Breaking Degeneracy in Semiconductor Nanocluster Assemblies for Tunable Chiroptics

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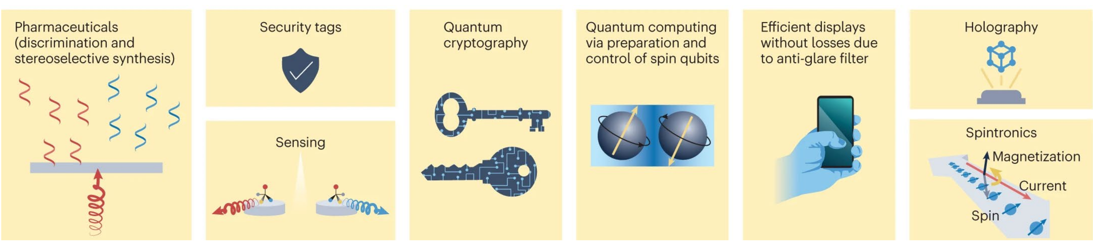
Background

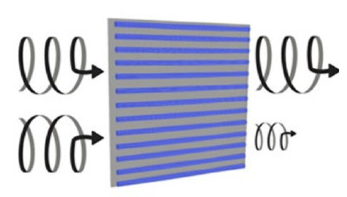


Nat. Rev. Mat. **8**, 365 (2023)

Circularly Polarized Light
- Additional degree of freedom for encoding information.
- Quantum optics, secure communication, 3D displays.

Motivation for Chiroptical Materials
- Scalable materials, with a large and tunable chirality.
- Understanding and leveraging structure-property relationships.

Circular Dichroism (CD) Spectroscopy
- $CD = A_{LCP} - A_{RCP}$
- Probe into chiral structure
- $g = 2(A_{LCP} - A_{RCP})/(A_{LCP} + A_{RCP})$ Figure of merit for chirality



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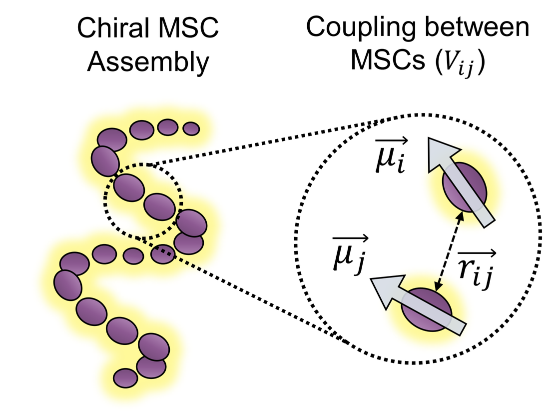
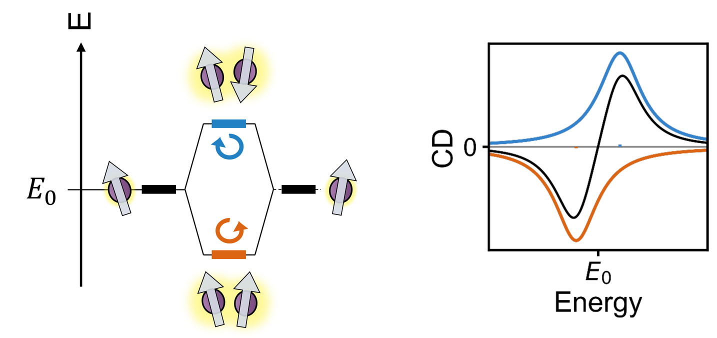
Modelling Circular Dichroism of MSC Assemblies

- Semi-classical model used to simulate CD and absorption spectra
- MSCs are approximated as point dipoles ($\vec{\mu}$) with a pairwise coupling potential V_{ij}



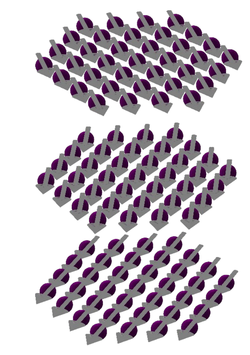
$$V_{ij} = \frac{1}{4\pi\epsilon}\left[\frac{\vec{\mu_i}\cdot\vec{\mu_j}}{|\vec{r_{ij}}|^3} - 3\frac{(\vec{\mu_i}\cdot\vec{r_{ij}})(\vec{\mu_j}\cdot\vec{r_{ij}})}{|\vec{r_{ij}}|^5}\right]$$

