



Hierarchically Assembled Bowtie-Shaped Hybrid Metamaterials with a **CHIRALITY CONTINUUM**

Kumar, P., Vo, T., Cha, M. et al. Photonically active bowtie nanoassemblies with chirality continuum. *Nature* 615, 418–424 (2023).



Nature detects friend or foe using polarized light

Mantis Shrimp
Unpolarized

Structure

Reflected

Polarization Rotation

Spike

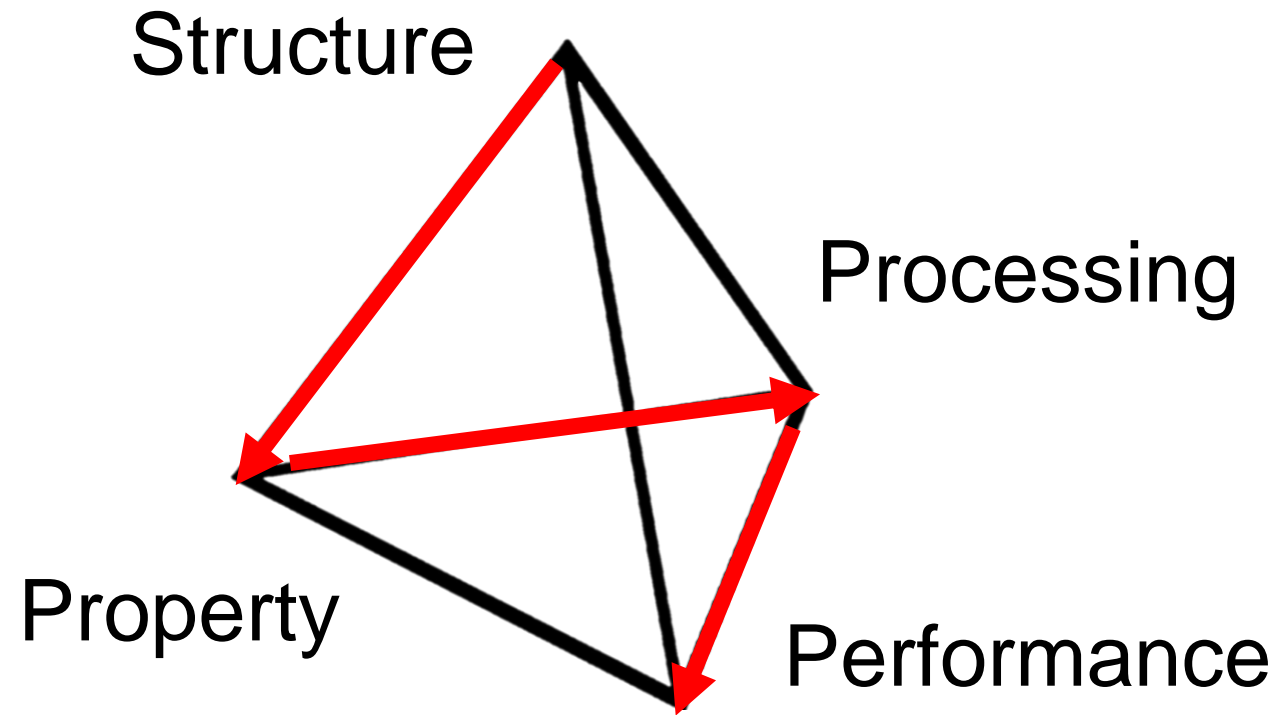
Tune the twist in a material, tune its polarization rotation

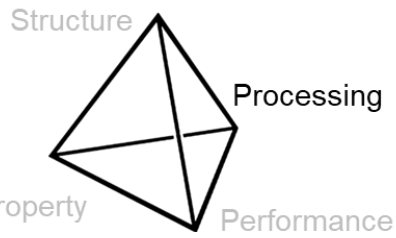
Tuning the twist / chirality while maintaining shape is not trivial

Gagnon, Yakir Luc *et al.* *Current Biology*, 25, (23) 3074 – 3078 (2015).

Youtube : Deep Look

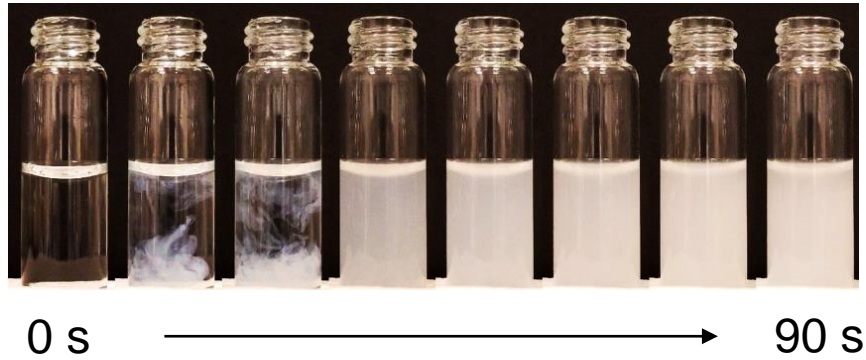
Shan Li *et al.* *ACS Applied Materials & Interfaces* 13 (15), 17380-17391 (2021)





Uniqueness of bowties (Cd + Cystine)

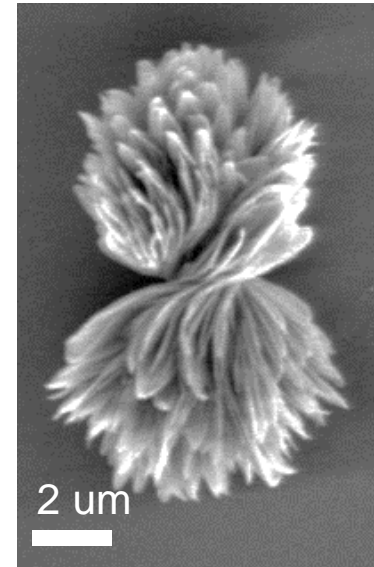
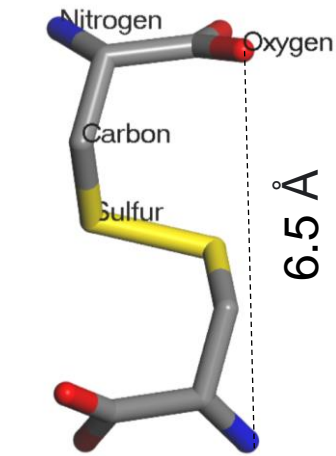
1. One-pot Synthesis in water



2. Monodisperse

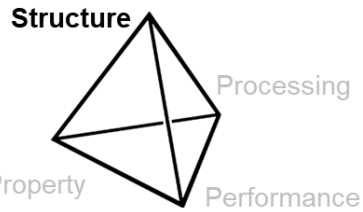


3. Molecule to Micron-sized particle



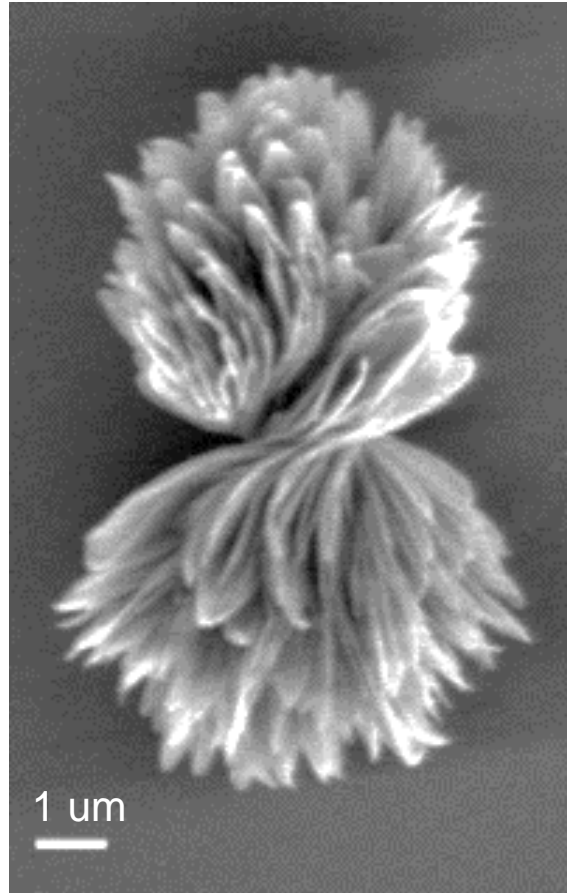
4. Scalable to gram of powder





Levels of hierarchy

Level 3
Stack of ribbons



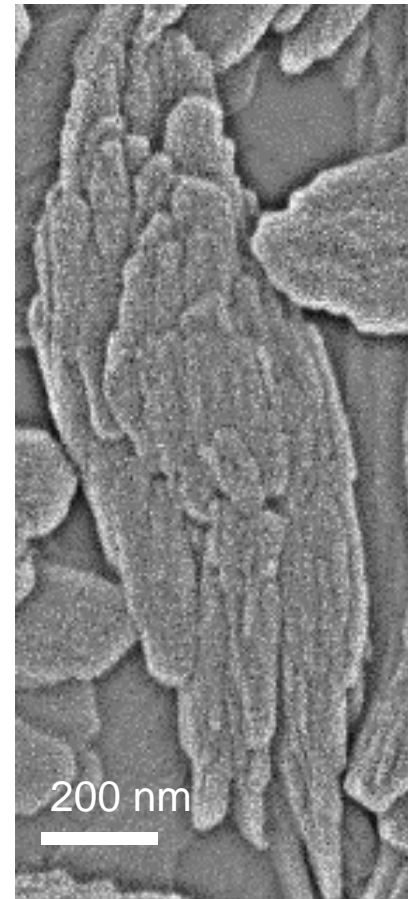
SEM image

Level 2
Single ribbon



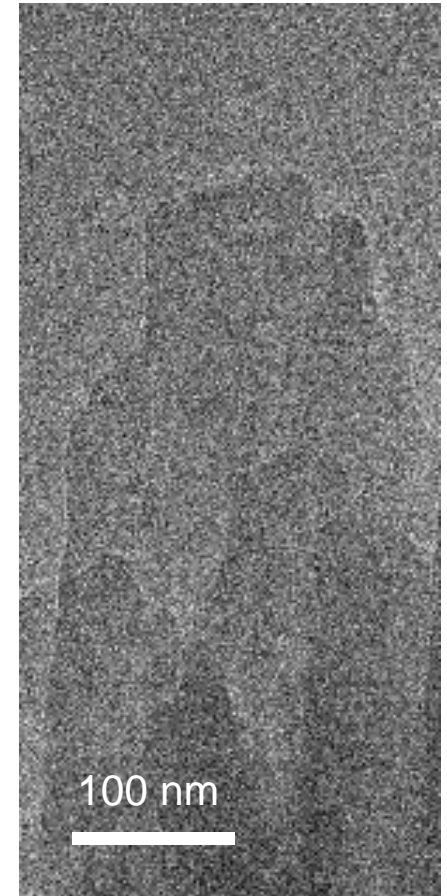
SEM image

Level 2
Domains within a ribbon

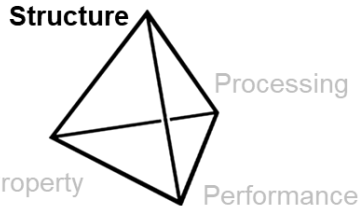


SEM image
Bandpass filtered

Level 1
Nanosheets



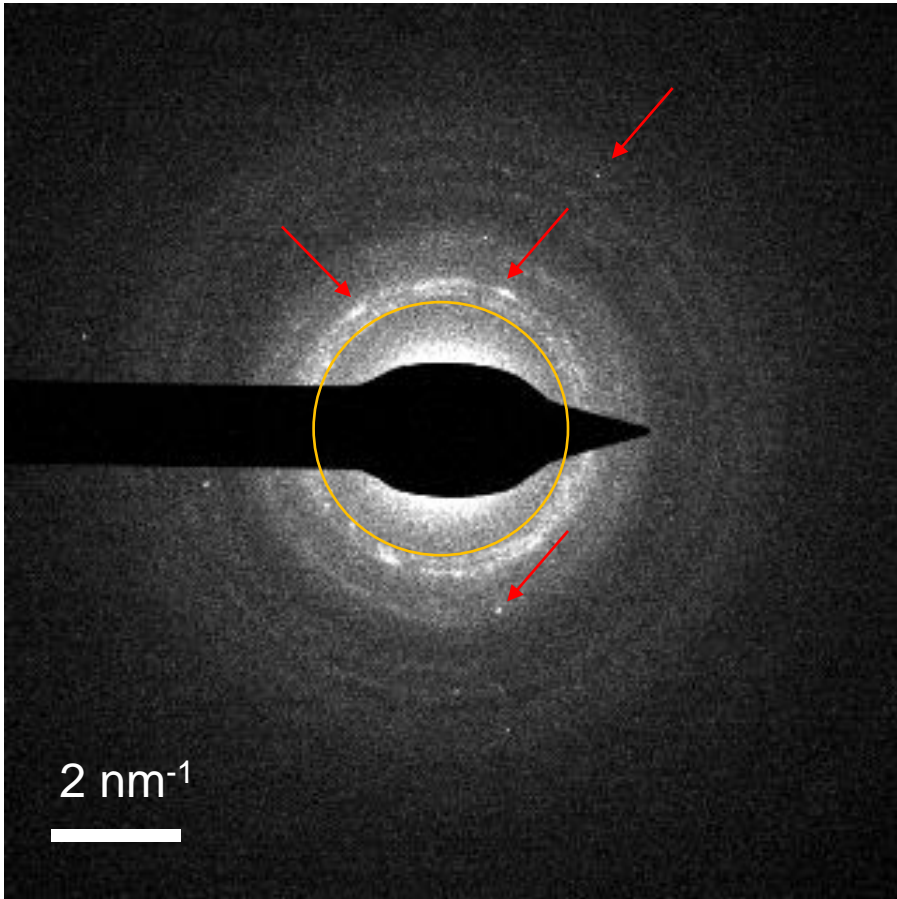
TEM image



What is level 1 made out of?

