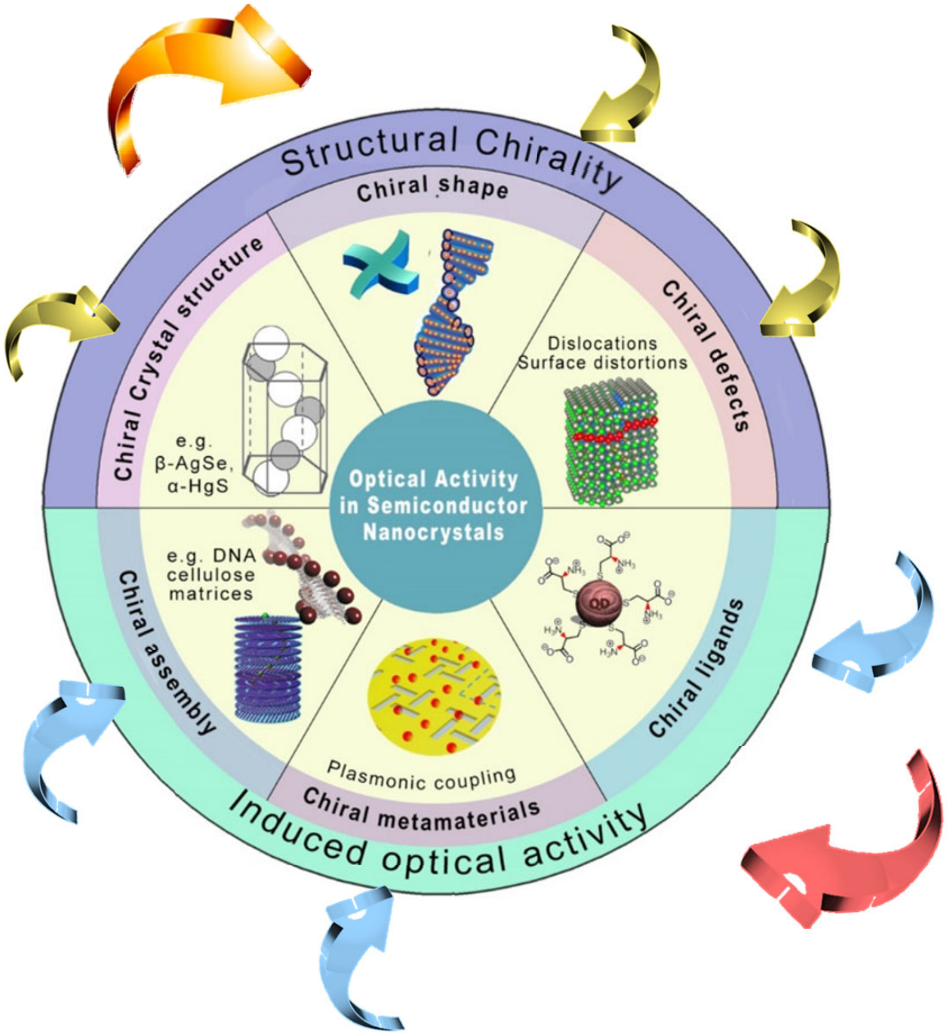
Chirality and QDs nanoobjects

Dr. Marie-Hélène DELVILLE

Ligand **induced chirality in QDs**



QDs : luminescent semiconductor NPs with outstanding tunability of the optical and physical properties thanks to quantum confinement effect (as a result of their band electronic structure which is size dependent.

QDs may exhibit high photoluminescent (PL), quantum yield (up to 100%); large extinction coefficients continuous across a wide spectral range, in addition to excellent photo- and chemical stability

Nanophotonics 2020, 10, 797-824,

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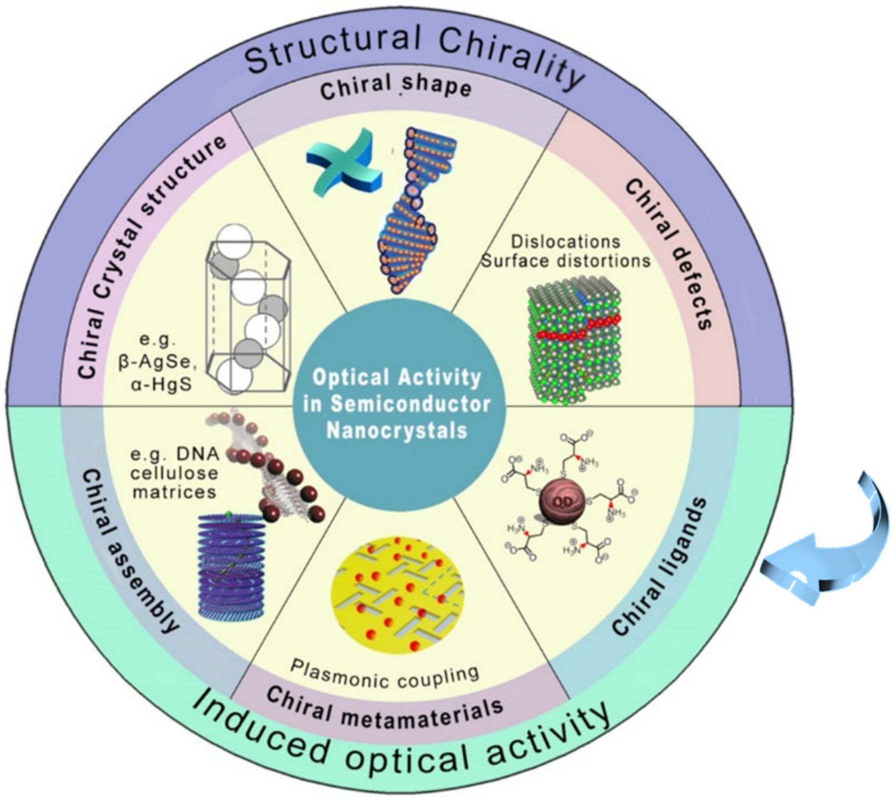


