Development of Next Generation Display Technologies – Quantum Dot LEDs

Material Synthesis and Processing, Device Design and Application

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Outline

- **Introduction to Fraunhofer Society and the Fraunhofer IAP**
- Contributions to OLED development
- QD design, synthesis and applications
- QD-LED devices
- Active matrix OLED (AMOLED)
- Summary

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- First Polymer OLED (1994)
- Organic Electronic (1999)
- Passive Matrix OLEDs (2001)
- OLED Printing (2006)
- **Indium Phosphid Quantum Dots (2009)**
- Pilot Line (2012)

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Outline

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- **Multilayer OLED solvent processing with polymers**
- QD design, synthesis and application
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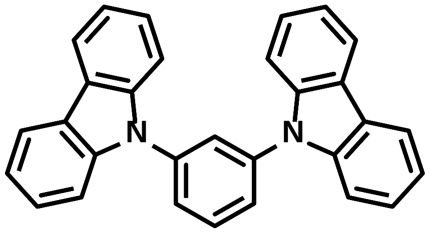
Charge Transport Materials in OLED Applications

Small molecules (SM)



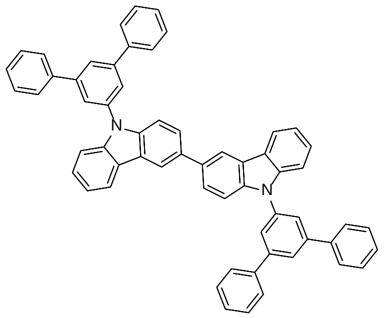
- Low T_g
- When applied from solution
  - Recrystallization problems
  - De-wetting

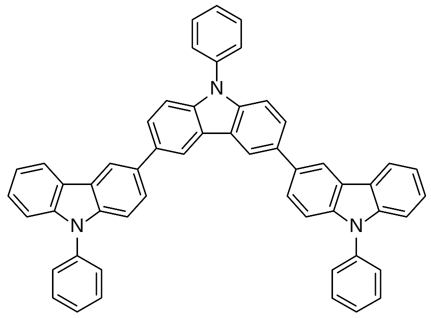
Increase of molecular weight

[1]

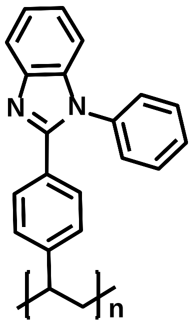
[2]

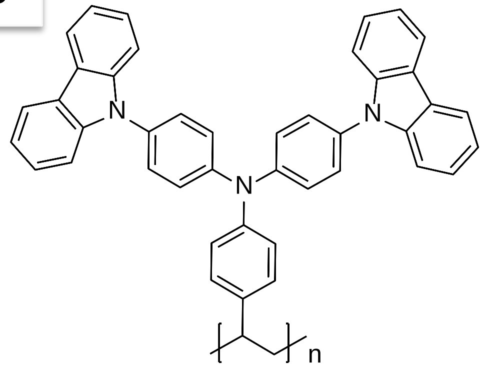
Dimerization / Extension





Side-chain polymers





Similar optoelectronic properties as SM

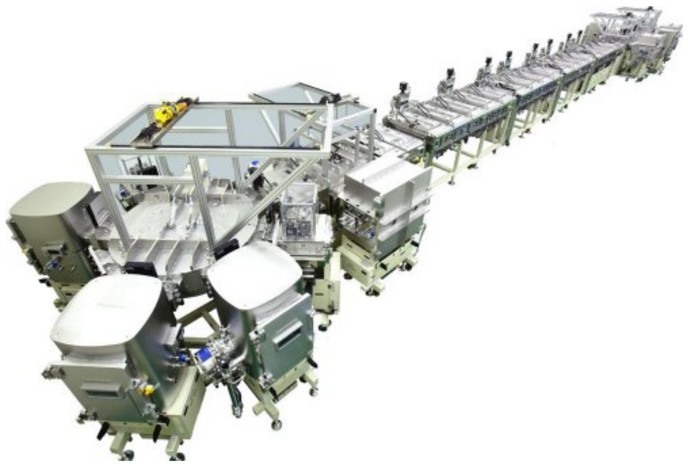
[1] Aizawa et al. *Nat. Commun.*, 5 (2014) 5756

[2] Suzuki et al. *Appl. Phys. Lett.*, 86 (2005) 103507

OLED Multilayer Processing

Evaporation in Vakuum

- Good performance and lifetime
- Reproducible multi-layer processing
- High invest
- Low materials exploitation



Sunic System has developed the large size inline system from Gen 1 to Gen 5.5 and using Sunic system's linear evaporation source, can supply over Gen 8 substrate.

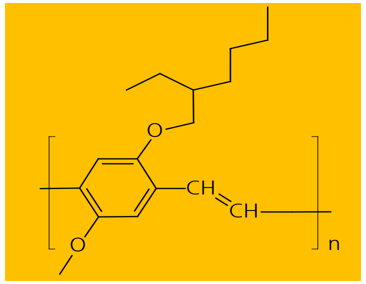
Solvent Processing and Printing

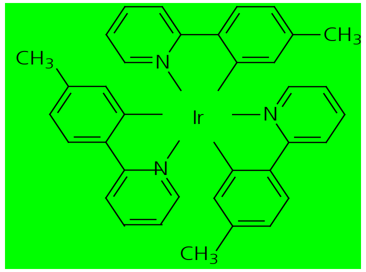
- Moderate performance and lifetime
- Multi-layer processing by crosslinking
- Lower invest
- High materials exploitation

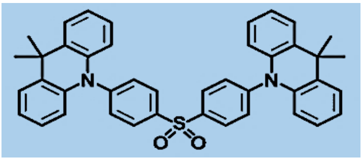
Tokyo Electron (TEL) announced a new OLED R&D inkjet printing system, the Elius 500 Pro that is capable of printing on 2-Gen substrates (370x470 mm).

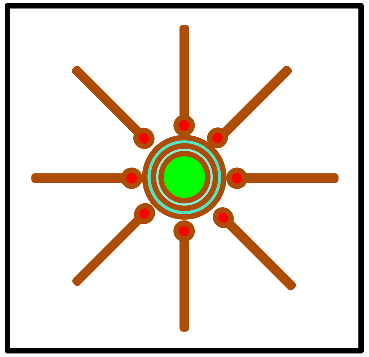
From OLEDs to the next generation: QD-LEDs

- **Singlet-emitters (PLED)**
  - Conjugated polymers MEH-PPV, low efficiency
- **Triplet-emitters (PhOLED)**
  - $Ir(ppy)_3$ as component, high efficiency, evaporate or soluble based
- **TADF Emitter**
  - Thermally activated delayed fluorescence
- **Quantum Dots (QDEF, QD-LED)**
  - Semiconductor nanoparticle with inorganic core/shell and organic ligand, tunable color and narrow FWHM





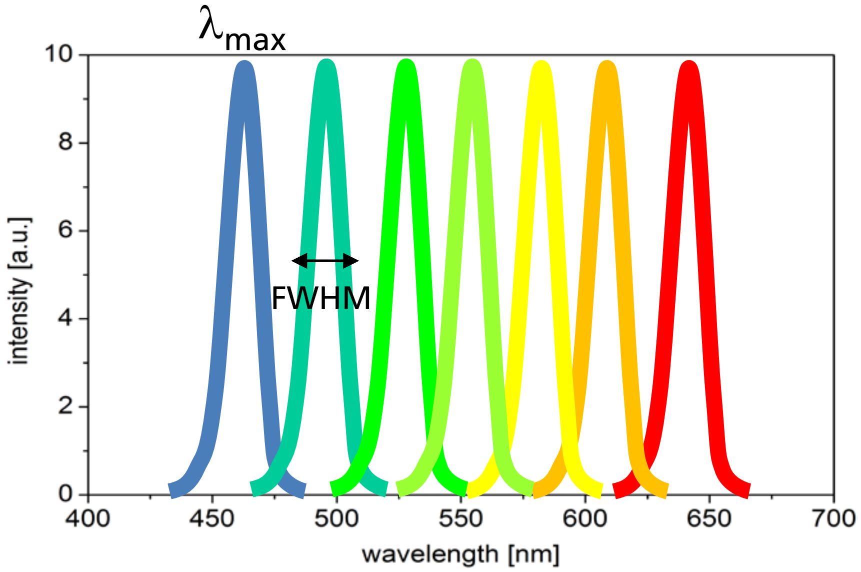


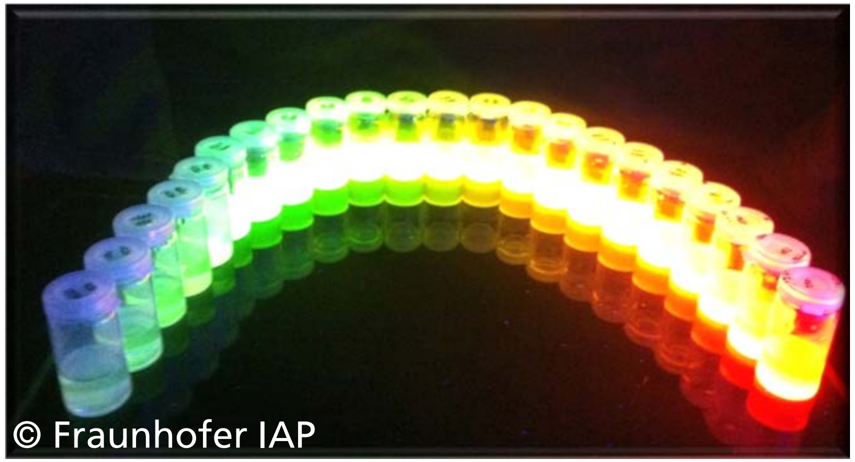


Quantum Dots – special semiconductor nanoparticles

Optical properties are depending on the following parameters:

- **Absorption- and emission properties** (l_{max} [nm]) are depending on the particle size
- **The full width at half maximum** (FWHM [nm]) is depending on the particle size distribution
- The **Luminescence and Quantum Efficiency** (QY [%]) is depending on the surface defects of the nanocrystal





