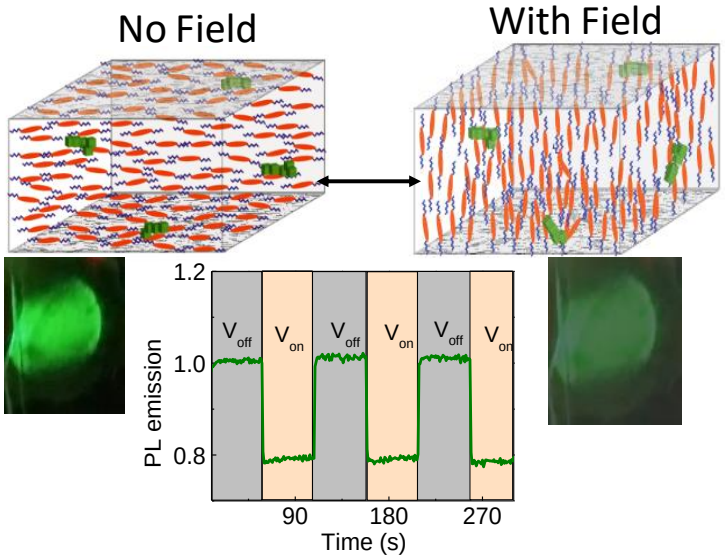
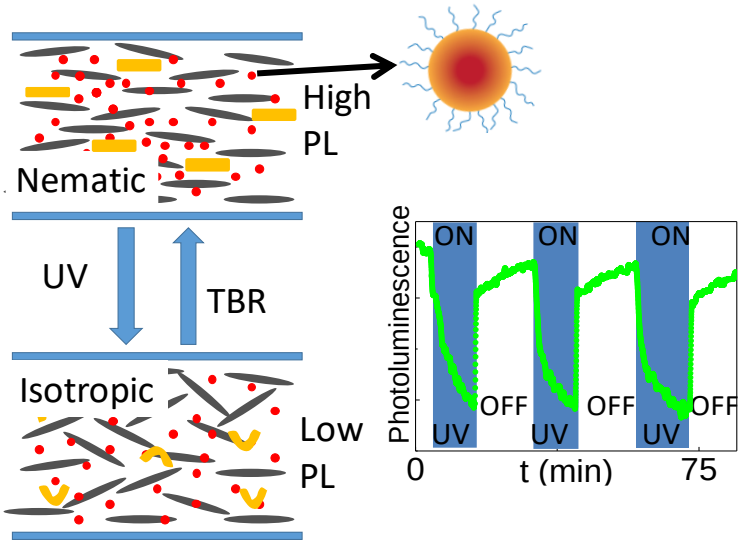
Multiple and efficient pathways for anisotropic photoluminescence modulation in soft nanocomposites





Adv. Opt. Mater. *2019, 7, 1801408*

Crystals. *2019 , 9, 378*

Chem. Photo. Chem. *2020,* 4, 413

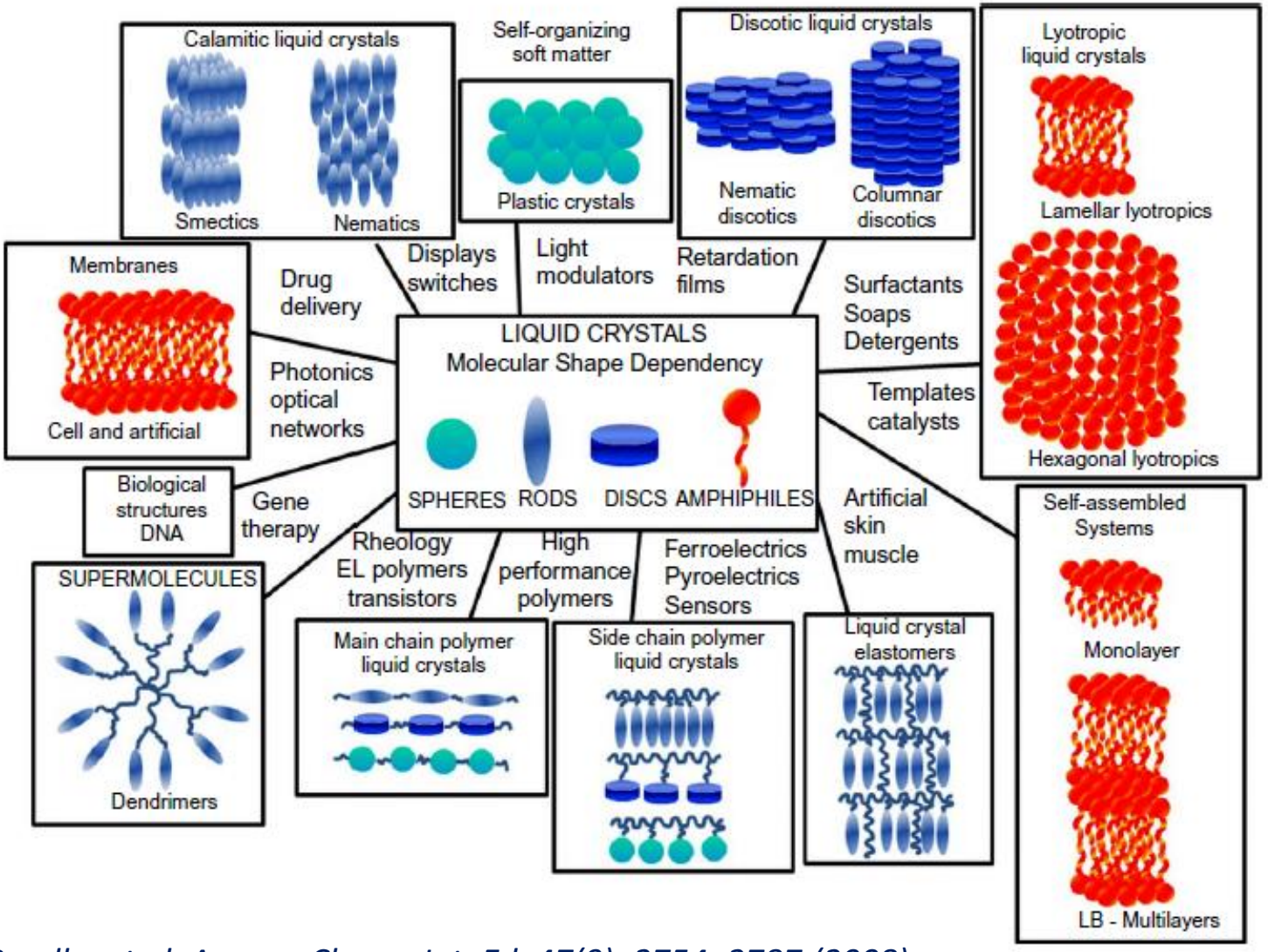
Pragnya Satapathy
CeNS
Bengaluru

Outline

- Introduction to Soft Nano composites
- Motivation
- Anisotropic emission
- Emission modulation
- Fast switchable display devices

Liquid crystals

Classes of Liquid crystals and their applications



J. W. Goodby et al. Angew. Chem., Int. Ed. 47(9), 2754–2787 (2008).

Nano materials in Liquid crystals

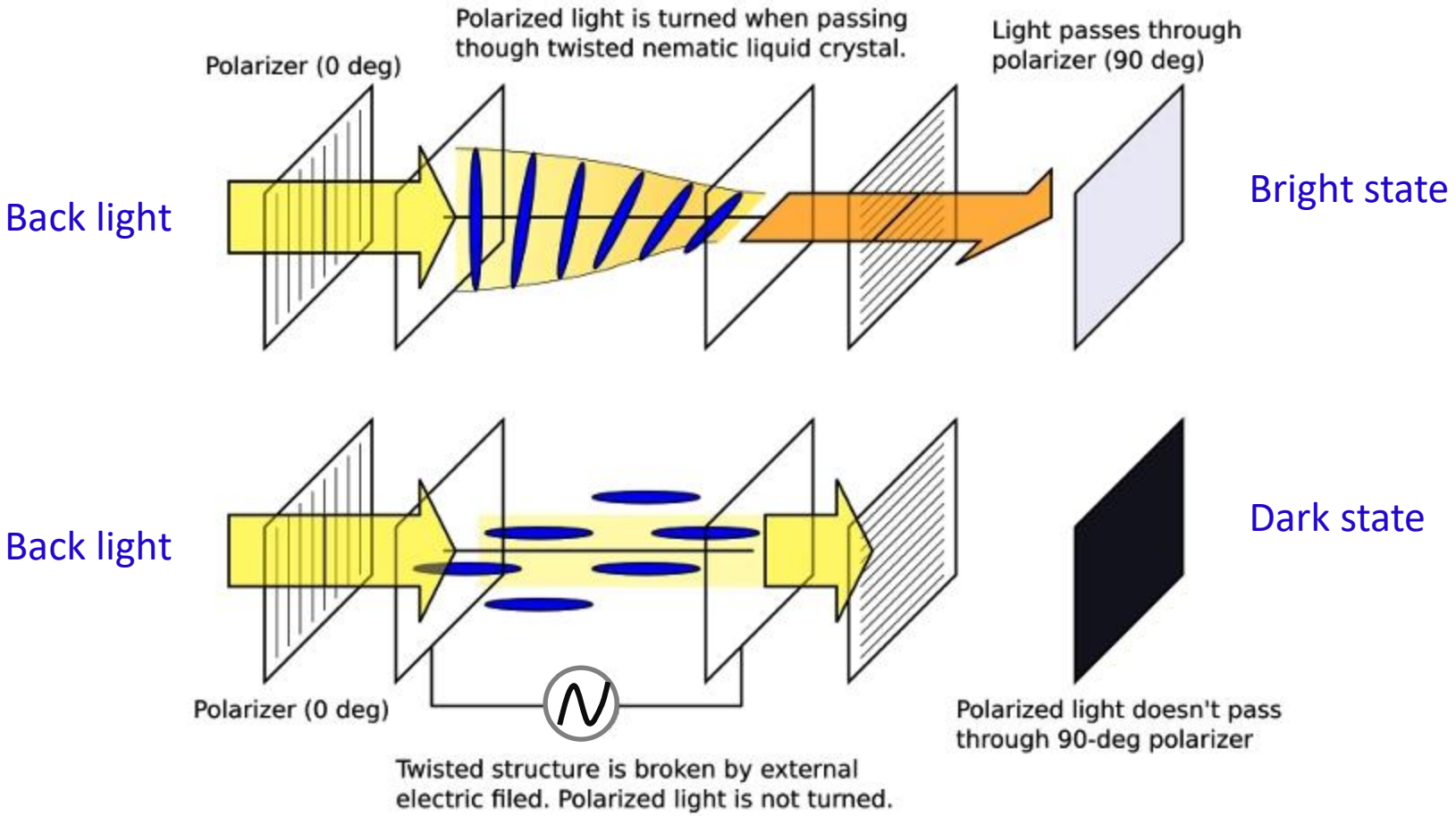
Nematic Liquid Crystals

- Anisotropic refractive index (n_e and n_o)
- Anisotropic permittivity
- Orientational ordering
- Stimuli responsive (easily tunable)

