Quantum Dot-Conducting Polymer Hybrids for Optoelectronic Devices

2010. 4. 5.

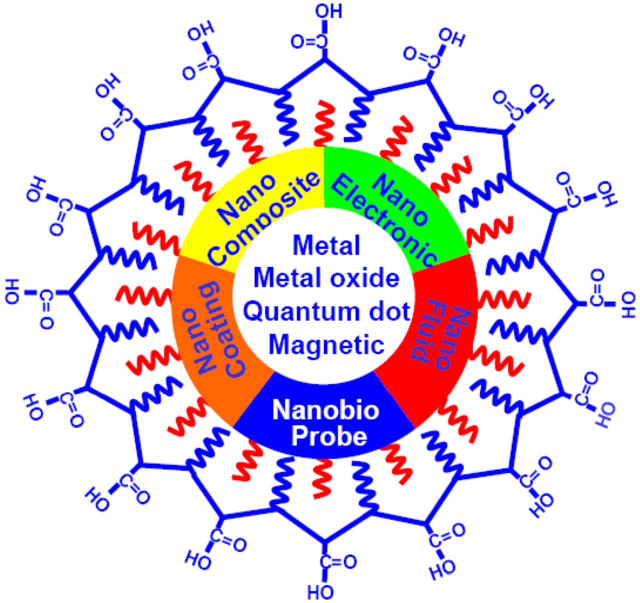
Changhee Lee
School of Electrical Engineering and Computer Science
Seoul National Univ.
chlee7@snu.ac.kr

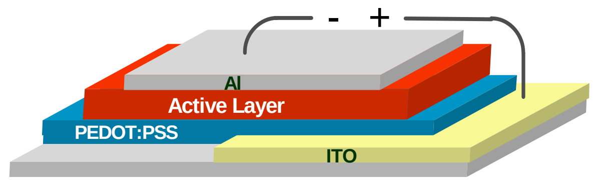
Contents

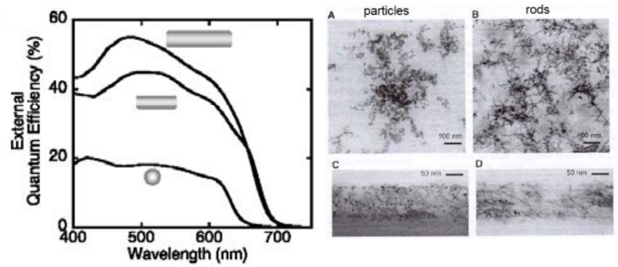
- *Introduction of semiconductor Quantum dots*
- *Quantum Dot / Conducting Polymer Hybrid Material*
- *Light-Emitting Diodes Based on QD-Polymer Hybrid Materials*
- *Summary*

Nanoparticle applications

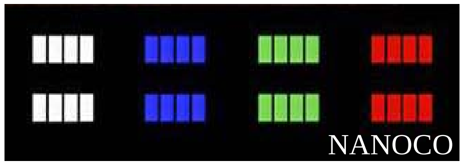
- **Quantum dots**
  - QDLEDs
  - Solar cells
  - Biomedicine
- **Magnetic nanoparticles**
  - Biomedicine: MRI. Hyperthemia, Drug delivery
- **Metal nanoparticles**
  - Biodetection (Au. Ag)
  - Electromagnetic shell (Fe, Ni, Co)
  - Nanofluid
- **Metal oxide nanoparticles**
  - Dielectrics
  - Nanocomposite
  - Nanocoating

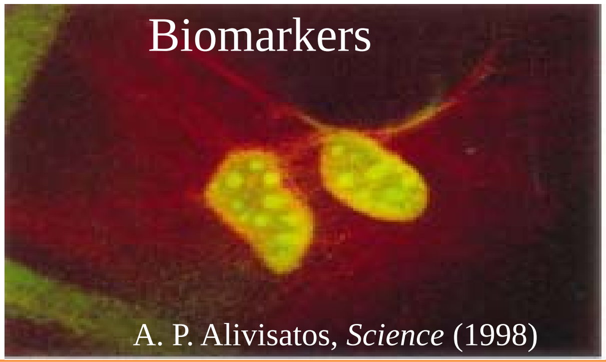






W. U. Huynh, J. J. Dittmer, A. P. Alivisatos, Science, 295, 2425 (2002)

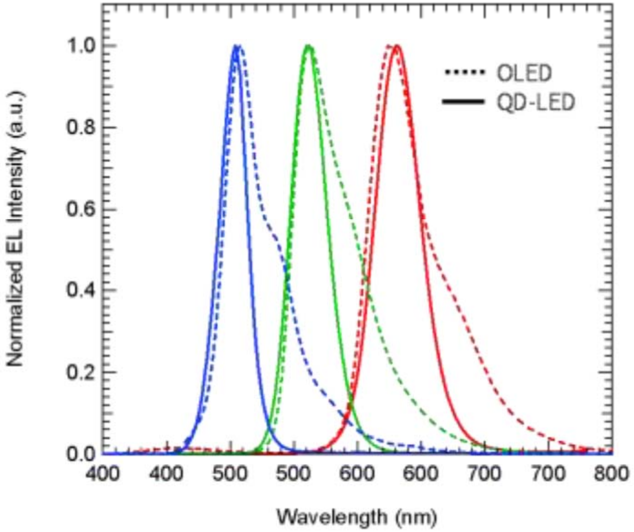




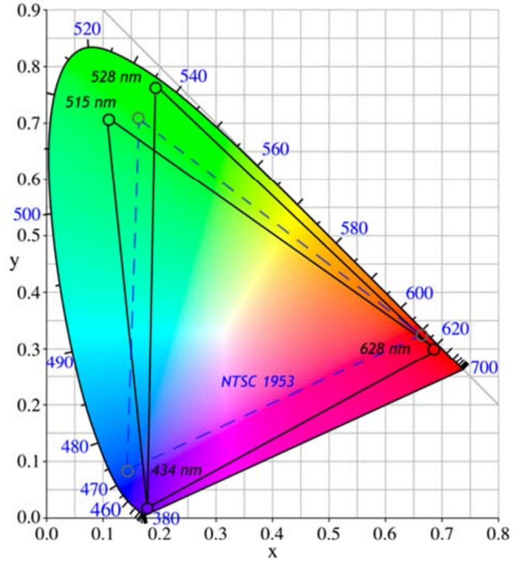
A. P. Alivisatos, *Science* (1998)

Comparison of QD-LED and OLED

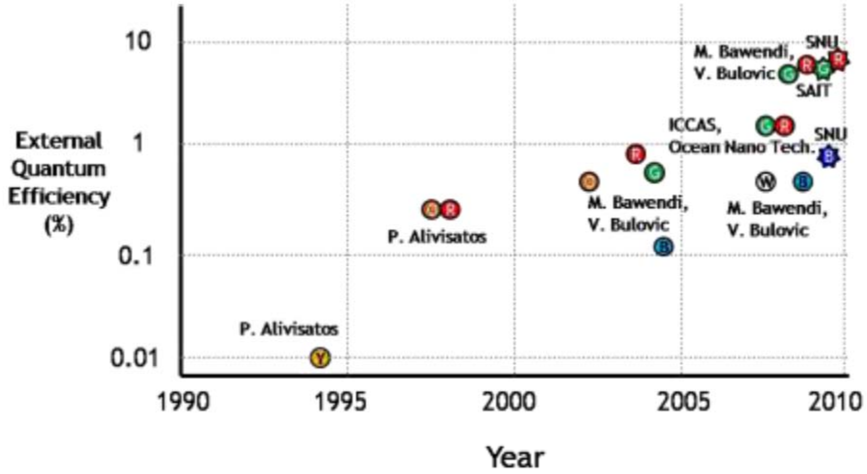
Feature	QD-LED	OLED
Efficiency	Low	High
Emission bandwidth (color saturation)	Narrow FWHM<30nm	Broad FWHM<50-100 nm
Color Tunability	Excellent: Change QD size	Low: Different emitter
Cost of Emitter	Low: One procedure for all RGB emitters	High
Manufacturing process	Solution-based	Vacuum deposition Solution-based
Large display area	Yes	Yes
Flexibility	Yes	Yes