CdSe-QDs

Quantum Dot Stream in Display

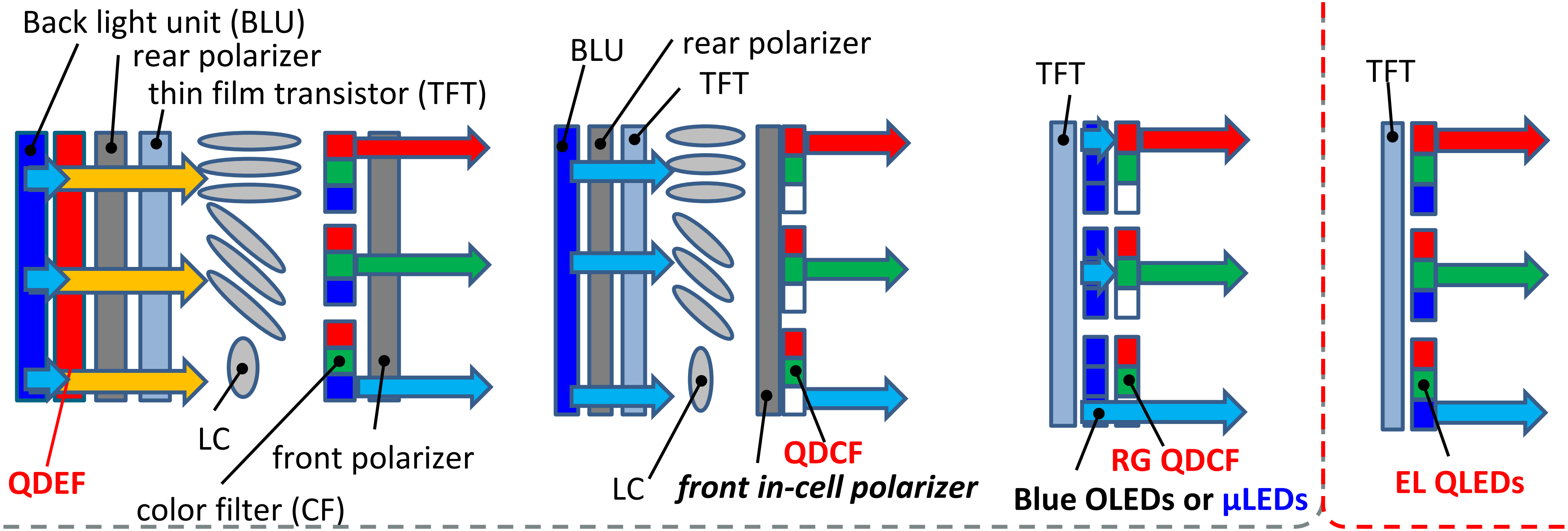
PL | EL

- **QDEF (QD Enhanced Film)**
- blue LED + red QDs + green QDs
- Samsung 8K UHD QLED TVs

- **QDCF (QD Color Filter)**
- 50% higher efficiencies
- widest viewing angles
- In-sell polarizer / high absorption

- **QDCF + Blue OLED**
- No BLU, polarizer & LC
- Low color distortion
- Thin & Flexible

- **EL-QLEDs**
- Self-emitting
- Wide color volume
- Conformable display
- Low cost



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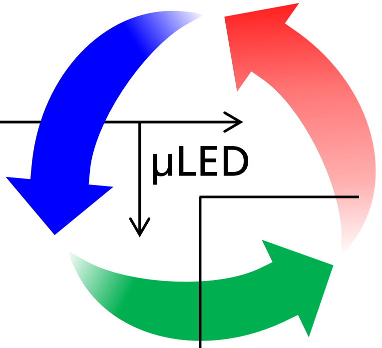
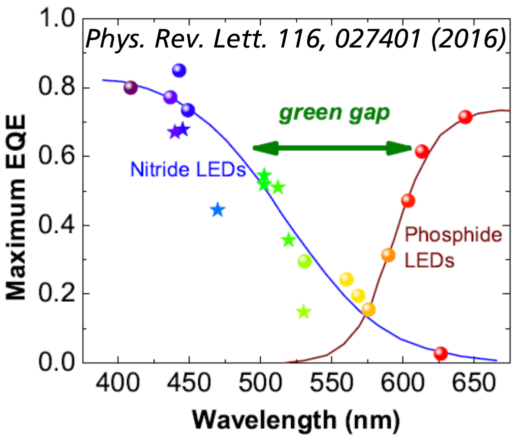
µLEDs with Quantum Dots - beyond the pick & place

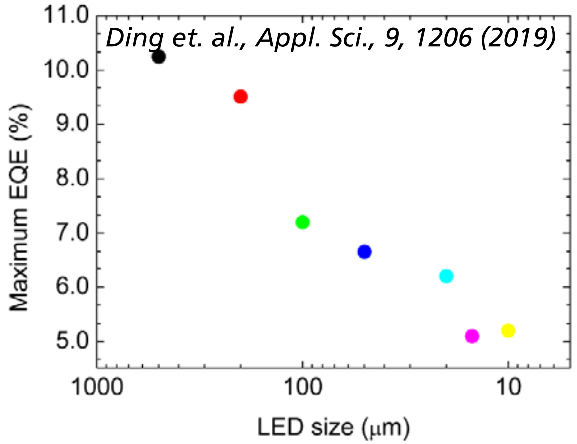
InGaN — **RED GREEN** — *Low EQE* → µLED ← *Drop of EQE with smaller size* — AlInGaP **RED**

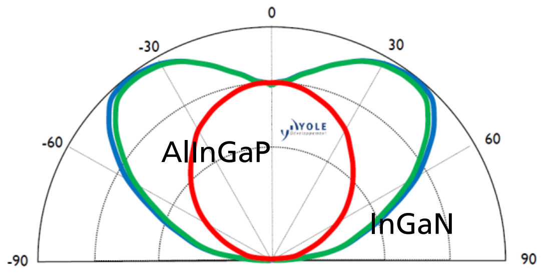




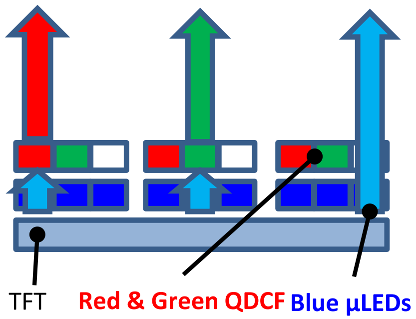
R & G QDs

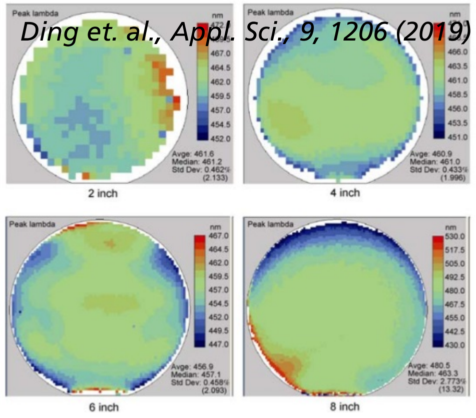
High efficiency
Color uniformity





Hypothetical beam pattern of Red, Blue and Green emitters (not actual, illustration purpose): the relative intensity of the red green and blue emitters at 0 degree and 30 or 60 degrees varies, resulting in a shift of color balance at those different angles.
(Source:Yole Development)
@ www.yole.fr





used under CC BY *Gadget Seoul*
https://youtu.be/2hQsJhMBdeQ
- modified with more information-

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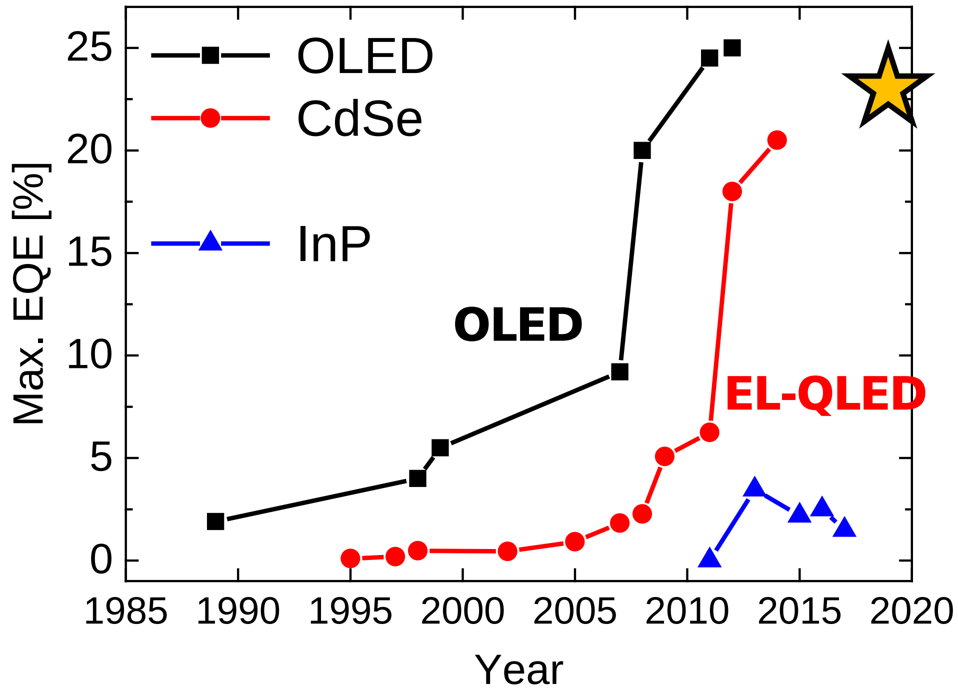
Challenges for EL-QLEDs

- **High performance with Cd-based QDs**
  - *EQE ~23% (63~100 cd/A)
  - *T50: 7k ~ 1700k hour at 100 cd/m^2

** Nature photonics 13, 2019, 192-197*

- **Cadmium-free QDs**
  - **InP**, **ZnSe**, $CuInS_2$, Perovskite…
  - relatively low performance and stability

RoHS



- **Efficiency roll-off, low brightness, life time** → sophisticated system design for carrier balance, low luminance quenching and recombination zone (RZ)
- **Color saturation for BT. 2020**

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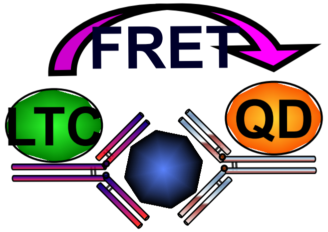
QDs @ Fraunhofer IAP - Technology and Application

- **QD based OLED**
  - OLED set-up and 4th generation of emitting materials
- **QD as converting material for lighting application**
  - QD based enhancement films (QDEF) for display application in LED backlights
- **QD as special material for security application**
  - QDs printed on paper or plastics
- **QD as highly sensitive sensor materials** for bioanalytical applications