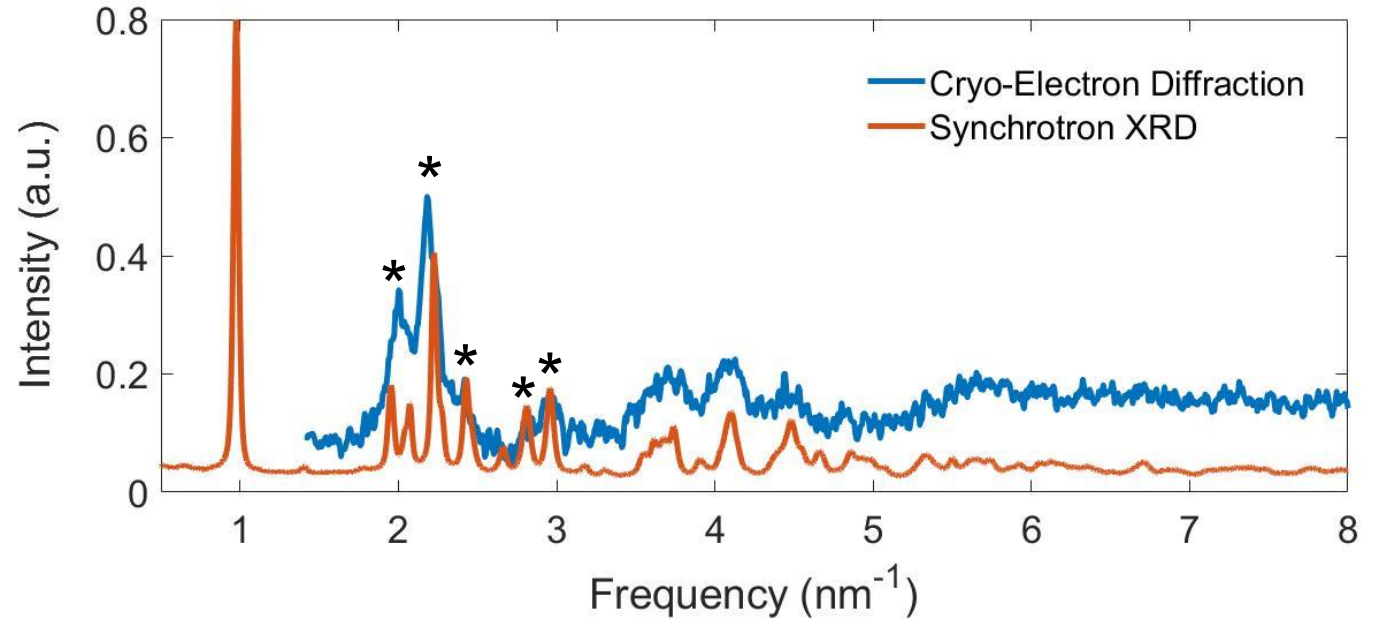
Understanding through Electron and X-ray diffraction

Level 0

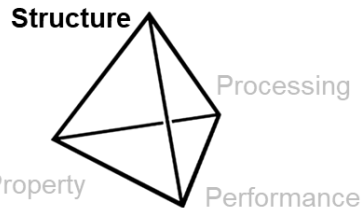


Cryo-Selected Area Diffraction Pattern

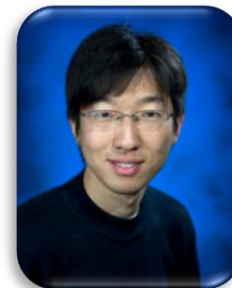
Cryo-SAED vs Synchrotron XRD



Material damages quickly under the electron beam at room temperature and converts to CdS nanoparticles

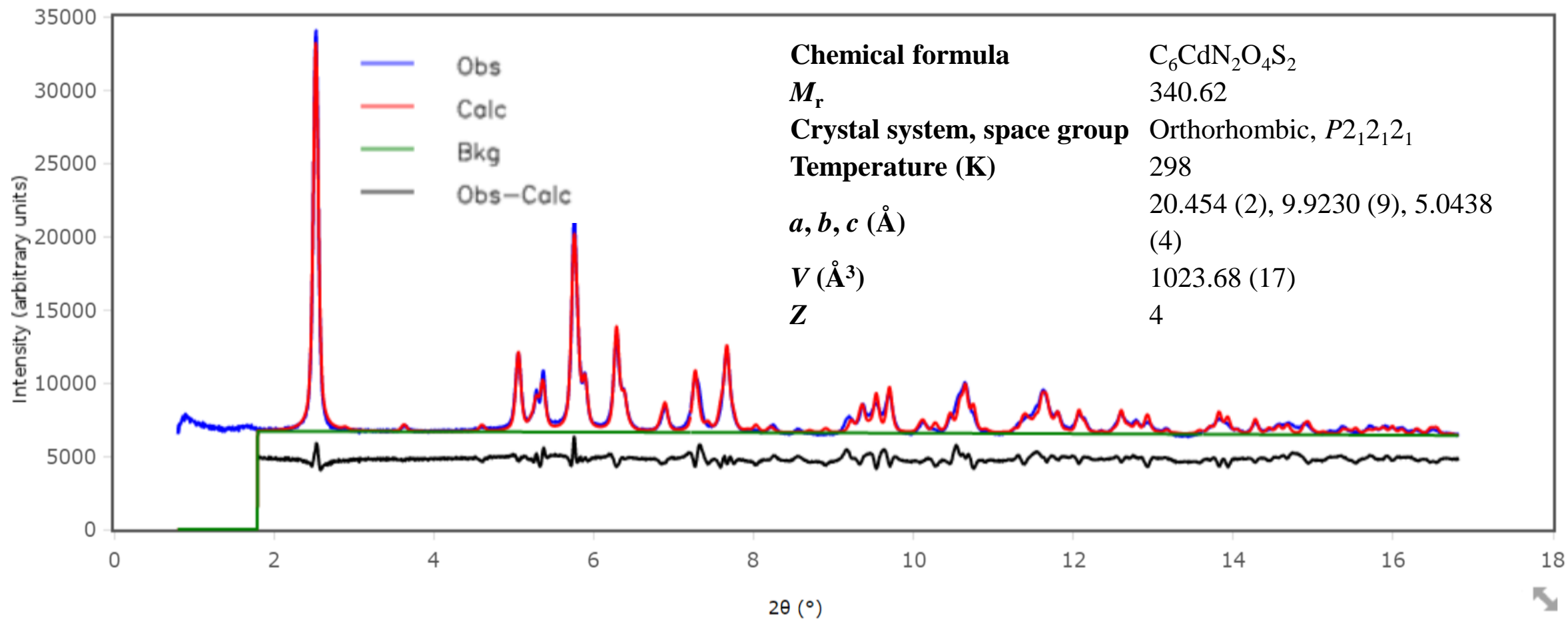


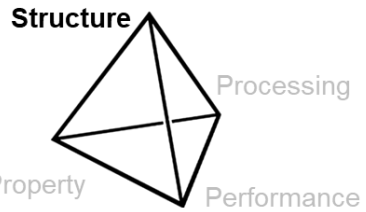
Unit cell of the structure at Level 0



Dr. Wenqian Xu

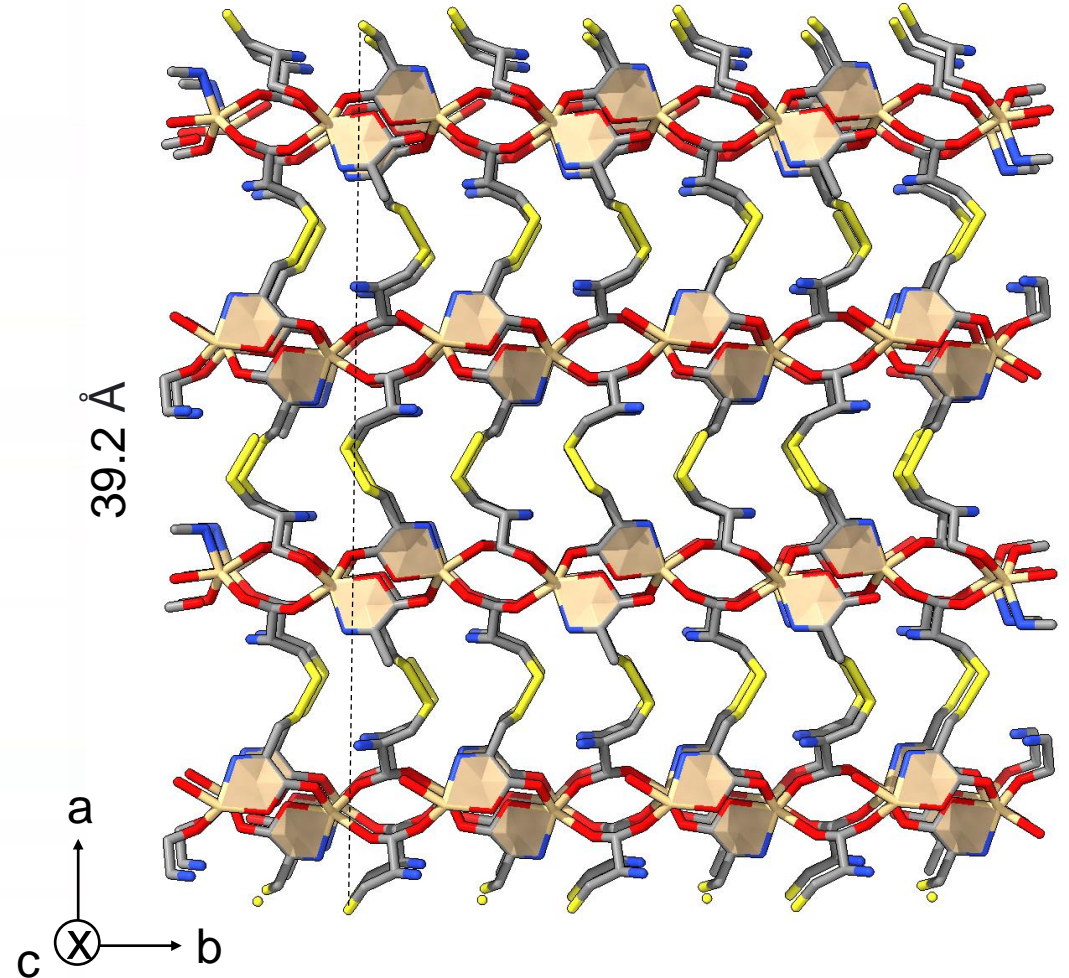
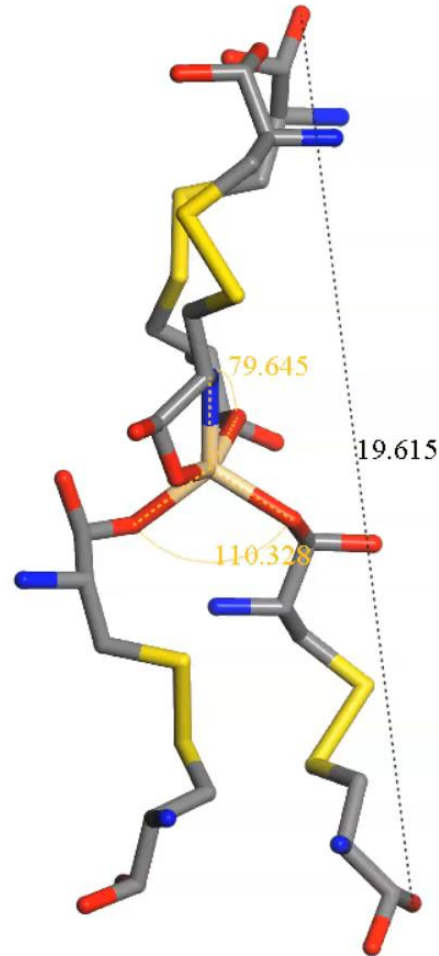
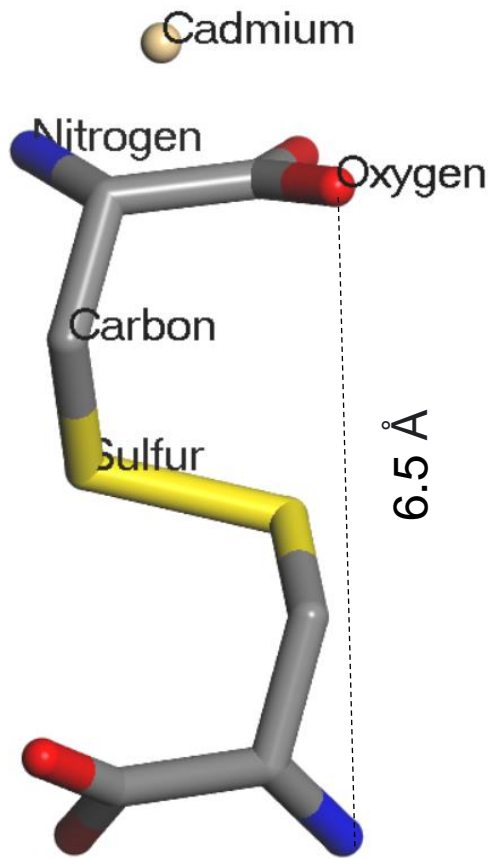
Through synchrotron X-Ray diffraction and structure solution