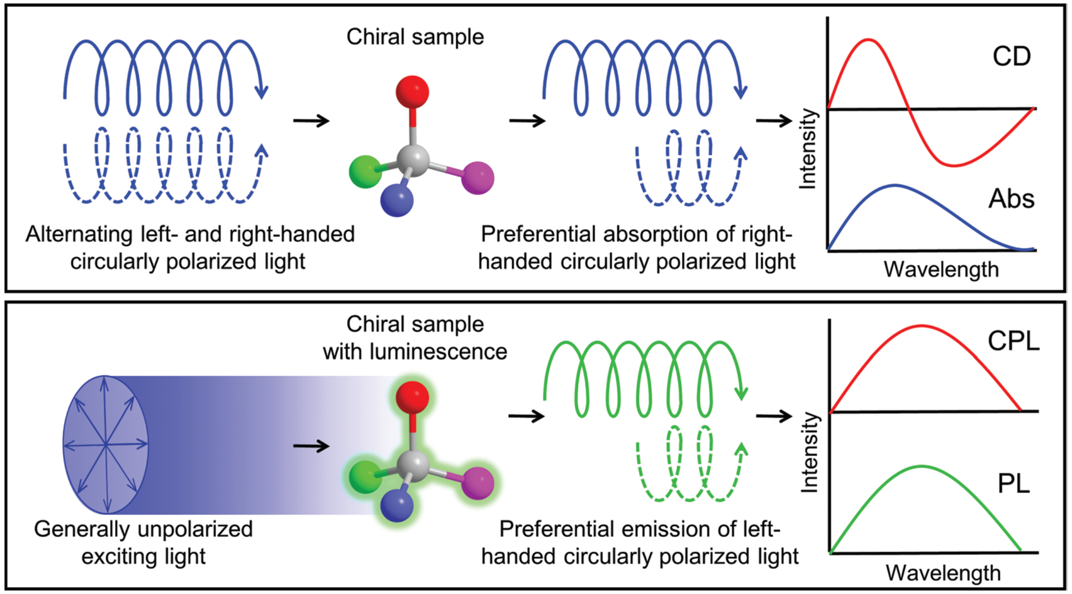
- Easy control of the NCs Shape
- Various types of chiral molecules
- Optical activity

Nanophotonics 2020, 10, 797-824,

CD & Circularly polarized luminescence (CPL) in QDs

1

$$g = | A_L – A_R | / A = \Delta A/A = \theta_{(mdeg)} / 32980*A$$



ground state chirality of the system,

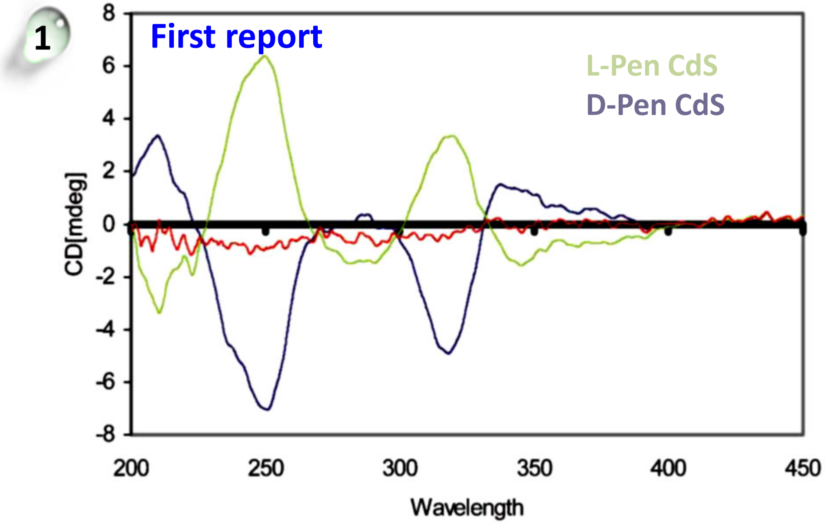
excited state chirality.

CD signals of a chiral luminescent system do not ensure CPL signals. **But**, CPL active materials normally display the Cotton effect.

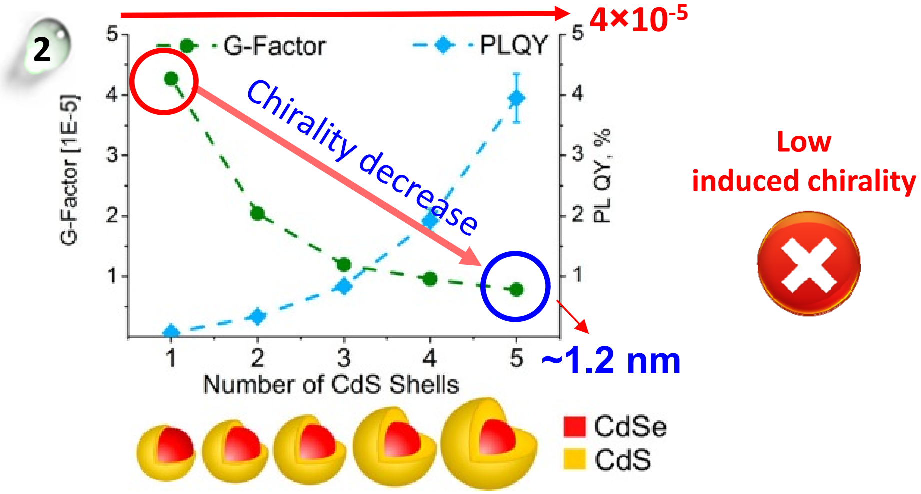
$$g_{lum} = 2(I_L – I_R)/(I_L + I_R) = \Delta I/I.$$