J. H. Kwak, Ph.D. Thesis (SNU, 2010)



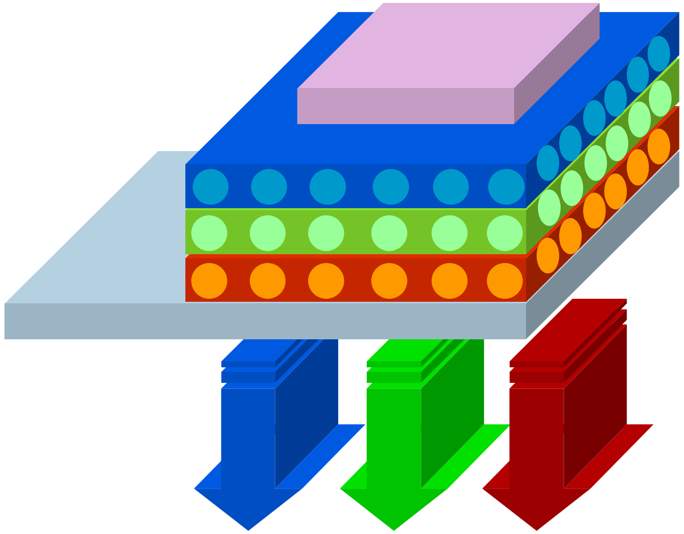
J. H. Kwak et al., SID 2010

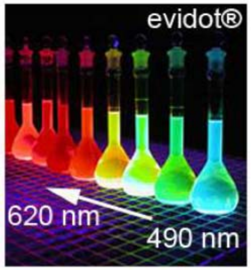


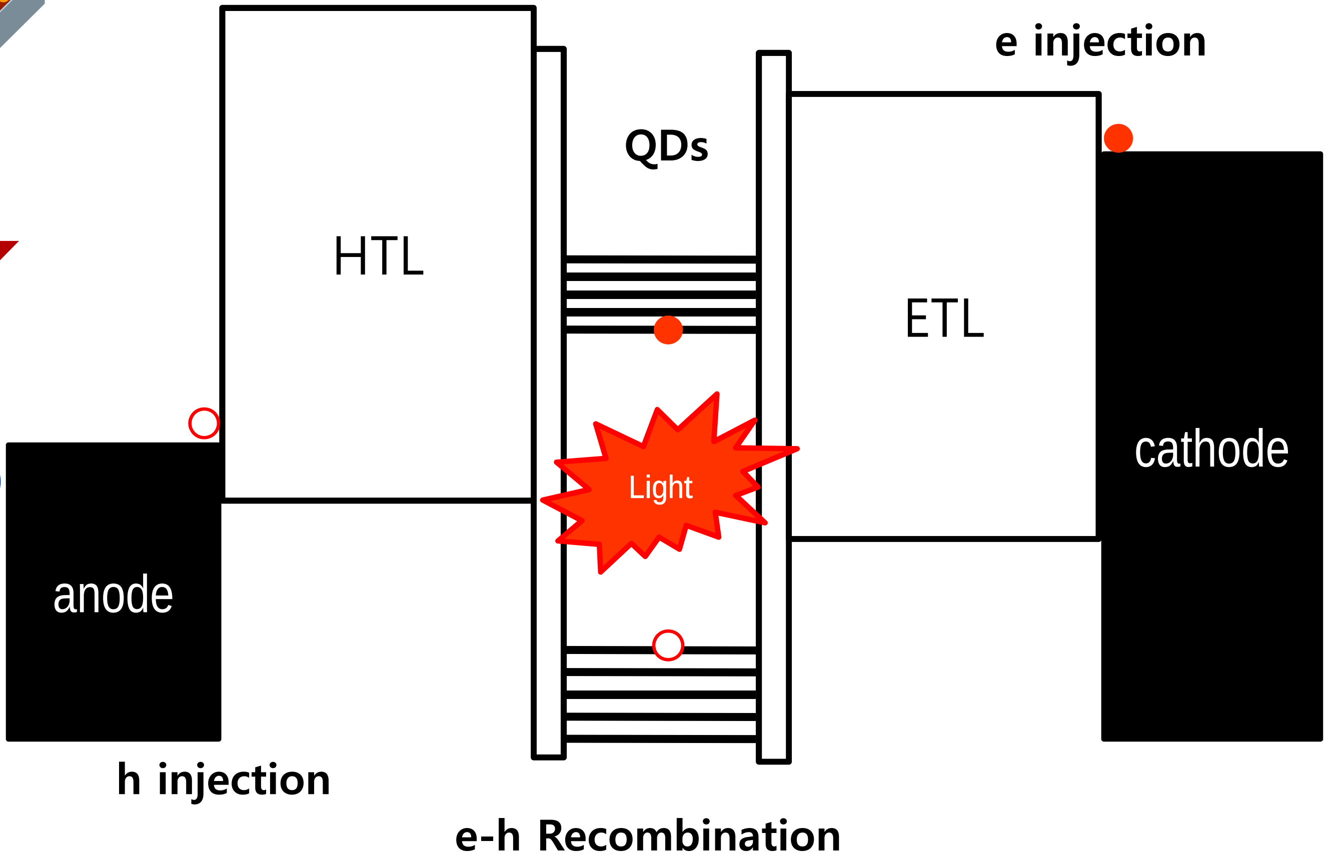
J. H. Kwak, Ph.D. Thesis (SNU, 2010)

LEDs based on colloidal quantum dots

QD-LEDs

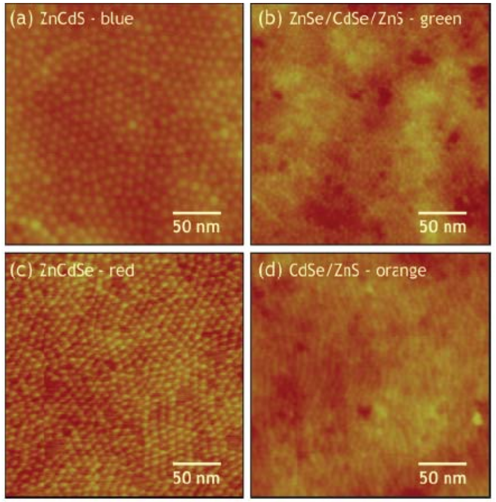


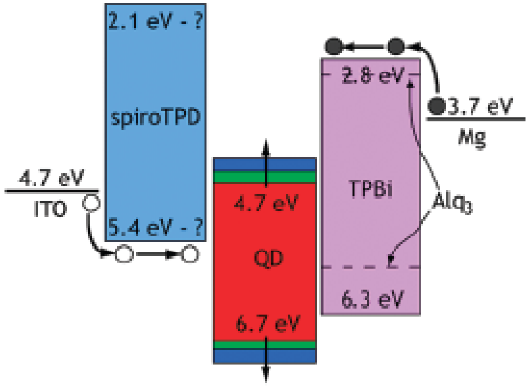




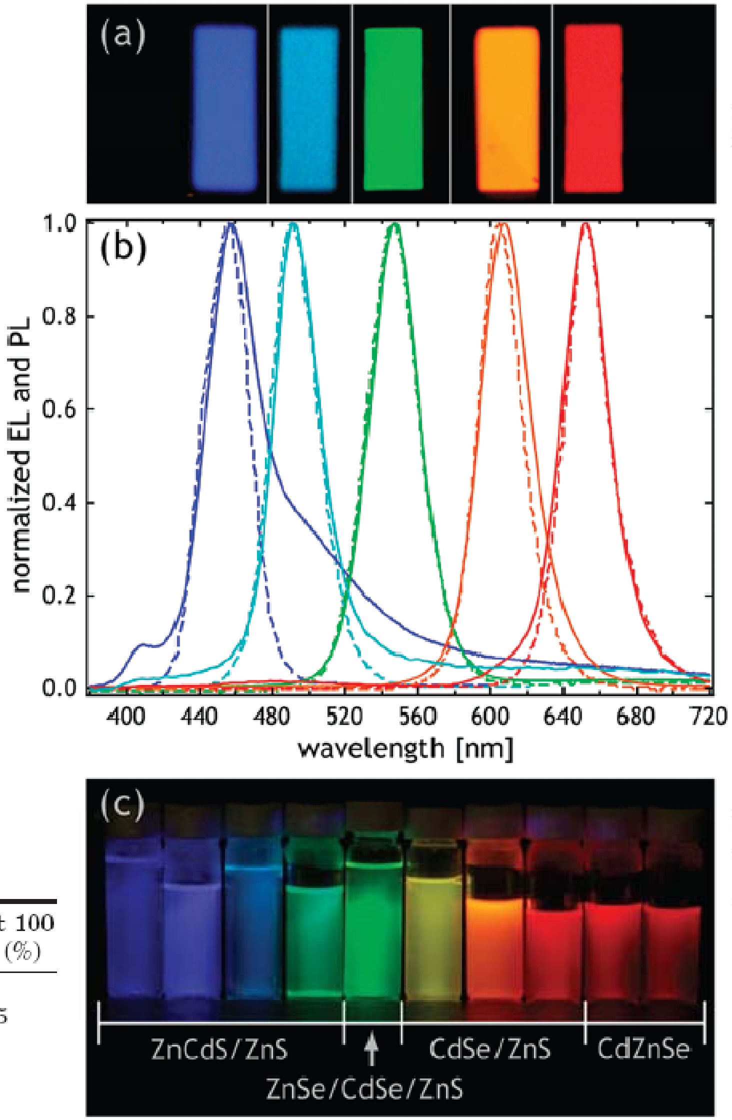
- Size-tunable band-gaps (Color tunability)
- High PL quantum efficiency
- Good photostability
- Narrow emission line widths (FWHM <30 nm)
- Compatibility with solution processing methods

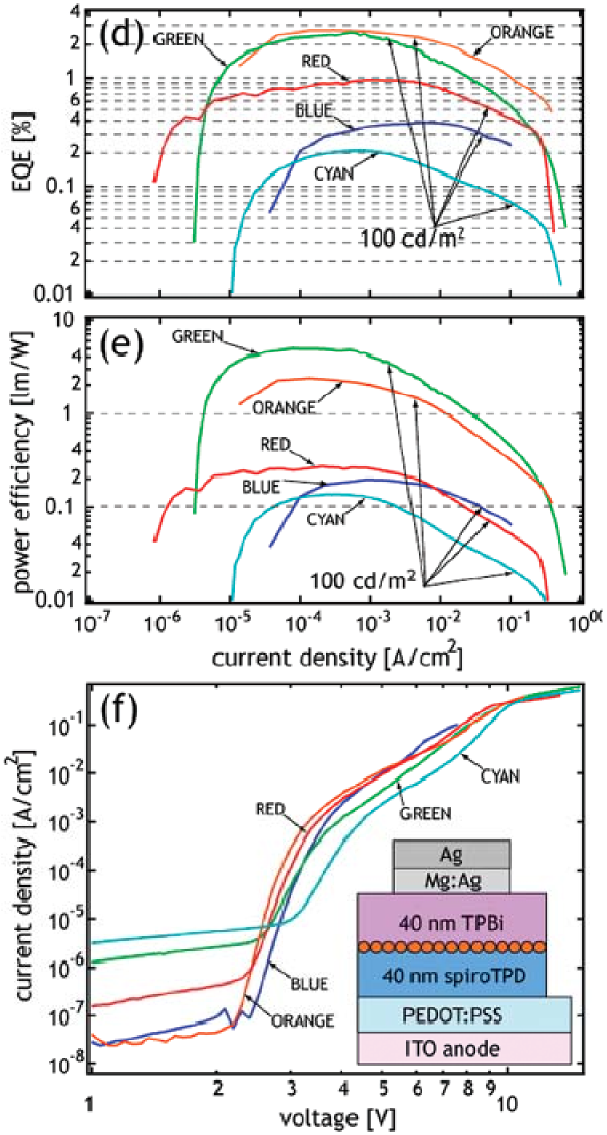
QD LEDs Tunable over the Entire Visible Spectrum





QD-LED color	peak EQE (%)	brightness at peak EQE (cd/m²)	EQE at 100 cd/m² (%)
blue (EL_{max} at 460 nm)	0.4	15	0.3
cyan (EL_{max} at 490 nm)	0.2	3	0.05
green (EL_{max} at 545 nm)	2.6	28	2.2
orange (EL_{max} at 600 nm)	2.7	13	2.3
red (EL_{max} at 650 nm)	1.0	7	0.5





