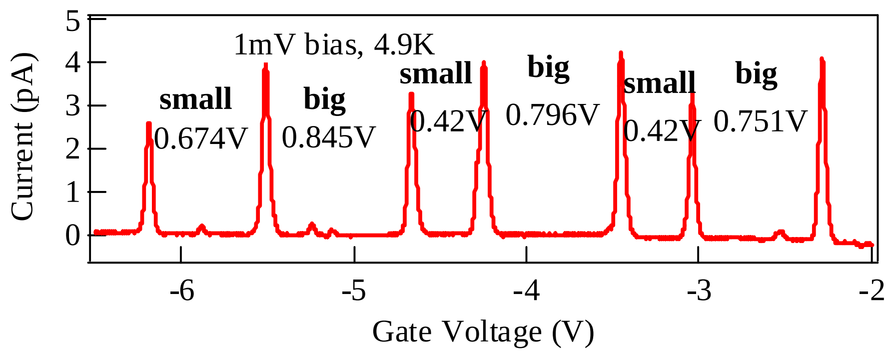
2). Periodic oscillations of current vs gate voltage at fixed bias.

(Yi Cui, Uri Banin and Paul Alivisatos, unpublished results)

Semiconductor Nanorod as a Single Quantum System

Differentiatial conductance vs bias and gate voltage (4.9K)