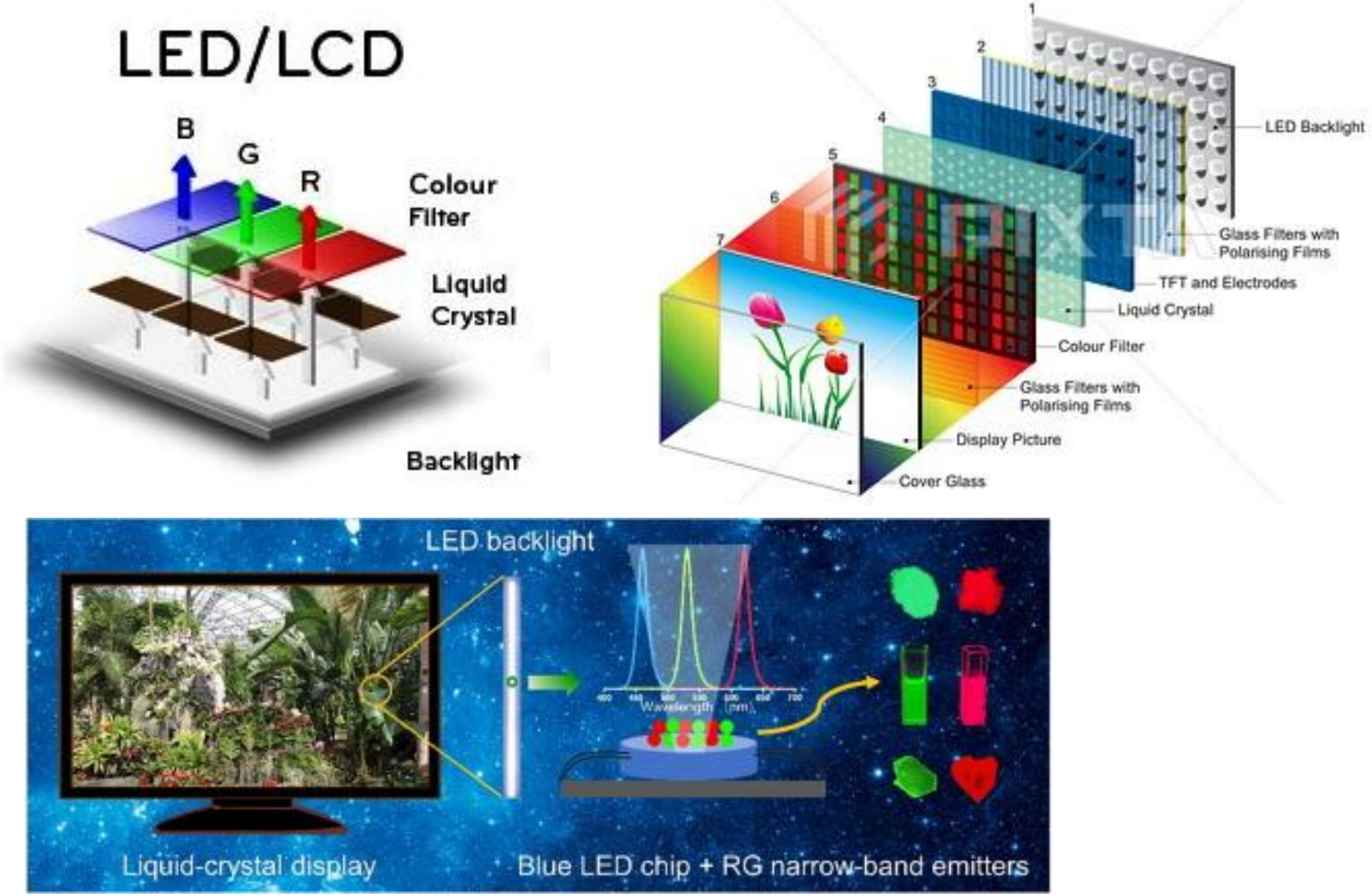
Nano materials ?

- Multifunctional properties to the soft materials
- Enhancing the inherent liquid crystalline properties
- Transferring the orientational/positional ordering to Nanomaterials (Macroscopically)
- Easily tuning the Nanomaterials property by changing LC properties

Liquid crystal displays



https://www.yaoyulcd.com/whatislcd.html



https://www.wepc.com/tips/ips-vs-led-monitor-difference/

https://doi.org/10.1016/j.mattod.2020.04.032

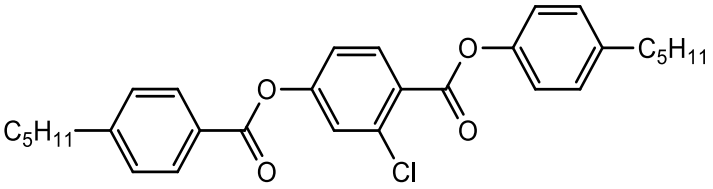
Motivation

- To make LCs self emissive (Removing the backlight)
- Transferring the structural anisotropy of the LCs to the emission characteristics (Removing the polarisers)
- Making a highly emissive, fast switchable emissive display device

Materials

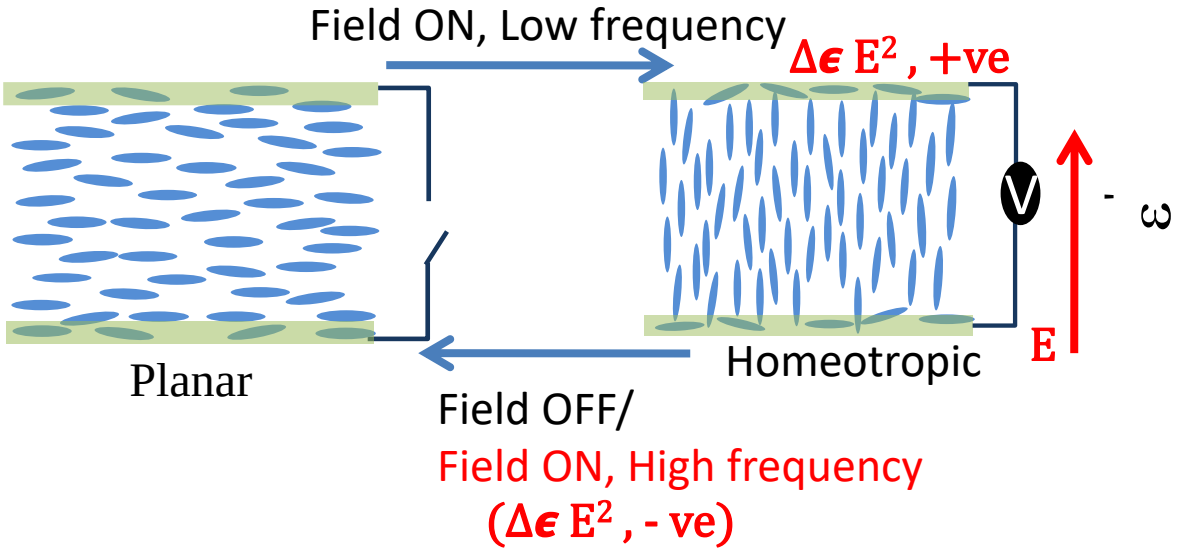
Liquid Crystal

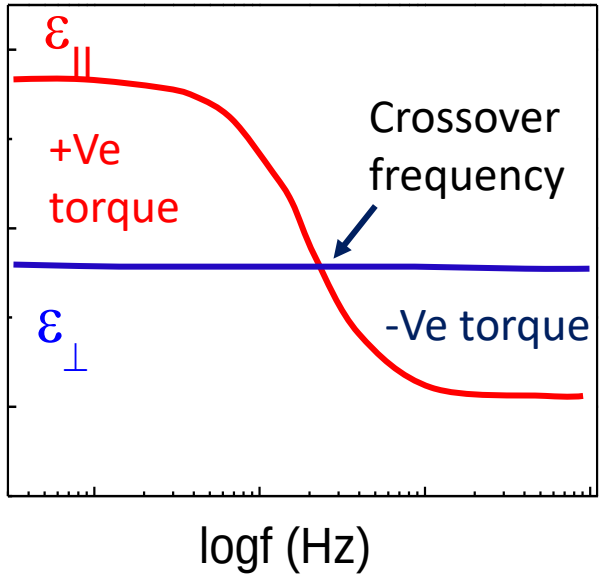
4-pentylphenyl 2-chloro-4-(4-pentyl benzoyloxy) benzoate or PCPBB



Phase sequence : Nematic (N) 123.9°C Isotropic (I)

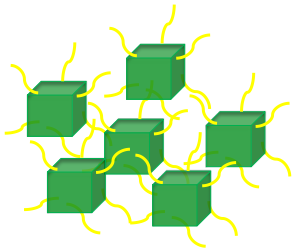
- Having structural anisotropy
- Can be switched with external field
- Dual frequency material



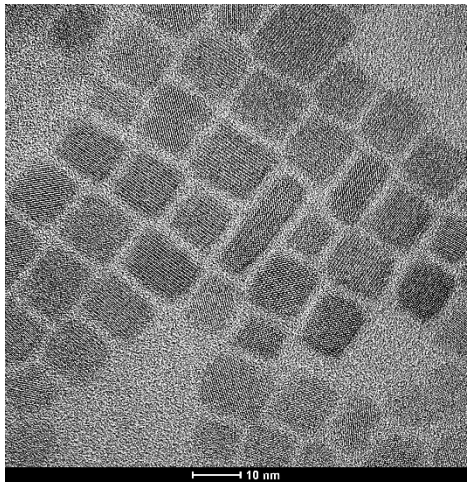


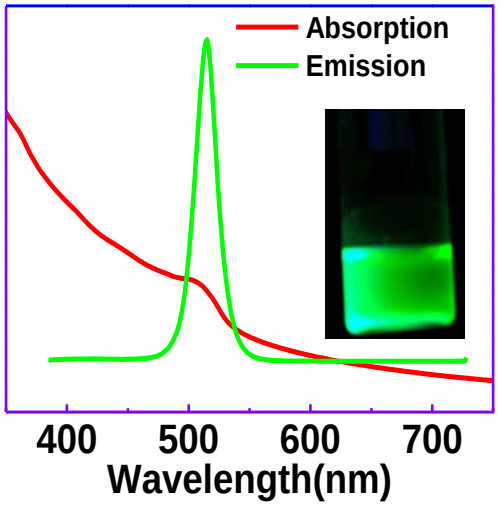
$CsPbBr_3$ Perovskite QCs

J. Phys. Chem. C 2018, 122, 13399-13406



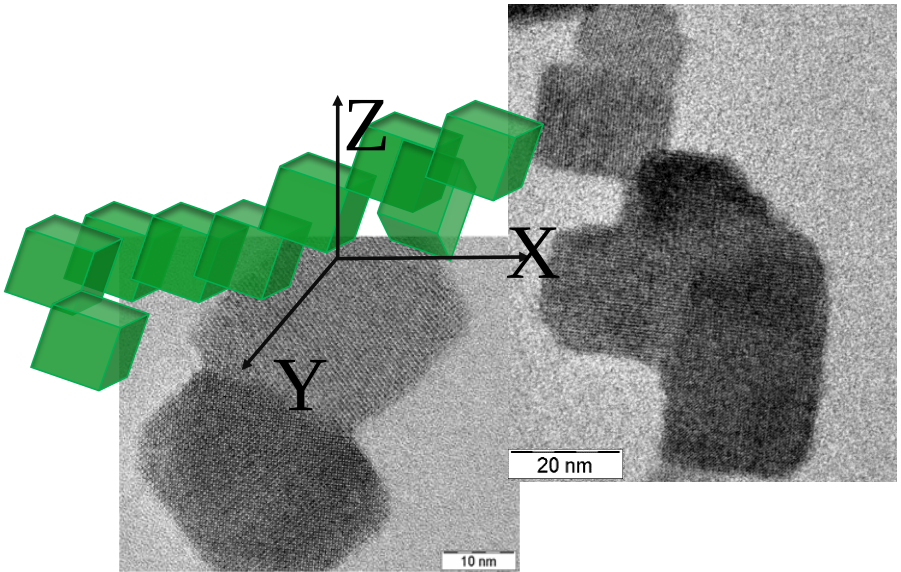
- Isotropic structures
- Highly emissive