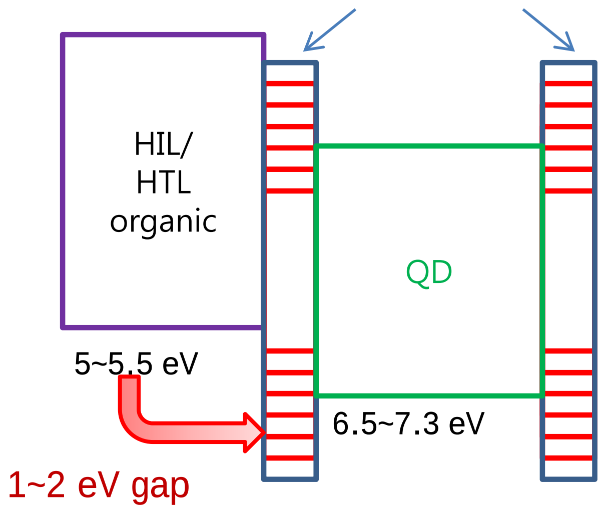
Polina O. Anikeeva, Jonathan E. Halpert, Moungi G. Bawendi and Vladimir Bulovic (**MIT**), Nano Lett., 2009, 9 (7), pp 2532–2536

Problems for low efficiency of colloidal QD-LEDs

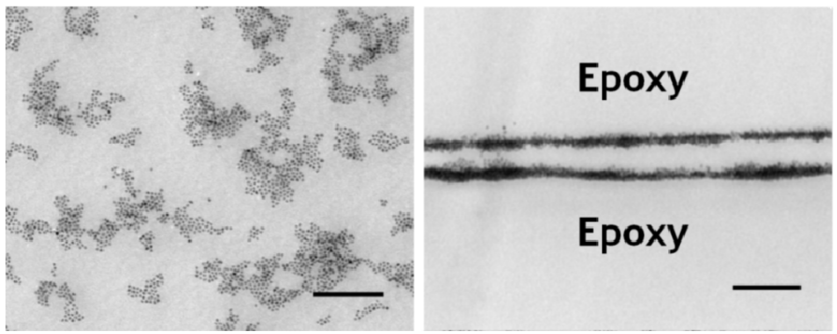
Poor charge carrier injection because

1) QDs generally have **an inorganic shell of a wide bandgap material** (e.g., CdS or ZnS) to increase photostability and improve emission quantum yields by passivating surface defects.
2) QDs are covered by **a layer of organic ligands**, which is needed during their growth and provides solubility in organic solvents to allow processing. However, these organic and inorganic layers form a tunneling barrier for charge injection.
3) The valence bands of the QDs are generally shifted to lower energy compared to the highest occupied molecular orbital (HOMO) levels of commonly used organic hole-injection layers. This introduces **significant energy barriers to hole injection**.
4) Massive QD aggregation occurs in blend film of QDs and polymers → **Poor morphology**

- **Wide energy band gap shell**
- **Organic ligands**
- **Surface traps**

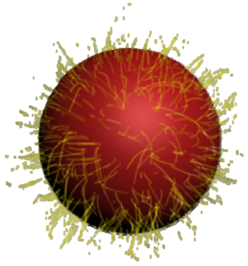


Top view X-section view



Conducting Polymer - Nanoparticle Hybrid System

Nanoparticle

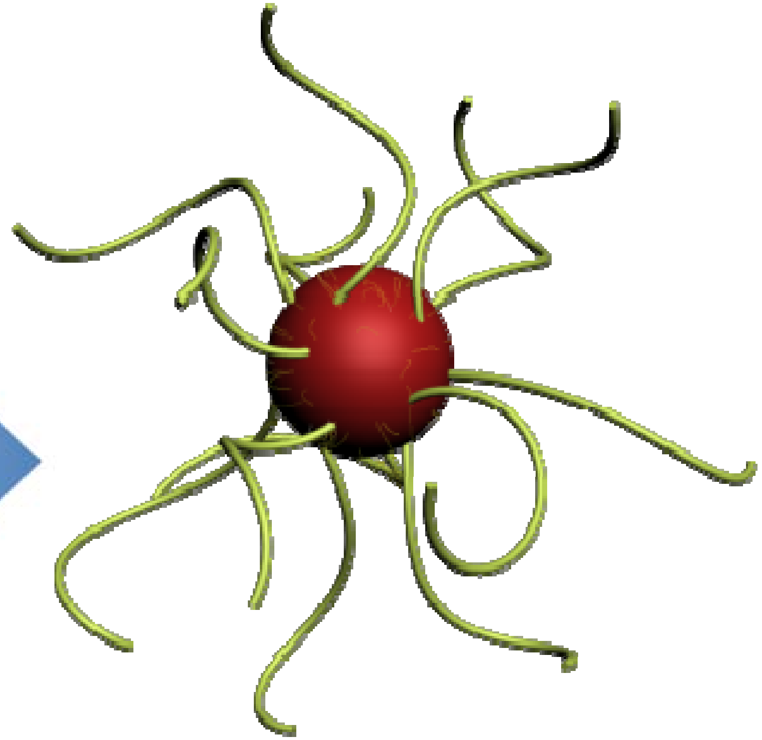


- High extinction coefficient
- High electron mobility
- Band gap & position tunability
- Solution process capability

Polymer

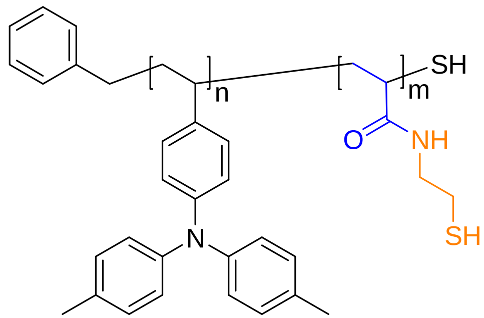
- High extinction coefficient
- High hole mobility
- Solution process capability
- Patterning capability
- Synthesis thru *RAFT, ATRP, NMP*

Conducting Polymer/NP Hybrid

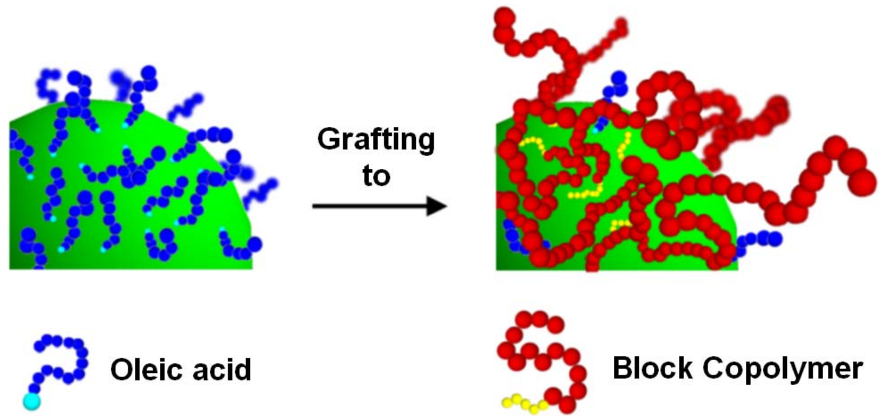


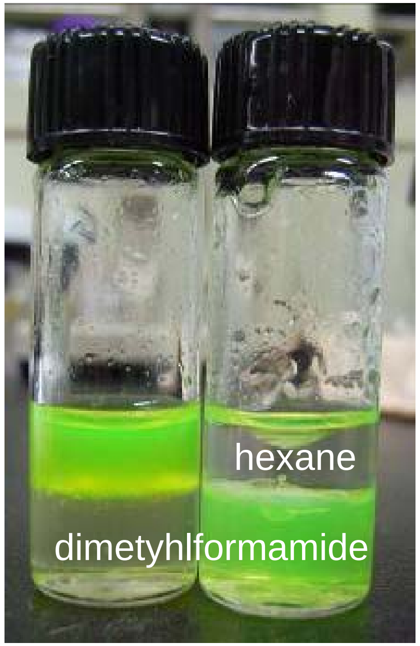
- High extinction coefficient
- Efficient charge separation
- Improved colloidal stability
- Solution process capability
- Patterning capability

Quantum Dot / Conducting Polymer Hybrid

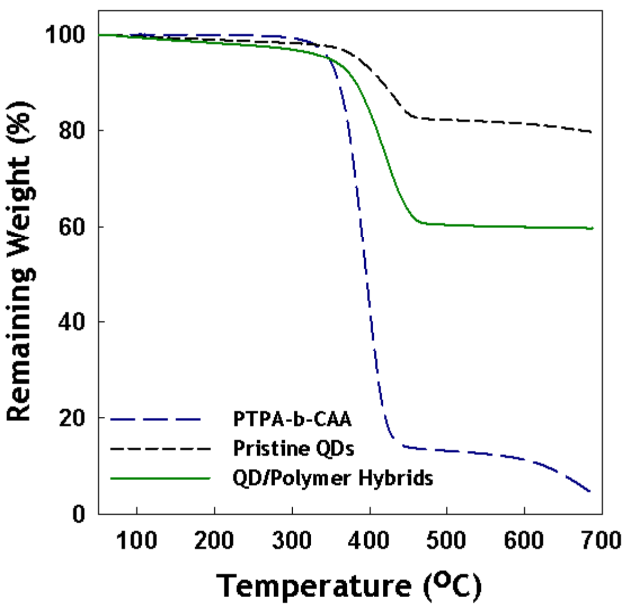


poly(TPA)-b-cysteaminacrylate

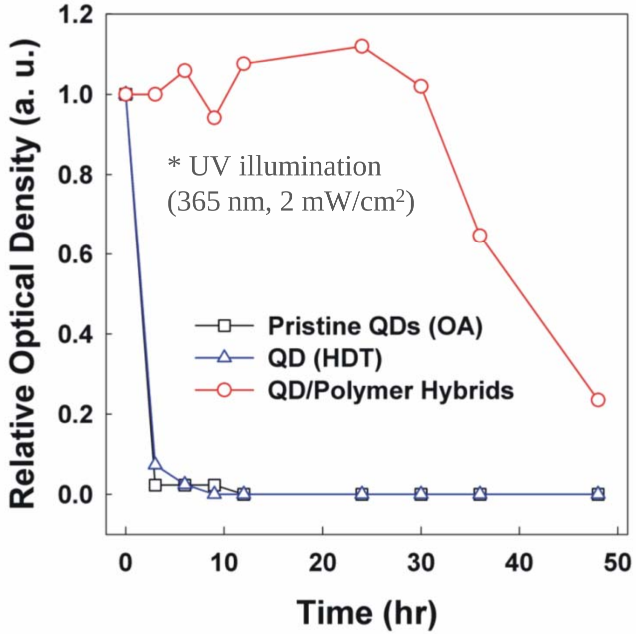




Evidence of hybridization



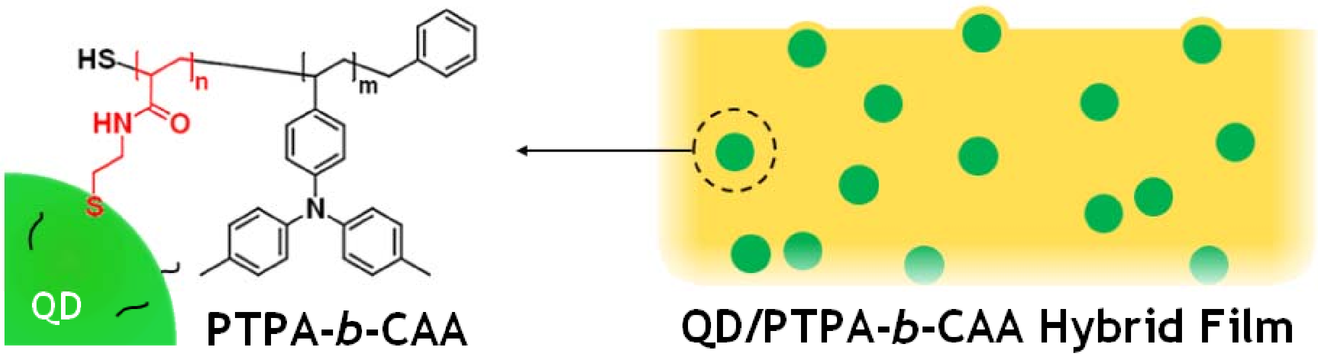
Improved colloidal stability with hybrids