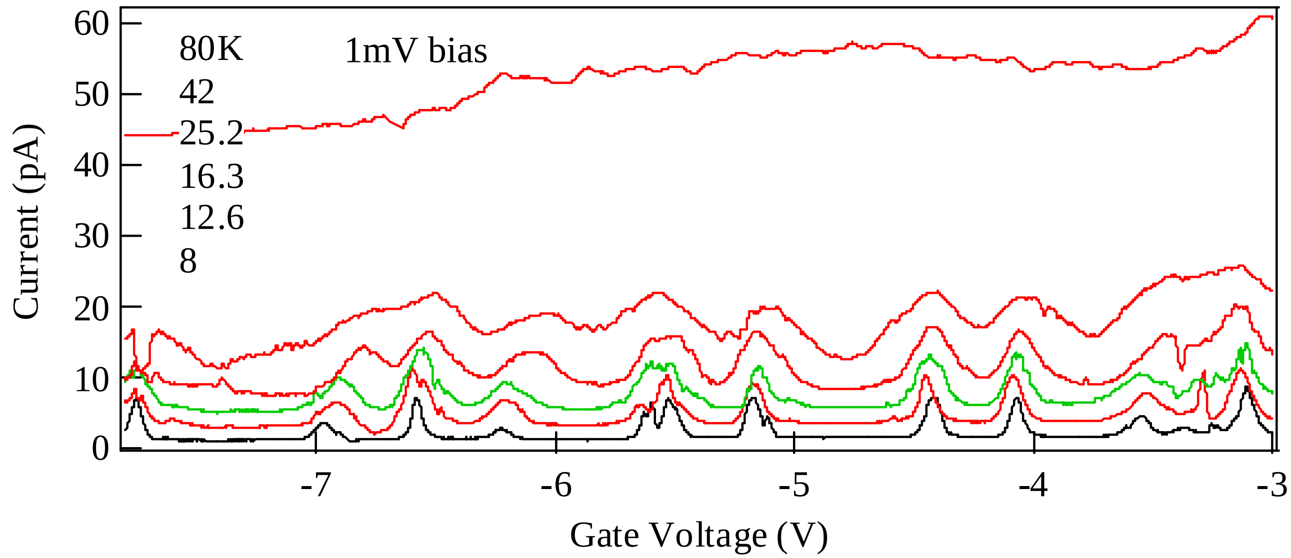




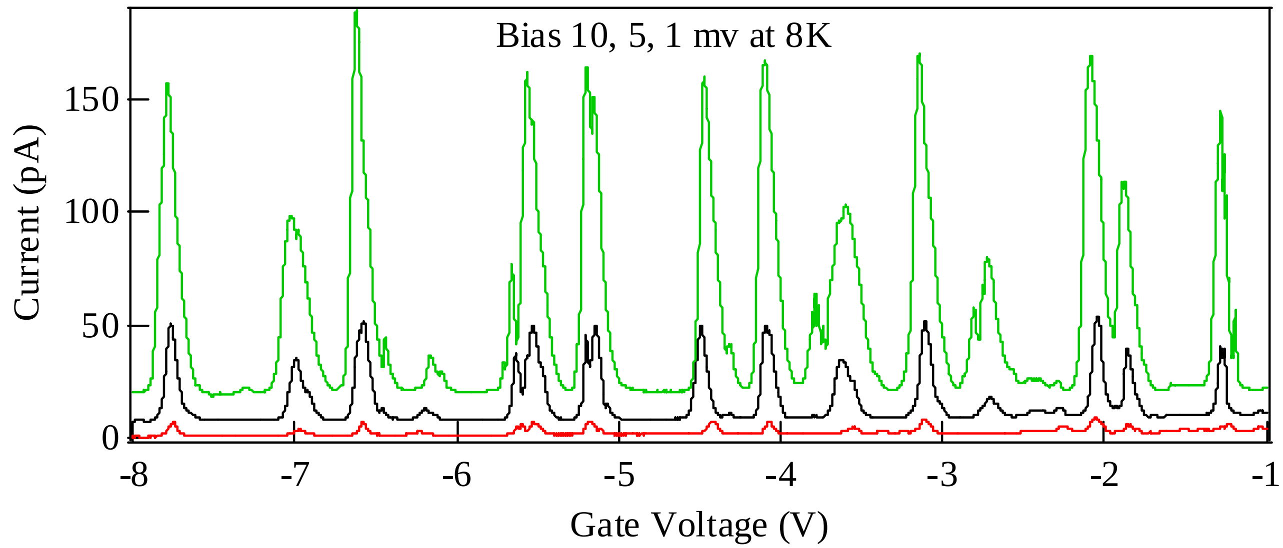
Individual well-defined Coulomb diamonds- single quantum dot behavior.
Arrows indicate sudden jumps of single charges