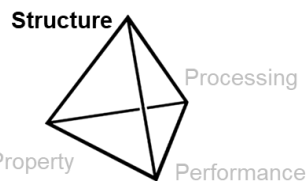




Unit cell of the structure at Level 0

Structure resolved from X-ray data



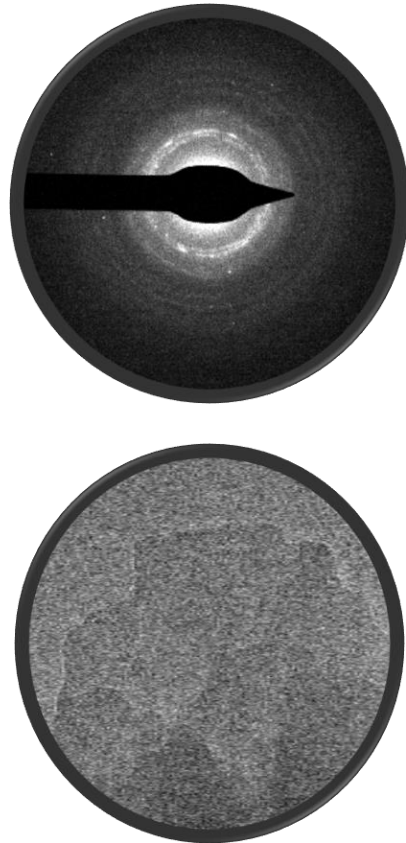


Multiscale Synthesis and Characterization

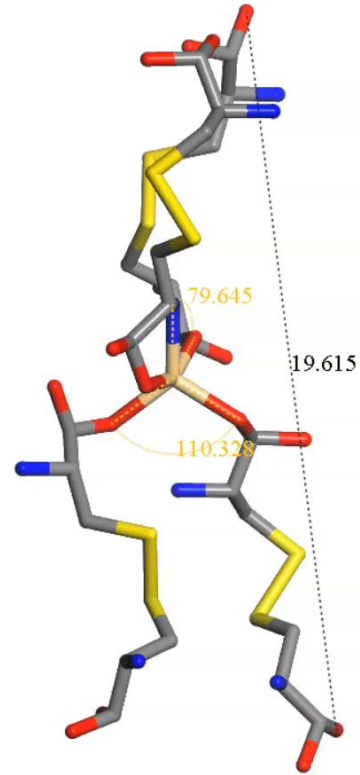
Colloidal Chemistry
(Self-assembly)



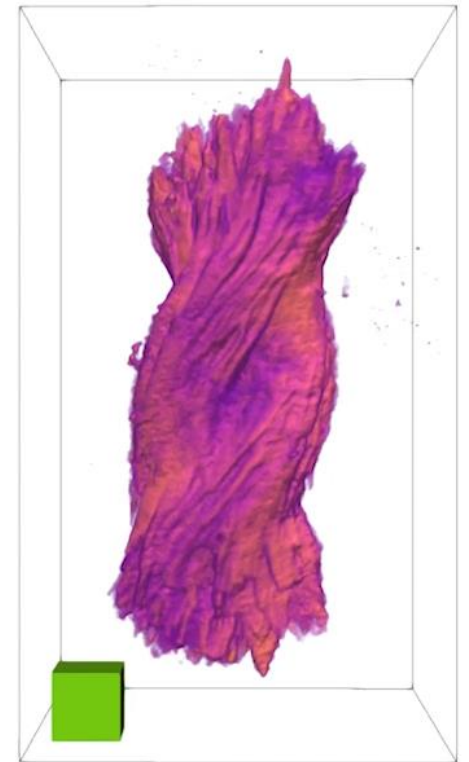
Imaging and Spectroscopy



Atomic Structure Solution
(XRD, TEM)



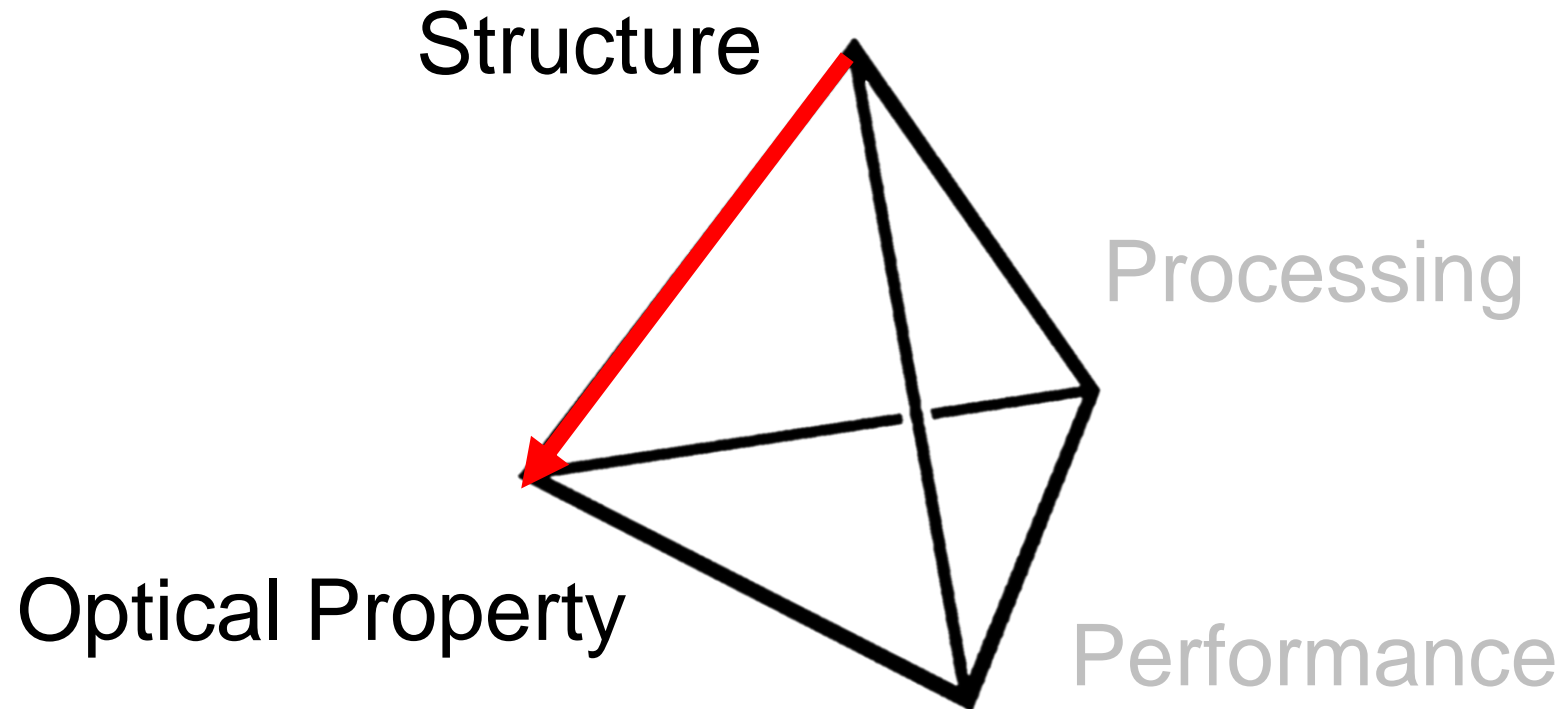
Tomography
(Cryo-TEM)



Å

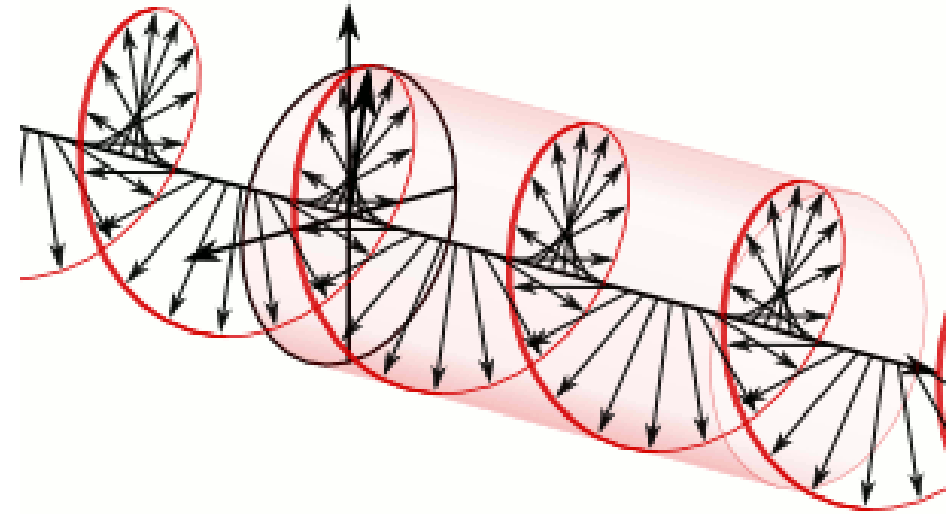
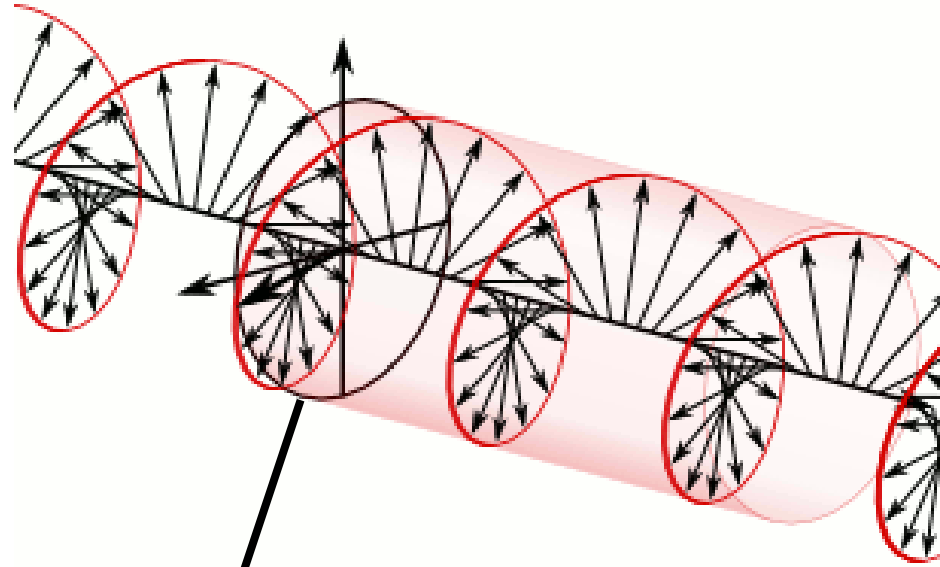
nm