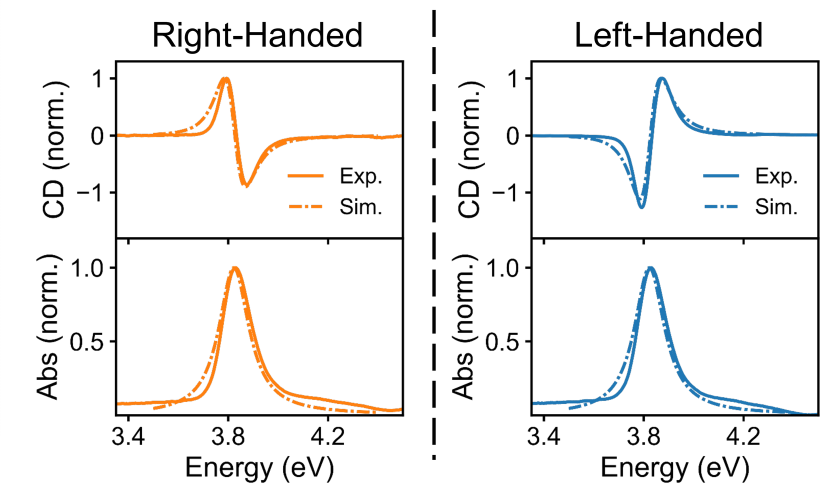
- Interaction Hamiltonian ($\hat{H}$) computes delocalized hybrid states.
- Light-matter interactions are calculated using Fermi's Golden Rule.
- For chiral dipole arrangements, hybrid states are chiral and have opposite symmetries, resulting in a bisignate CD.



$$\hat{H}\psi_k = E_k\psi_k \qquad \hat{H} = \begin{bmatrix} E_1 & V_{12} & \cdots & V_{1N} \\ V_{21} & E_2 & & \vdots \\ \vdots & & \ddots & \vdots \\ V_{N1} & \cdots & \cdots & E_N \end{bmatrix}$$

- To simulate our material, we use a hexagonal lattice, with dipoles of each layer oriented by an angle α to the layer below
- Model predicts inversion of bisignate when handedness of the structure is changed – supports the structural hypothesis.