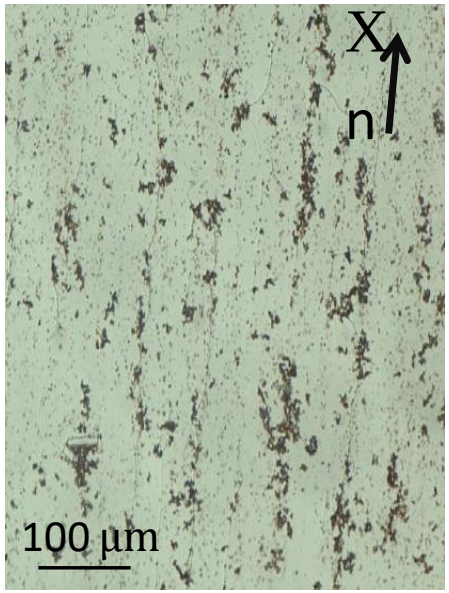


TEM image of the CsPbBr3 cuboids with an average edge length of 13.7 ± 3.1 nm

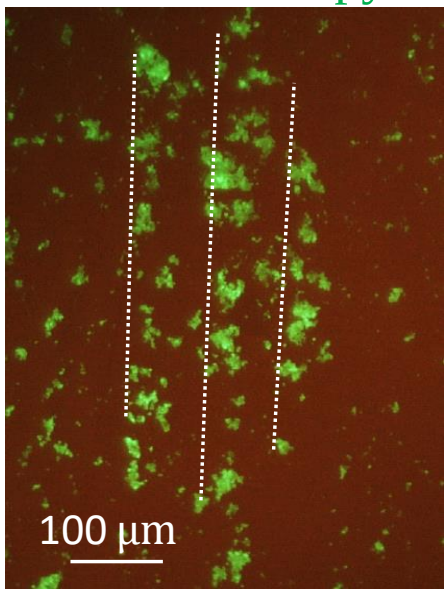
Liquid Crystal + QCs



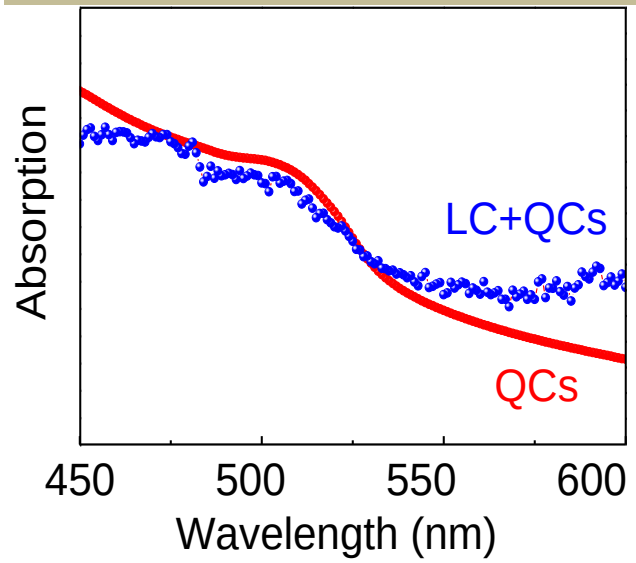
Optical microscopy

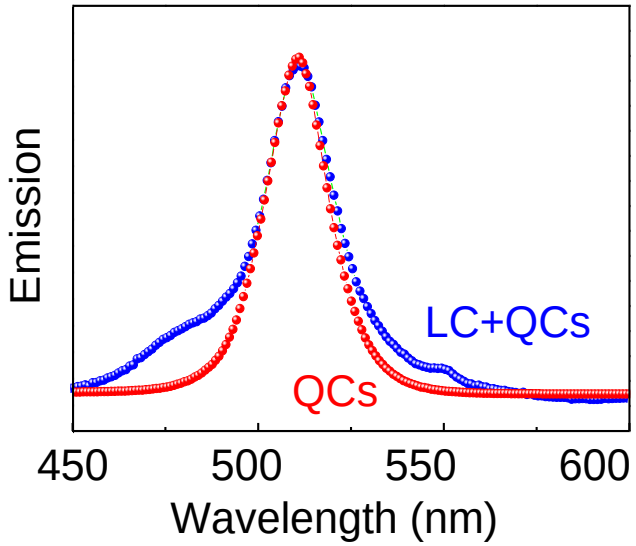


PL microscopy



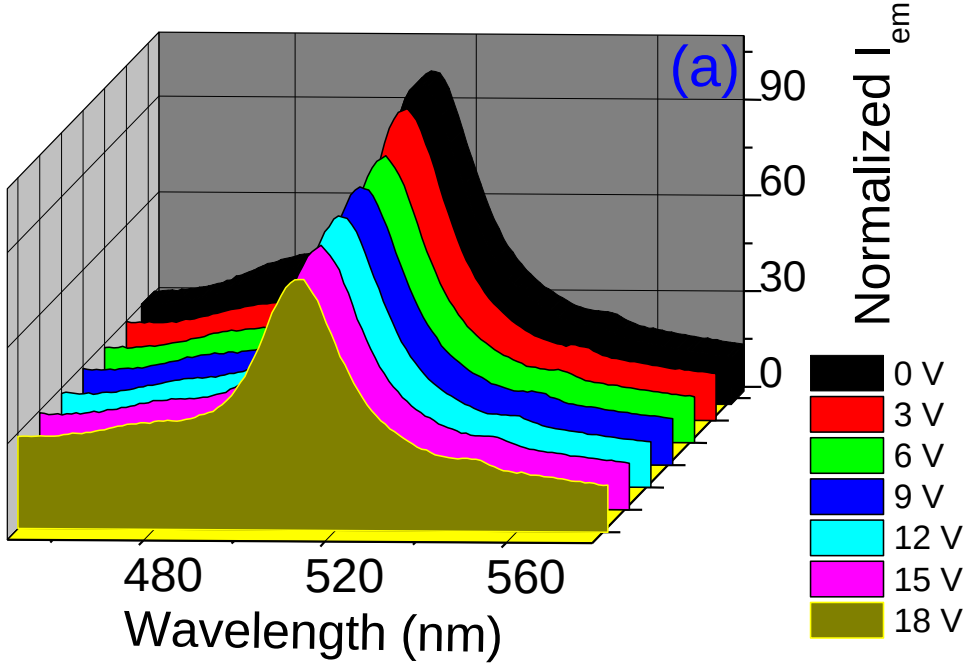
Absorption and emission spectra of QCs and LC+QCs composite



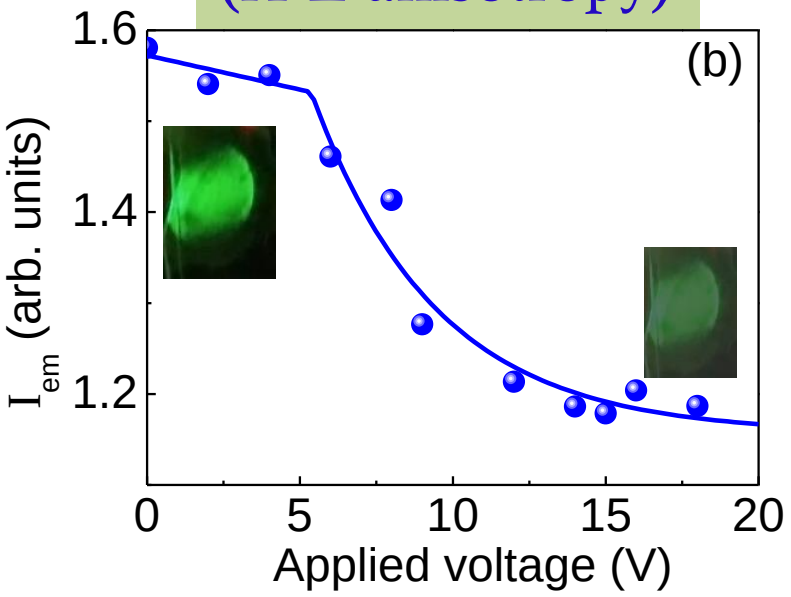


- The band edge emission at 512 nm of the QDs is clearly seen in the LC+QDs composite
- The peak wavelength and FWHM remain same in the composite

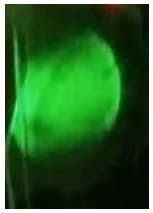
Field-driven PL modulation

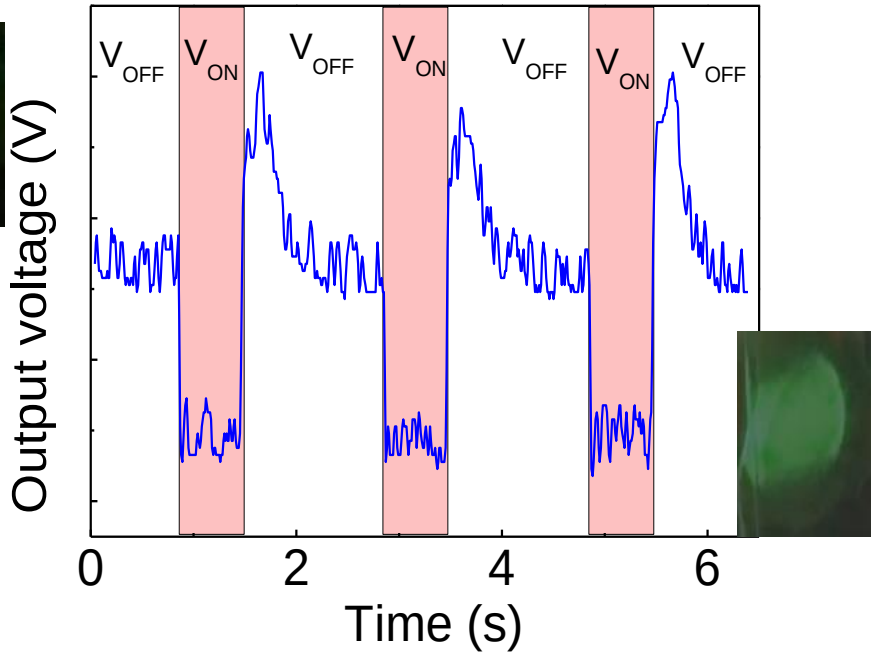


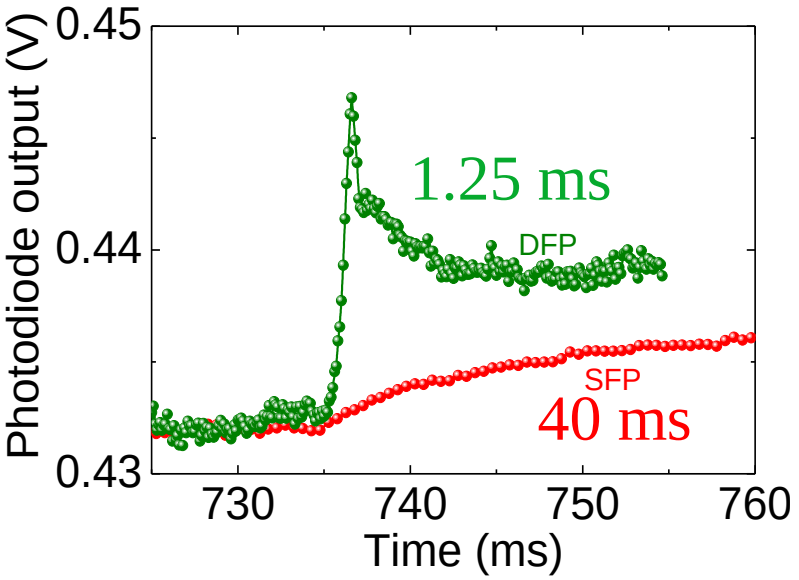
(X-Z anisotropy)