µm

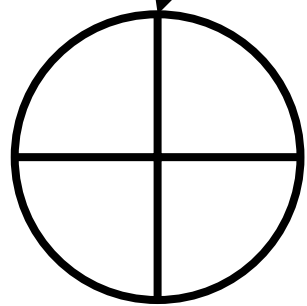


RCP – Right circularly polarized light

LCP – Left circularly polarized light

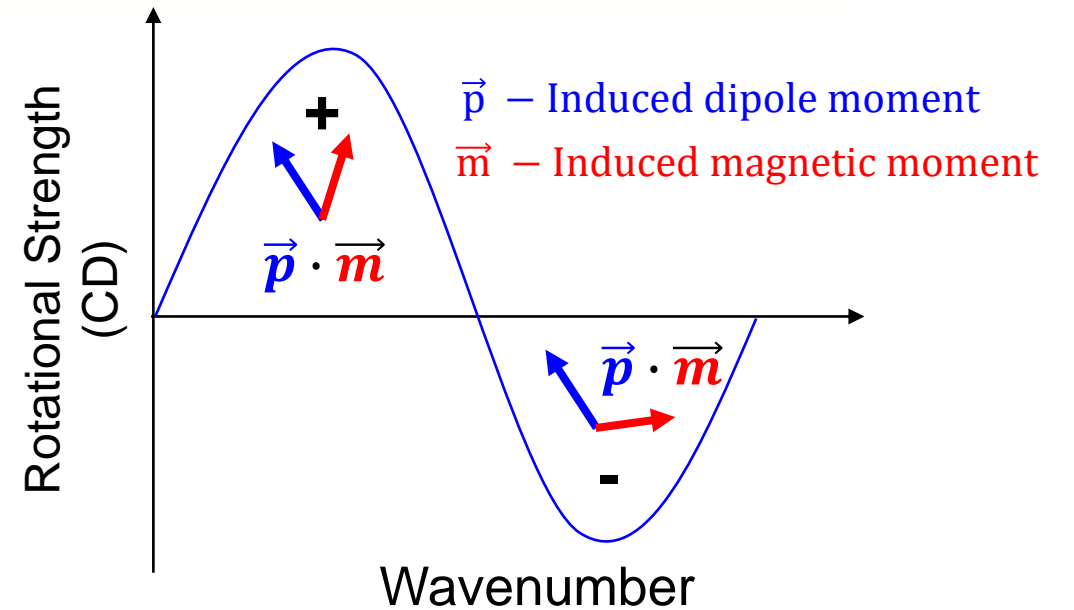
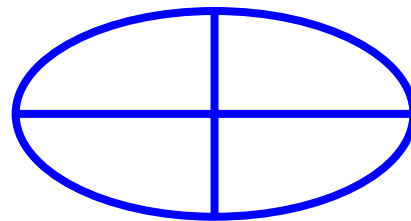


Incident
Circularly
Polarized Light



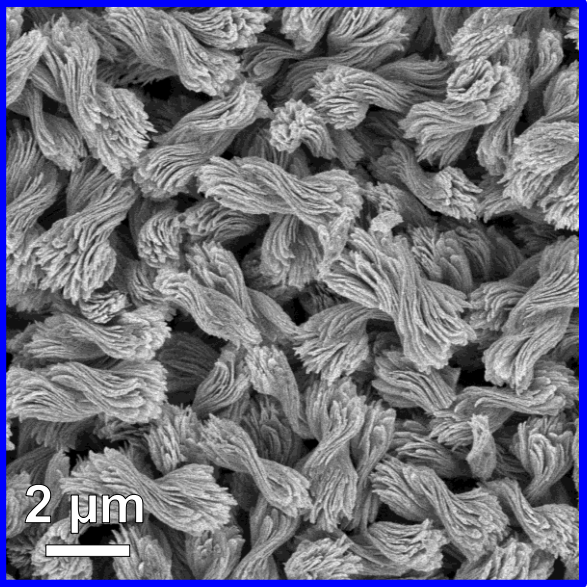
Material

Exit Elliptical
Polarized Light

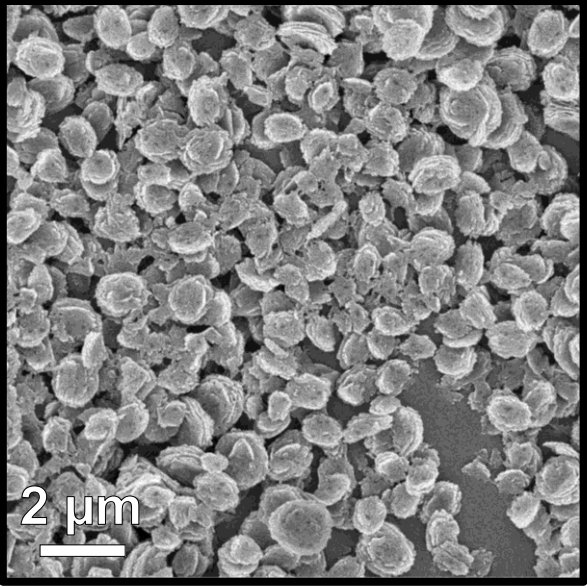


Understanding the chiroptical response

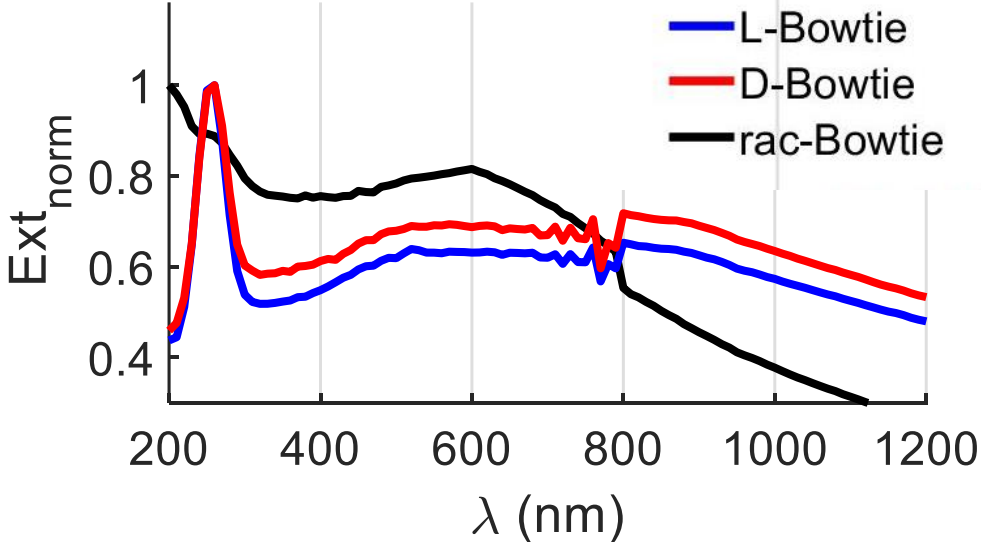
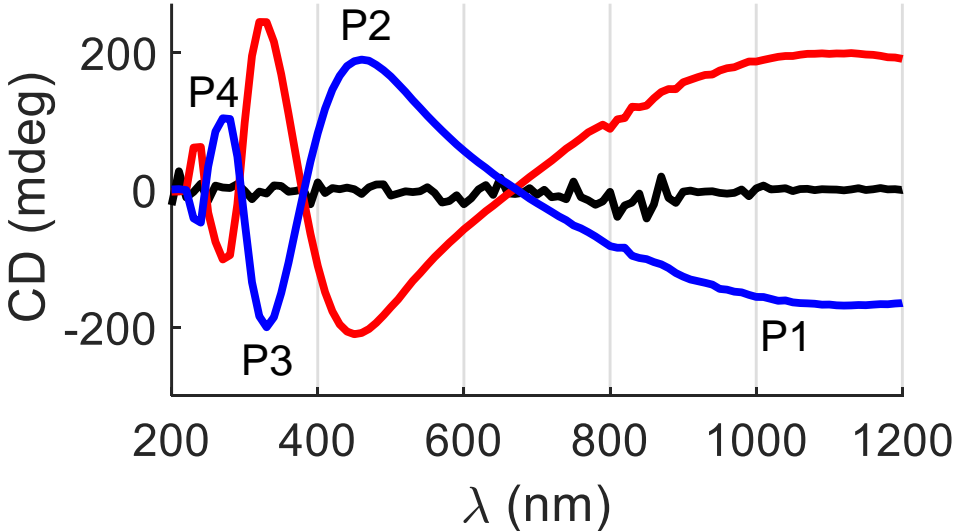
L-Bowtie
Right - handed