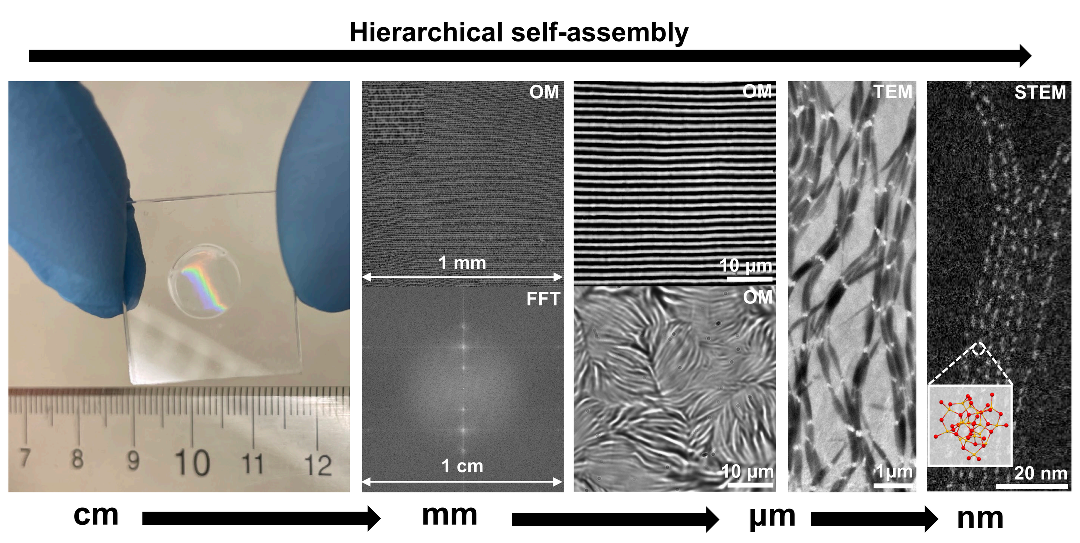


Parameters

μ	7D
a_z	3nm
a_{hex}	3nm
α	1°
n_z	100
n_{hex}	3

Chiral Self-Assembly of MSCs

- CdS Magic-Sized Clusters (MSCs): Atomically Precise, perfectly monodisperse nanocrystals stabilized by an organic mesophase.
- Monodispersity of MSCs favors the formation of self-assembled films with structural order up to the centimeter scale.



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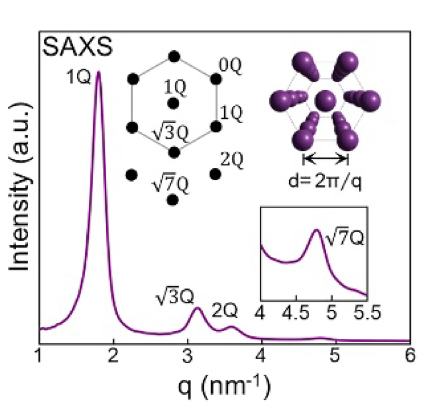
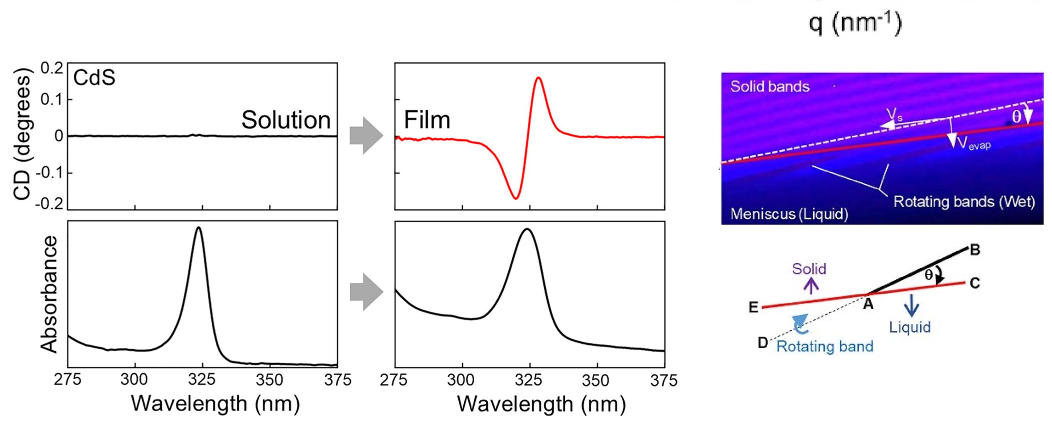
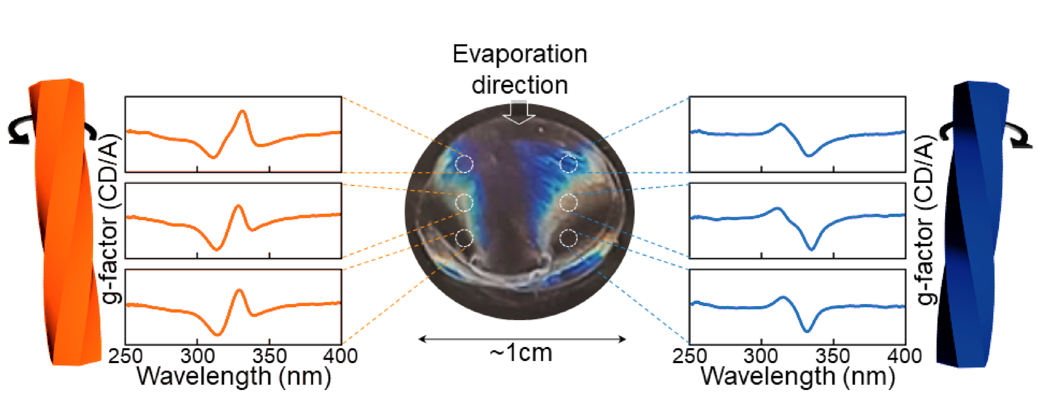
- MSCs assemble into hexagonal filaments which group into ~µm fiber bundles.
- Fiber bundles align and form linear patterns by meniscus driven deposition.