1. Adv. Mater. 2019, 32 (41), 1900110;

Ligand **induced chirality**



Ligands induced chirality



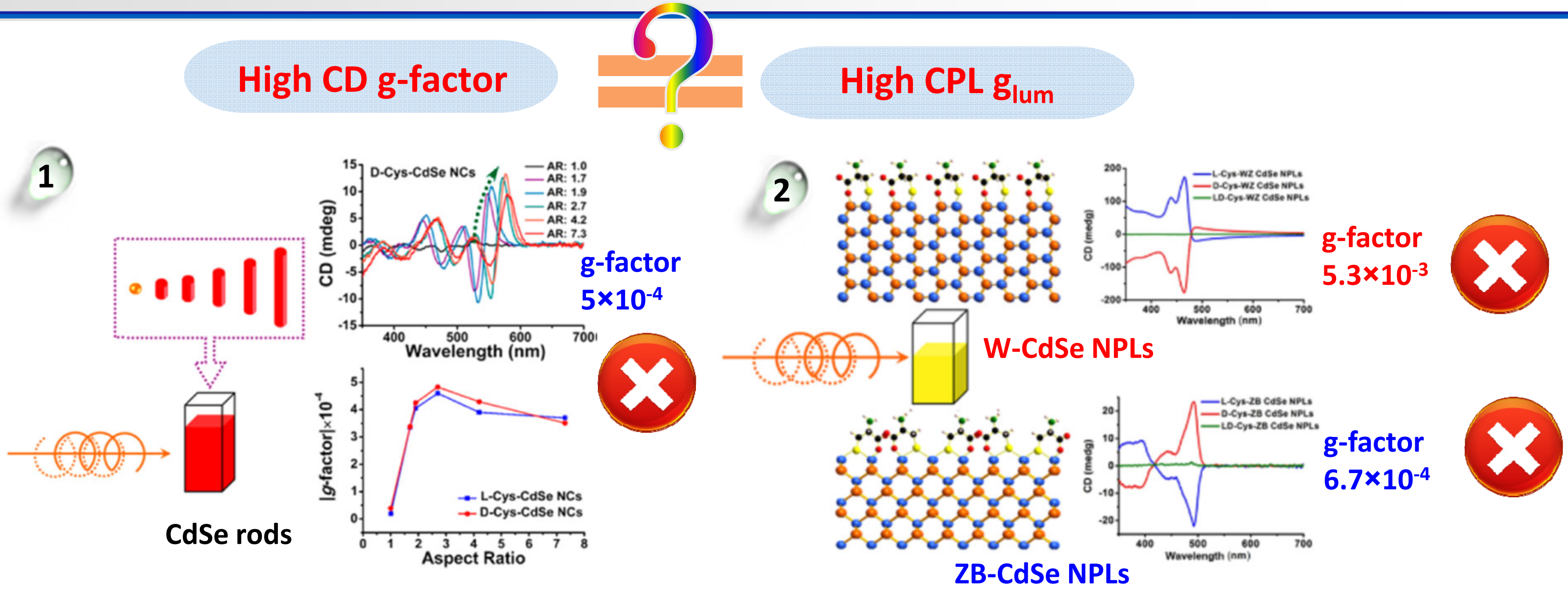
Shell thickness effect on the chiral transmission distance

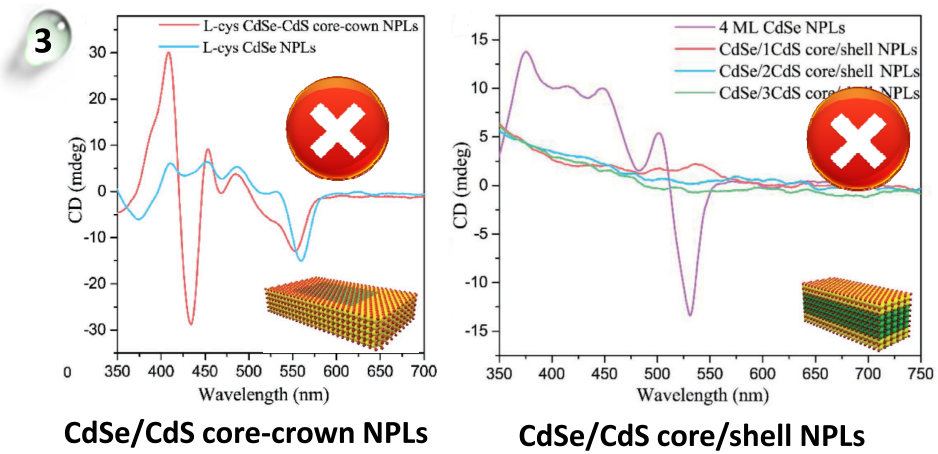
$$g\text{-}factor = \frac{\Delta\varepsilon}{\varepsilon} = \frac{\Delta A}{A} = \frac{\theta_{mdeg}}{32980 \cdot A}$$

- **Φ** Hybridization between the ligand highest occupied molecular orbitals (HOMO) and the hole levels of valence band (VB) of the quantum dots
- **χ** NPs: an undistorted and achiral core, CD signals arise from near-surface Cd atoms that are enantiomerically distorted by chiral ligands

1. Gun'ko Chem. Commun. 2007, 38, 3900-3902;
2. ACS Nano 2017, 11 (9), 9207-9214.

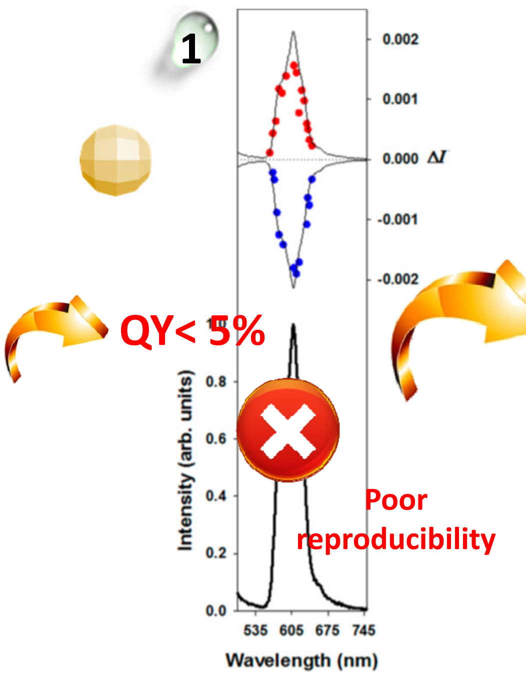
Bottlenecks **of** Circularly Polarized Luminescence (**CPL)**