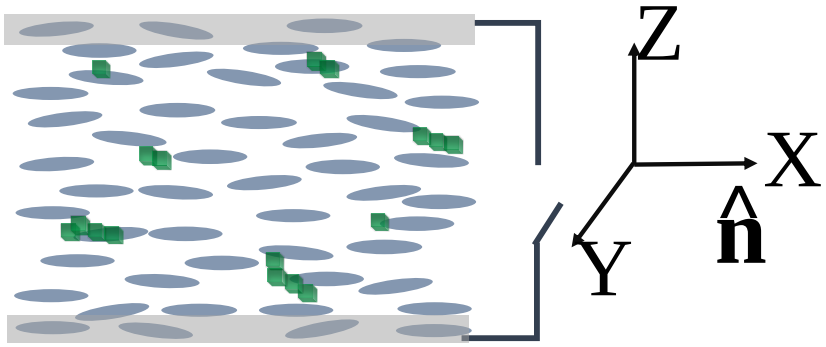
Switchable emission

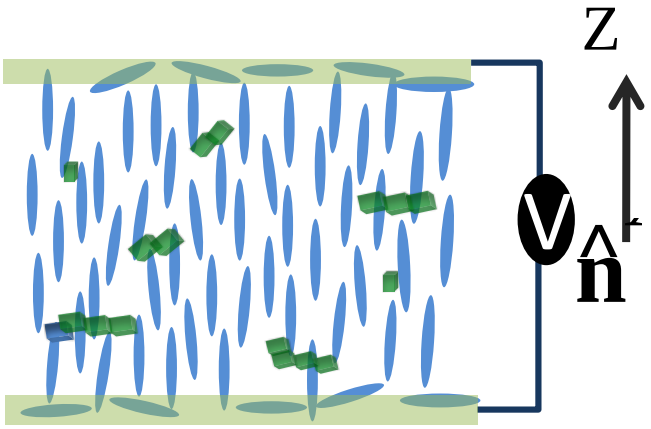






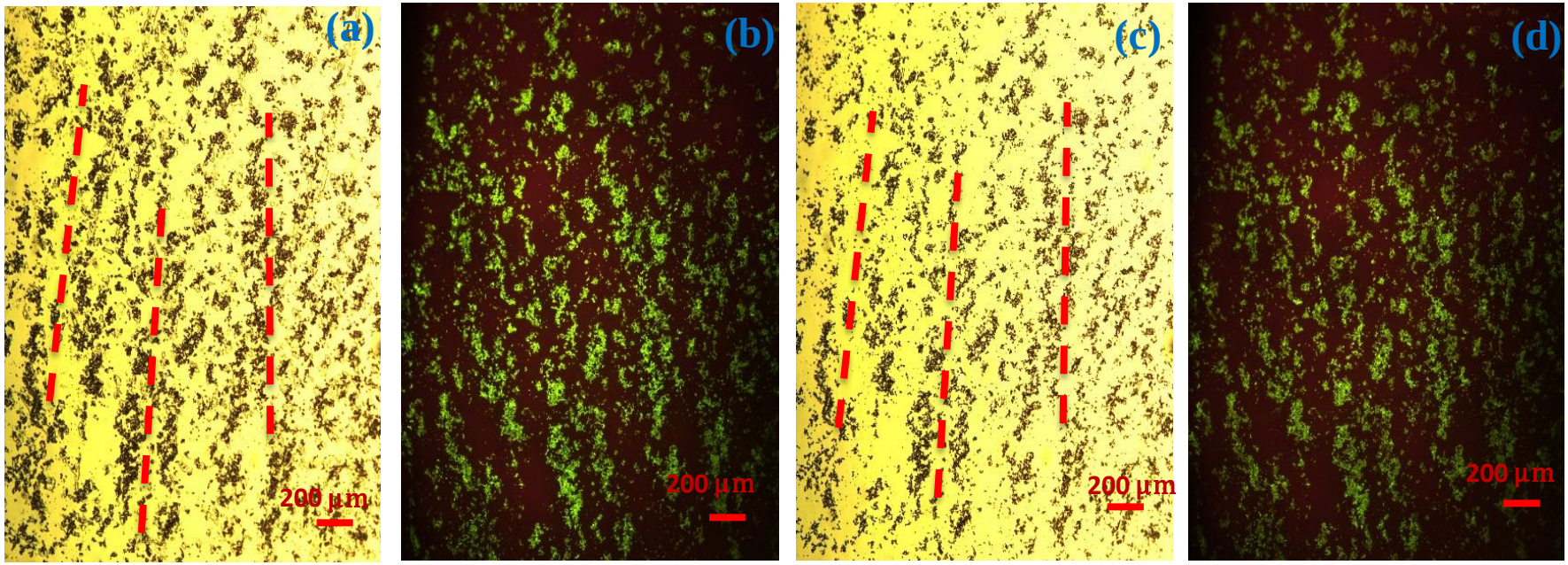
Possible reason for X-Z anisotropy





Field Off

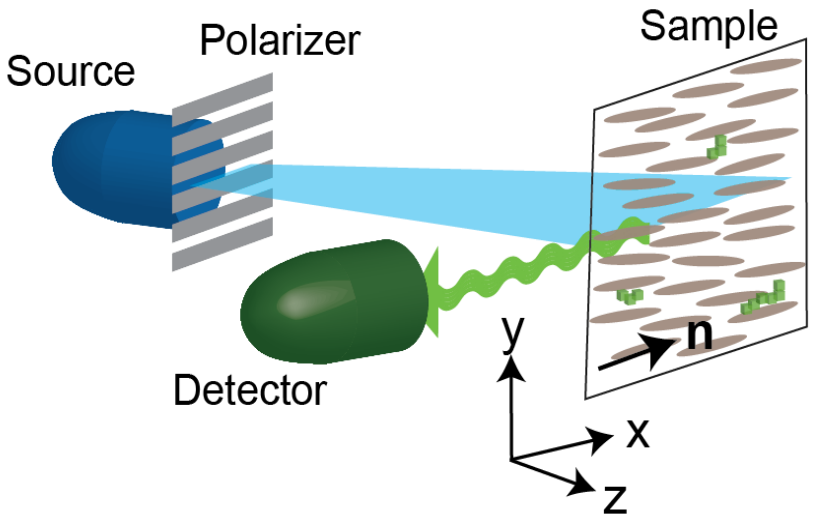
Field On

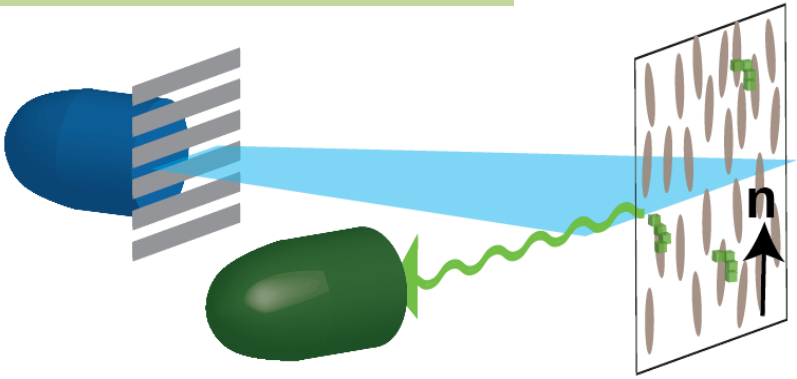


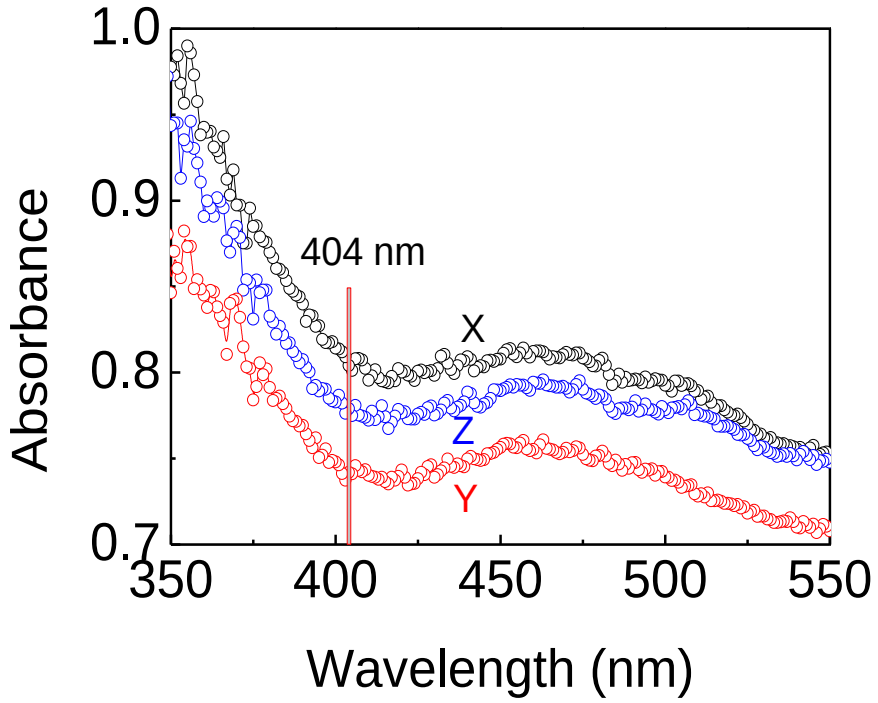
Optical microscopy

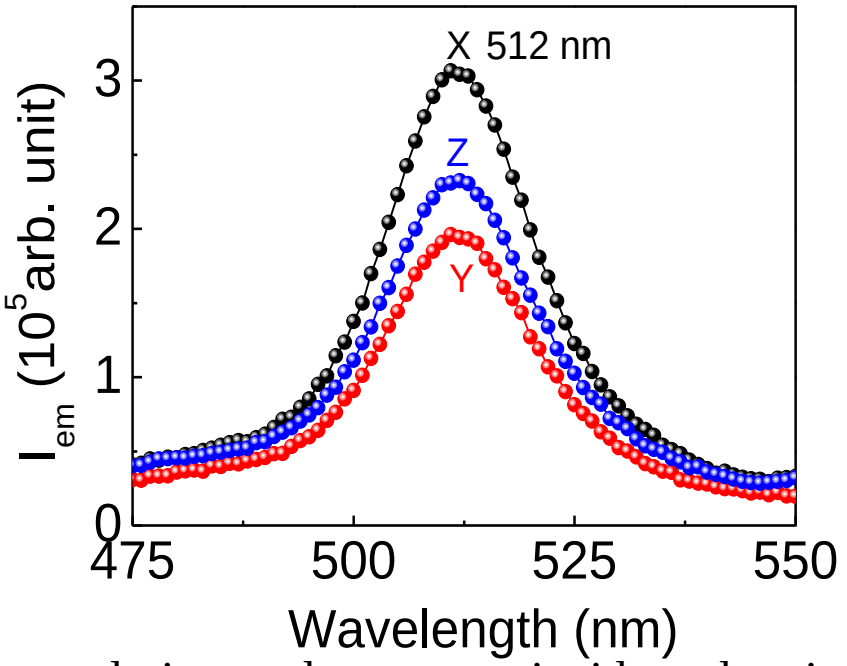
Emission microscopy

X-Y anisotropy









The self-assembled QCs behave like miniature bar polarizer and attenuates incident electric fields polarized orthogonal to the long axis and diminishes A_Y