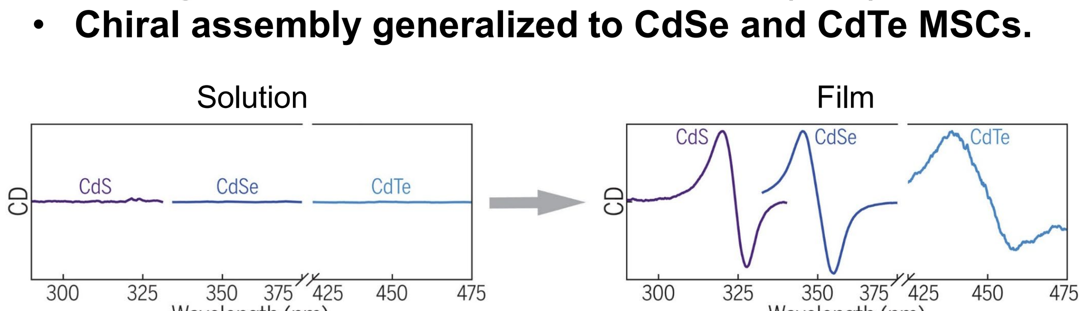




- Chirality attributed to twisting fibers that arises from fluid flows during deposition.
- Assembled MSCs exhibit a 'bisignate' CD signal with the zero crossing at the exciton energy, characteristic of 'exciton coupling' seen in organic aggregates.
- By controlling the solvent evaporation, films with large homochiral domains can be engineered.



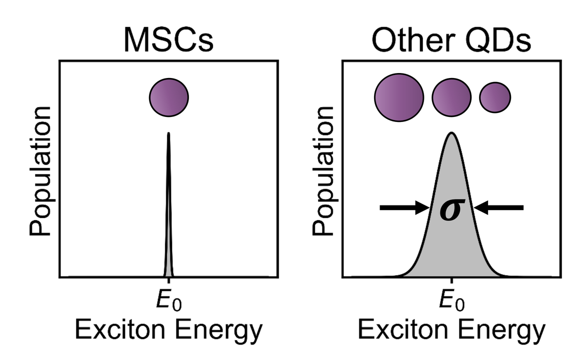
- CdS MSC films have the highest reported g-factor among semiconductor-based materials (1.30).
- Chiral assembly generalized to CdSe and CdTe MSCs.



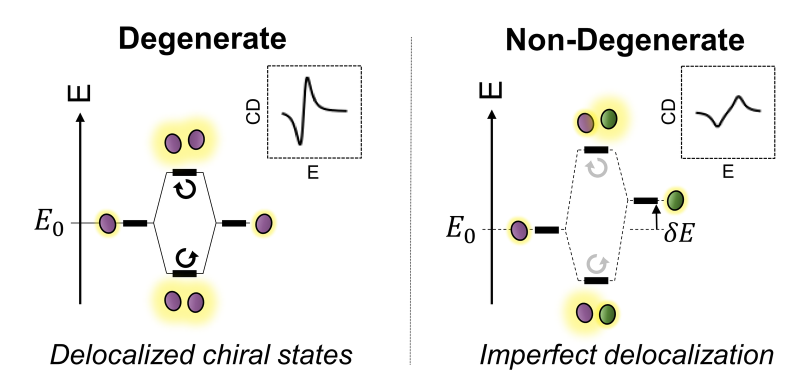
Science 387, eado7201 (2025)