Temperature and Voltage Dependence

Temperature-dependence

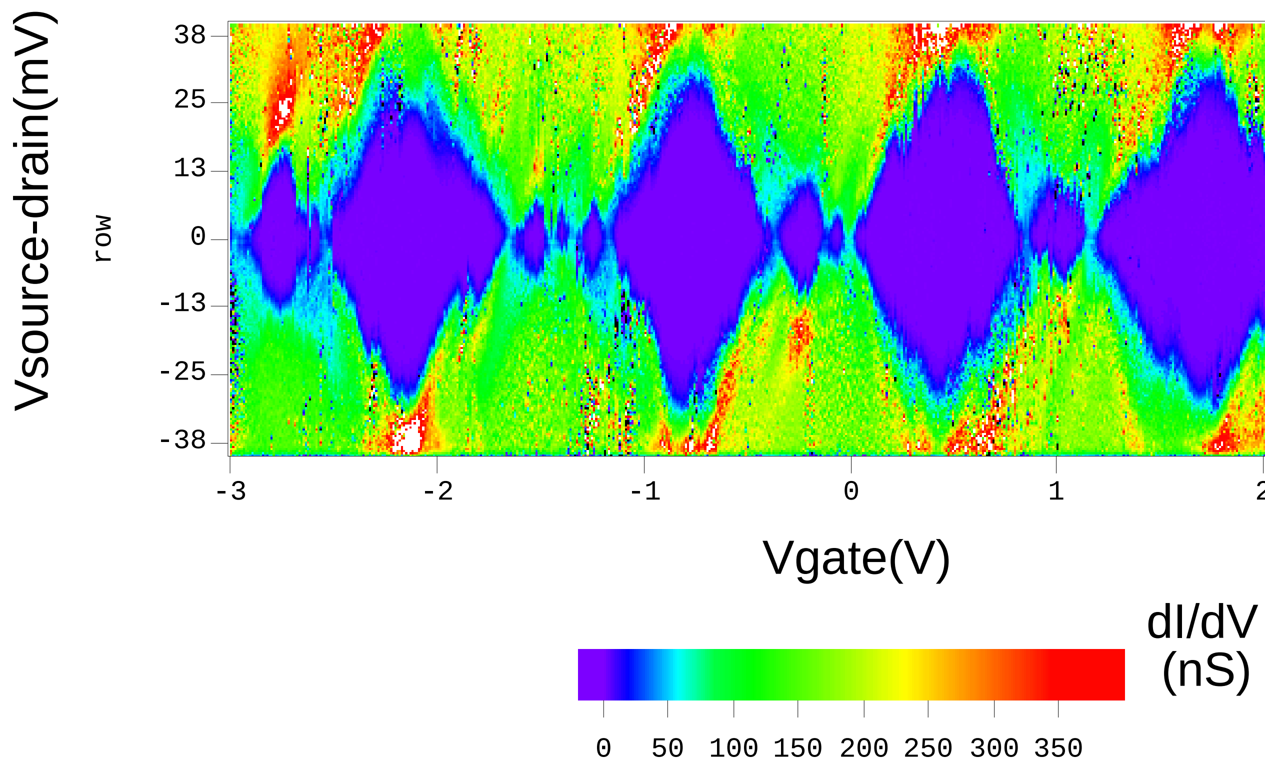


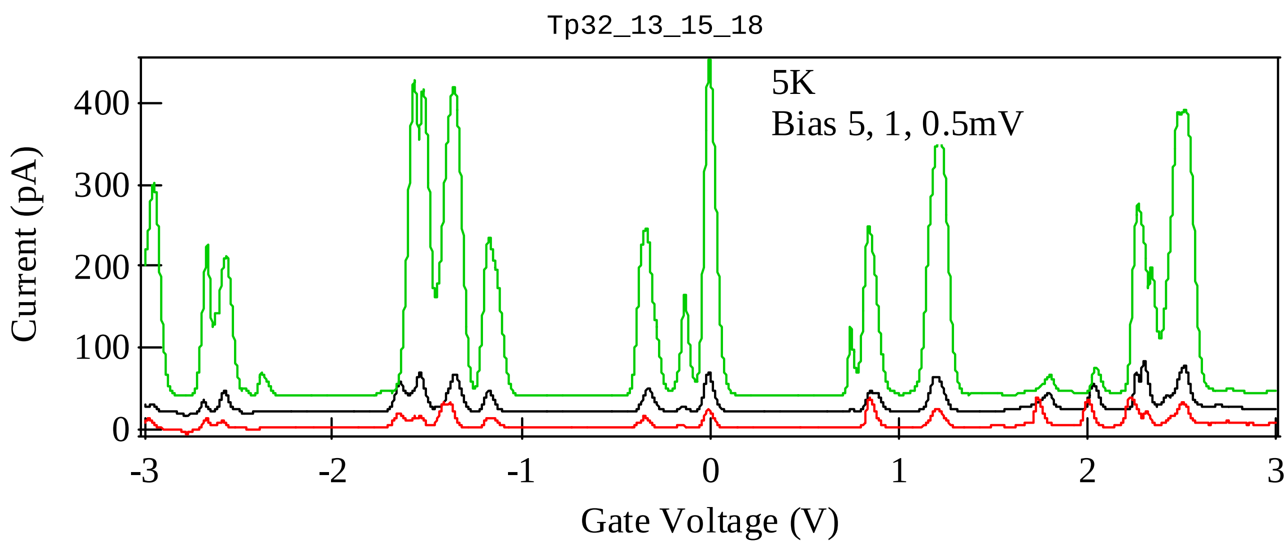
Voltage-dependence



Number of conductance peaks constant vs. T and V, suggesting a single dot behavior.