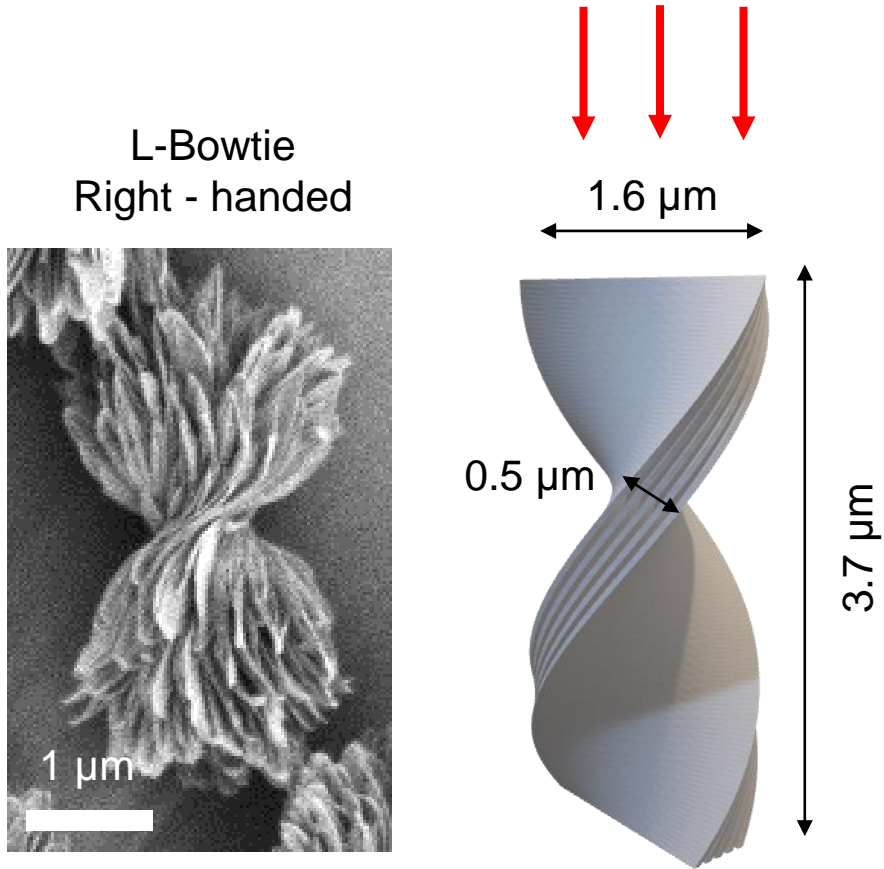
rac-Bowtie
Flat pancake



D-Bowtie
Left - handed

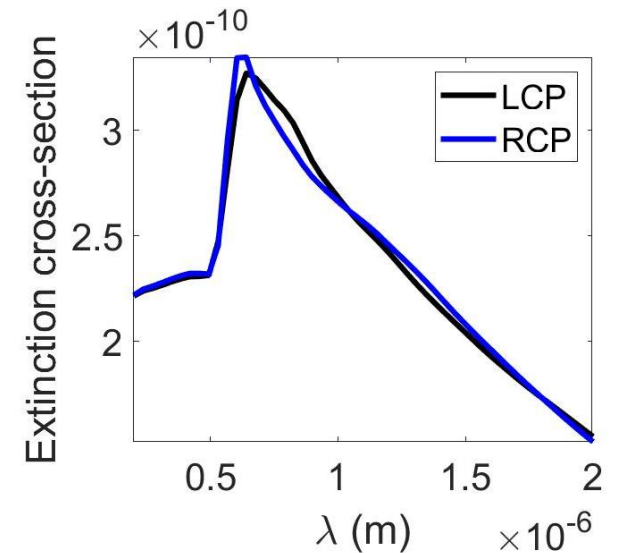
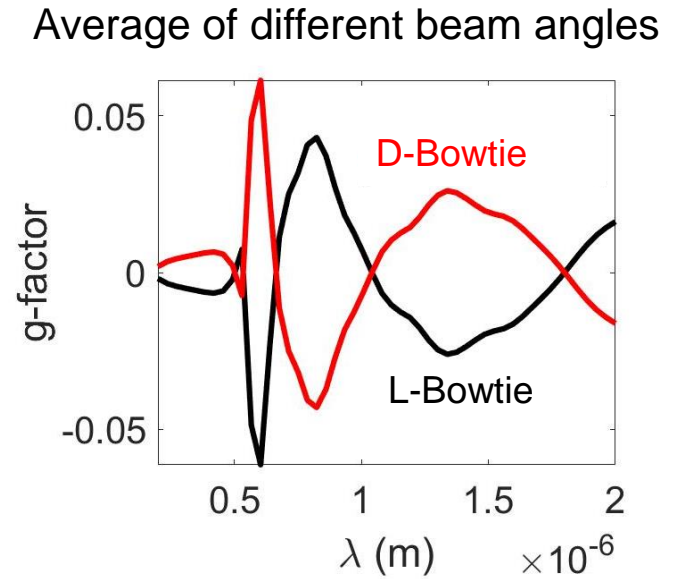
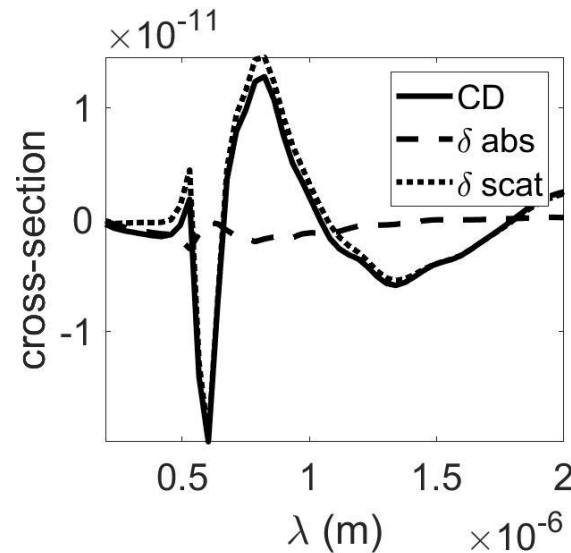
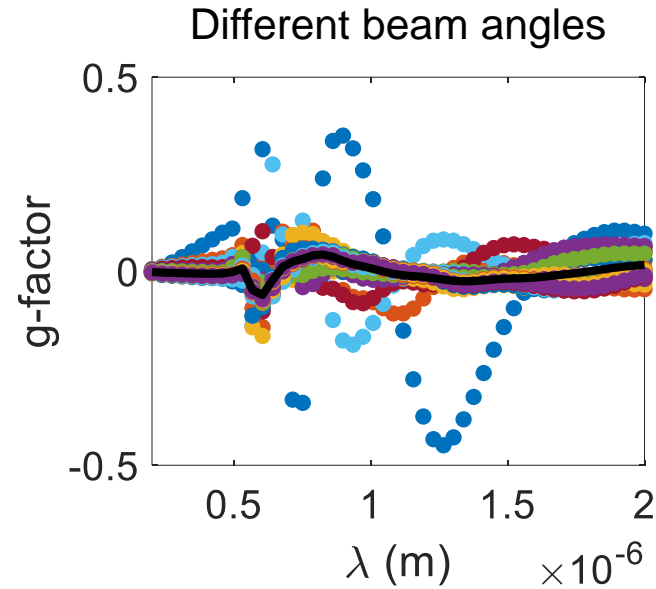


Understanding the chiroptical response



$$g - factor = \frac{CD}{extinction}$$

Lumerical FDTD, 3dS Max Simulation software were used. Michigan Supercomputing facility was leveraged

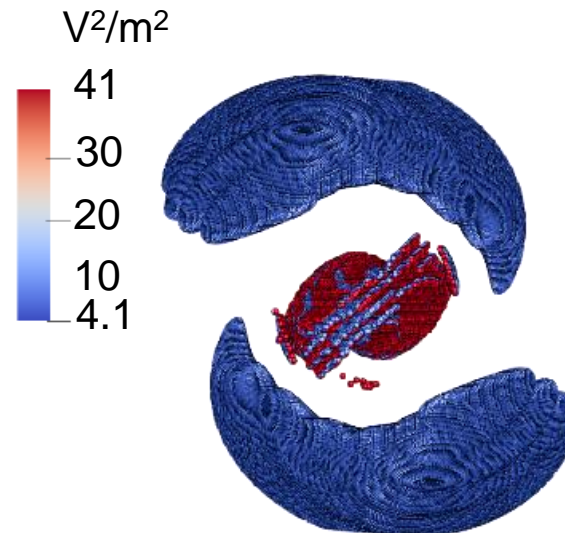
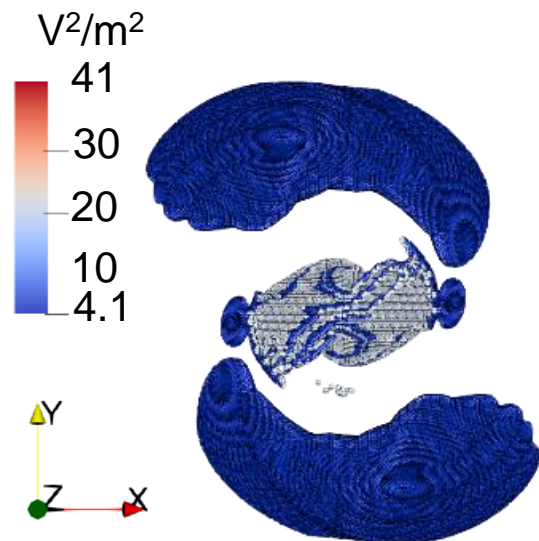
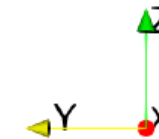
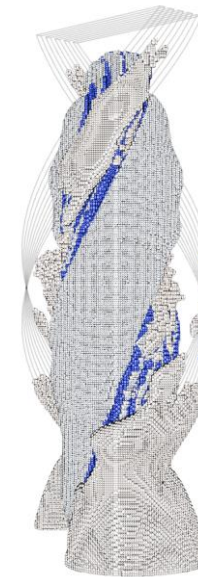
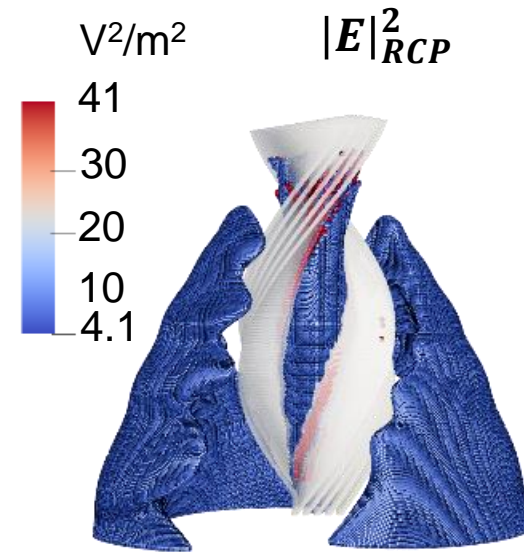
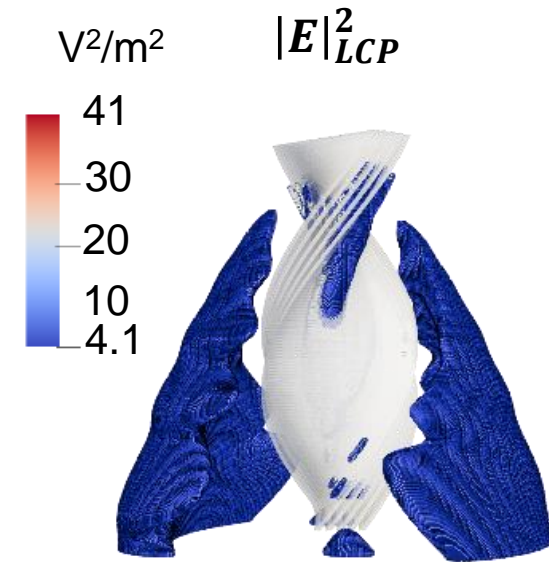


Scattered Electric Field Distribution

$\lambda = 1550 \text{ nm}$

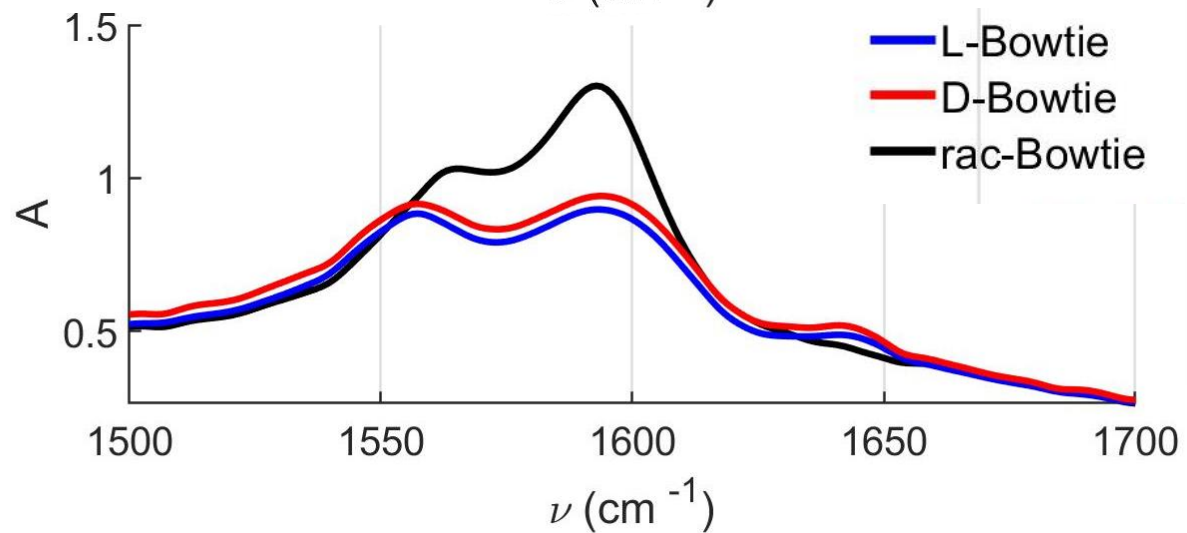
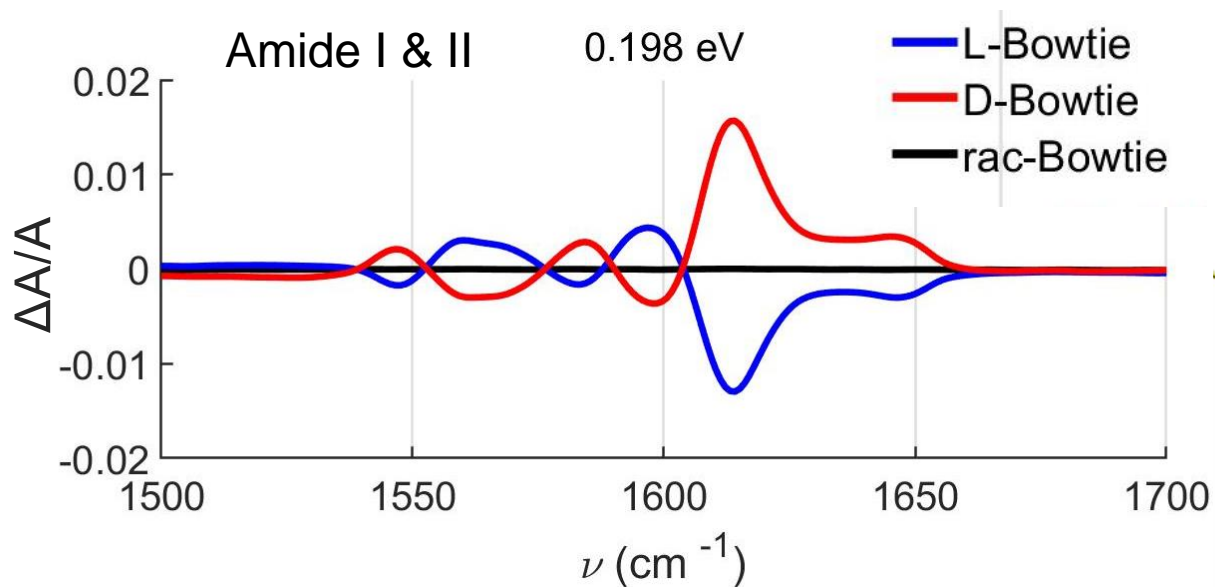
LCP – Left circularly polarized light
RCP – Right circularly polarized light