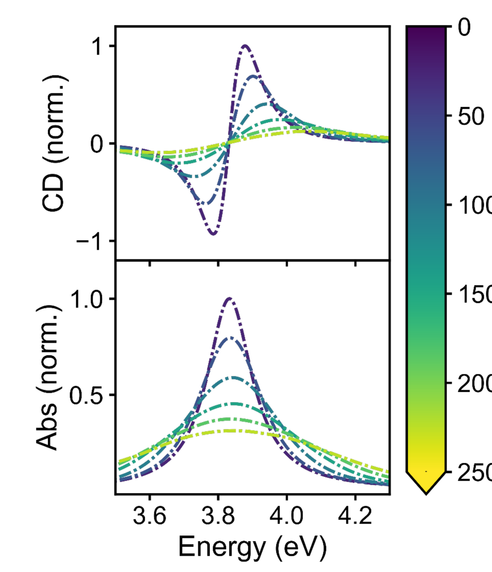
Significance of Degeneracy in Chiral Assemblies

Strong CD of MSC assemblies from:
- Monodispersity ⇒ structural order
- **Degeneracy of Excitons**



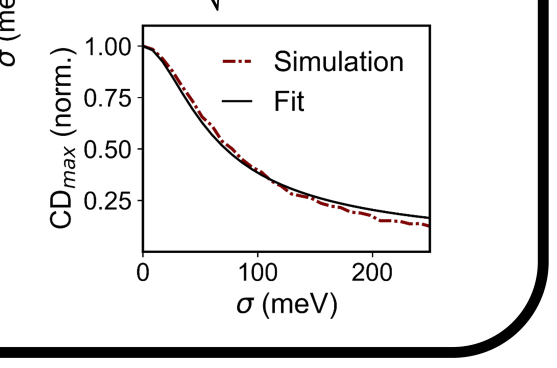
Theory predicts weaker delocalization of exciton from non-degenerate coupling, leading to a weaker chiral response





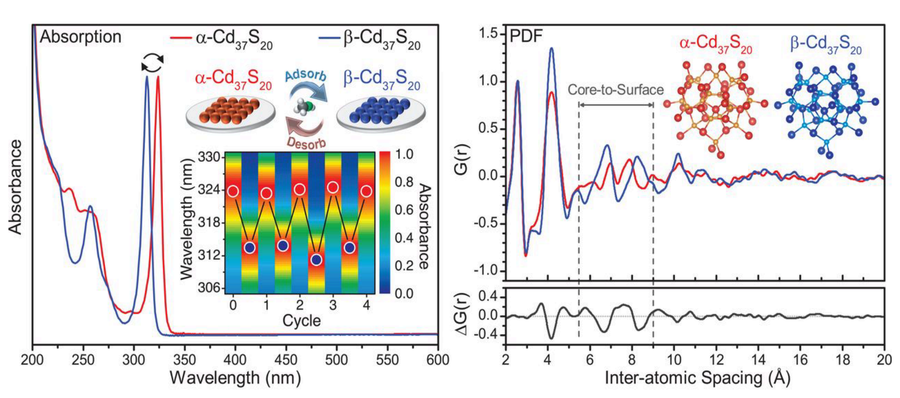
Model predicts rapid decay of CD with dispersity (σ), fitted to:

$$CD \sim \frac{1}{\sqrt{1+\left(\frac{\sigma}{k_{fit}}\right)^2}}$$



Inducing Discrete Non-Degeneracy

A non-degenerate state can be introduced by isomerization of MSCs.