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Outline

- Introduction
- Multilayer OLED solvent processing with polymers
- **QDs: synthesis approaches and design principles**
- QD-LED devices
- Active matrix OLED (AMOLED)
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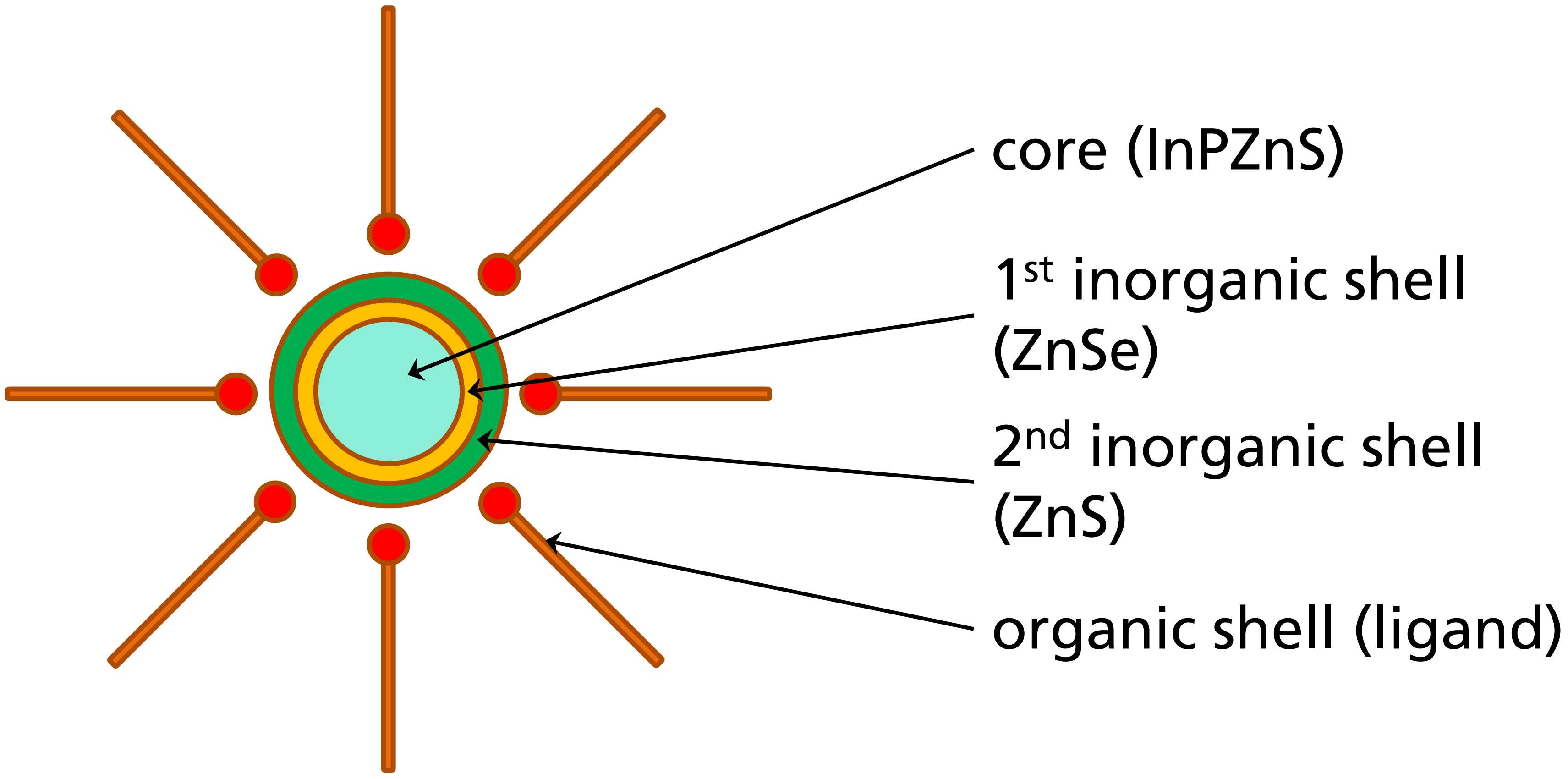
Quantum Dot System Structure

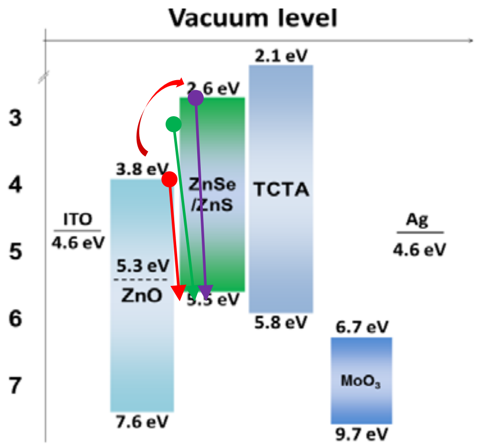


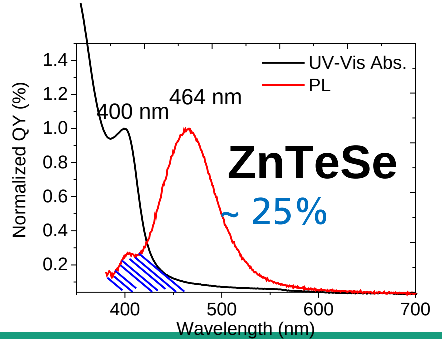
[1] DE 102012203036 A1
[2] DE 102013206077, EP 2 787 057 A1, US 2014/0353579 A1

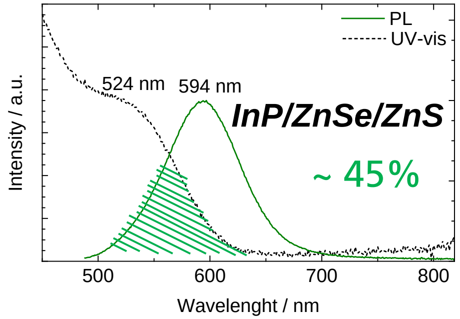
ZnSe/ZnS QDs for blue QDs – current issues

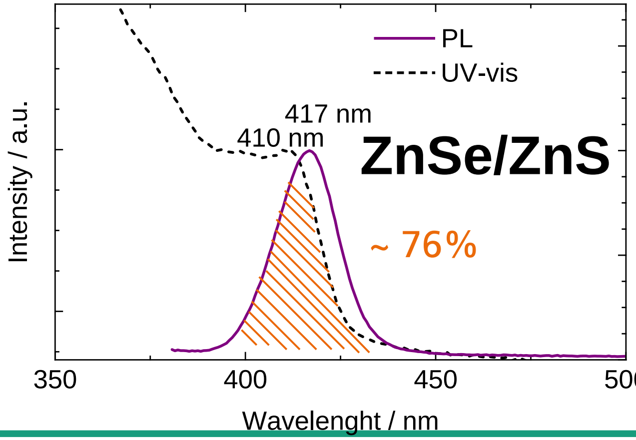
Q. what is the main reason of low efficiency and parasitic emissions?

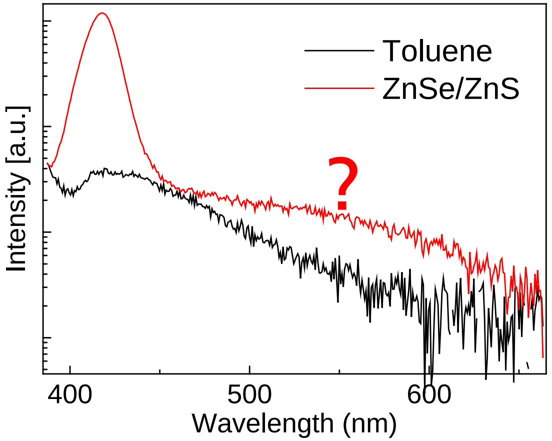
- A. Inverted: not efficient electron injection by energy barriers ~ 1.2 eV
  → Other ETLs for low injection barriers… PEIE, ZnMgO
- B. The defects (shown in PL) of QD disturb the charge injection?
  → Further passivation of QDs ~ thicker ZnS, alloyed ZnSeS/ZnS shell
- C. Stronger overlap between PL & UV-Vis Absorption ~ 76% (45% w/ InP)
  → Stronger self-quenching?
  → Te doping..











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Status QD synthesis @ Fraunhofer IAP | Focus on InP and ZnSe

- **CdSe**
  - Best performance for green and red
- **Cd free QDs (green and red)[1]**
  - QY comparable for green and red
  - FWHM to be improved
- **Cd free blue QDs[2]**
  - ZnSe for blue in development
  - QY about 30%, FWHM < 30 nm
- **General approaches**
  - Color tuning via reaction conditions
  - Ligand tuning to adjust solubility