Matthias Zorn, Wan Ki Bae, Jeonghun Kwak, Hyemin Lee, Changhee Lee, Rudolf Zentel, Kookheon Char, ACS Nano **3** (5), 1063 (2009)

Comparison of QD/Polymer Hybrid and Blend

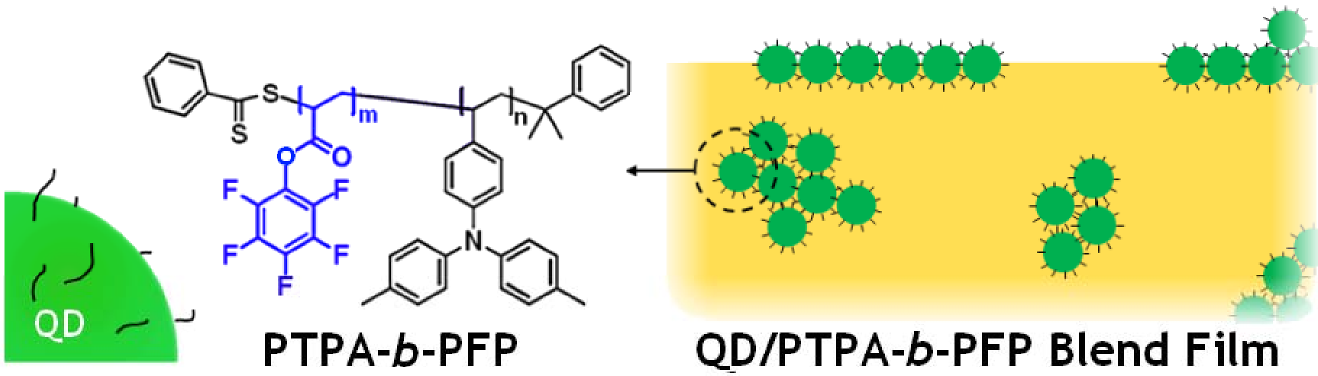
- Quantum Dot / Conducting Polymer ***Hybrids***



The thiol anchor groups in the CAA block replace the surface ligands (oleic acid) of QDs, leading to QD/conducting polymer ***hybrid*** films.

* poly(*para* methyl triphenylamine-*b*-cysteamine acrylamide)

- Quantum Dot / Conducting Polymer ***Blends***

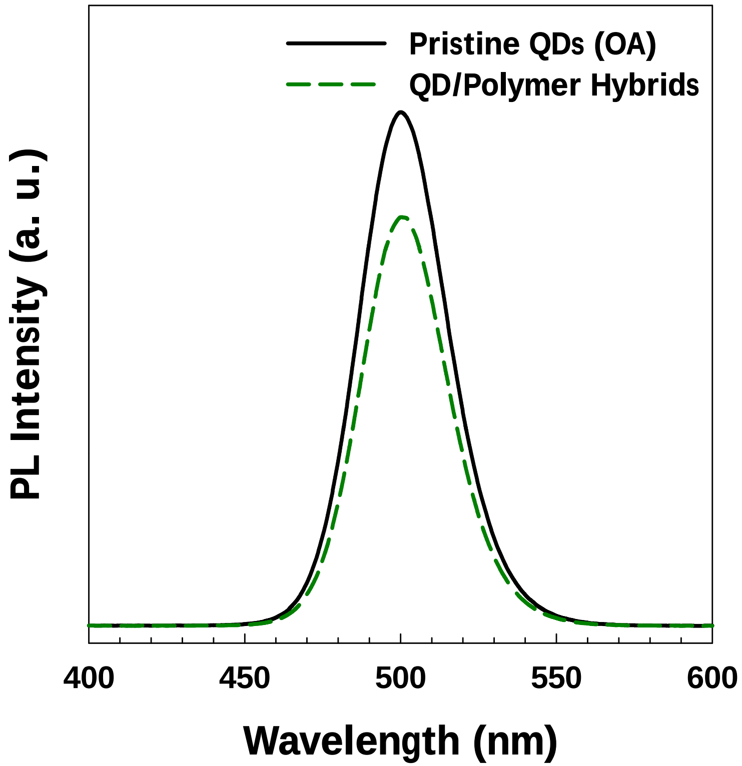


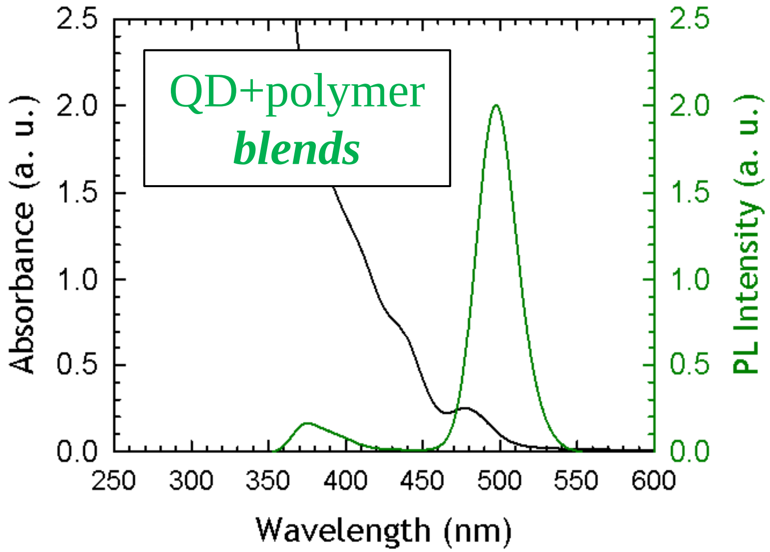
The fluorinated block (PFP) with low surface energy does not have specific interactions with QDs, resulting in QD/conducting polymer ***blend*** films.

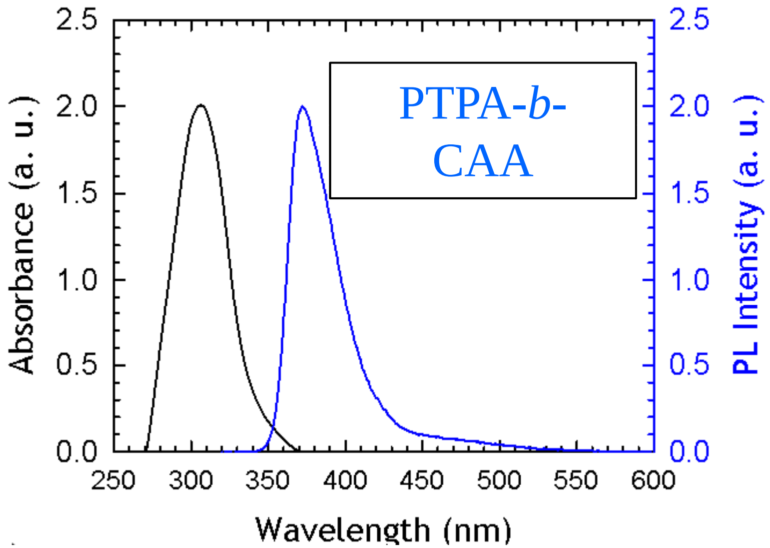
* poly(*para* methyl triphenylamine-*b*-pentafluorophenole)

Jeonghun Kwak, Wan Ki Bae, Matthias Zorn, Heeje Woo, Hyunsik Yoon, Jaehoon Lim, Sang Wook Kang, Stefan Weber, Hans-Jürgen Butt, Rudolf Zentel, Seonghoon Lee, Kookheon Char, Changhee Lee, Adv. Mater. **21** (48), 5022 (2009)

Comparison of QD/Polymer Hybrid and Blend



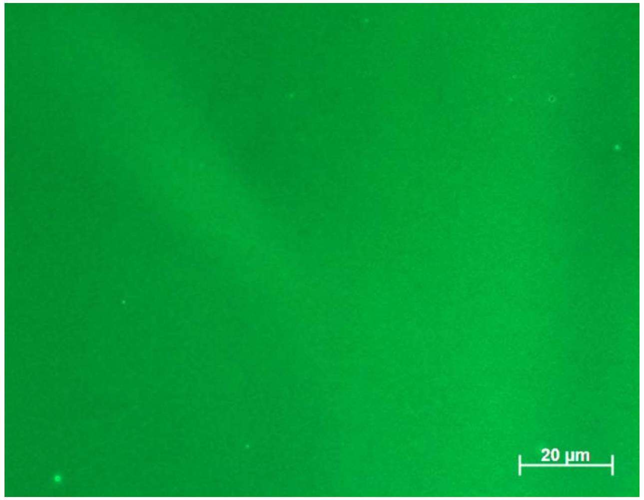


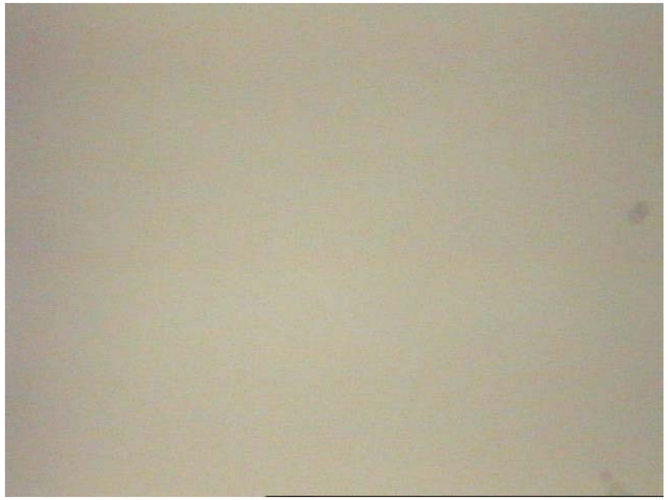


About 80 % of the PL intensity remains after grafting the QD surfaces with block copolymer.