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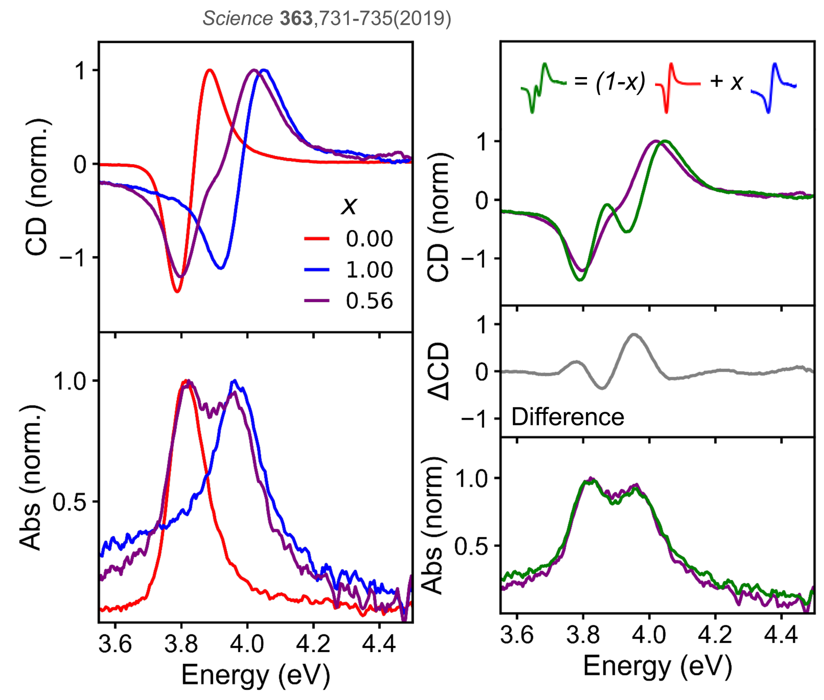
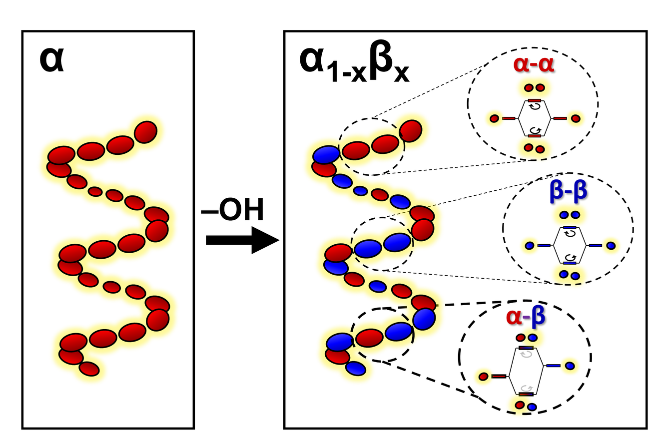
Isomerization:
Coherent transformation of MSCs induced by chemical modification of surface ligands with -OH

α-MSC ⇋ β-MSC
3.82 eV 324 nm | 3.97 eV 313 nm

MSC films are treated with MeOH vapor to induce isomerization, while maintaining the chiral mesostructure.
If the reaction proceeds to completion, CD and absorption shift to 3.97 eV. (Unary β-MSC assembly)
However, an incomplete reaction creates an $\alpha_{1-x}\beta_x$ binary assembly with a modified lineshape.



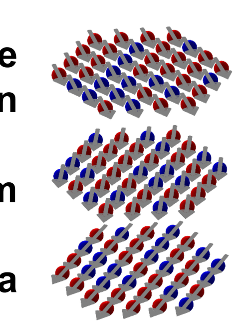


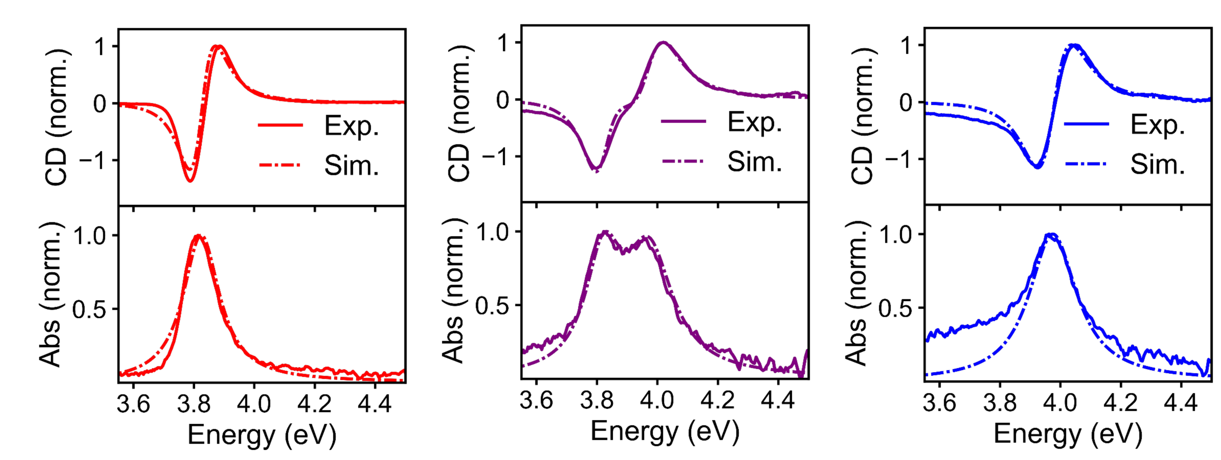
A linear combination of the CD spectra of single phase systems fails to match the binary $\alpha_{1-x}\beta_x$ CD.