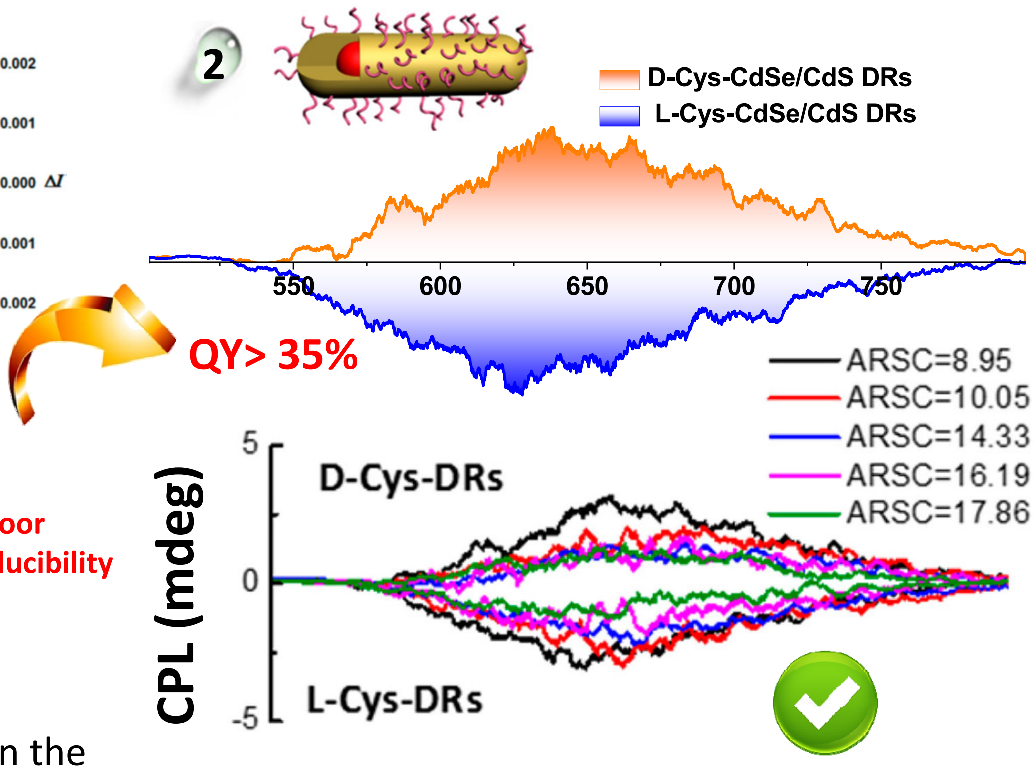


1. J. Am. Chem. Soc. 2017, 139 (25), 8734-8739;
2. Nano Lett. 2018, 18 (11), 6665-6671;
3. Adv. Funct. Mater. 2018, 28 (28), 1802012.

Circularly polarized luminescence (CPL)



First report on the induced CPL in Cys-CdSe NCs



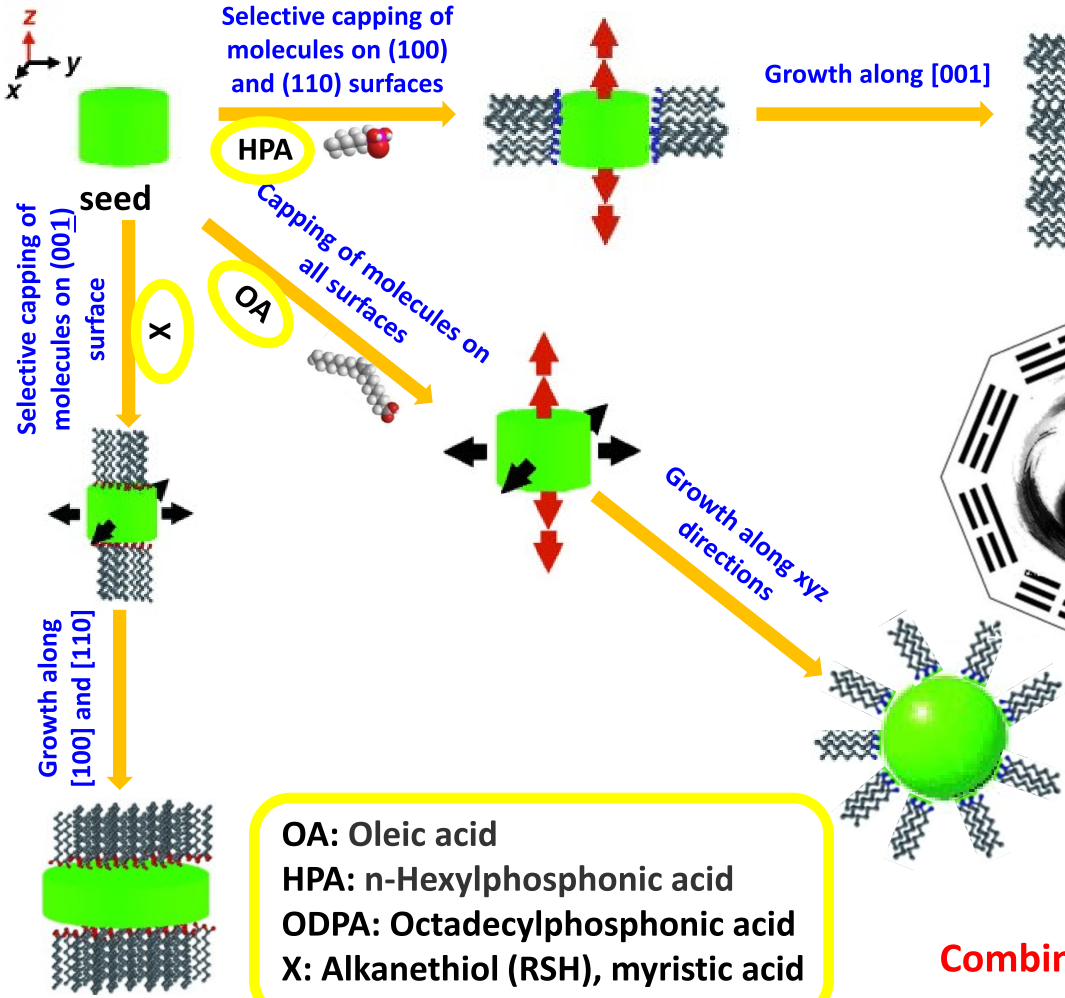
The excellent **luminescence properties** of Cys-CdSe/CdS DRs improve the **reproducibility** of CPL.

How can we expand the range of nanocrystals exhibiting a CPL signal?