$$CD \propto |E|_{LCP}^2 - |E|_{RCP}^2$$

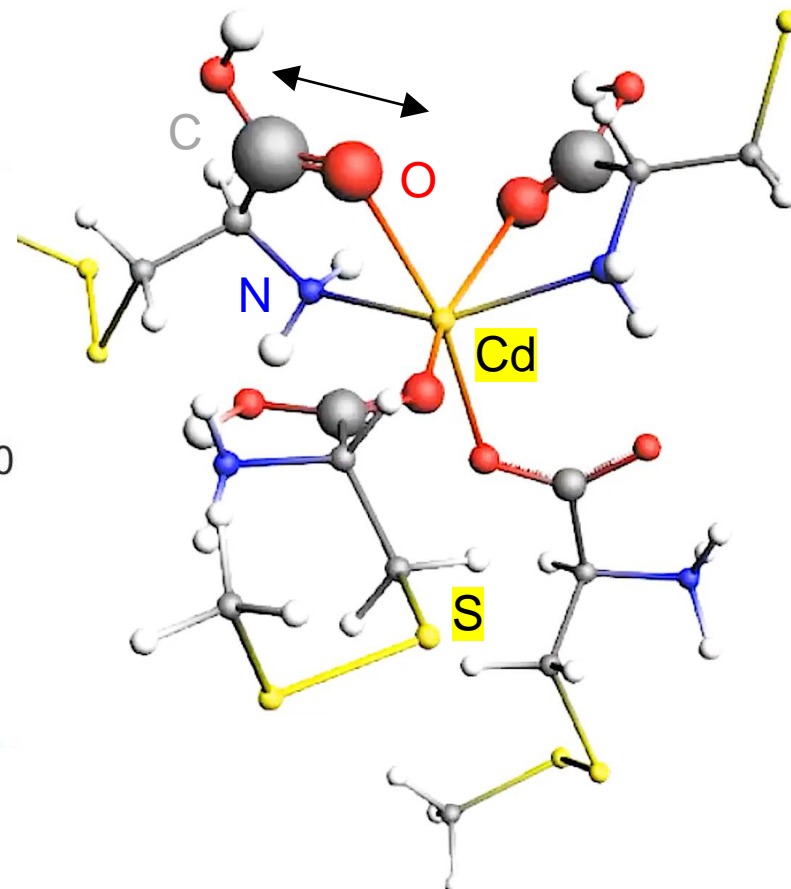


Higher scattering when the handedness of light matches the handedness of the bowtie

Vibrational CD



DFT Simulation



Prof. Paul Nicu

Cysteine has a bi-signate VCD pattern.

-COO Bonding with Cd splits the 2 peaks further in to 5 bands

-COO stretching modes

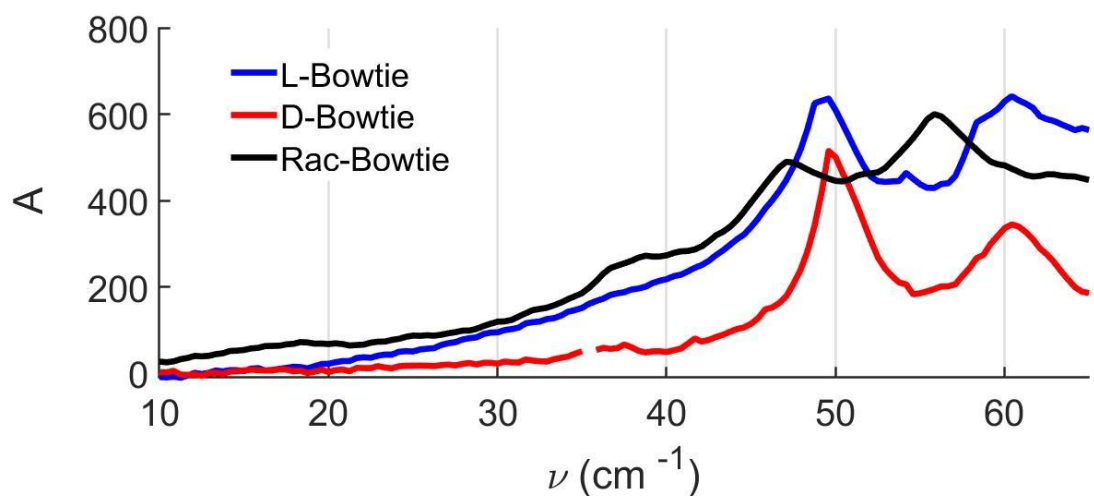
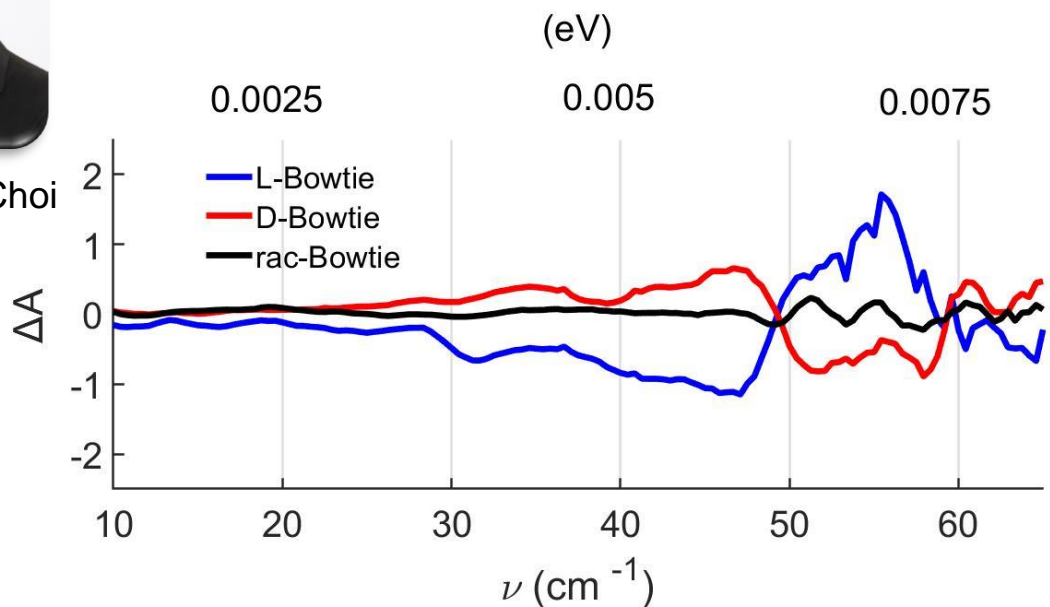
+