Non-degenerate α-β coupling results in a synergetic chiroptical response.

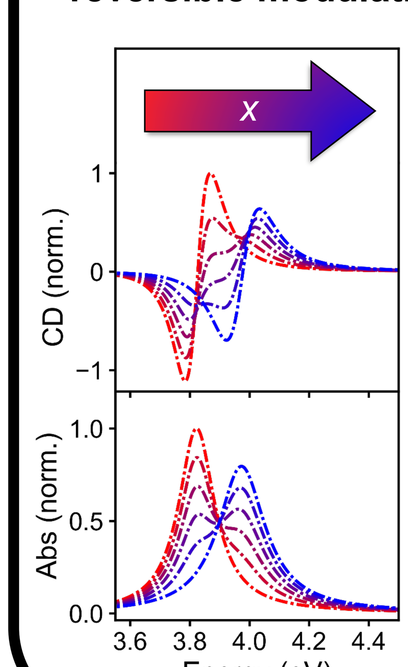
Model Predictions

The $\alpha_{1-x}\beta_x$ binary assembly is modeled by changing the energies of a fraction of MSCs, randomly distributed in the structure.
The fraction of isomerized MSCs (x) is extracted from the experimental absorption.
Excellent agreement with the experimental data suggests that β-MSCs are indeed uniformly distributed.



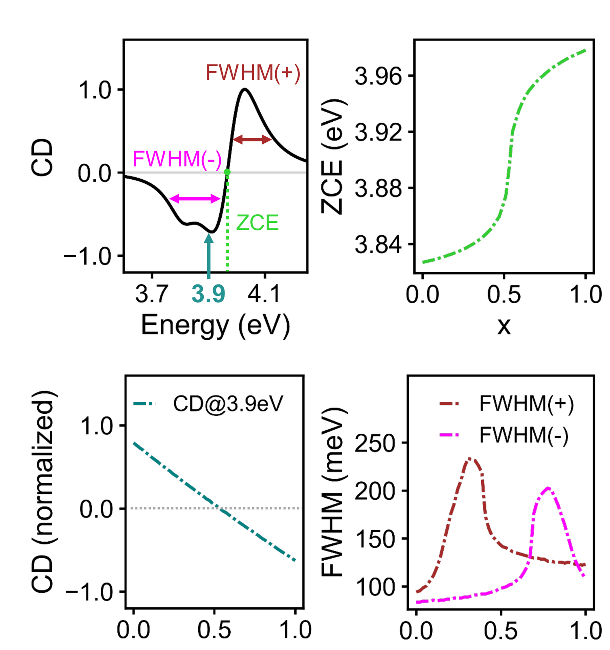


This validated model predicts the potential of dynamic and reversible modulation of the CD spectra by controlling x.



Modulation of:
- Full Width at Half Maximum (FWHM)
- Zero Crossing Energy (ZCE)

"Chiral continuum": Continuous modulation of CD between positive and negative extremes



Conclusions

- CdS magic-sized clusters (MSCs) form cm-scale hierarchical assemblies exhibiting exceptionally strong circular dichroism (CD).
- CD spectra are closely replicated by modeling the material as a chiral hexagonal assembly of interacting dipoles.
- Degeneracy, while being critical for a strong CD signal, can be strategically broken to extend the functionality of the material.
- Isomerization is leveraged to develop binary and ternary non-degenerate MSC assemblies, exhibiting a synergetic CD response.
- Non-degenerate exciton coupling in MSC assemblies has the potential of enabling dynamic and reversible control over the CD lineshape.

Expanding to Ternary Systems

Under different processing conditions, an isomerization intermediate (β') at 3.6 eV can be stabilized, leading to an αββ' ternary system, which offers further potential to improve functionality.