Possible reasons of anisotropic absorption and emission

The total absorption *A* can be represented as

$$A = \phi_1 n_{QC} + \phi_2 n_{LC}$$

ϕ_1 and ϕ_2 are prefactors

n_{QC} and n_{LC} are the refractive indices of QCs and the LC

$n_e > n_o$

$$A_X = \phi_1 n_{QC} + \phi_2 n_e$$

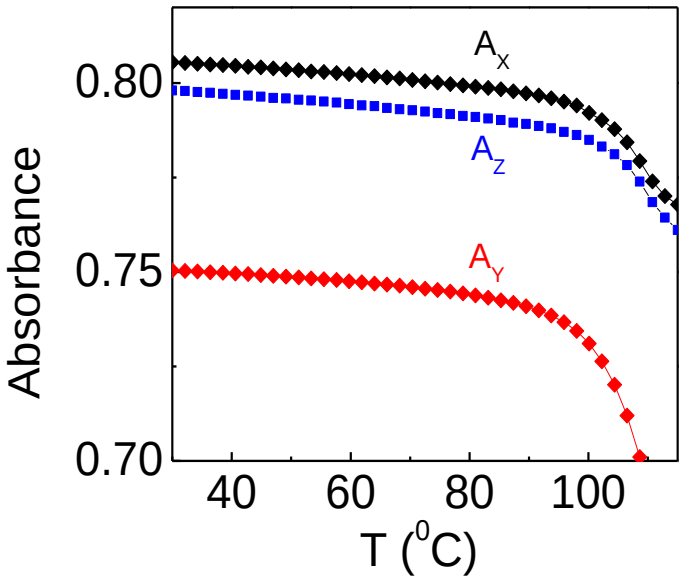
$$A_Y = \phi_3 n_{QC} + \phi_2 n_o$$

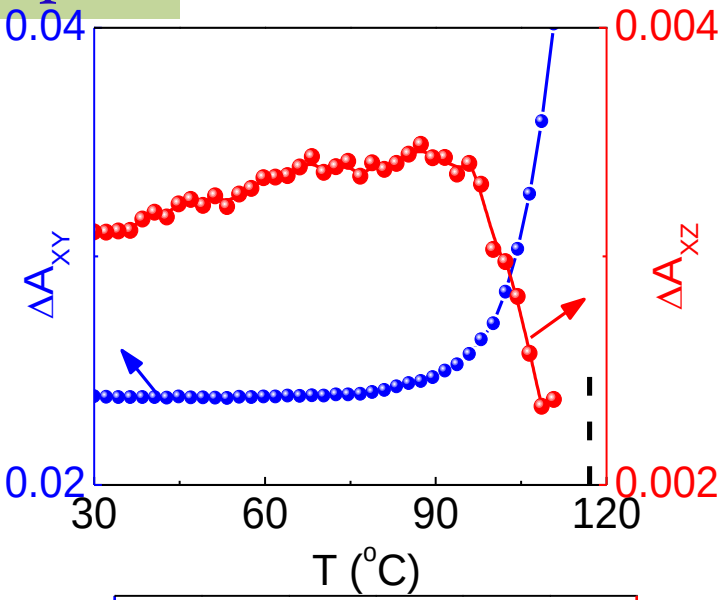
$$A_Z = \phi_1 n_{QC} + \phi_2 n_o$$

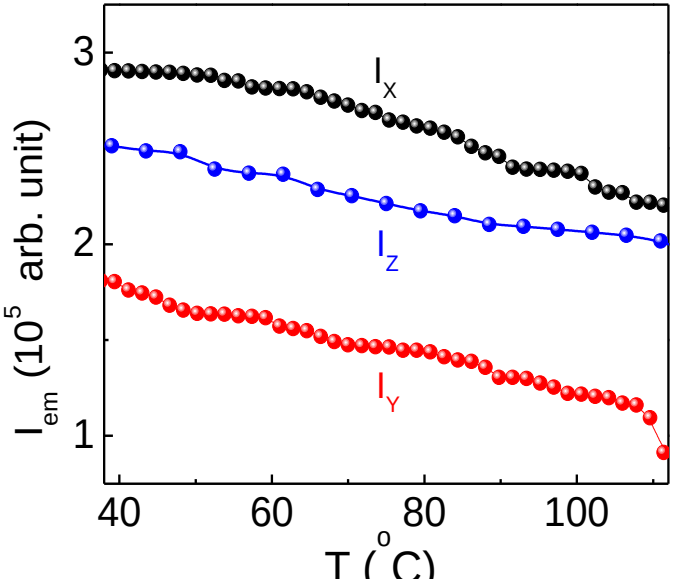
$$\Delta A_{XY} = (A_X - A_Y)/(A_X + 2A_Y) \qquad \Delta I_{XY} = (I_X - I_Y)/(I_X + 2I_Y)$$

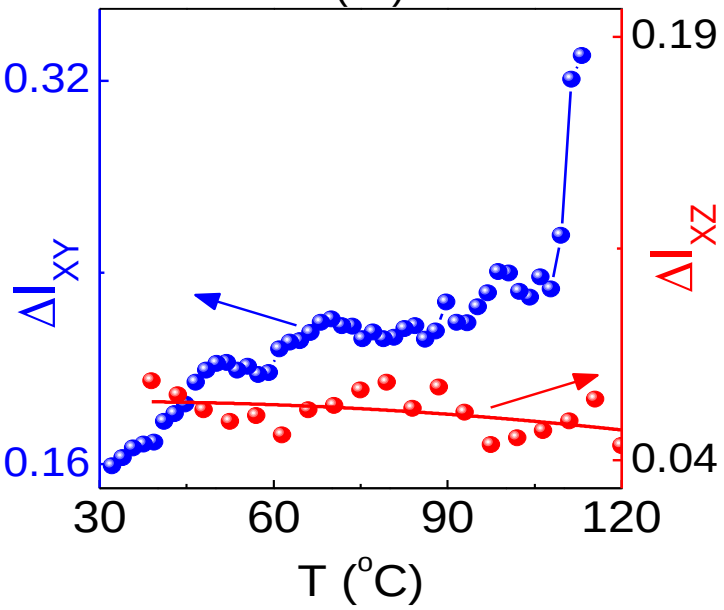
$$\Delta A_{XZ} = (A_X - A_Z)/(A_X + 2A_Z) \qquad \Delta I_{XZ} = (I_X - I_Z)/(I_X + 2I_Z)$$

Temperature dependent anisotropies



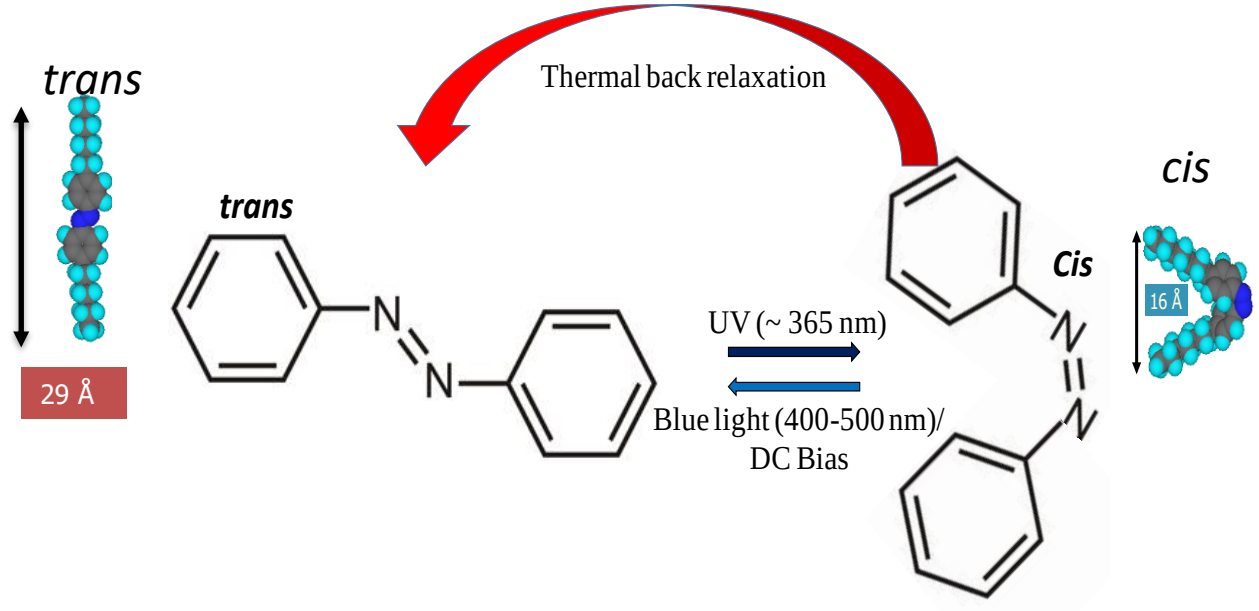






Photoisomerization (PI)

Photo-driven shape transformation



J. Hu et al. Smart Mater. Struct. ***2012****, 21 (Smart textiles)*

A. Raman et al. New J. Chem. ***2018****, 42, 9300 (Biosensing)*

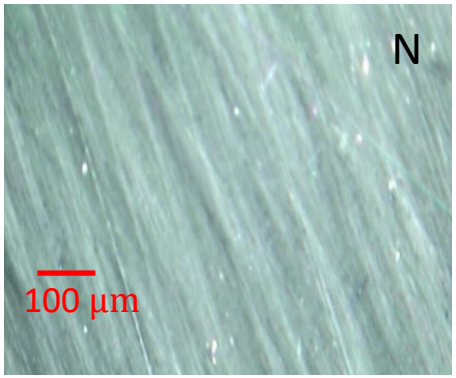
J. Garcia-Amorós et al. J. Mater. Chem. C ***2014****, 2, 474 (Photochromic switches)*

H. Shahsavan, L. Yu, A. Jákli, B. Zhao, Soft Matter ***2017****, 13, 8006 (actuator)*

S. K. Prasad, P. L. Madhuri, P. Satapathy, C. V Yelamaggad, Appl. Phys. Lett. ***2018****, 112, 253701 (Memory device)*

Photoisomerization

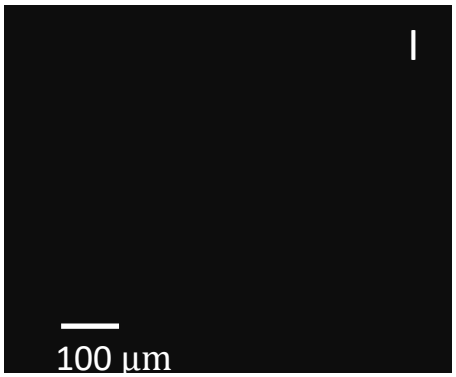
(a) Nematic (N)