CdSe	green	red
QY (%)*	> 81	> 85
FWHM (nm)*	< 26	< 34

InP	green	red
QY (%)*	> 85	> 77
FWHM (nm)*	< 42	< 58

ZnSe	blue
QY (%)*	~ 30%
FWHM (nm)*	< 20

*all data measured in solution

[1] DE 102012203036 A1
[2] DE 102013206077, EP 2 787 057 A1, US 2014/0353579 A1

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Outline

- Introduction
- Multilayer OLED solvent processing with polymers
- QD design, synthesis and application
- **Complex material setups in QD-LED devices and the optimization challenge (ETL, QDL, ETL vs QDL, QDL vs HTL)**
- Active matrix OLED (AMOLED)
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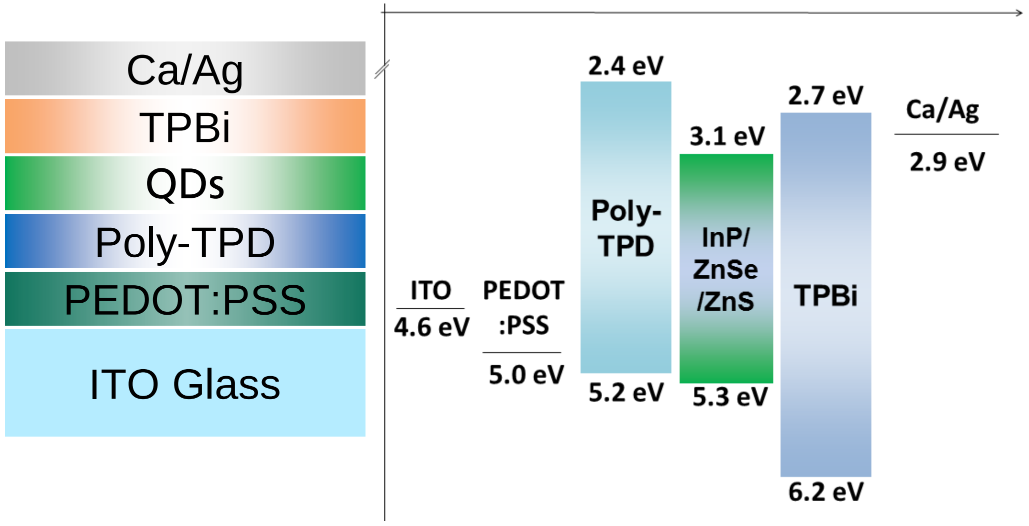
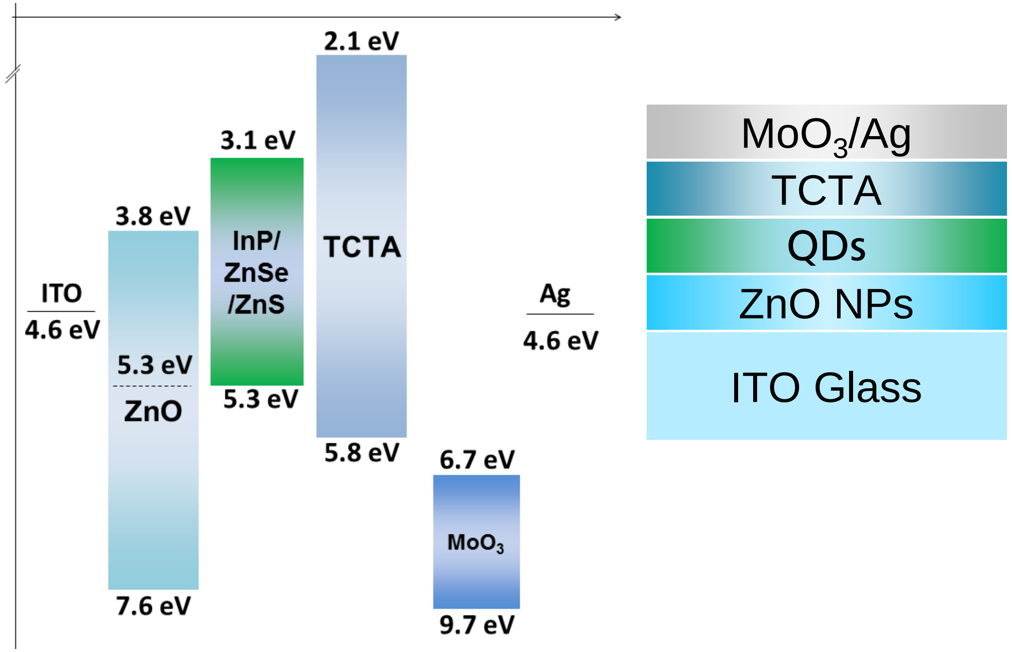
Device architectures of QD-LEDs

conventional



inverted



- Multi-layer device structure, orthogonal solvent process
- Uniform film, efficient charge carrier balance (injection, transport, block)
- ZnO NPs: Auger assisted electron injection, charge neutralization effect

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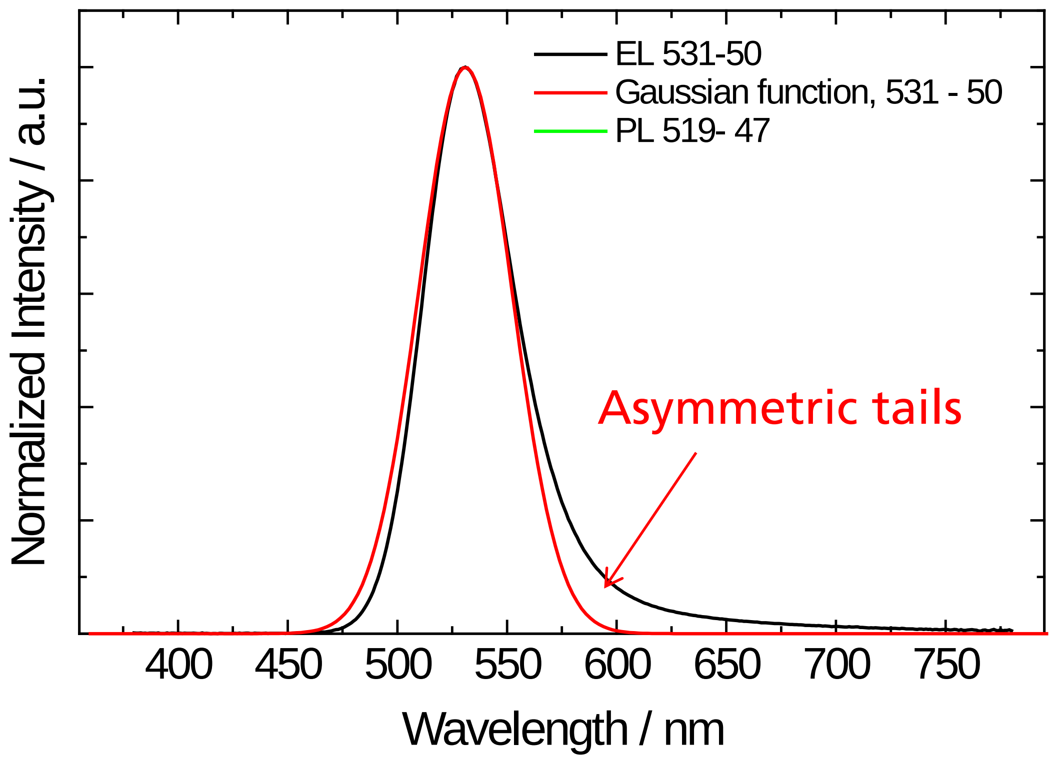
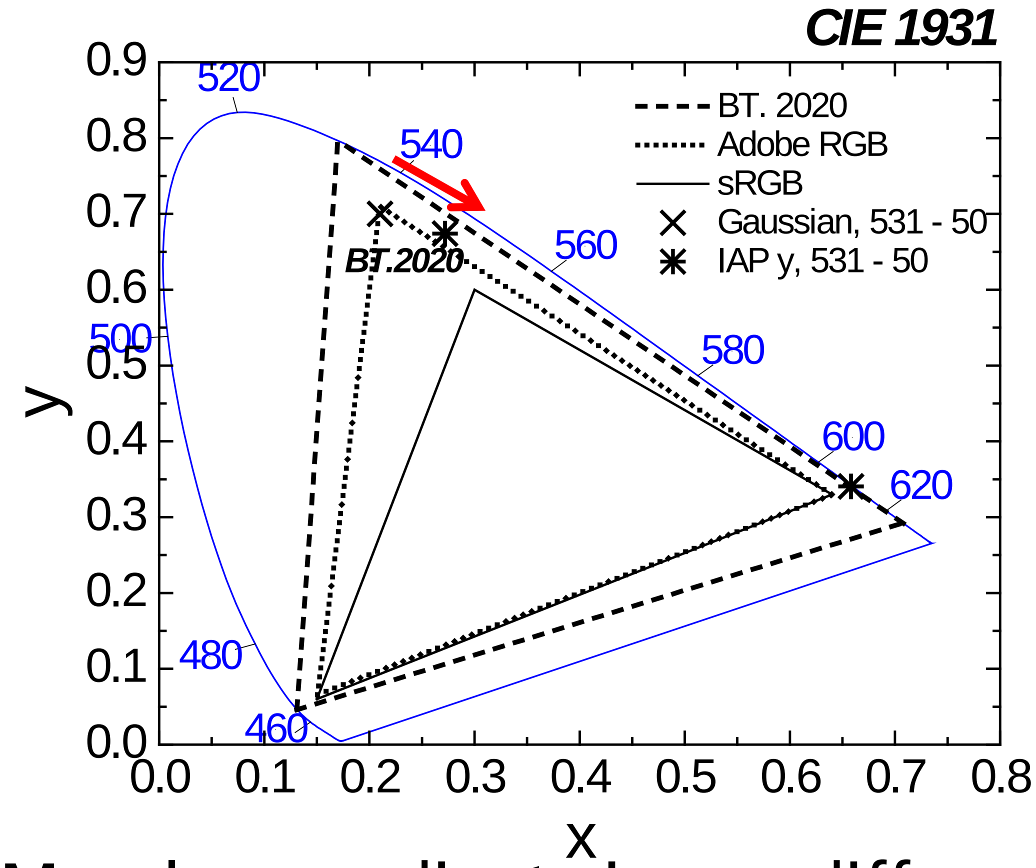
CIE1931: Green with Gausian vs. QD spectrum





- Even though the same λ_{peak} and FWHM, color coordinate is very different
- Asymmetric tails from QDs → Green is sensitive to color purity