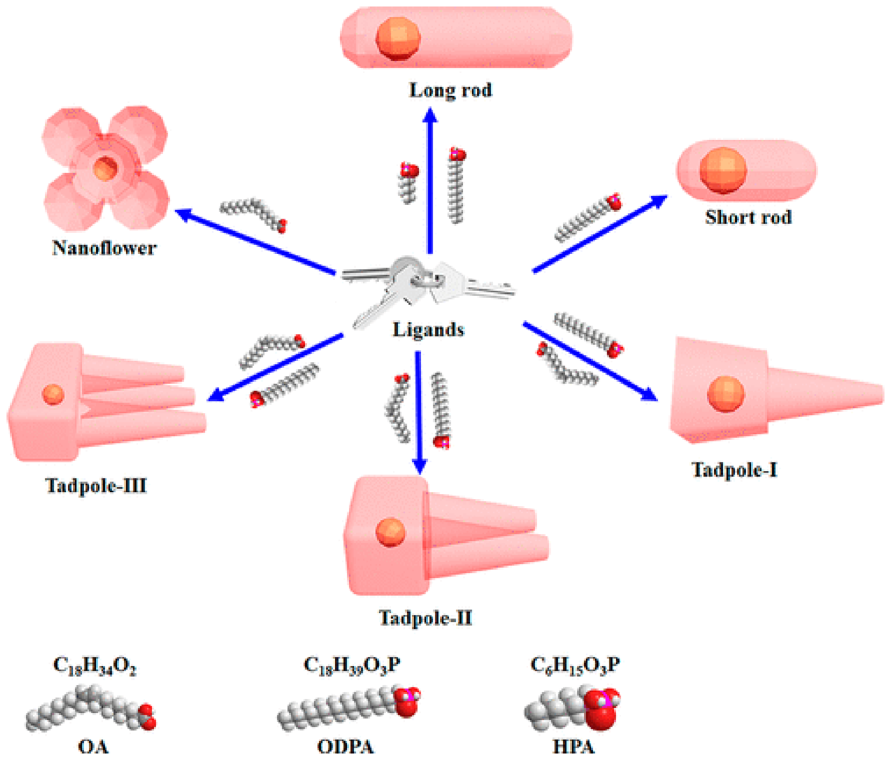
ARSC: A_{shell}/A_{core}, absorption ratio of shell to core geometry-dependent CD and CPL phenomena

1. Balaz, ACS Nano 2013, 7 (12), 11094-11102;
2. Cheng, ACS Nano 2018, 12 (6), 5341-5350.

Circularly polarized luminescence (CPL)



OA: Oleic acid
HPA: n-Hexylphosphonic acid
ODPA: Octadecylphosphonic acid
X: Alkanethiol (RSH), myristic acid



Combine ligands?

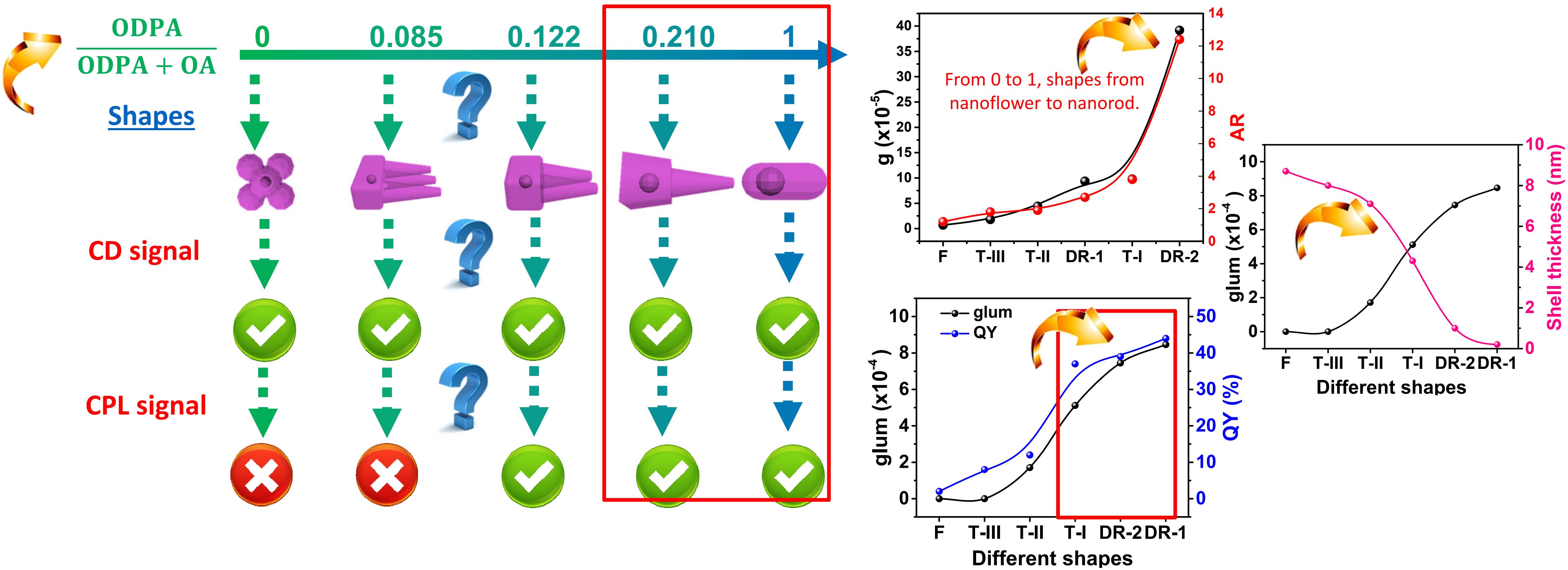
Time, temperature & AI

Angew. Chem. Int. Ed. 2006, 45, 3414.

ACS Nano 2020, 14 (8), 10346-10358.

Ligand-Induced Chirality in Asymmetric CdSe/CdS Nanostructures 1D

■ **The chirality evolution with shape in the case of core-shell semiconductor NCs**