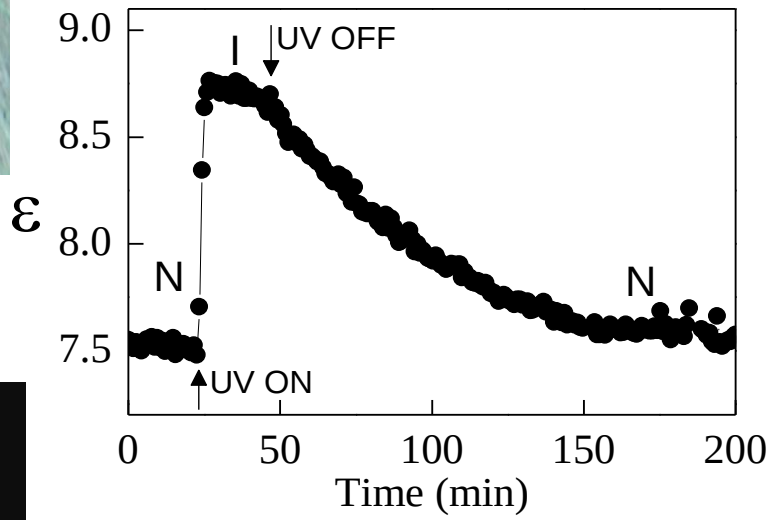


UV irradiation

Thermal back relaxation (TBR)/ Blue light/ DC bias

(b) Isotropic (I)



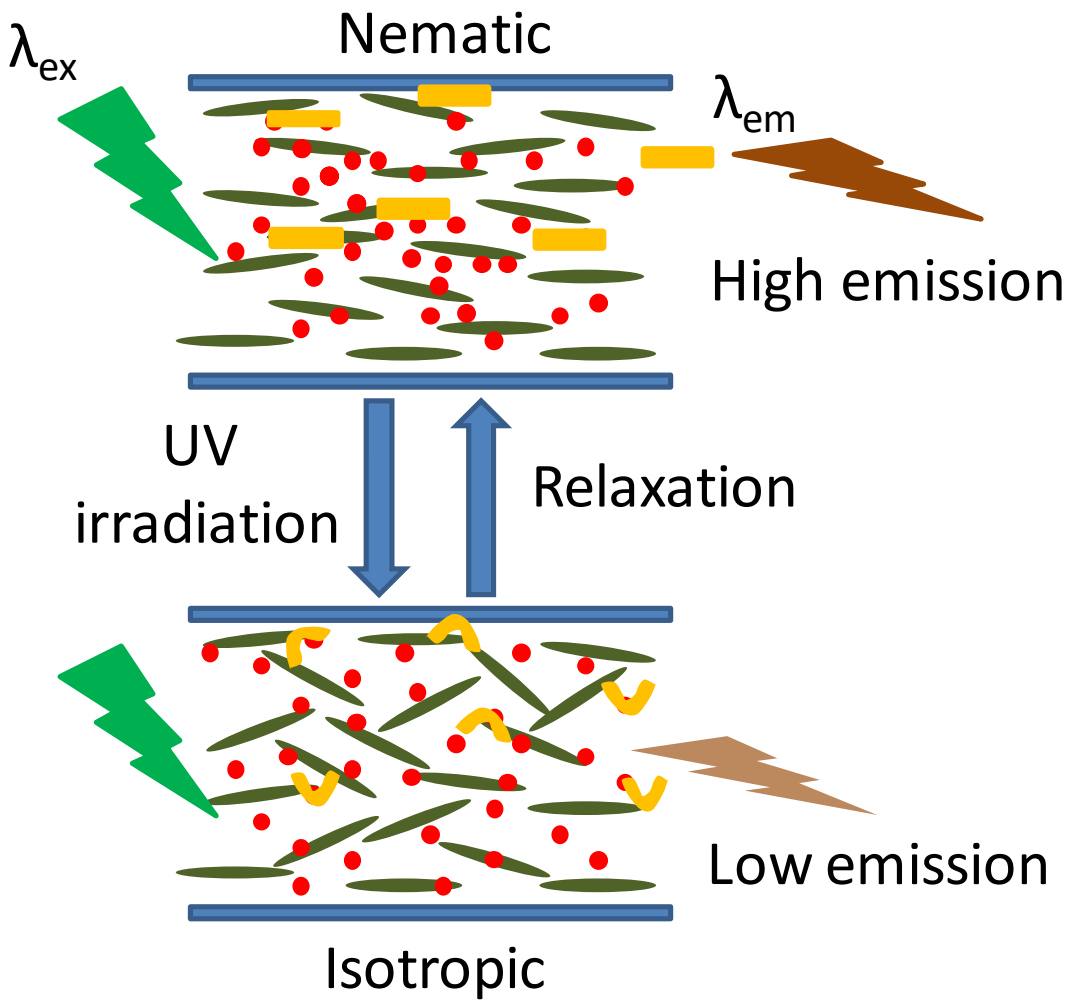


Guest azo molecule
"*trans*" confomer
"cis" confomer

S. K. Prasad et al. Appl. Phys. Lett. ***2018****, 112, 253701*

S. K. Prasad et. al. Adv. Mater. ***2008****, 20, 1363*

Isothermally driven photo modulation due to photoisomerization ? (Motivation)

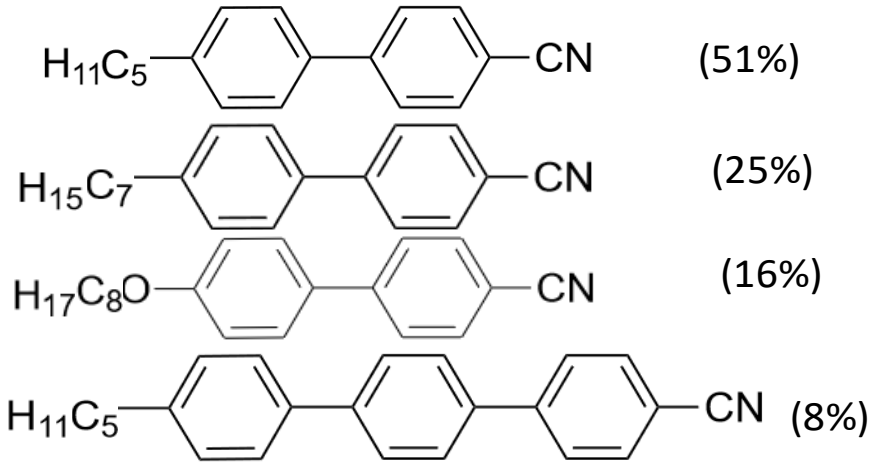


- *trans-cis* photoisomerization decreases the orientational ordering isothermally
- Decrease in ordering can reduce the emission
- Emission can be modulated isothermally by PI process
- Spatially addressable PL modulation