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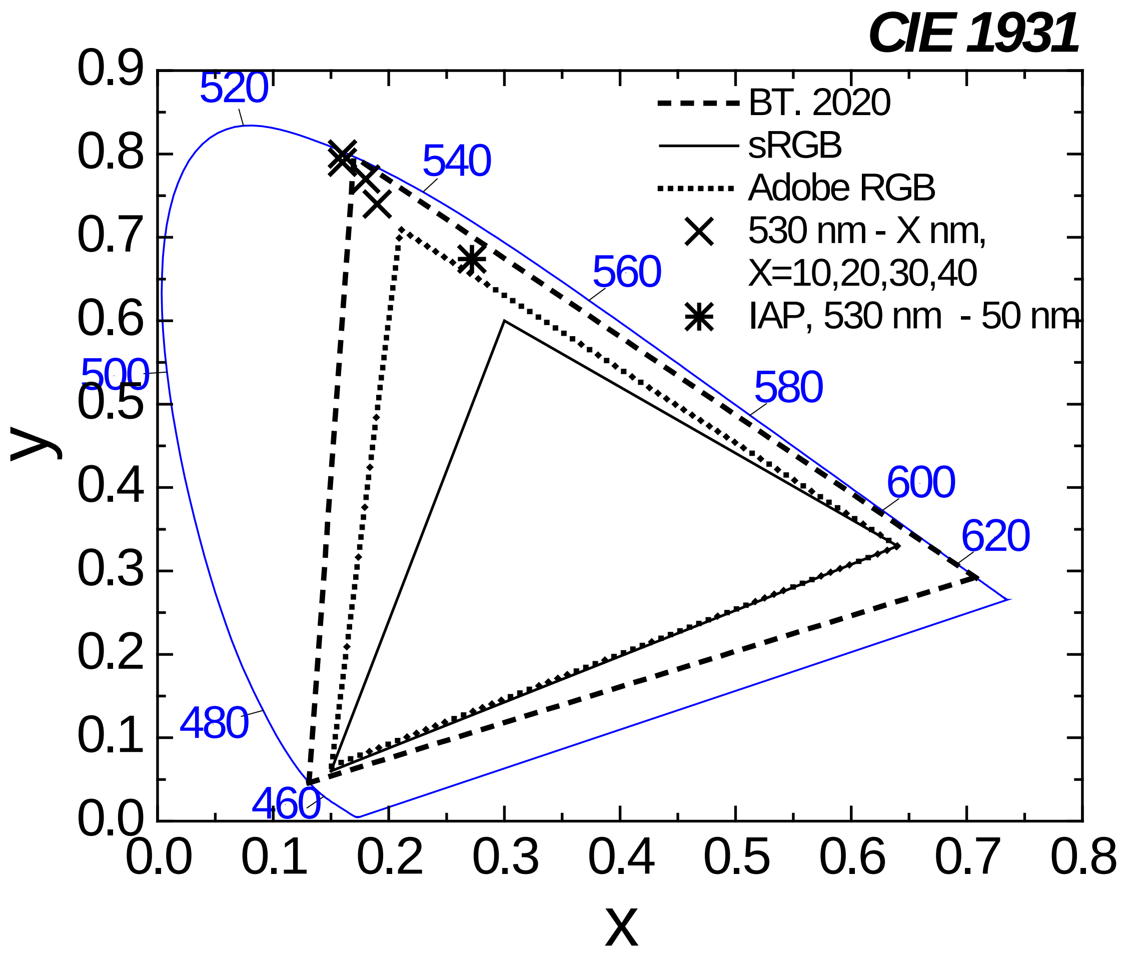
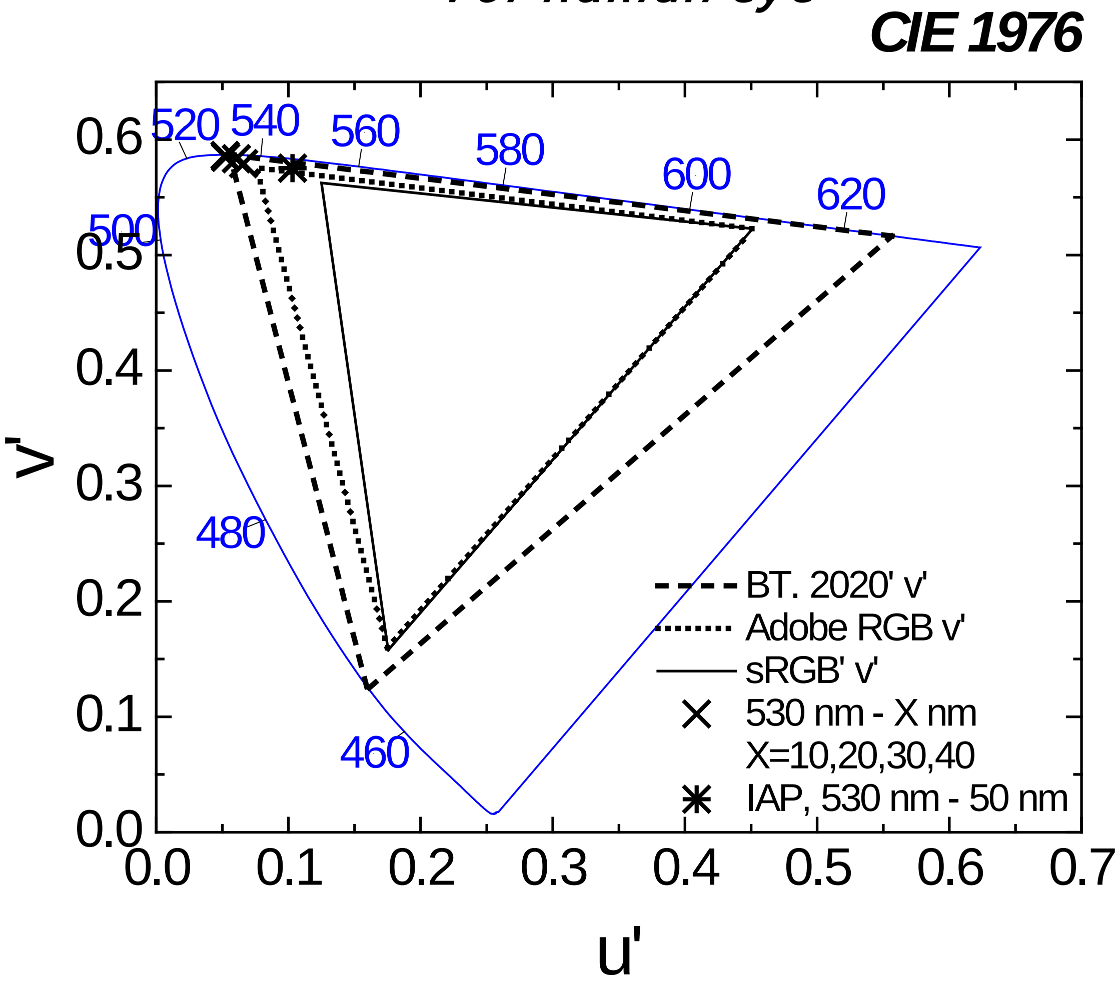
CIE1931 vs CIE1976 (Gaussian spectrum and IAP QDs)

For measurement



For human eye



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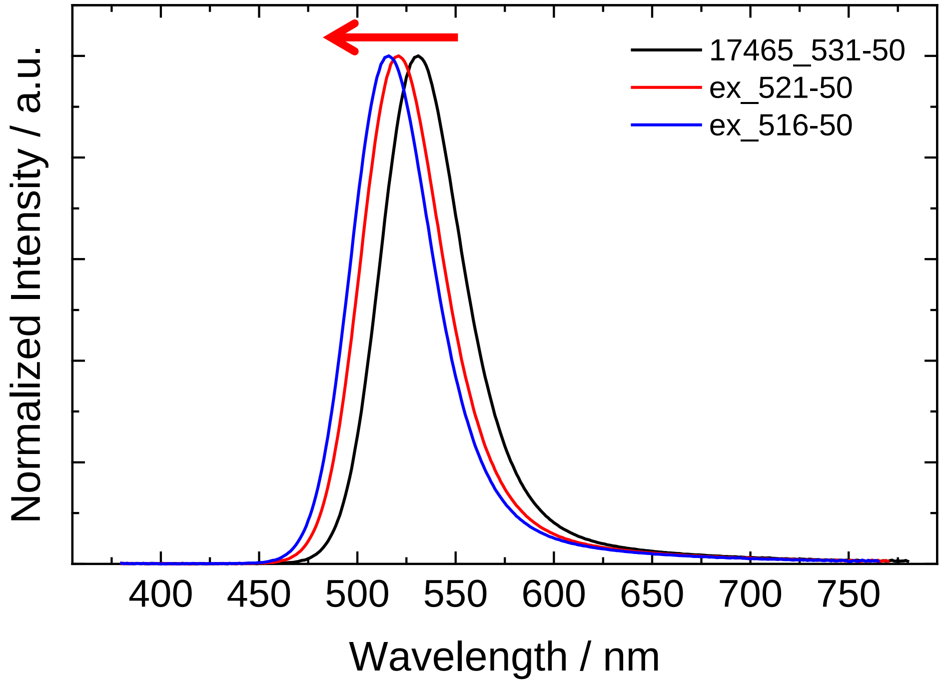
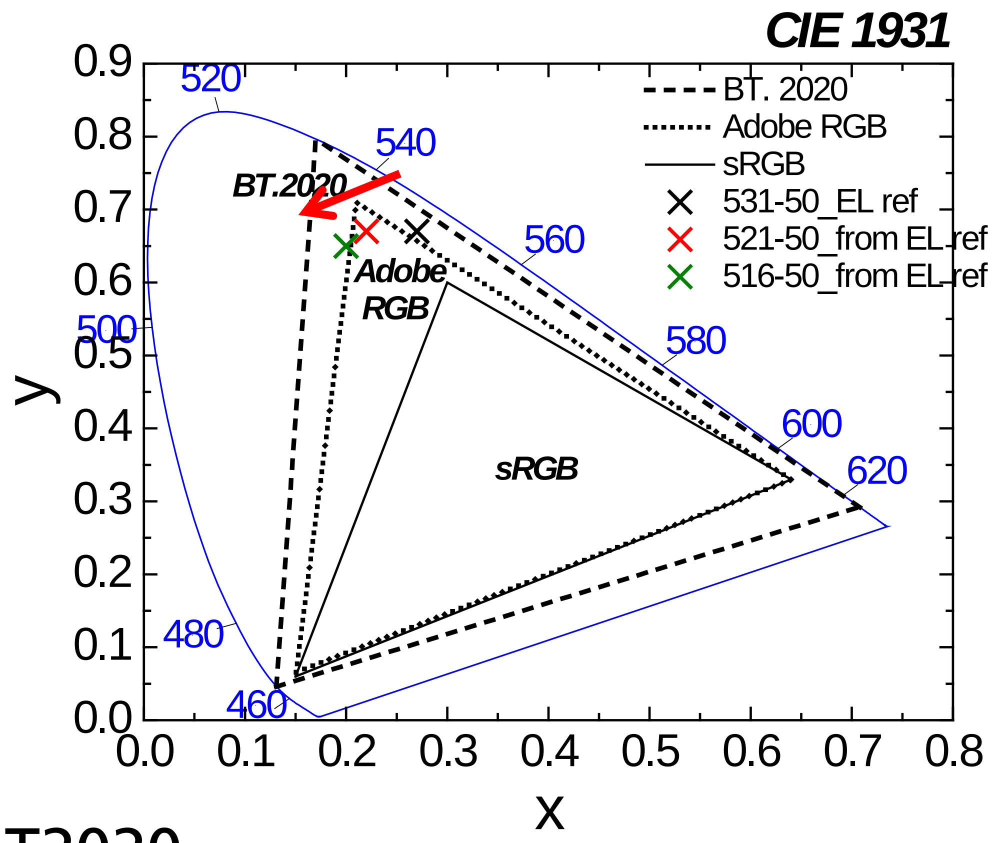
Peak wavelength shift with reference EL spectrum