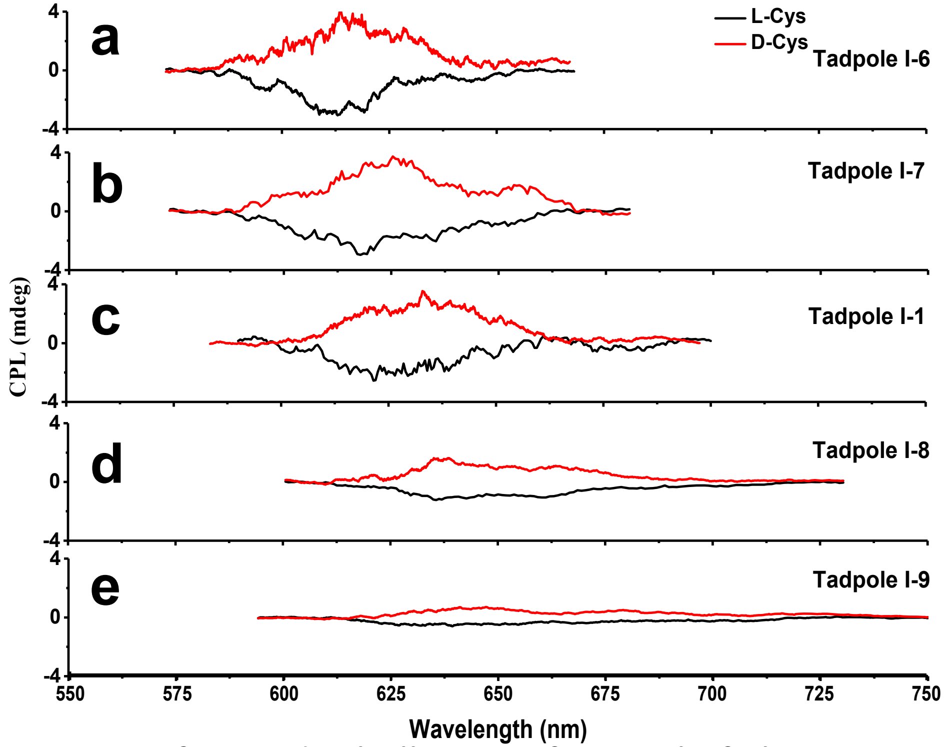


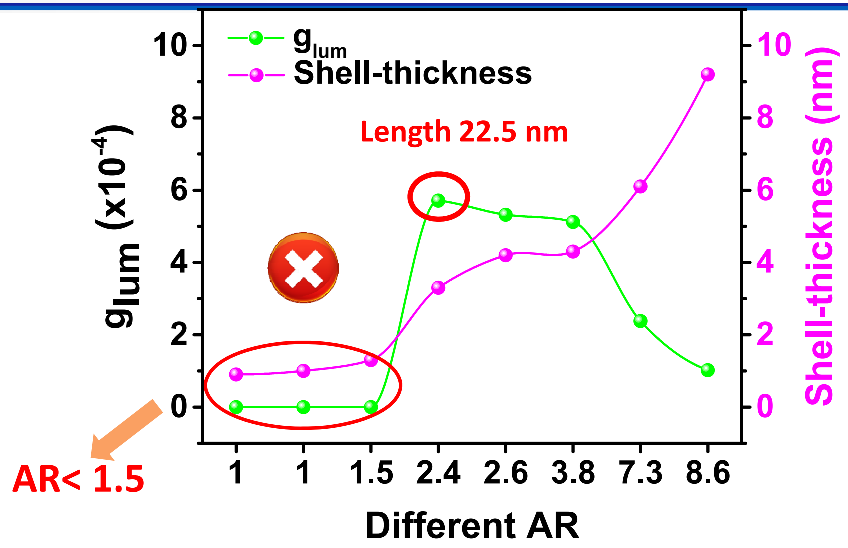
> ➢ CD chirality increases with increasing anisotropy (aspect ratio) & Short separation between core and L
> ➢ High luminescence is usually needed for the **reproducibility** of CPL (let's say >10%)

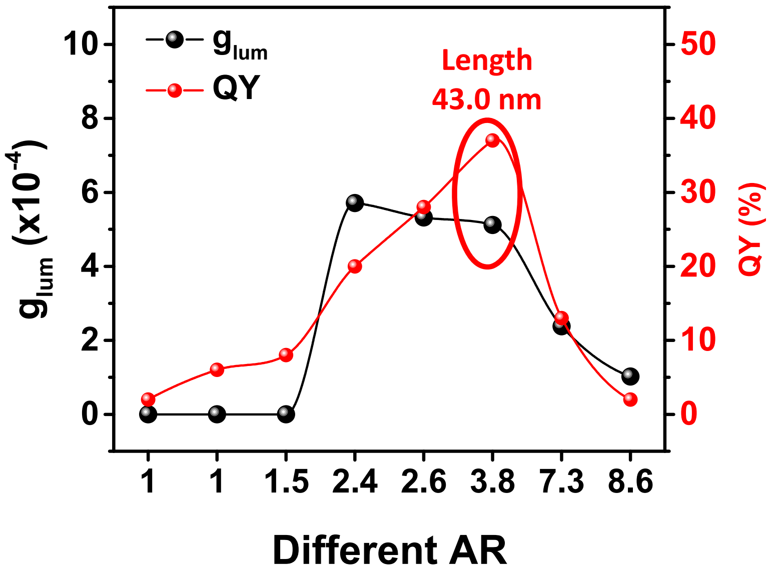
ACS Nano 2020, 14 (8), 10346-10358.

Ligand-Induced Chirality in Asymmetric CdSe/CdS Nanostructures, 1D

■ **Dependence of g_{lum} on AR**







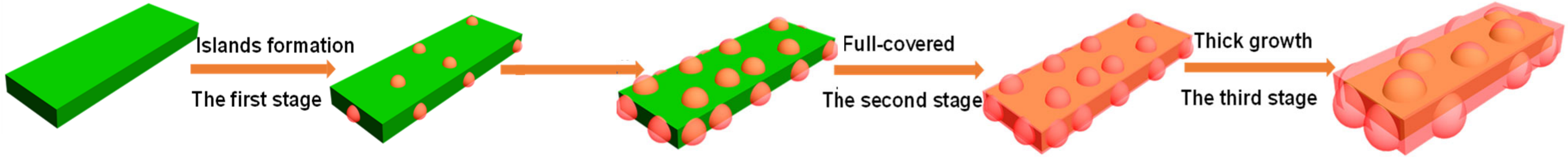
CD response from CdS shell is max for a tail of about 45 nm (λ/10 of the incident light

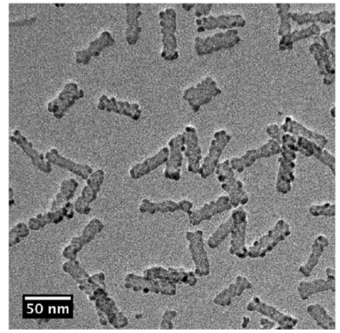
CPL activity from CdSe core, and the activity benefits from a thin CdS shell with a relatively high photoluminescence QY

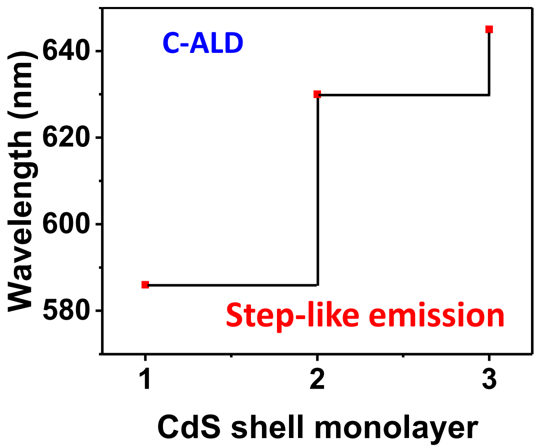
ACS Nano 2020, 14 (8), 10346-10358.