Materials

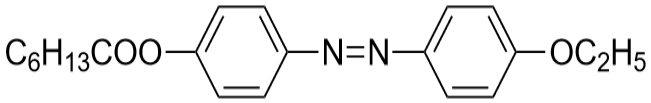
Host LC

E7



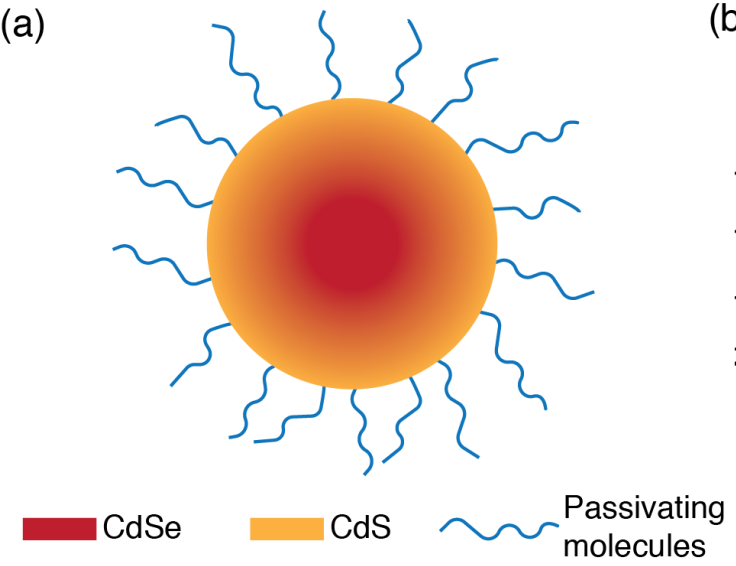
Guest azo molecule

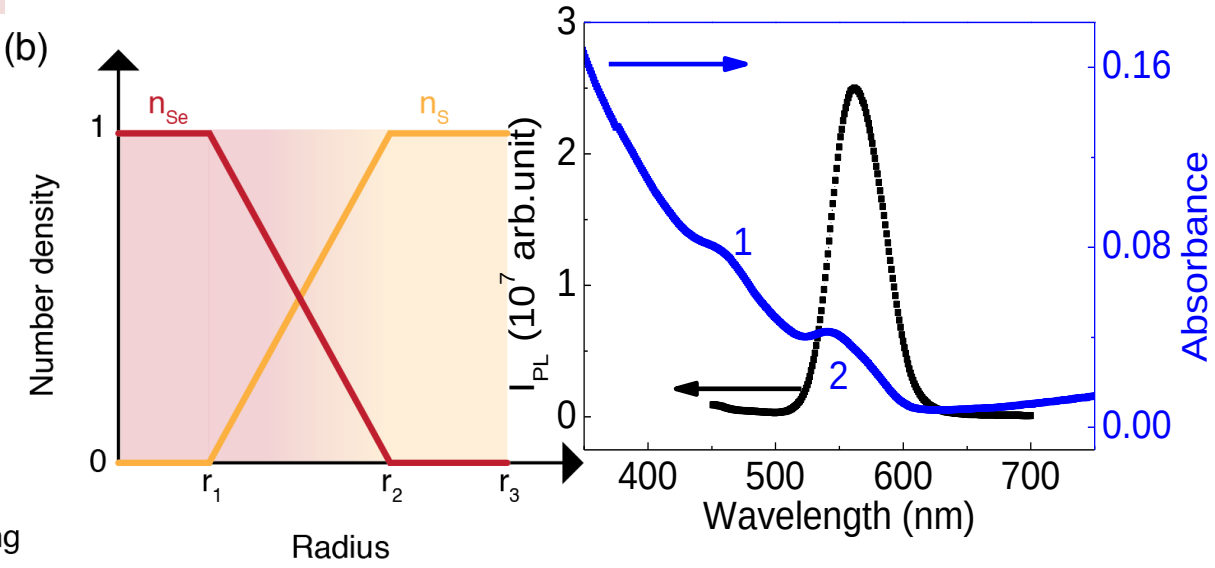
EPH



- 4.5% of EPH in E7
- I to N at 58.3 °C

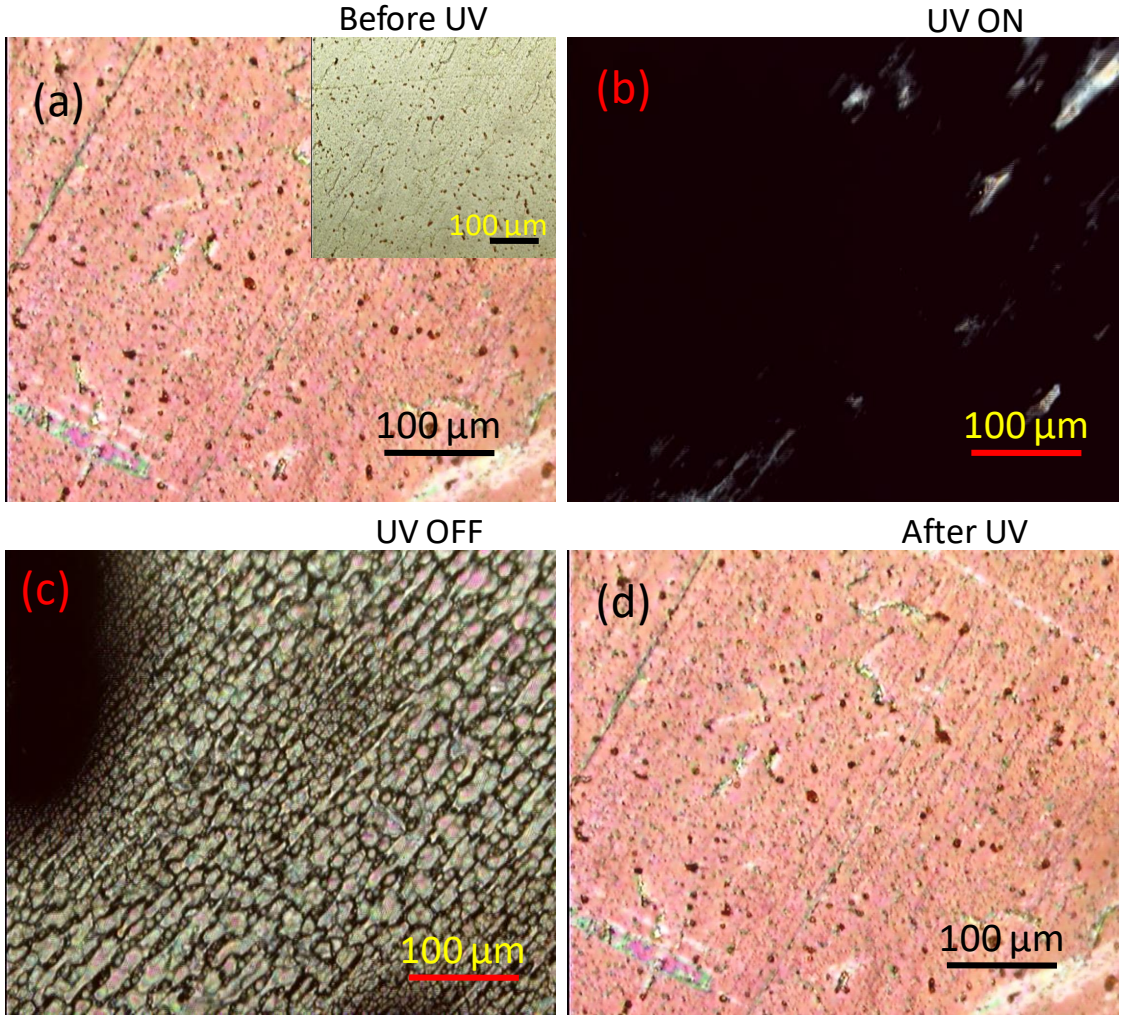
Gradient controlled QDs





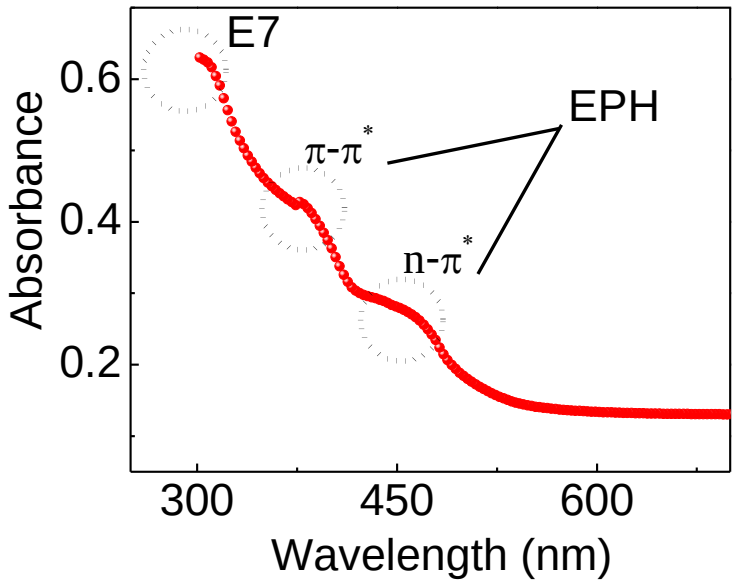
E. Jang, S. Jun, L. Pu, Chem. Commun. ***2003****, 2964*

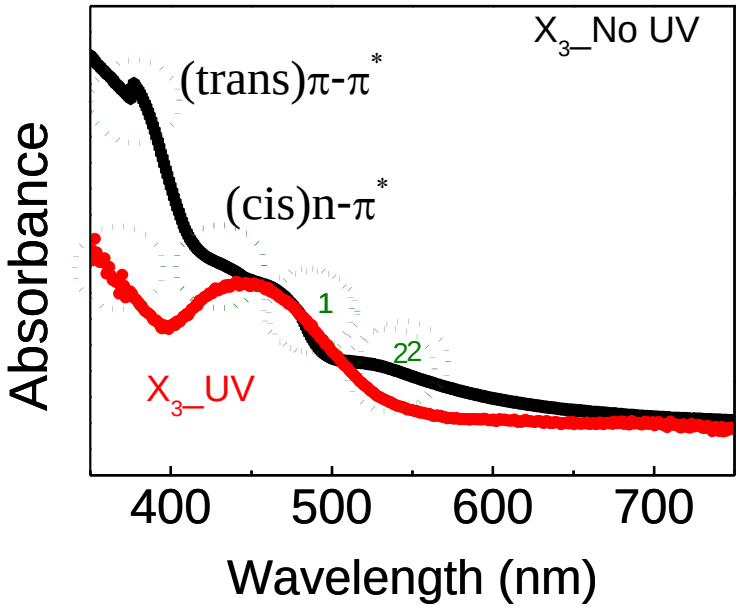
Polarizing optical microscopic observations



- PI phenomena in X_3 is pictorially evidenced from the POM images (birefringence images)
- The presence of QDs can be clearly visualized by removing one of the polarizers
- There is no such self-assemblies of QDs as seen for CsPbBr3 QC systems

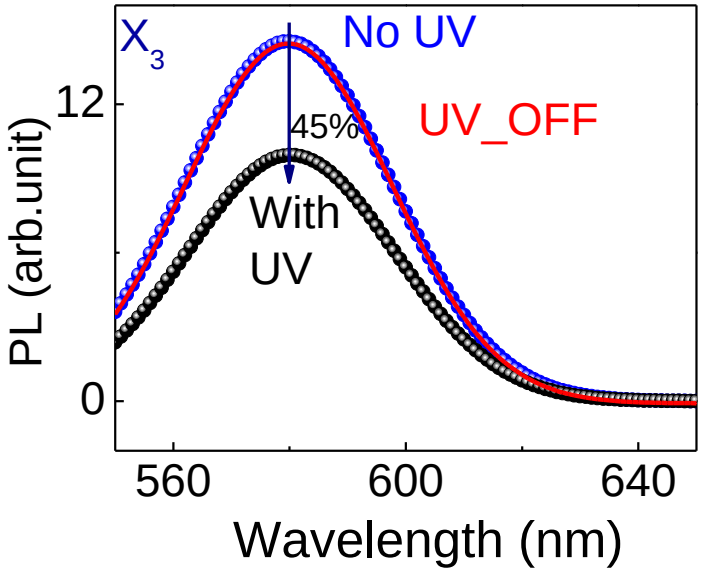
UV-Vis Absorption





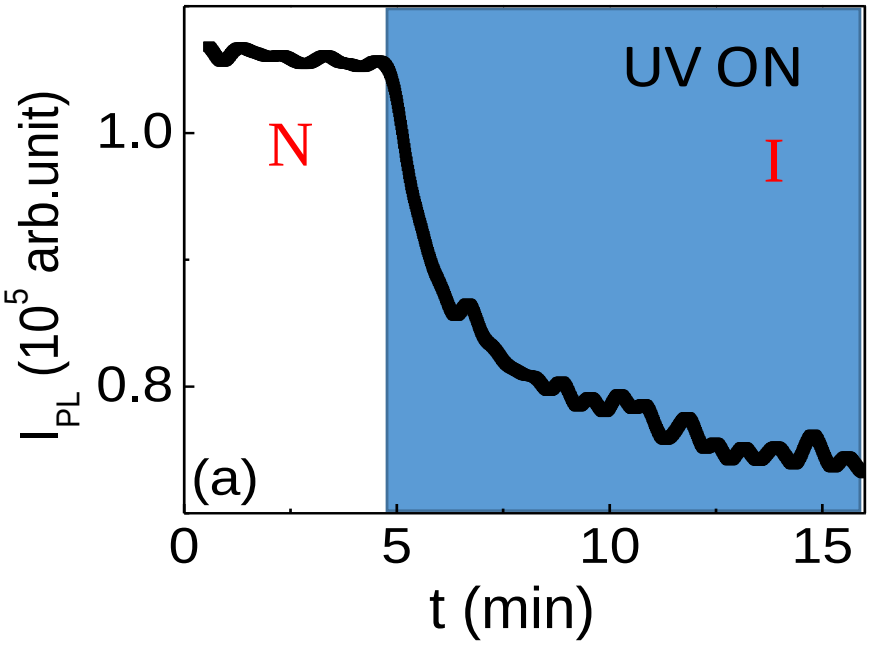
- 1 and 2 are the excitonic peaks of QDs
- Excitation of samples at a wavelength near the second absorption band of QDs (~ 532 nm) to stay away from the *cis* absorption.