Comparison of QD/Polymer Hybrid and Blend

Hybrid Film

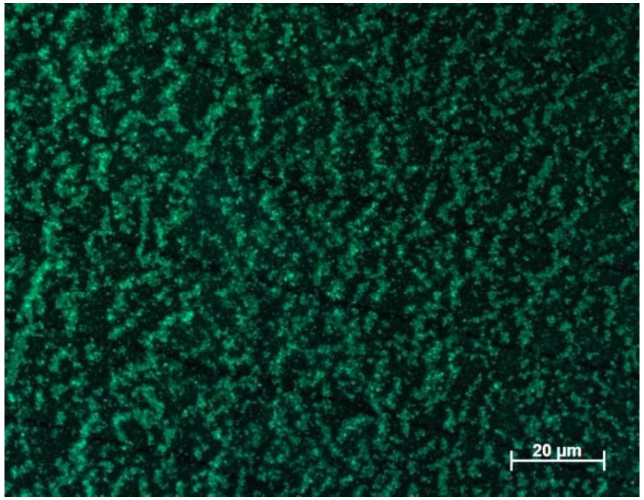


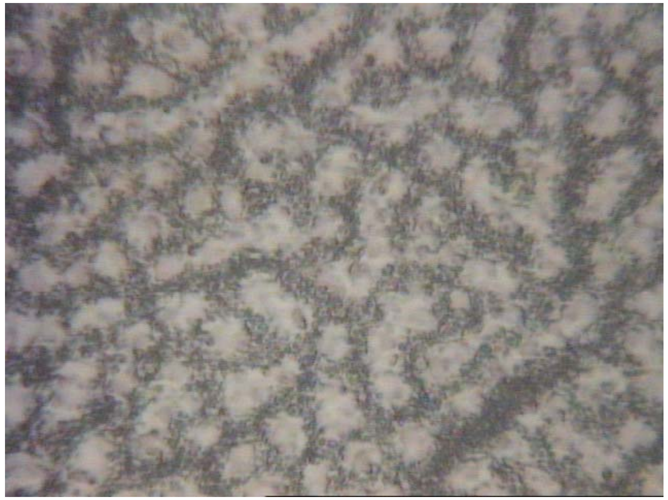


Fluorescent Optical Microscopy

Optical Microscopy

Blend Film





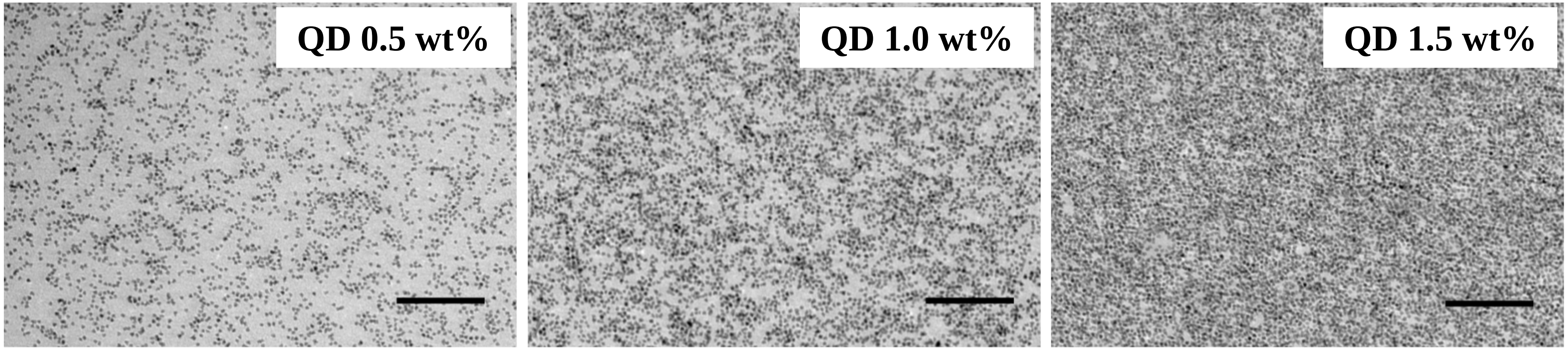
* All films were fabricated by spin-coating.

Comparison of QD/Polymer Hybrid and Blend

Hybrid Films

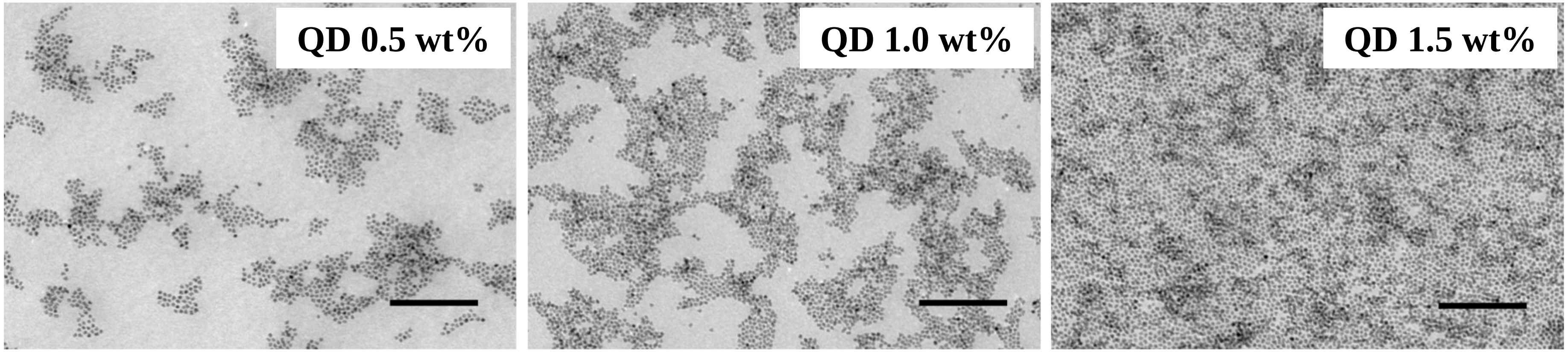
TEM top view

* All films were fabricated by spin-coating.



Blend Films

* Scale bars in the figure are 200 nm.



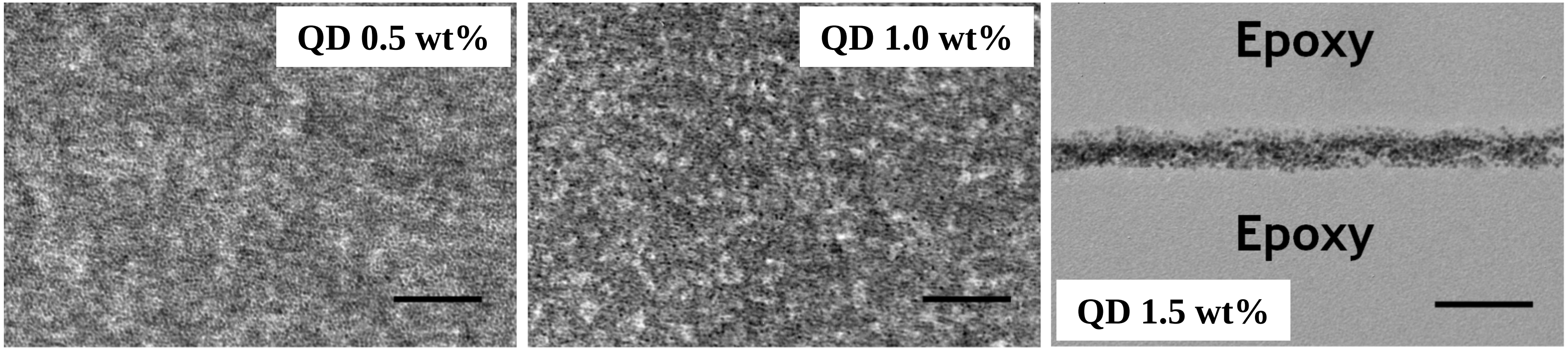
Hybrid and Blend films show drastic differences.

Comparison of QD/Polymer Hybrid and Blend

Hybrid Films

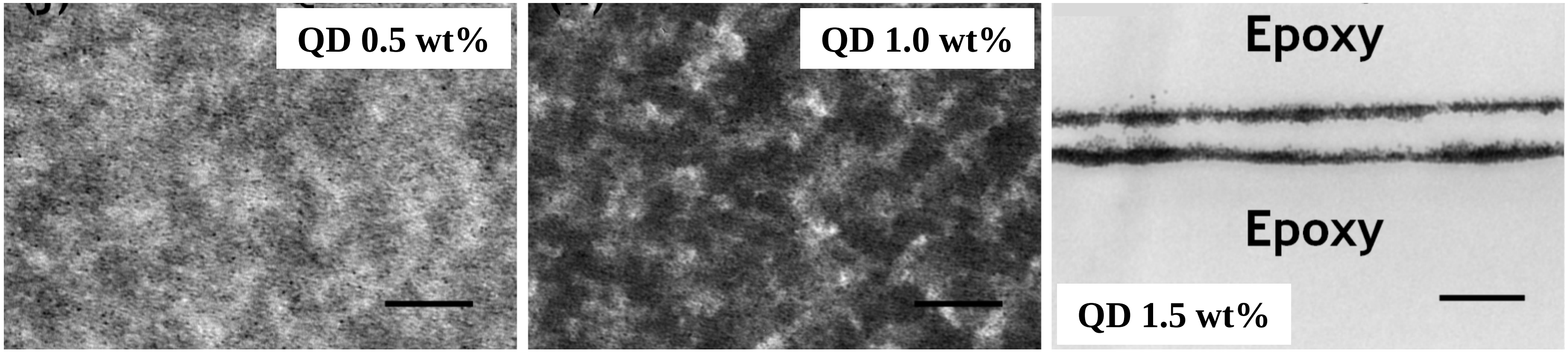
TEM top view

TEM cross-section view



Blend Films

* Scale bars in the figure are 200 nm.