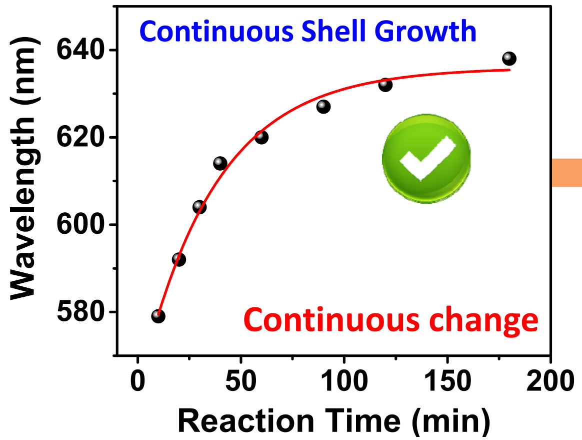
Optically Active 2D CdSe/CdS Nanoplatelets Exhibiting Both CD and CPL

- **One-pot approach synthesis**









Finer tuning:
Gives rise to the precise regulation of the nanoparticle morphology and the chiral signal

- Simplicity "one pot", less time for thick shell
- High quantum yield, ~60%
- Narrow emission spectra with FWHM, 20 nm
- Polytypism, stacking variations, anisotropy may enhance chirality

Adv. Optical Mater. 2021, 10.1002/adom.202101142

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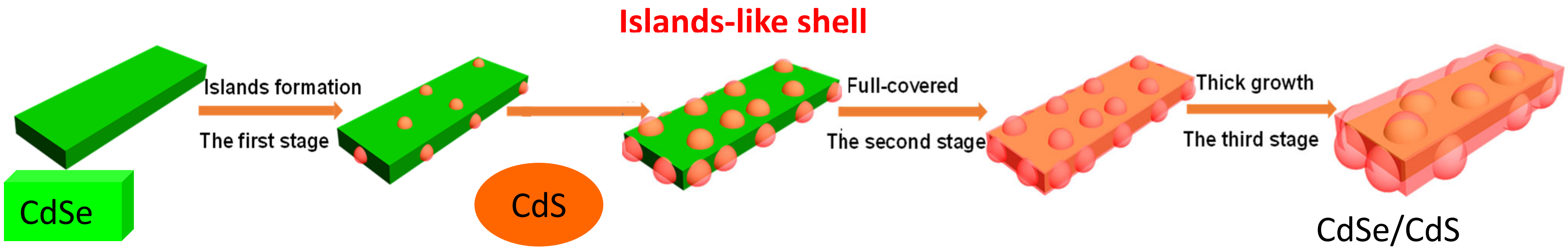
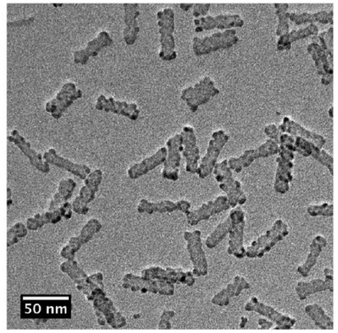
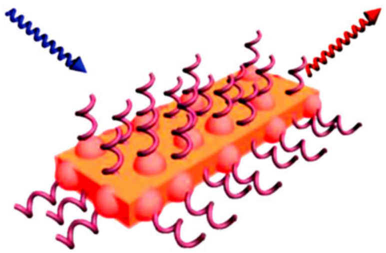