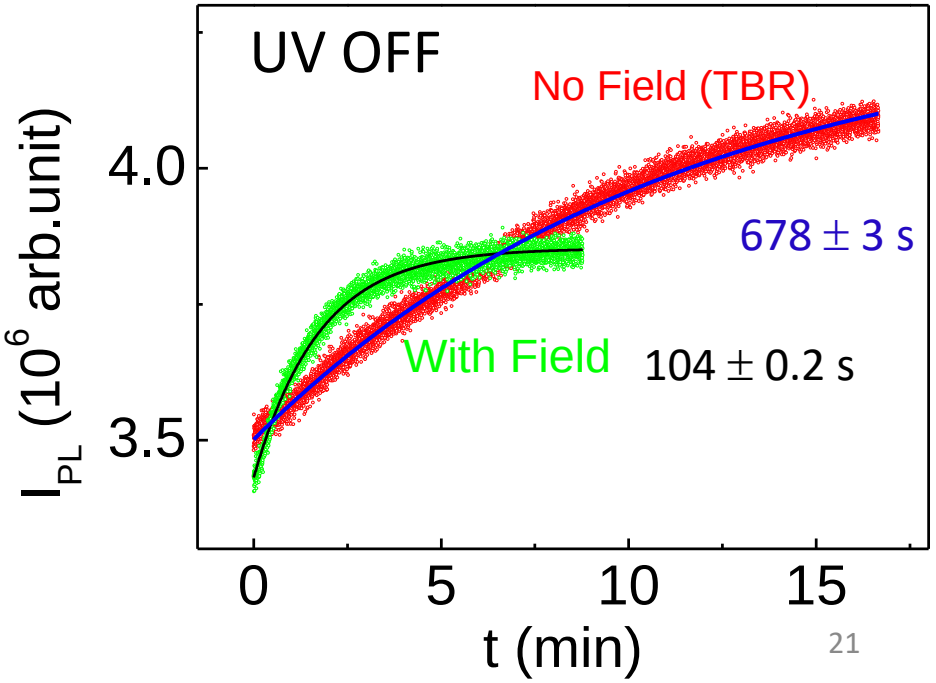
Photoluminescent measurements



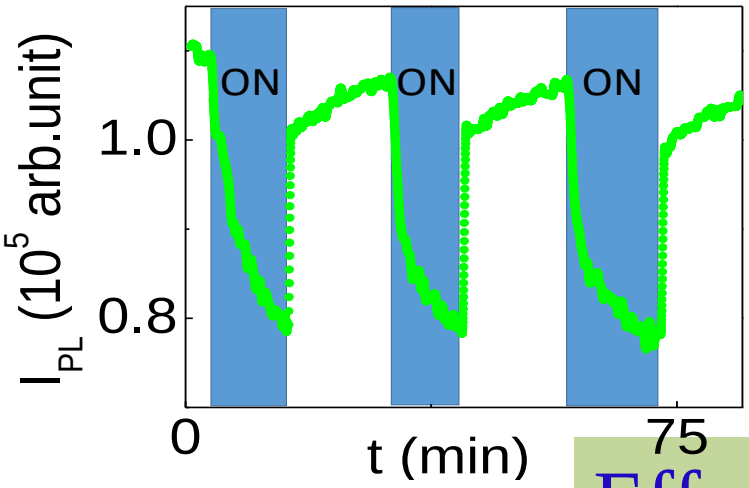
- The PL intensity gets drastically reduced (45%) due to the photoisomerization of the EPH molecules

PI driven photomodulation



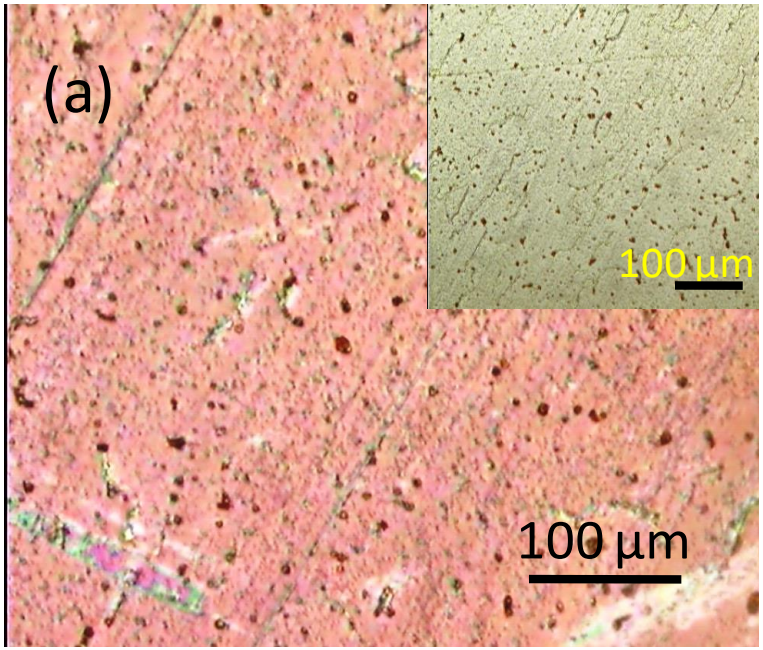


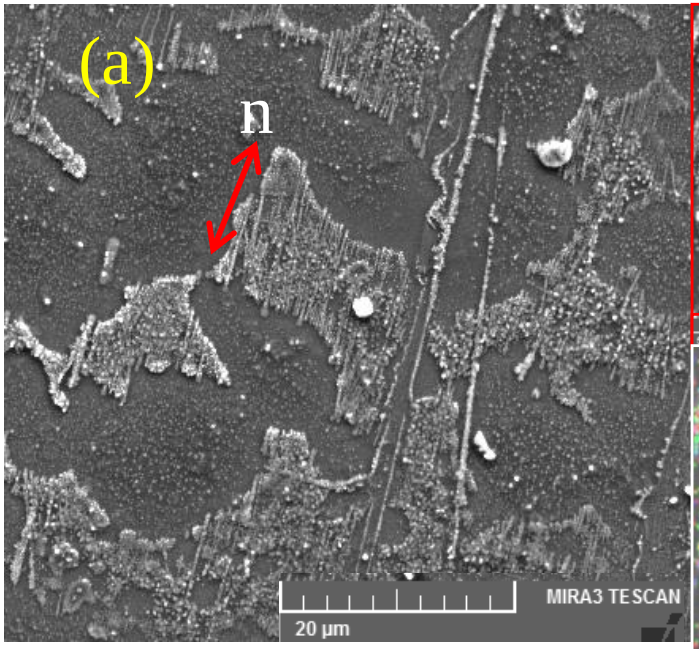
PI driven photomodulation

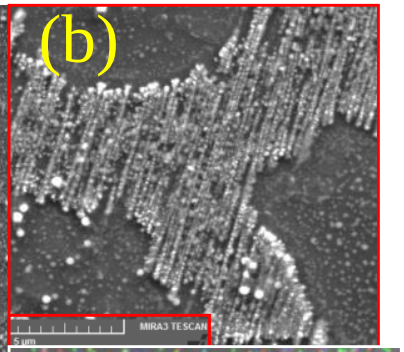


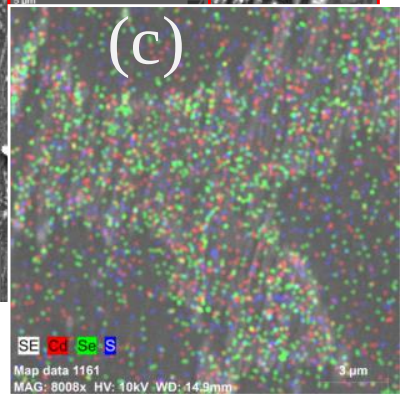
- An exponential was fitted to PL recoveries through TBR and with field
- Time scales for relaxation ~678 s (TBR) and ~ 104 (with field)
- 6 times faster recovery
- A fatigue free PL switching with faster recovery due to the field

Effect of polymer in LC+QD



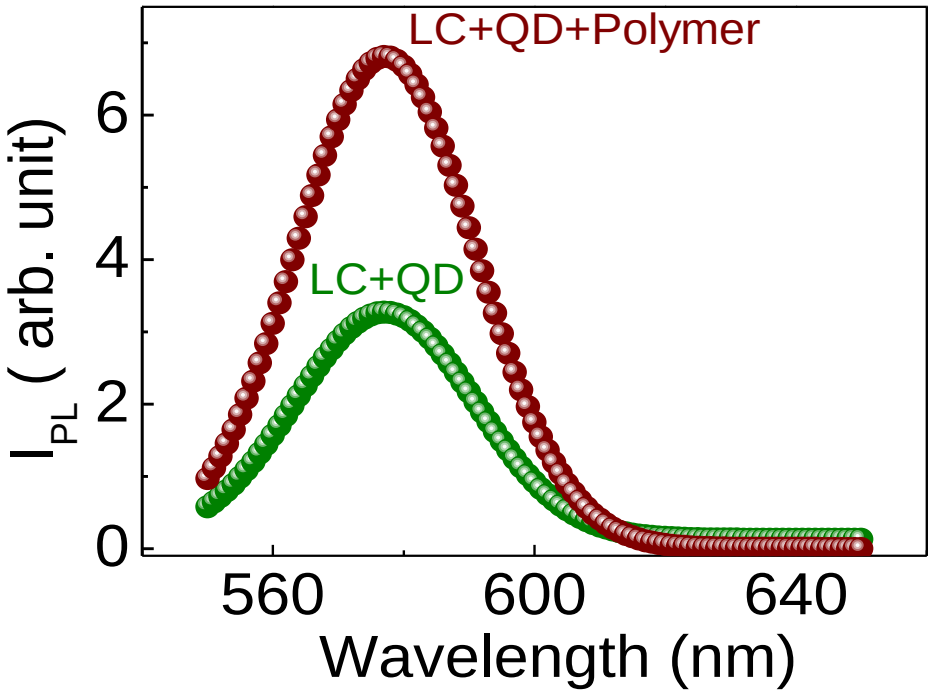


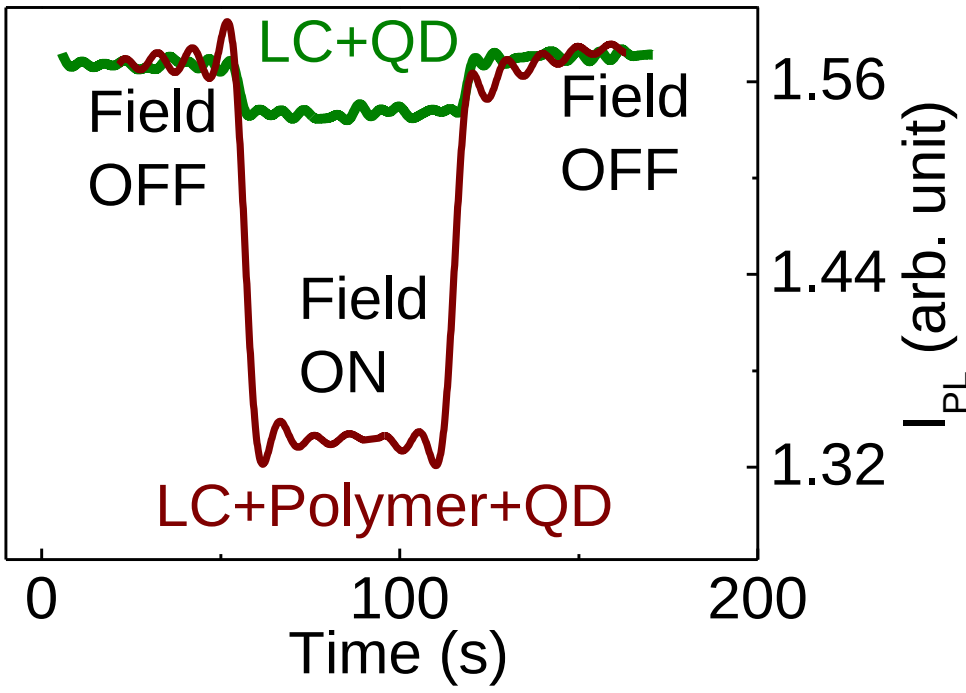




5 wt% of Poly(methyl methacrylate) PMMA

Effect of polymer on PL





Summary

- ❑ Dual anisotropic optical characteristics from structurally isotropic QDs
- ❑Fast-switchable display device
- ❑Actinic light modulated PL devices
- ❑Enhancing base PL by incorporating polymers

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