516 ← 521 ←531

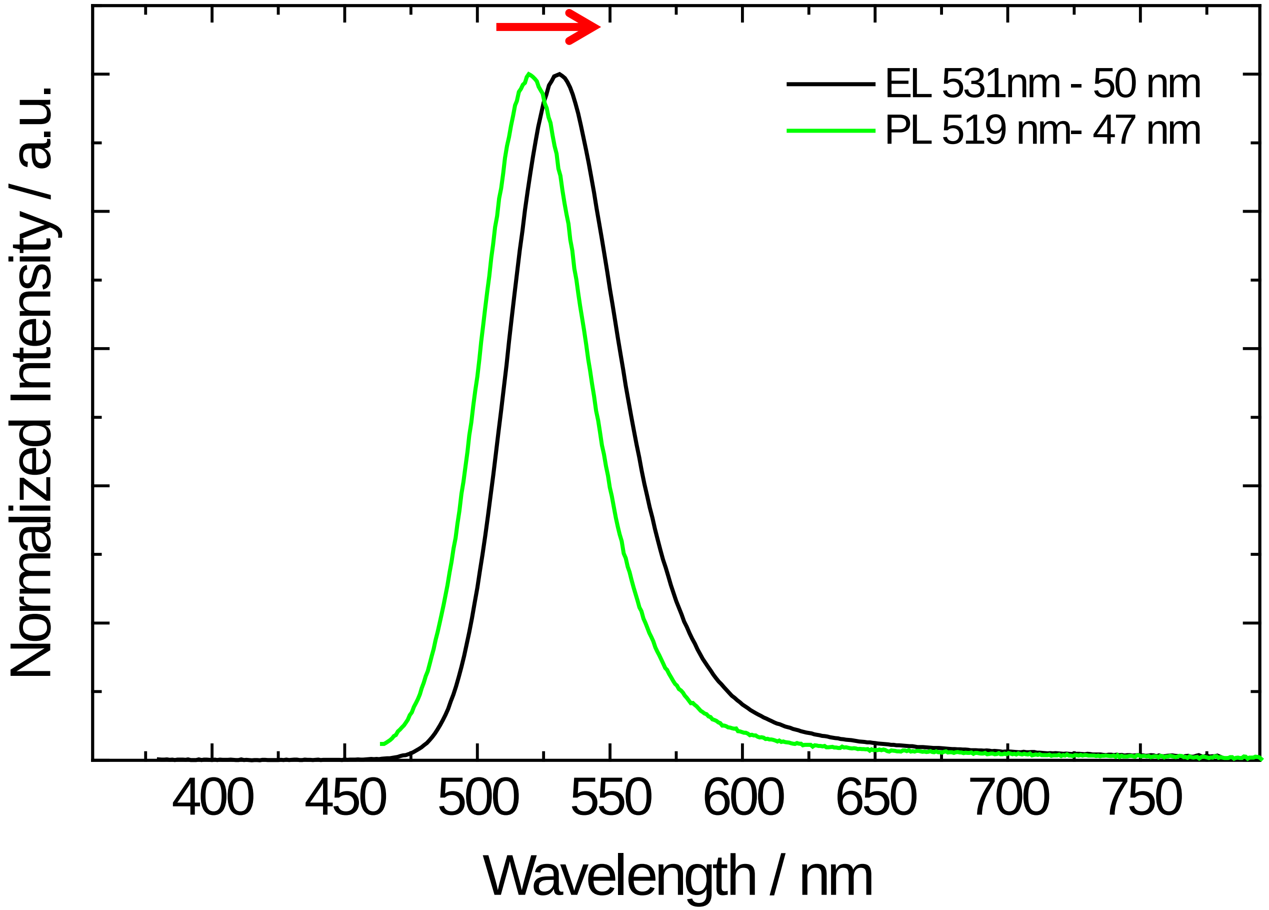




To reach green color coordinate for BT2020

→ FWHM should be narrow down to ~ 30 nm

Red-shift from PL to EL λ_{peak} >10 nm



For the design QD, red-shift must be concerned.

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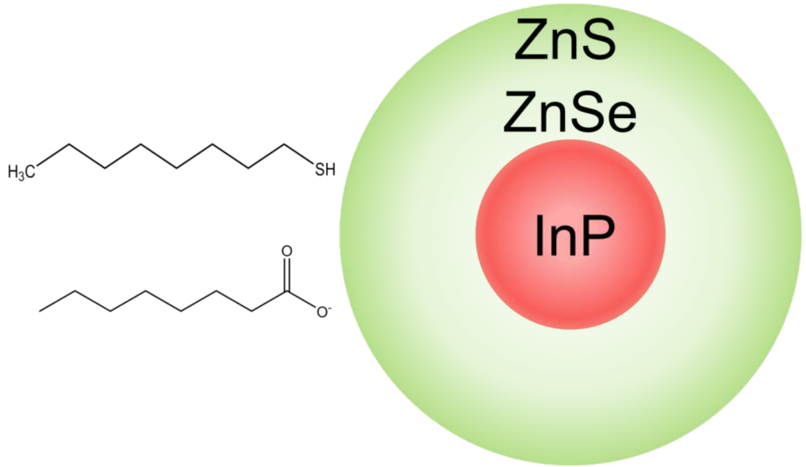
QD spectrum target for BT2020

Color	BT2020, monochromatic (nm)	CIE 1931 coordinate (x,y)	98.4% of BT2020 DOI:10.1364/OE.23.023680		95% of BT2020 DOI:10.1364/OE.23.023680	
			λ_{peak} (nm)	FWHM (nm)	λ_{peak} (nm)	FWHM (nm)
Red	630	0.708, 0.292	634.3	20	634.3	30
Green	532	0.170, 0.797	530.6	20	530.6	30
Blue	467	0.131, 0.046	465.8	20	465.8	30

Conventional QD-LEDs → Inkjet printing



QD design for QD-LEDs

Structure: InP/ZnSe/ZnS

Multi-shell design

Ligand design

Quantum Yield (QY) & Purity

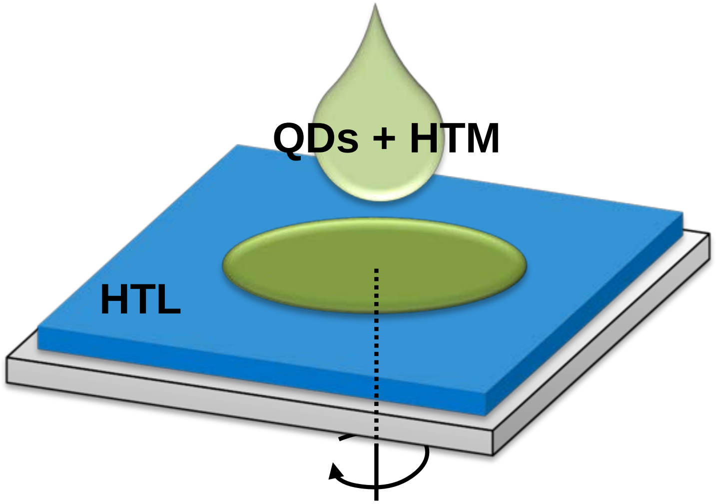
Crosslinkable hole transport layer

Thermal crosslinking

Orthogonal solvent process

Avoiding interfacial mixing

Enhanced film stability



Crosslinked HTLs
+ QD Spin-coating / **Inkjet printing**

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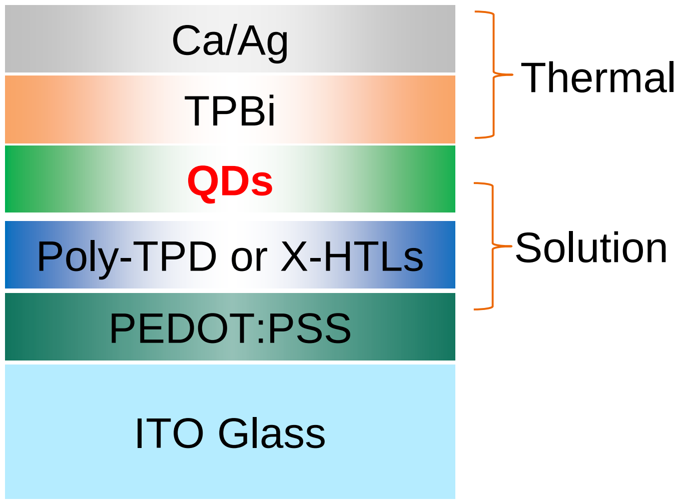
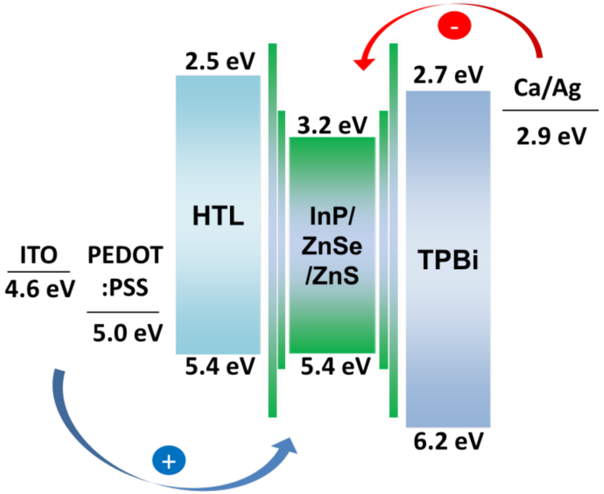
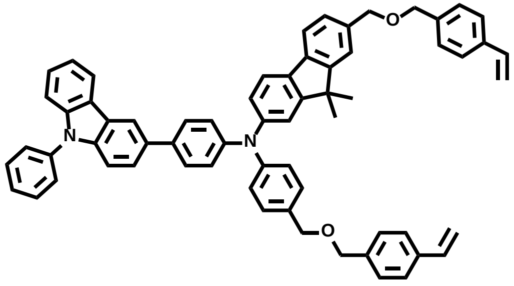
X-linked HTLs + different ligands and Zn precursor



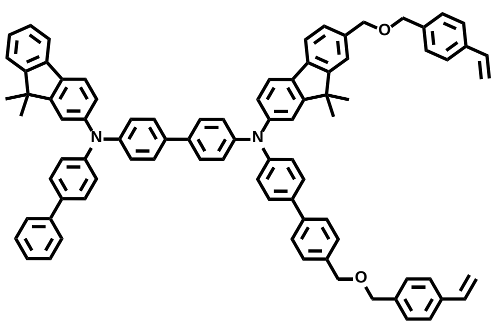
HTL layer	R_q / R_{pv} (nm)	HOMO (eV)	Max. CE (cd/A)	Luminance @ 7 V (cd/m^2)
Poly-TPD	1.70 / 51.59	5.18	10.1	890
SHTM-1118	0.60 / 8.45	5.48	11.5	800
SHTM-1133	0.60 / 7.80	5.54	13.7	1400
SHTM-1301	**0.65 / 5.41**	**5.42**	**11.6**	**2200**