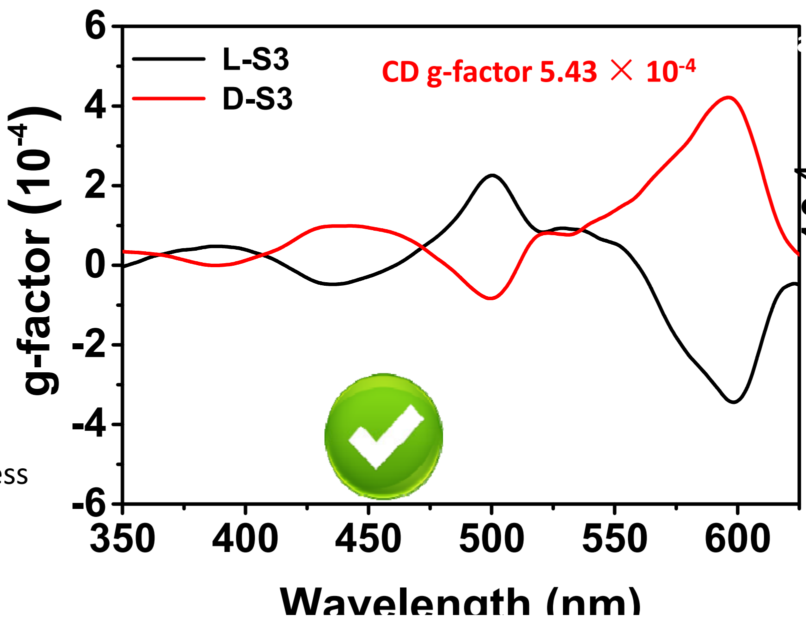


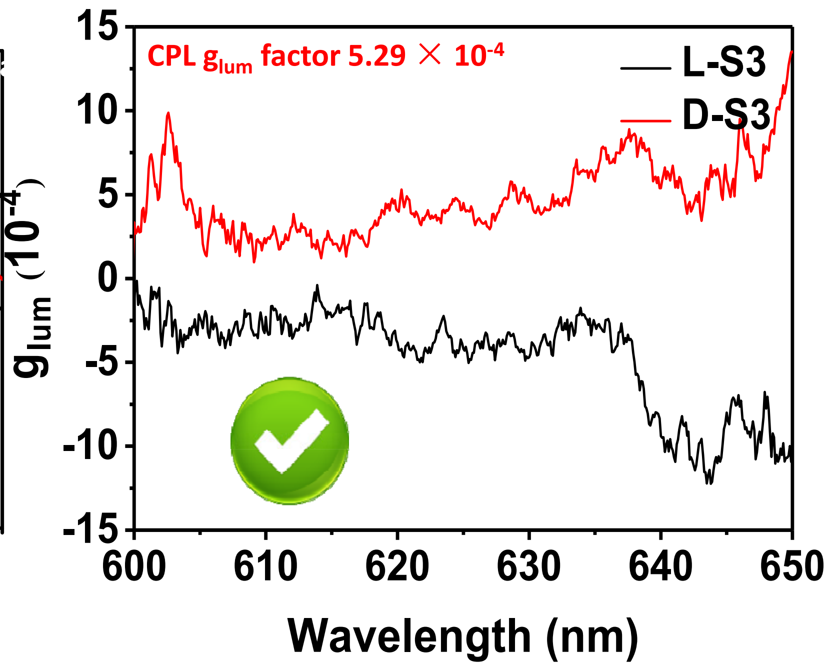
QY~ 20%



Island-like shell effect of CdS in the CdSe/CdS NPLs

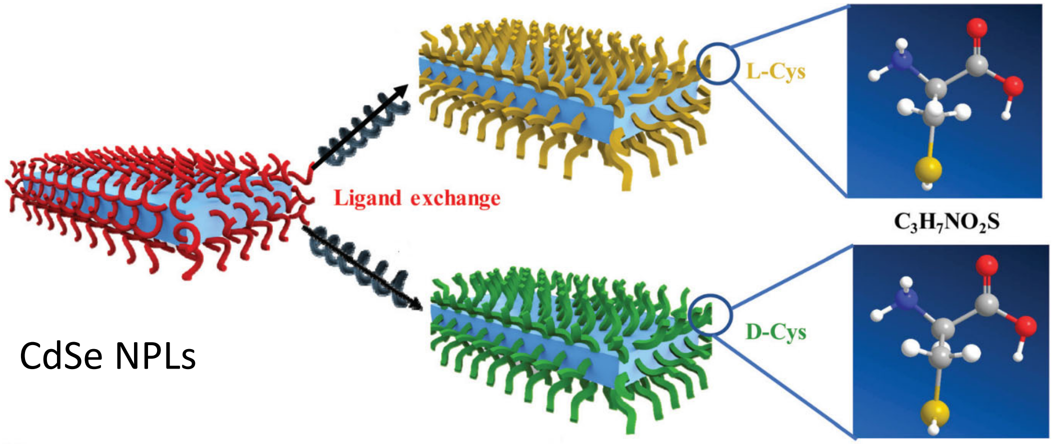
Reduction of the lattice Dislocation stress

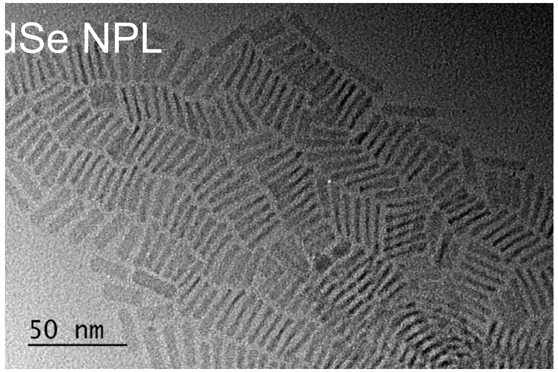


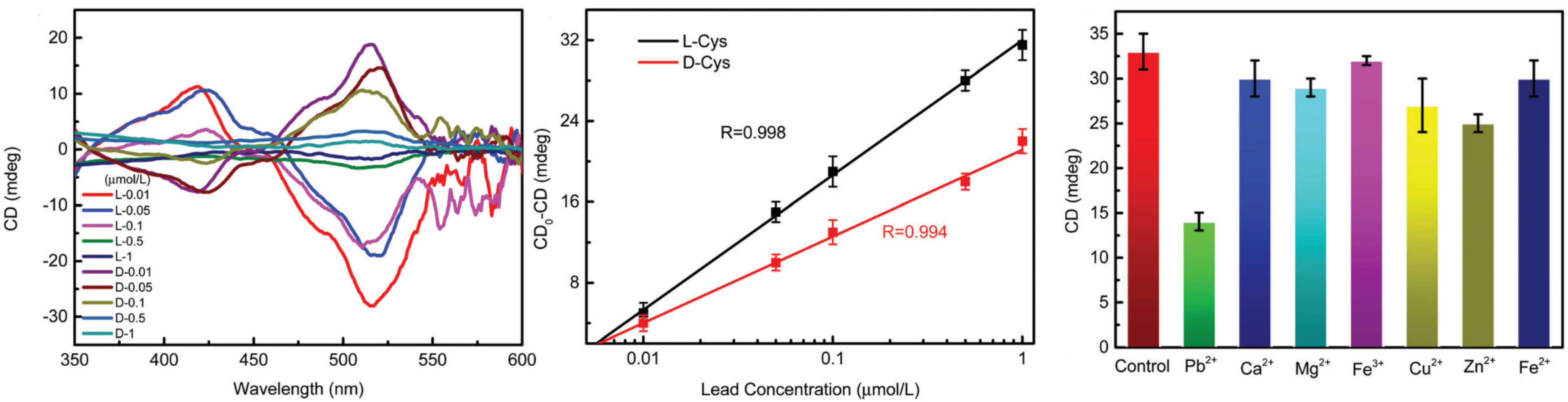


Adv. Optical Mater. 2021, **10.1002/adom.202101142**

Chiral application : ionic sensor







The highly sensitive chiroptical sensing for **lead ions detection** with high selectivity was demonstrated. LOD = 4.9 ± 0.3 nM

Nanoscale 2019, 11 (19), 9327-9334.

Next step:

- **Study of AR working on the control of the thickness which controls the degree of interaction of the Ligand MO with the QD core!**

- **Work on the controlled etching of mother solutions of DRs to control the solution concentrations and have access to the unique particle chiroptical properties in solution**

acknowledgments

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