H-N-H scissor oscillations

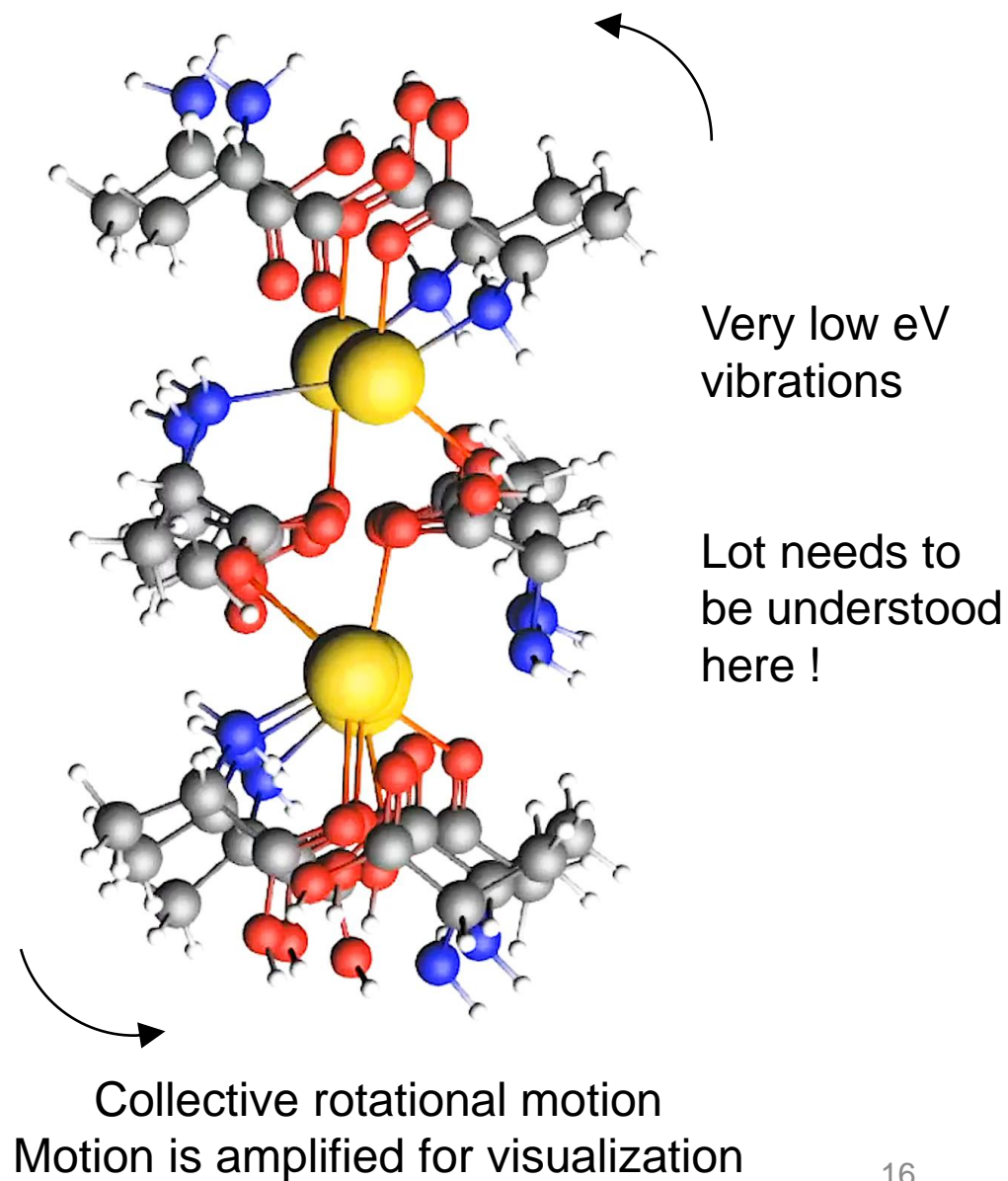


Dr. Wonjin Choi

Terahertz CD



Simulation



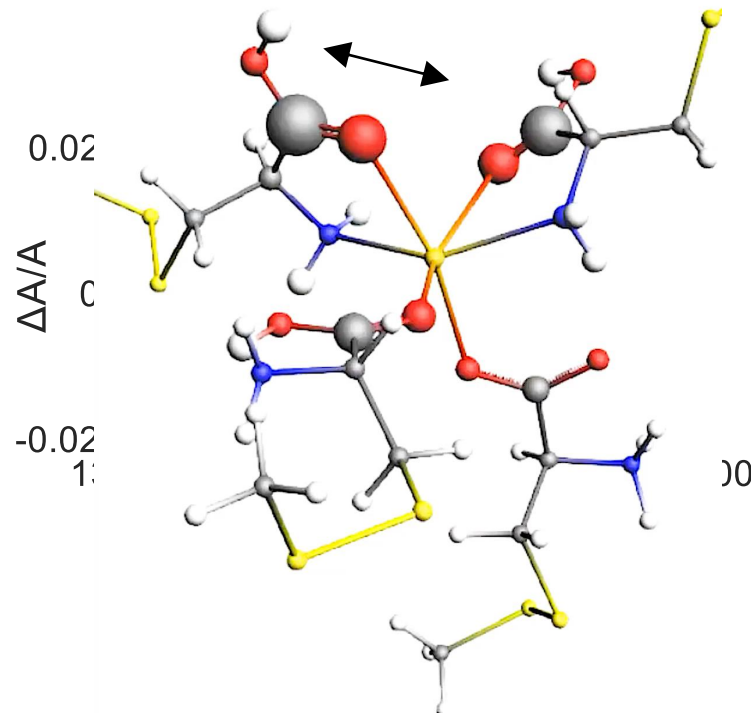
Experiment \leftrightarrow Simulations

Dielectric Response (UV-Vis, IR)
Scattering Modes



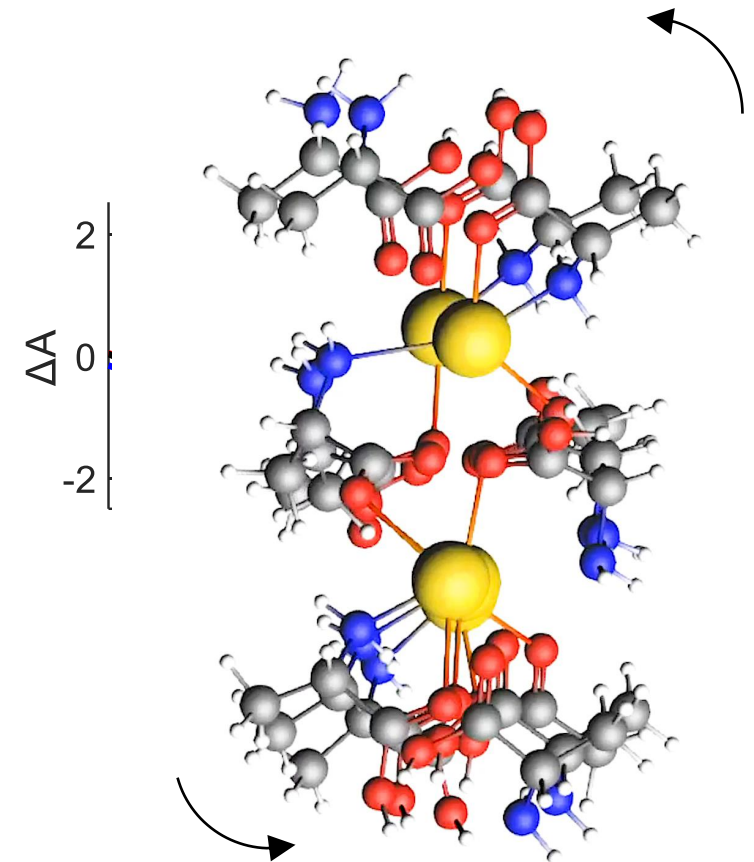
10,000 cm^{-1}

Chiral Vibrations (Far-IR)
Absolute conformations

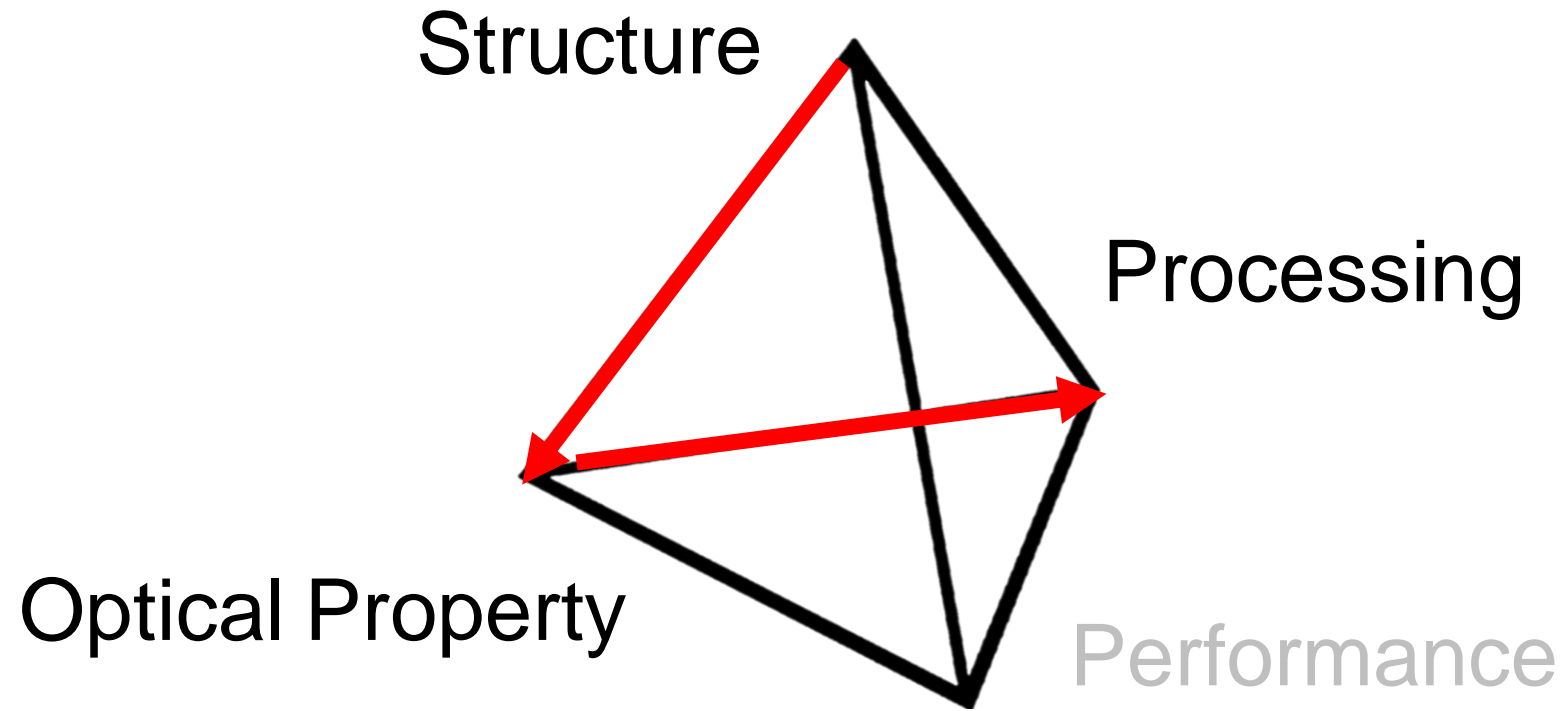


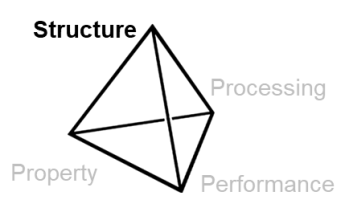
1,000 cm^{-1}

Phonons (THz)