μ_h : SHTM-1118 > SHTM-1133 > SHTM-1301

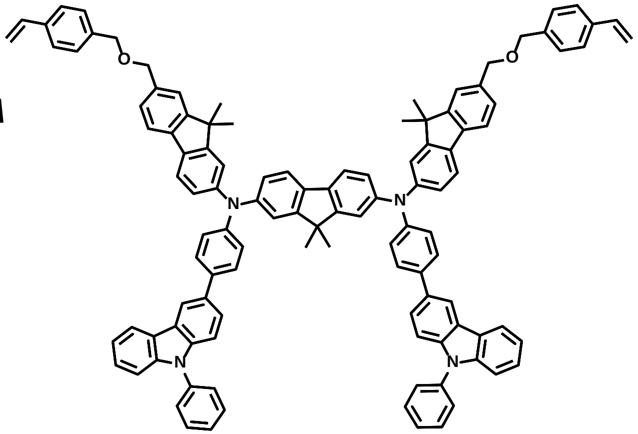




SHTM-1118



SHTM-1133



SHTM-1301

DS Neolux
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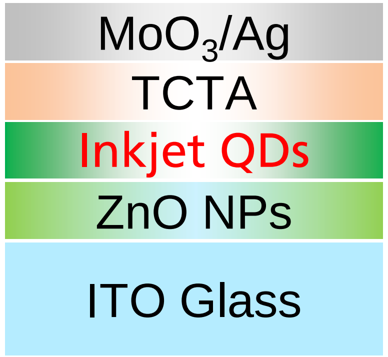
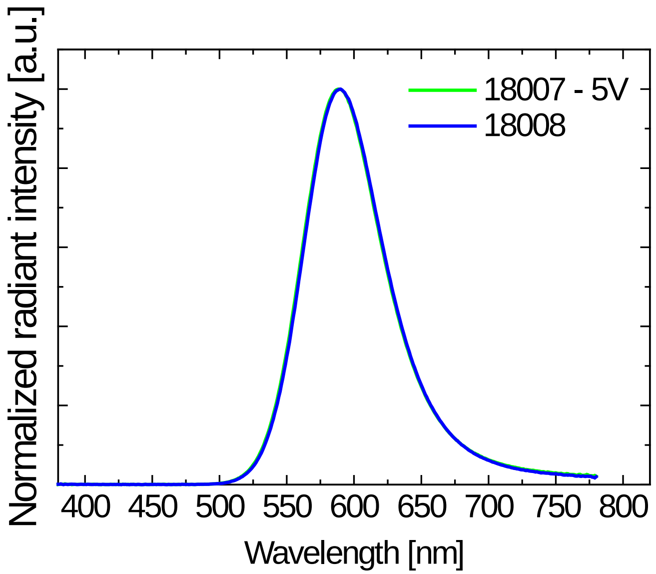
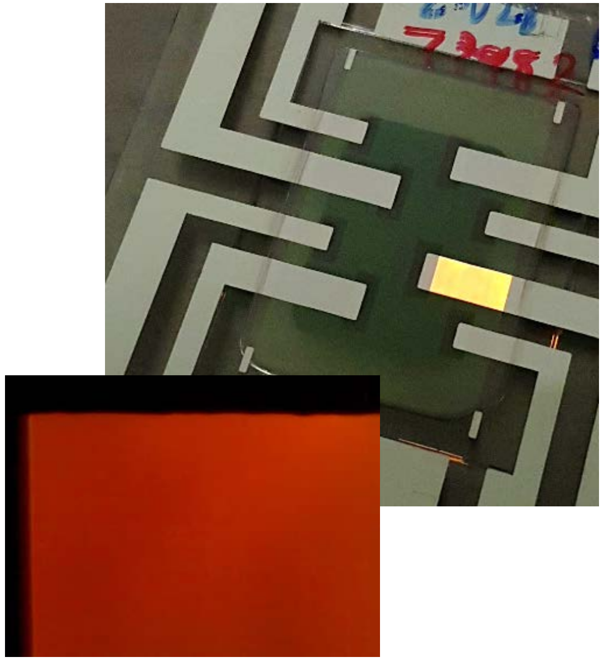
Inkjet printed (in air) inverted EL-QLEDs

Device results







- QD layer with QD ink –600 dpi vs. 500 dpi
  - All device show pure EL spectrum
  - V_{th} ~ 2 V (similar to spin-coated one)
  - Max. efficiency and luminance: 1.400 cd/m^2
  - Current efficiency is rather poor compared to the spin-coated devices in N_2.

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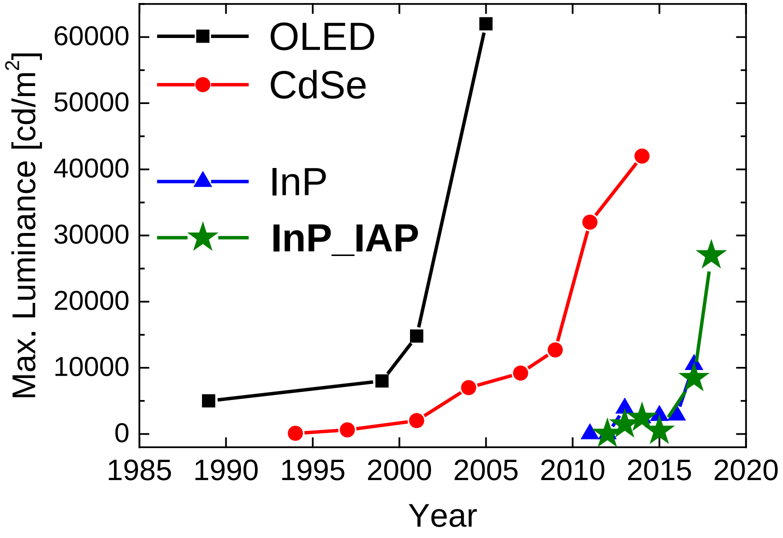
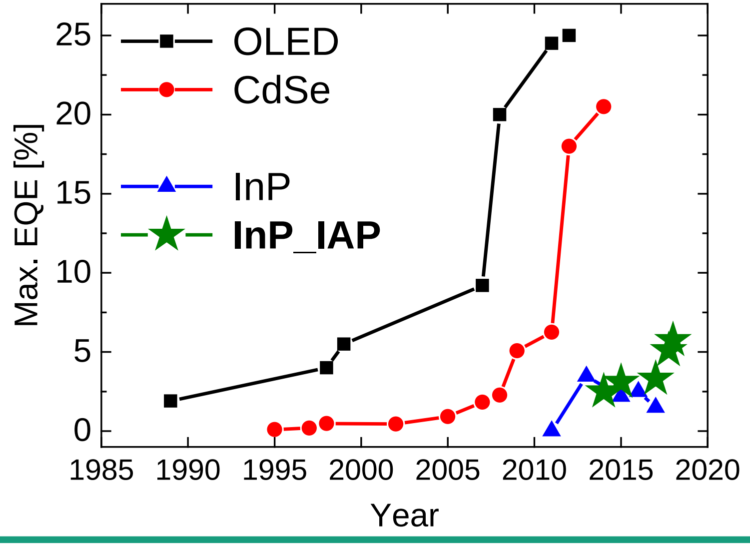
Summary of InP-based QD-LEDs

- Remarkable increase of brightness of QD-LEDs
  - **20.000 ~ 28.000 cd/m²**
  - **3.3 ~ 5.7 % EQE**
- **Interaction between QDs and mid-gap states of ZnO NPs is the key!**
  - **QD layer thickness is important**
  - **Good performance requires smooth and stable ZnO NP layer**
- The feasibility of InP/ZnSe/ZnS QDs as the future source of Cd-free QD-LEDs





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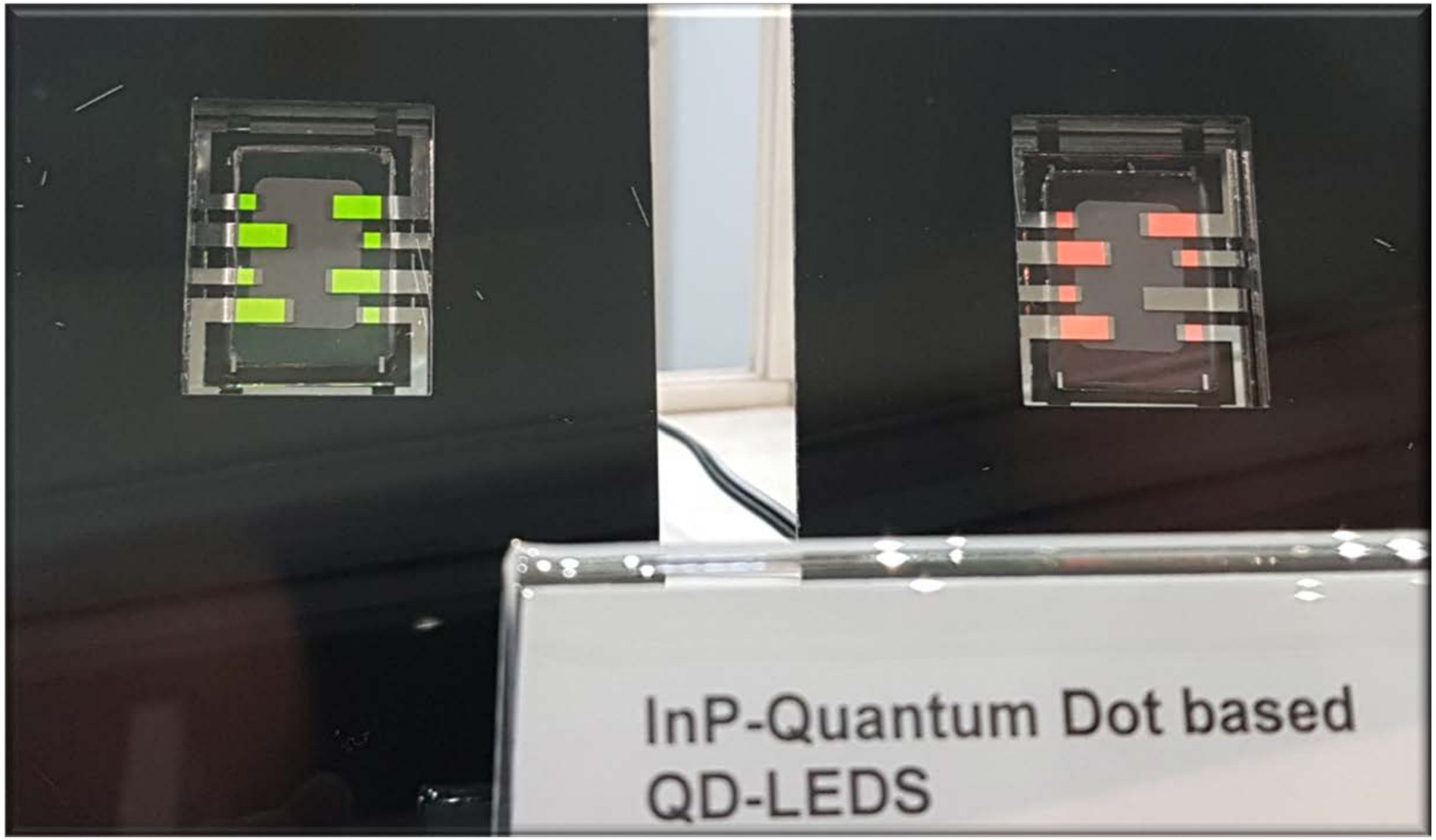
Devices running for days straight