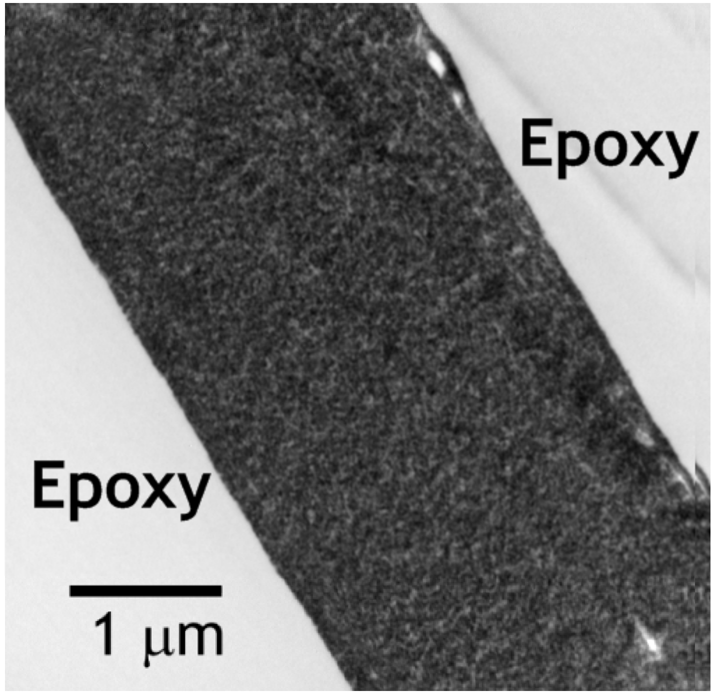


Aggregation & phase separation within blend films.

Comparison of QD/Polymer Hybrid and Blend

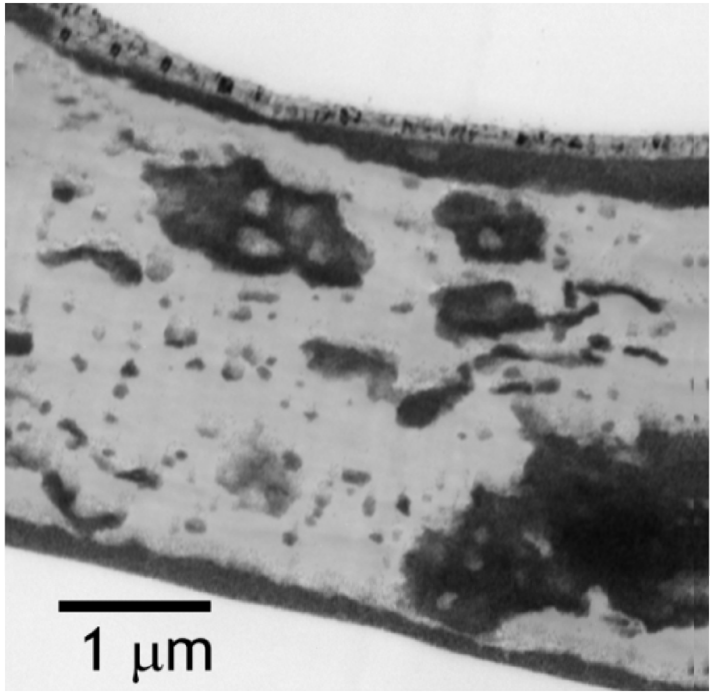
QD / Polymer Hybrids: Drop-casted Morphology

Hybrid Film



TEM cross-section view

Blend Film

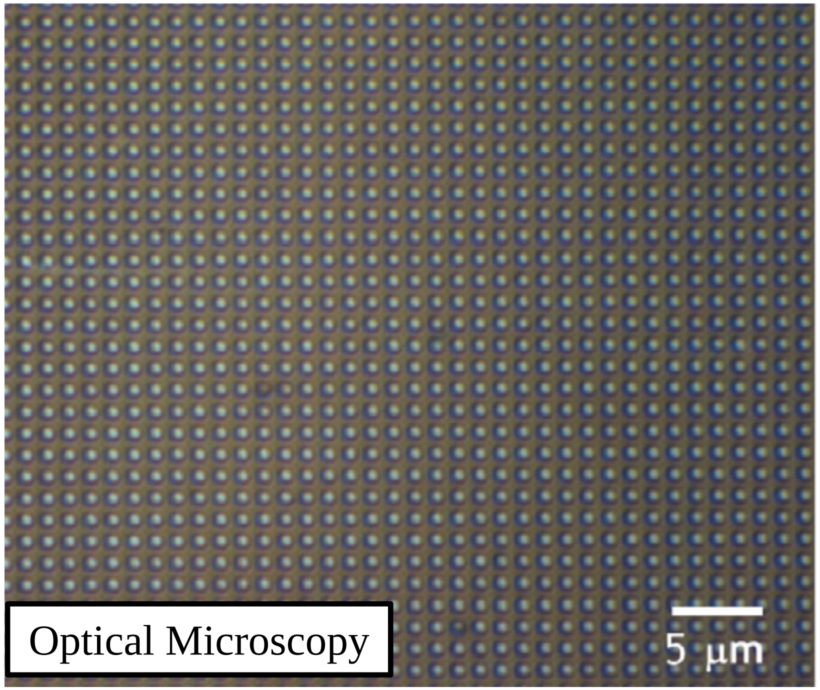


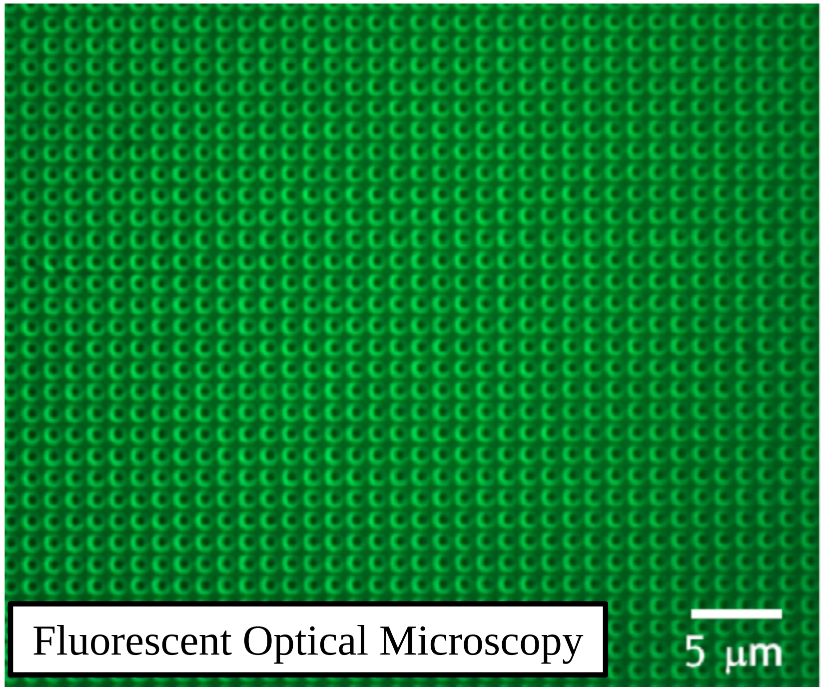
TEM cross-section view

- *Drastic differences can be observed within drop-casted samples.*
- *This result is extendable to similar solution process (e.g., Ink-jet)*
- *Aggregation & phase separation in Blend film.*