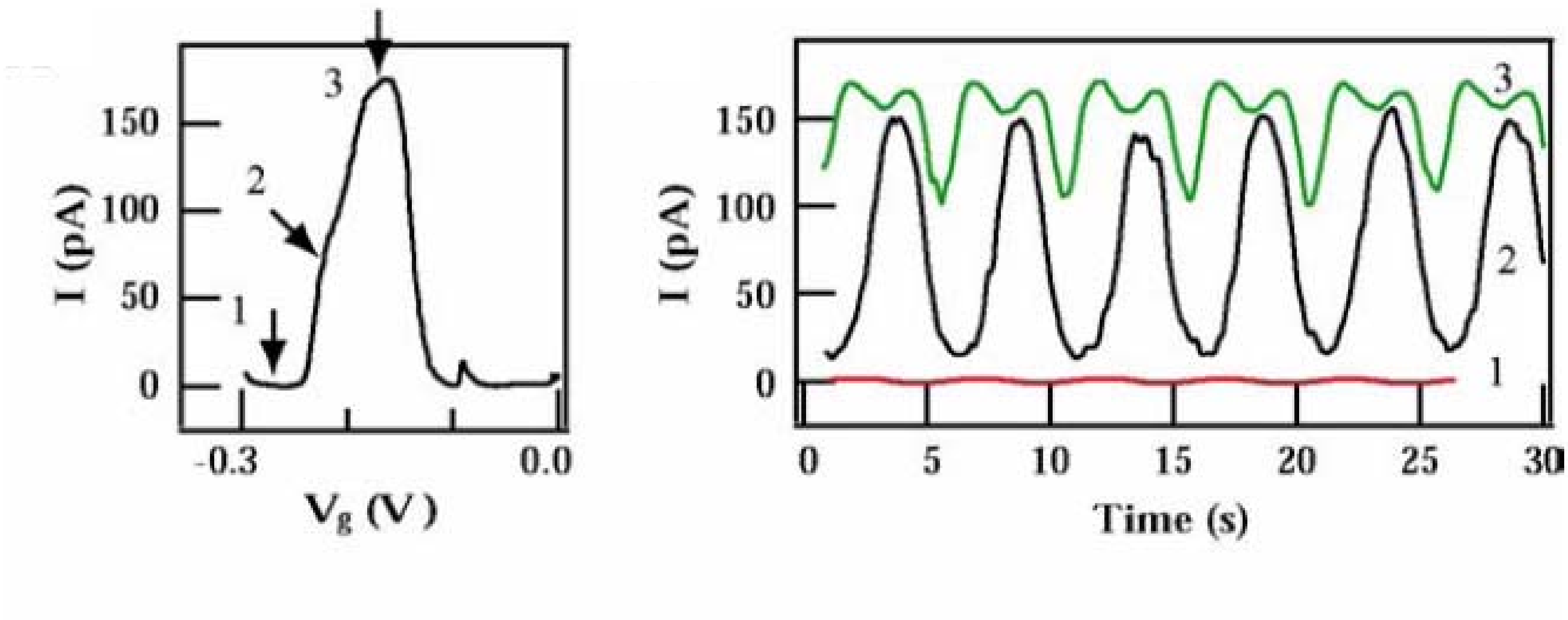
Strong Coupling Example





Future studies with Tetrapod transistors

3rd arm gate experiment



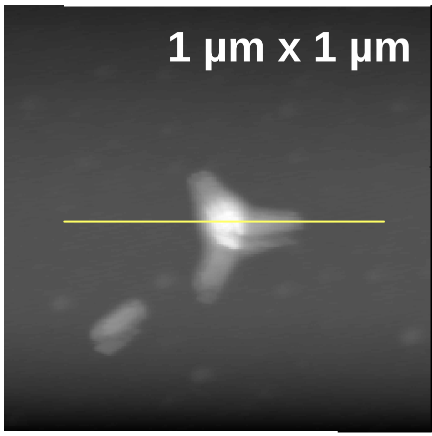
- Chemical or Mechanical Modulation with the 4th arm
- Umbrella Motions

Reversible vs Irreversible Deformation of Tetrapods

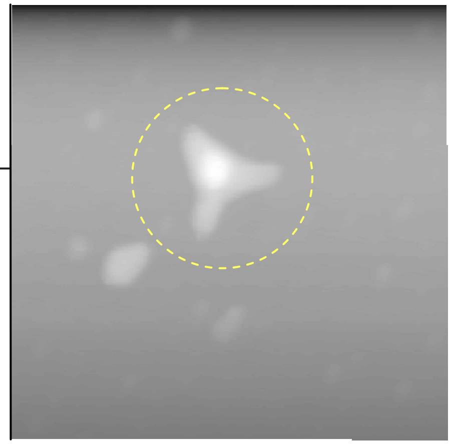
Maximum Deflection: 40 nm; Maximum Load : 73 nN

Compression experiments:

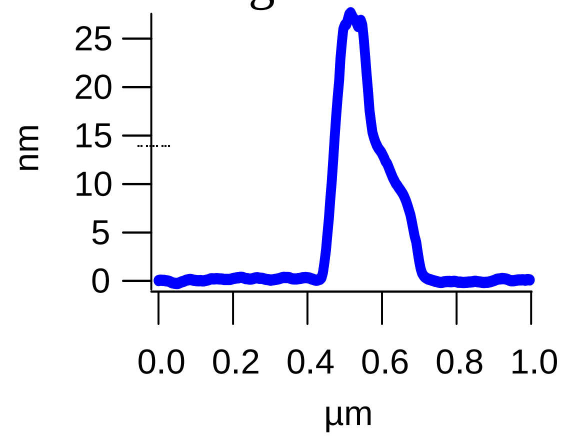
Before



After



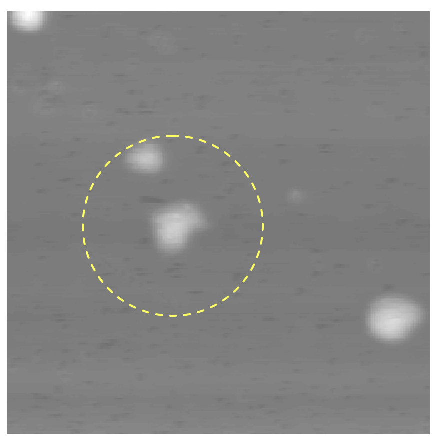
Height Profile



Maximum Deflection: 100 nm; Maximum Load : 183 nN

Before

After



Lang Fang and
Miquel Salmeron

- Nanorod polymer solar cell

  (Wendy Huynh, Janke Dittmer), Delia Milliron, Ilan Gur

  Collaboration with Prof. Jean Frechet

- Tetrapod Electrical Measurements

  Yi Cui, Prof. Uri Banin

Synthesis: Libero Manna, Erik Scher, Delia Milliron, Steven Hughes, Haitao Liu Antonis Kanaras

P. Alivisatos
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Molecular Foundry, Lawrence Berkeley National Lab