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Summary

- **InP/ZnSe/ZnS QD design** for improved performance
- QD **design and purity** trump QY
- Good performance requires **smooth and stable ZnO NP layer**
- **Thickness of QD layer** is very important for device performance
- **Complex device systems** require different optimizations depending on material combinations (reverse trends observed)
- Device performance: **20,000 ~ 27,260 cd/m^2** , 10~11 cd/A, up to 5.7% EQE
- First steps towards **ESJET printable AMQD-LED** devices

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ToDo’s

- QD and QD-LED: efficiency, stability, design
- profound understanding of:
  - processes in a driven device (non-radiative losses, charge effects, etc.)
  - how to tune charge carrier balance effectively
  - how to design the recombination zone
  - how to reduce luminance quenching
  - degradation(?) of QDs
- **New device concepts (tandem structure) with regards to material choice (move away from OLED optimized materials) and maybe even stack design**
- **Full-color R.G.B. patterning process (Inkjet-printing, lithography….)**

Current project (ELQ-LED)

ELQ-LED: Exploring quantum materials - new ways to realize innovative optoelectronic components (2017 – 2020)

BMBF project ELQ-LED for basic research on quantum materials as light sources / 2018

Researching New Highly Efficient OLEDs with Quantum Materials

Press release of the BMBF joint project ELQ-LED / Merck KGaA / 1.2.2018

"Exploring quantum materials - new ways to realize innovative optoelectronic components (ELQ-LED)" is the title of a joint project funded by the German Federal Ministry of Education and Research (BMBF) with 5.5 million euros. The aim of the project is to develop quantum materials for innovative applications in the display and lighting industries. The total budget of the project amounts to 9.1 million euros.

MORE INFO

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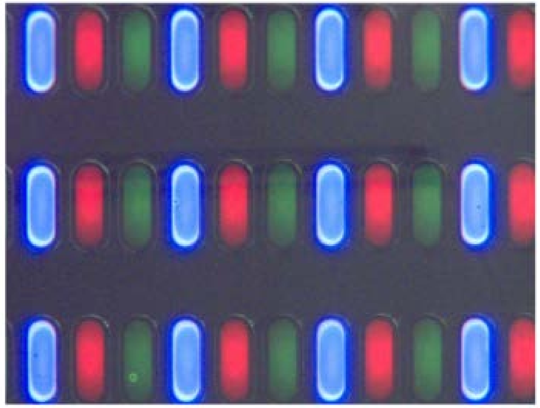
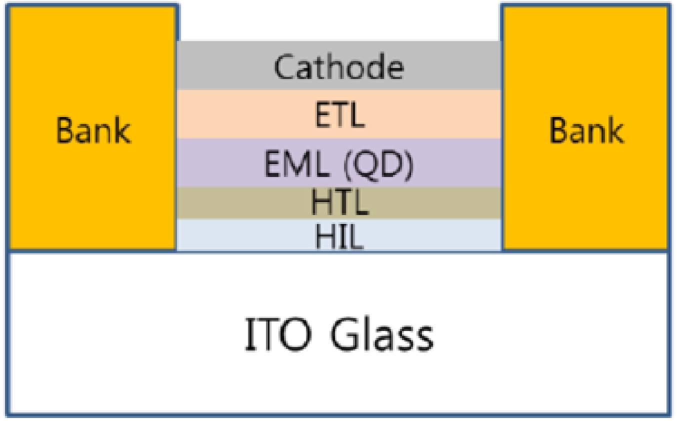
Current project (FiPaQ)

FiPaQ: **Fi**ne-**Pa**tterned eco-friendly **Q**uantum dot light emitting diode (2019 - 2022)

Development of materials and process technology for fine-patterned eco-friendly quantum dot light emitting diode

German-Korean
joint R&D project





R.G. display
88 inch 8K-Resolution
~ 100 ppi

Federal Ministry
for Economic Affairs
and Energy

Ministry of Trade,
Industry and Energy

Fraunhofer IAP

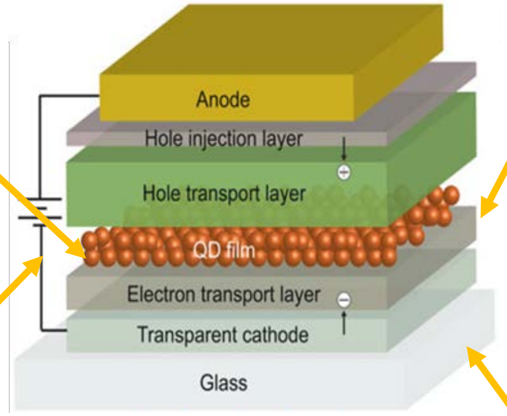
FiPaQ

Eco-friendly QD Light Emitting Materials

LT Materials

Optimization of EL-type QD-LED

KETI Fraunhofer IAP



Electron Transport Layer (ETL)

KETI KGU 경기대학교 KYONGGI UNIVERSITY

Inkjet materials/device & process

Fraunhofer IAP NOTION SYSTEMS

LG Display

Current project (CoCoMe)

CoCoMe: **Co**lor **Co**nverting **M**icro-L**E**Ds (2019 - 2023)

Ultra high luminance(> 50knit) Micro Displays with 2,000 ppi, for AR application

New research project between Fraunhofer IAP and Korea Electronics Technology Institute (KETI) / 2019

QD color filters for microLEDs

Press release / Text: Julia Consten / 6.9.2019

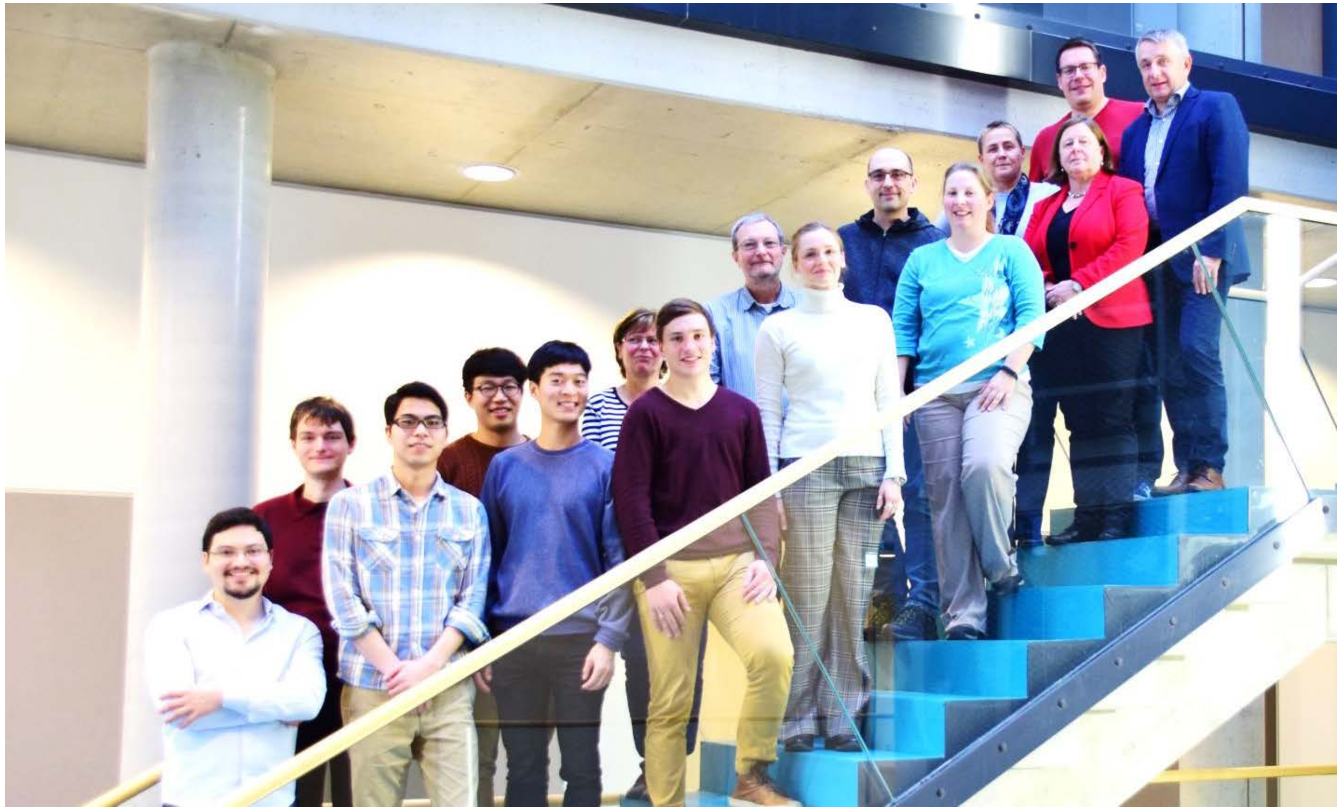
Quantum dot-based color filters for micro-LEDs are one of the most promising future technologies for displays. This technology makes displays even more brilliant, more efficient and even thinner, compared to displays with conventional color filters. The Fraunhofer Institute for Applied Polymer Research IAP and KETI have started working together on the development of printed QD color filters microLEDs in the new research project »CoCoMe«.

MORE INFO

KETI

Ministry of Trade, Industry and Energy

Acknowledgement



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Dr. Yohan Kim - **Device**

Printing Team (OLED & OPV)
Dr. Christine Boeffel - **Leader**
Dr. Manuel Gensler - **ES-JET**
Bert Fischer - **Ink-jet**
Franziska Ebert, Stefan Kröpke, Stefanie Kreißl - **Applications**

SPONSORED BY THE
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Project funded by the EUROPEAN UNION
KETI
DS Neolux

Thank you for your attention!

Want to know more?

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