QD / Polymer Hybrids: Patterning Test

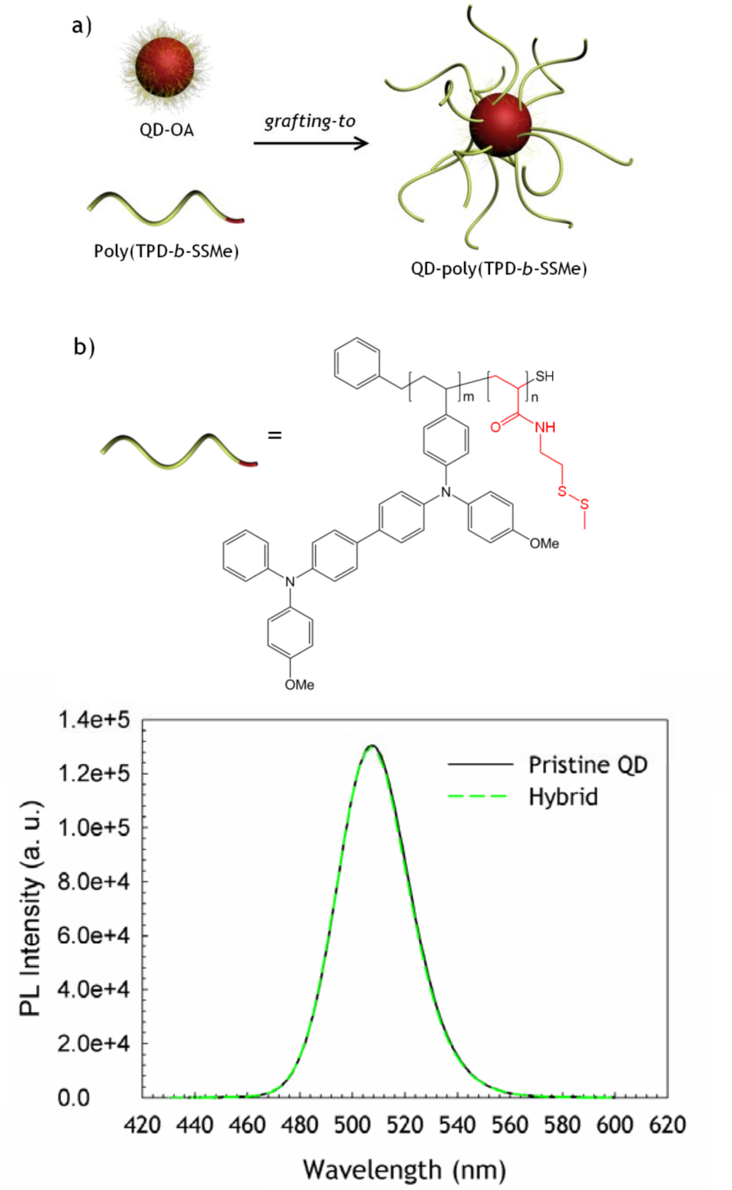
Capillary force lithography

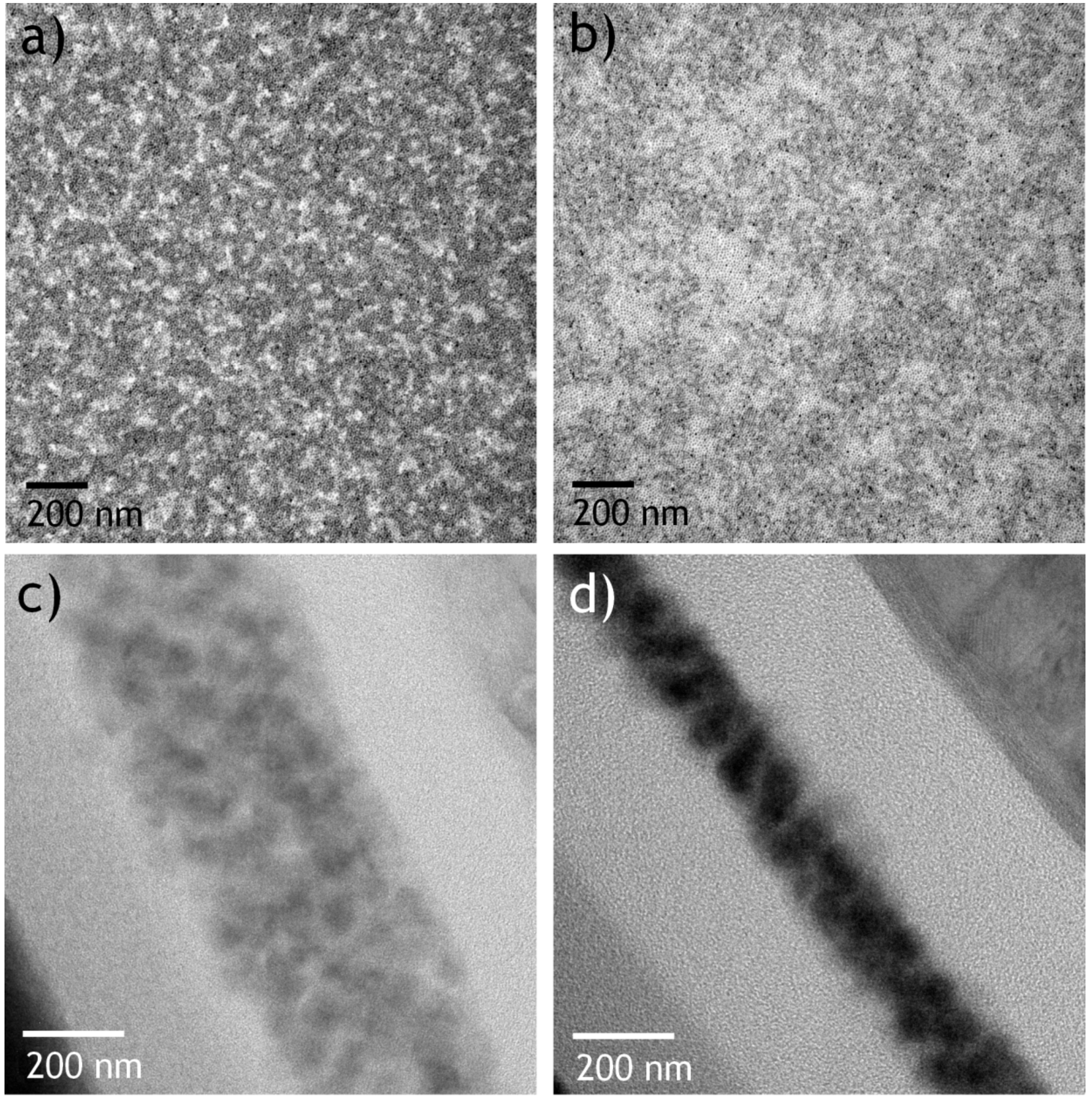




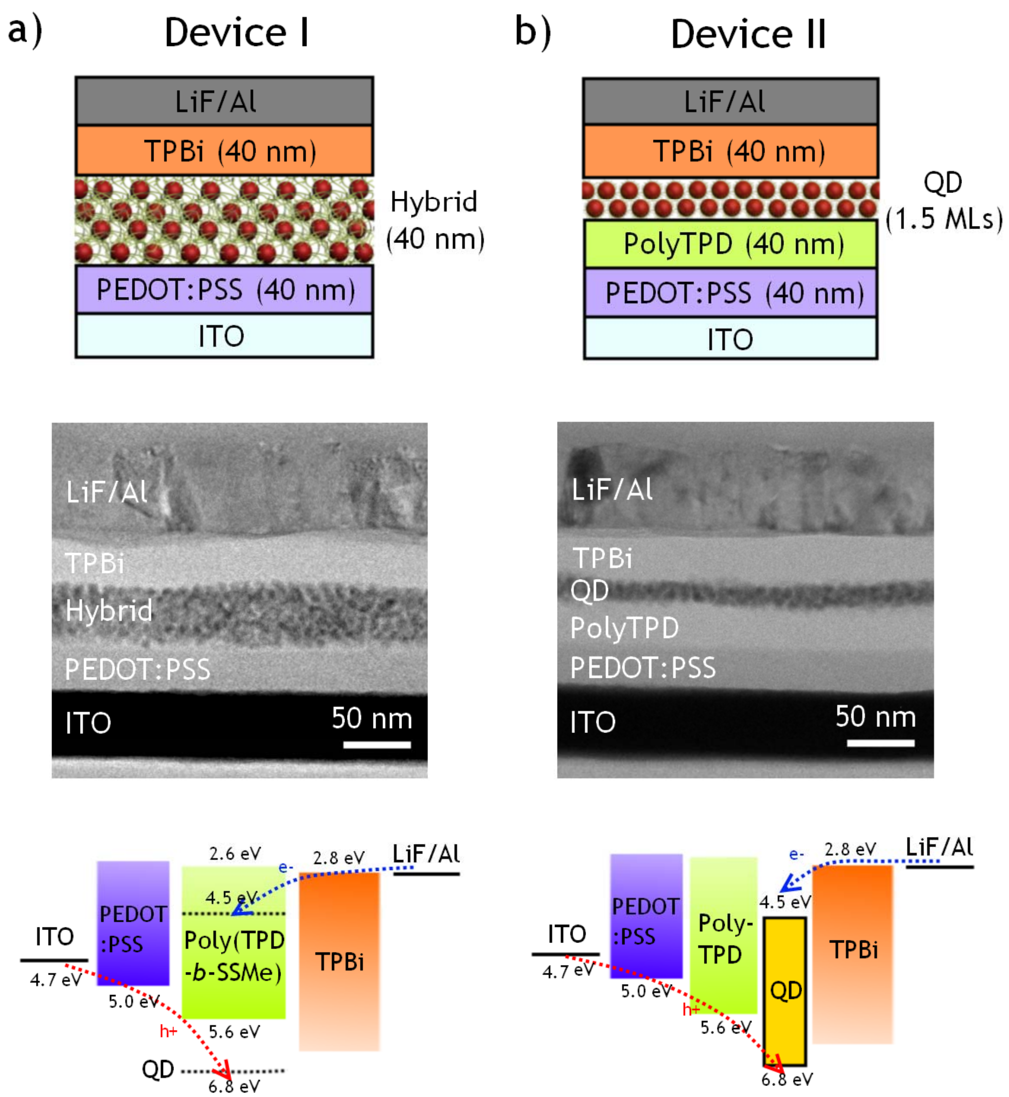
- regular hole patterns (hole diameter: 1 μm, hole distance: 0.3 μm)
- conventional solution-based process (ink-jet, roll-to-roll, etc.) compatible

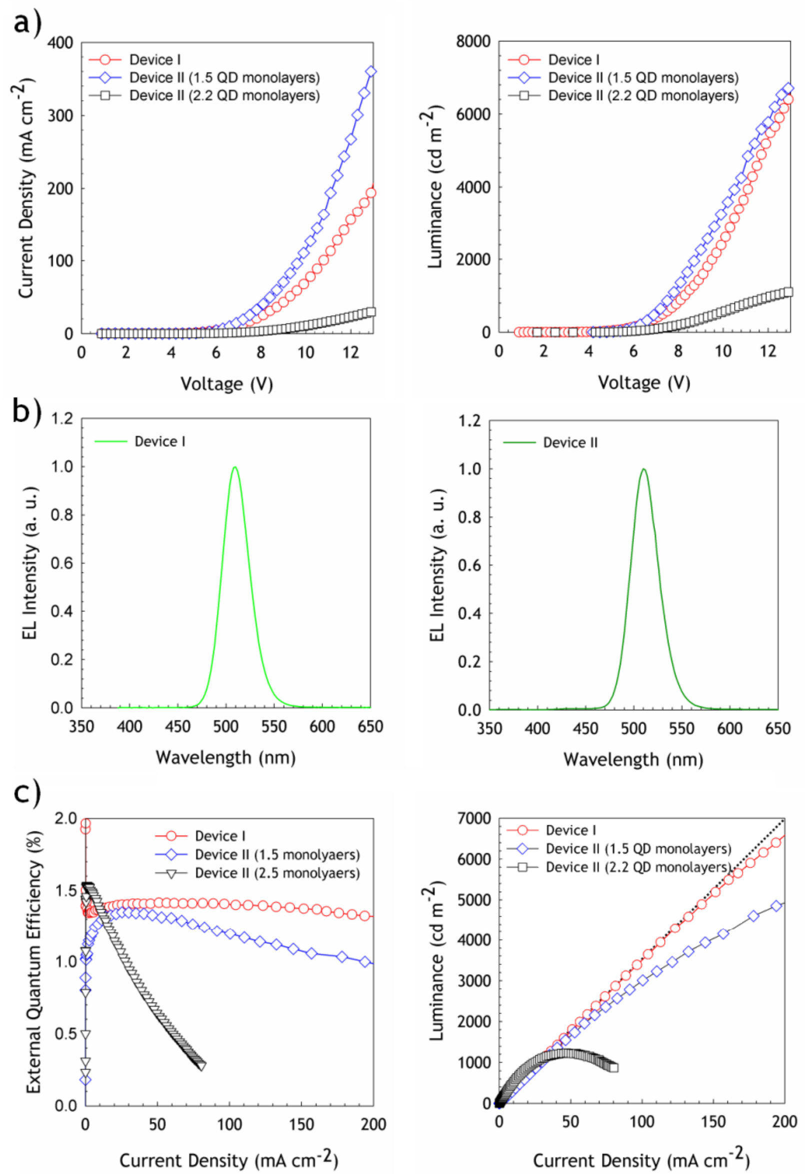
QD/Polymer hybrid films for efficient QD-LEDs





QD/Polymer Hybrid LEDs

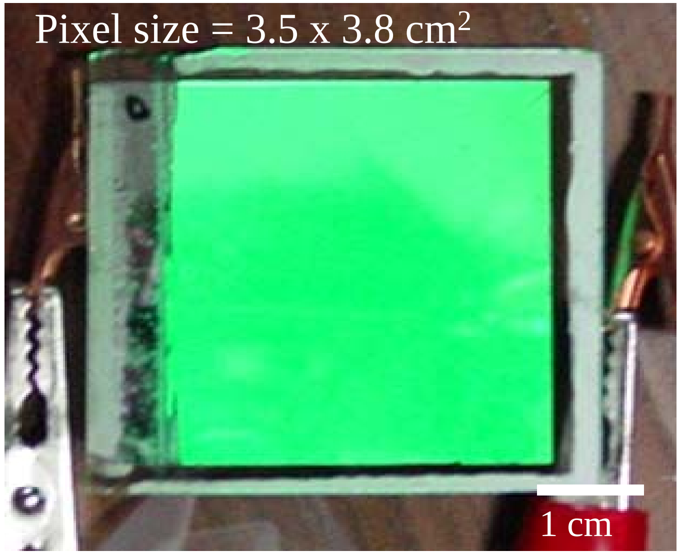




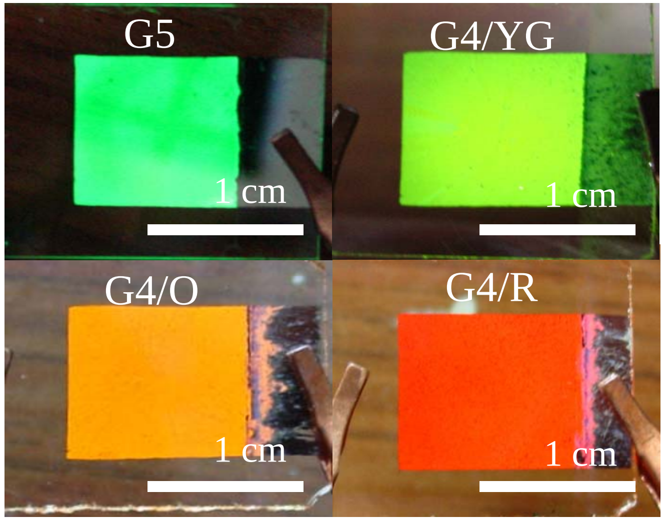
Wan Ki Bae, et al., Angew. Chem. Int. Ed. (submitted)

Multicolor QLEDs

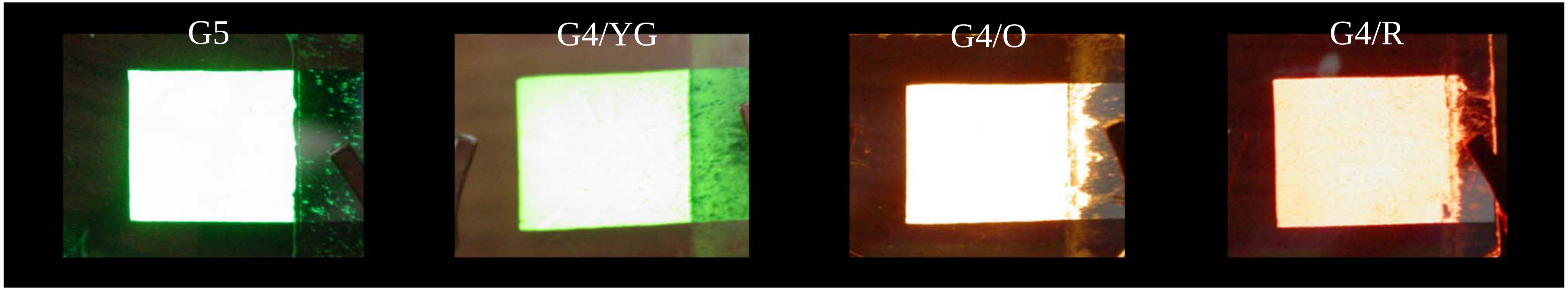
QLED in Large Area



Multicolored QLEDs

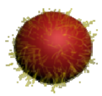


QLED with Strong EL Emission



QD-Polymer Blend *vs* Polymer/NP Hybrid

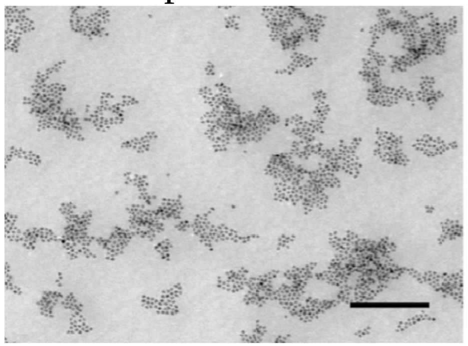
QD-Polymer blend



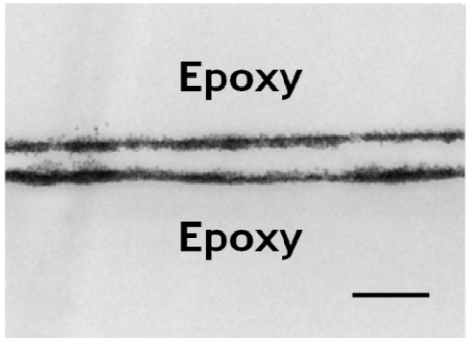
NP

Polymer

Top view



X-section view

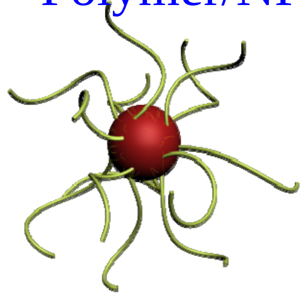


- Physical mixing of NPs & polymers
- Massive QD aggregation
- Poor morphology control
- Surface states of NPs

P. Alivisatos(U.C. Berkeley), R. Jenssen(Eindhoven)

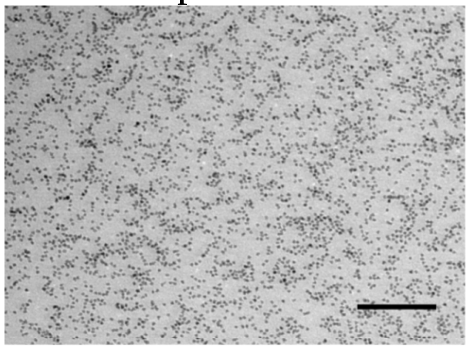
Limited efficiency & poor reproducibility

Polymer/NP Hybrid

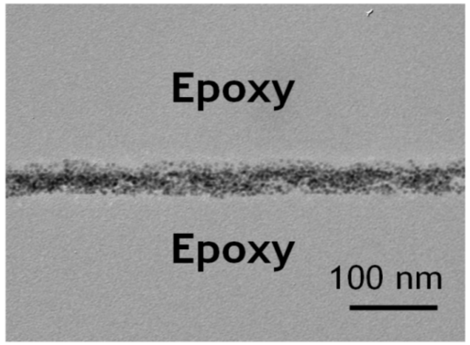


Polymer/NP hybrid

Top view



X-section view



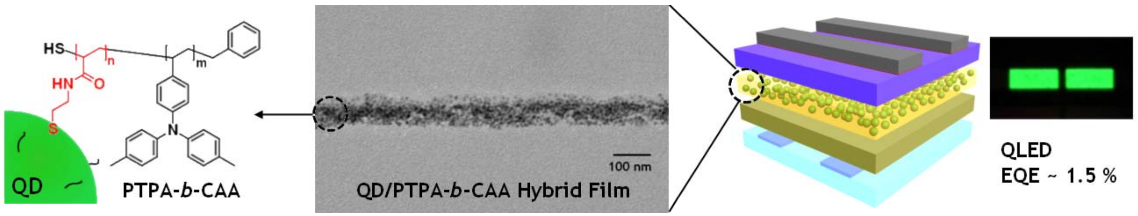
- Chemical binding btw NPs & polymers
- Nanoscopic morphology control
- Extensive process capability
- Surface state passivation with polymers
- Improved colloidal stability

High efficiency & reliability!

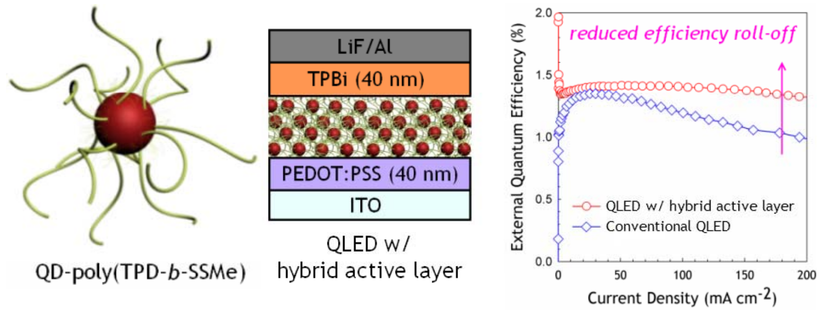
Jeonghun Kwak, *et al*., Adv. Mater. 21 (48), 5022 (2009)

Summary

- Quantum Dot / Conducting Polymer Hybrid Material
  - *QD/conducting polymer hybrid* materials have been prepared by grafting conducting polymer with anchor group.
  - *Hybrid films* show improved surface/bulk morphology and stability compared to QD/conducting polymer *composite films*.
- Light-Emitting Diodes Based on QD-Polymer Hybrid Materials
  - *reduced turn-on voltage, high efficiency, reduced efficiency roll-off* and *high color purity*.
- Compatible with *conventional solution/patterning process* and Applicable to another *optoelectronic devices such as solar cells, photodiodes, etc.*



Jeonghun Kwak, *et al*., Adv. Mater. 21 (48), 5022 (2009)



Wan Ki Bae, et al., Angew. Chem. Int. Ed. (submitted)

Acknowledgements

Prof. Seonghoon Lee
(School of Chemistry, SNU)

Prof. Kookheon Char
(Dept. of Chemical Engineering, SNU)

Prof. Rudolf Zentel
(Univ. of Mainz)

Dr. Wan ki Bae (SNU)

Dr. Jeonghun Kwak (SNU)

Dr. Matthias Zorn (Univ. of Mainz)

Mr. Donggu Lee (M.S. student, SNU)

Mr. Min Ki Nam (M.S. student, SNU)

Mr. Jaehoon Lim (M.S. student, SNU)

Brain Korea 21 Program (SNU/MEST)

International Research Training Group (IRTG)

Thank you very much for your attention.