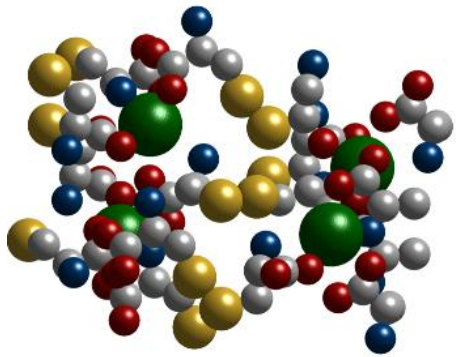
100 cm^{-1}



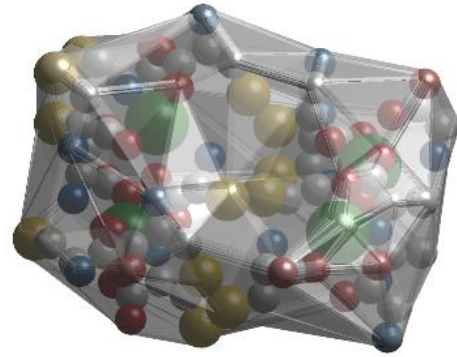


Monte-Carlo Modeling of Self-Assembly

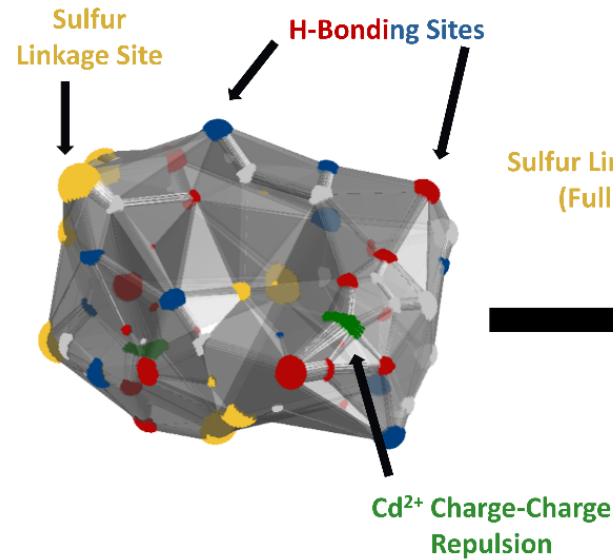
Atomic Coordinates from XRD



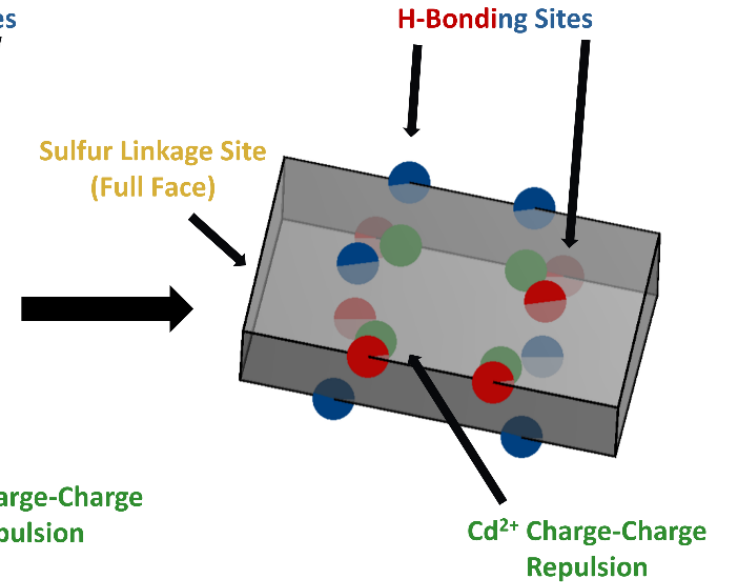
Convex Hull



Primary Interaction



Generalized building block



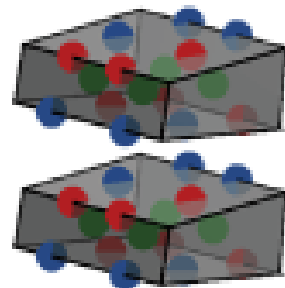
Dr. Thi Vo



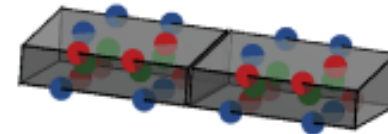
Prof. Sharon Glotzer



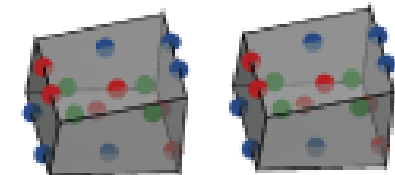
H-Bonding

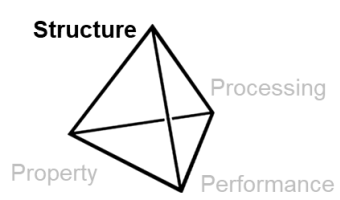


S-S

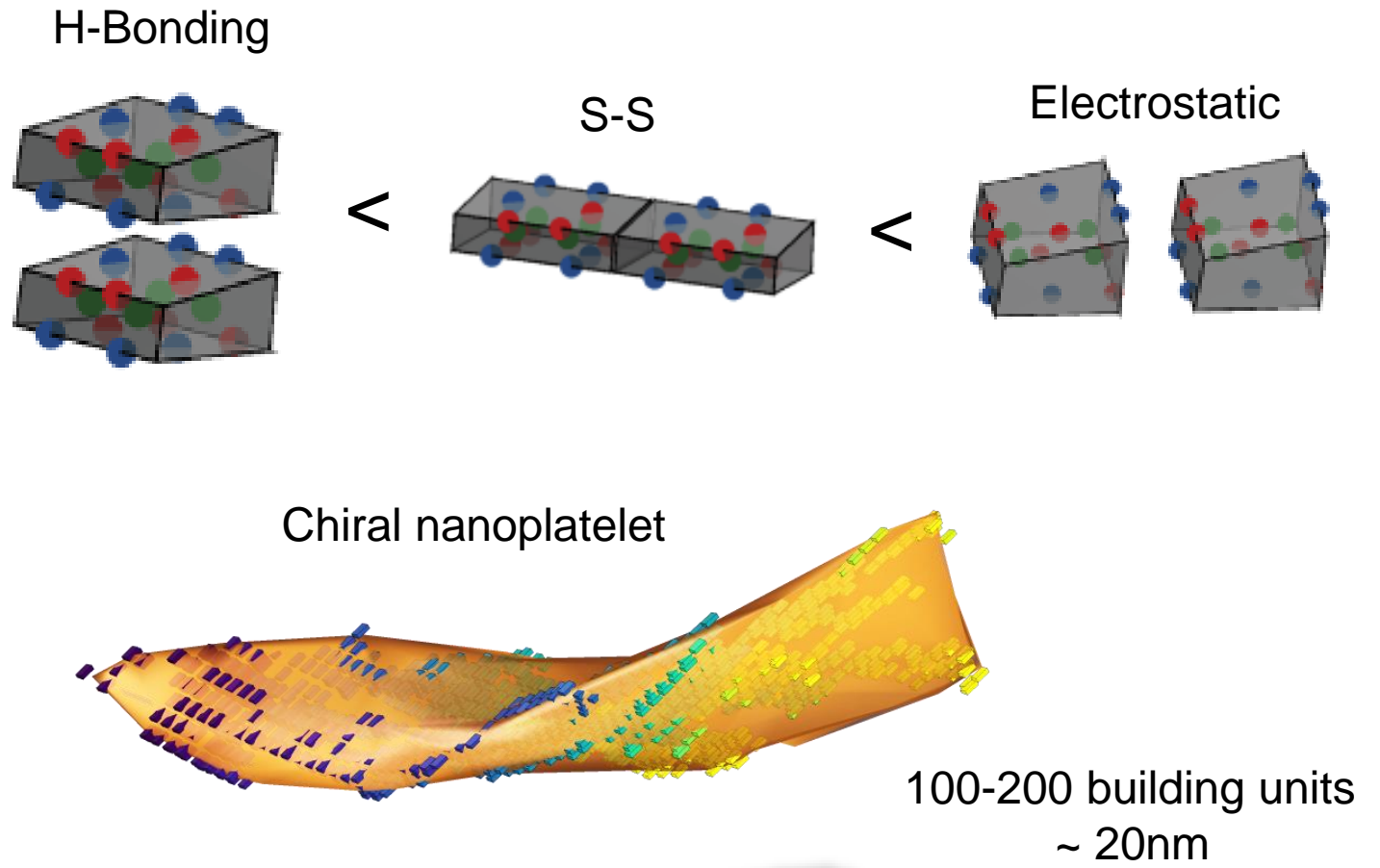
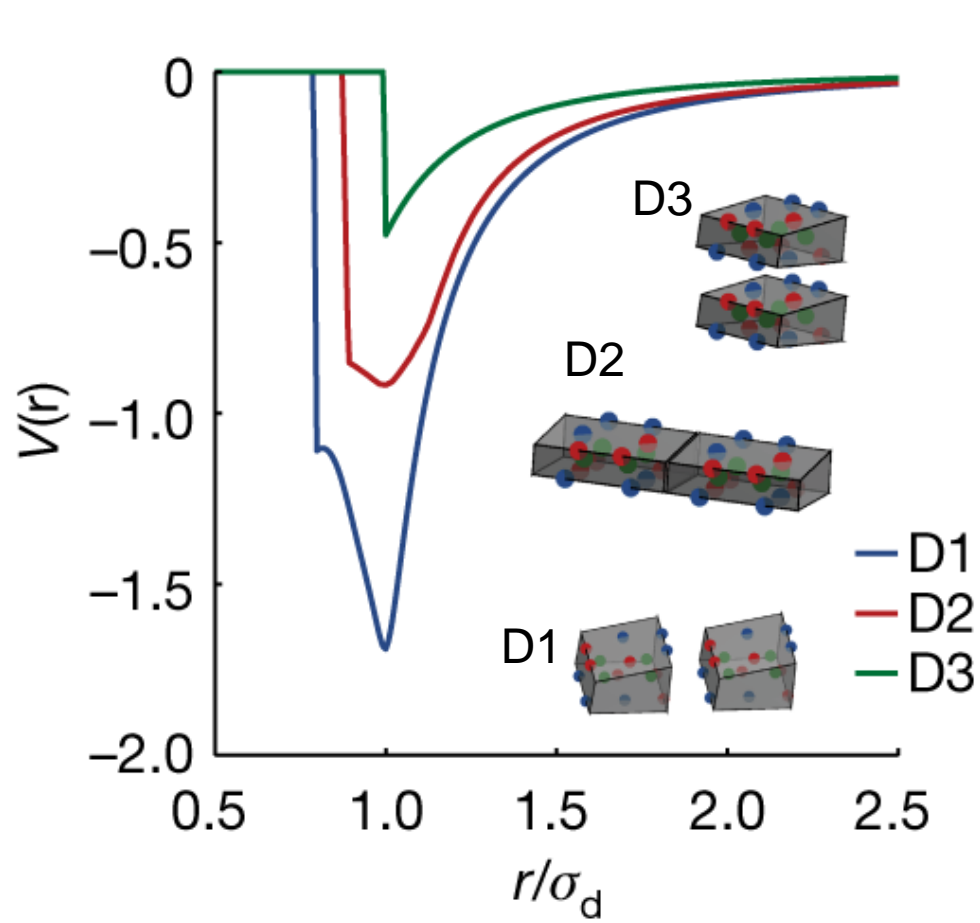


Electrostatic





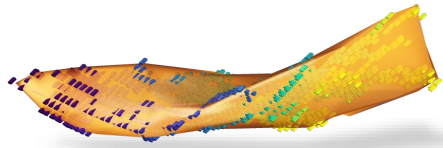
Monte-Carlo Modeling of Self-Assembly



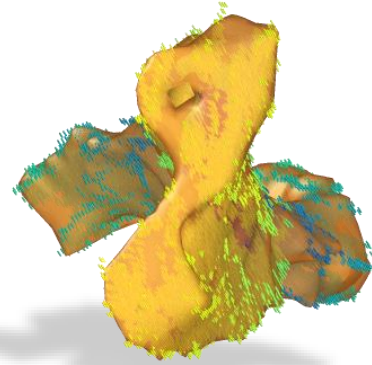
Charged building blocks and interaction between them

Monte-Carlo growth Models

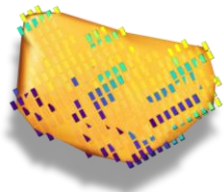
Chiral nanoplatelet



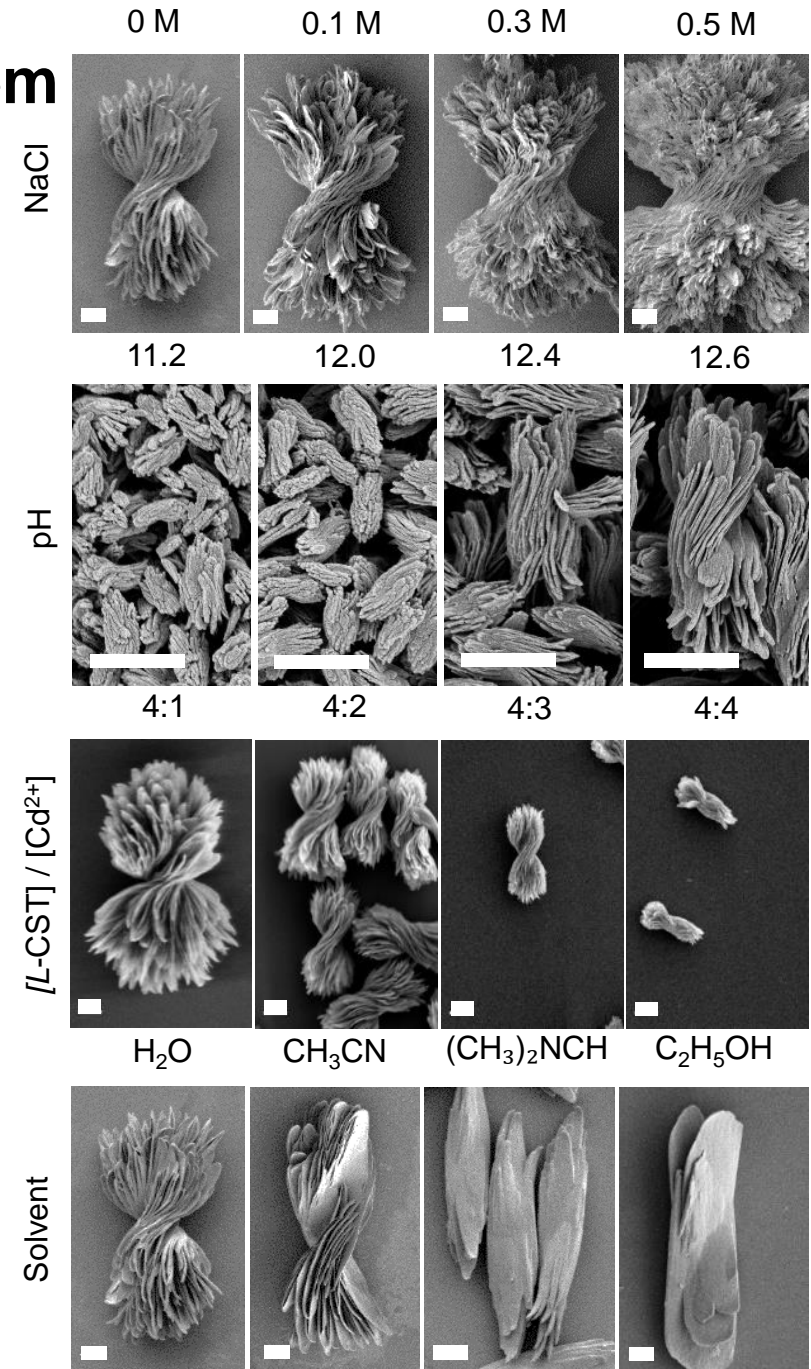
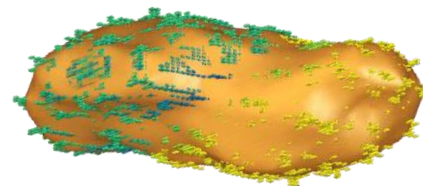
100-200 building units
~ 20nm



100000 building units
~ 200 nm

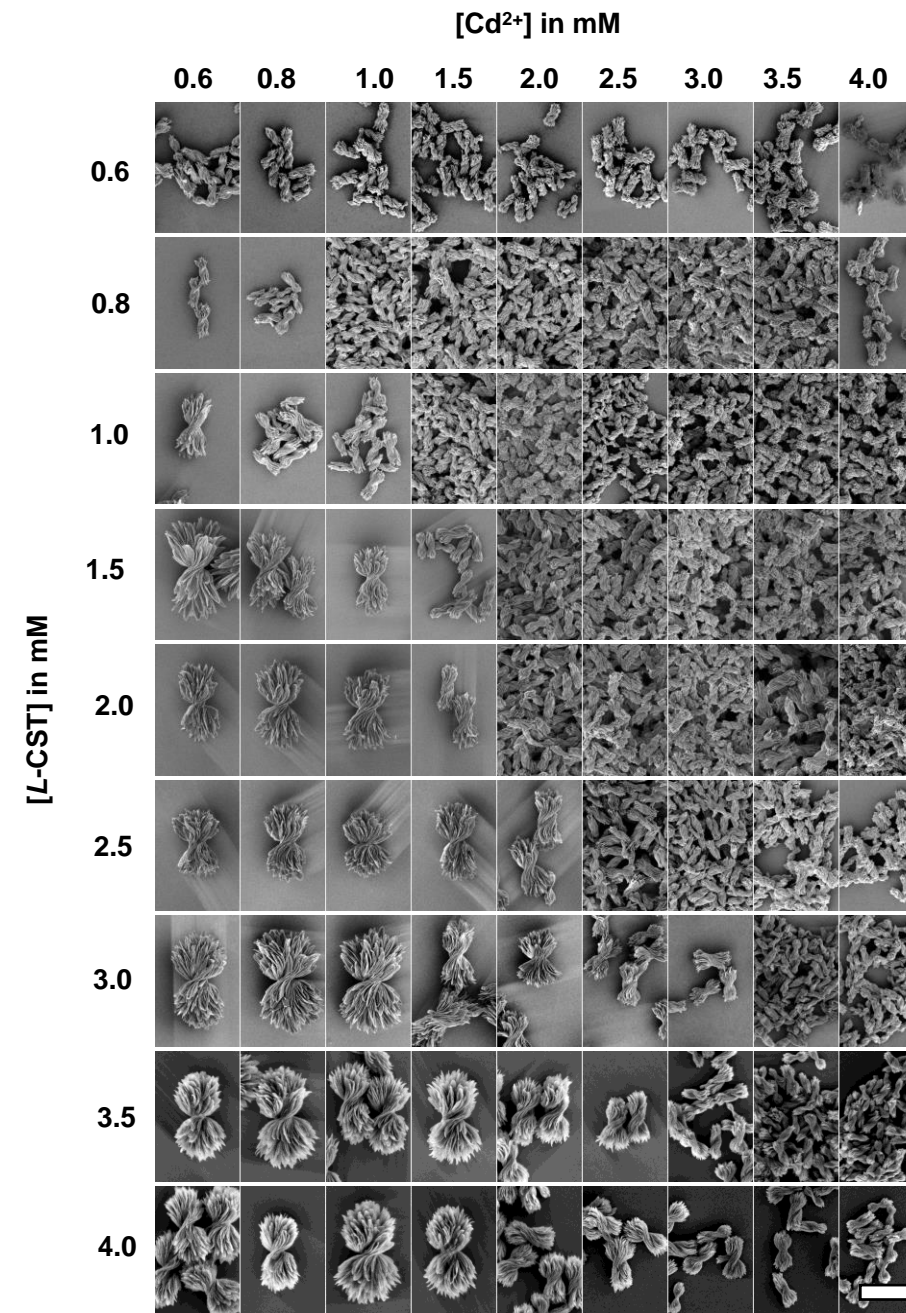
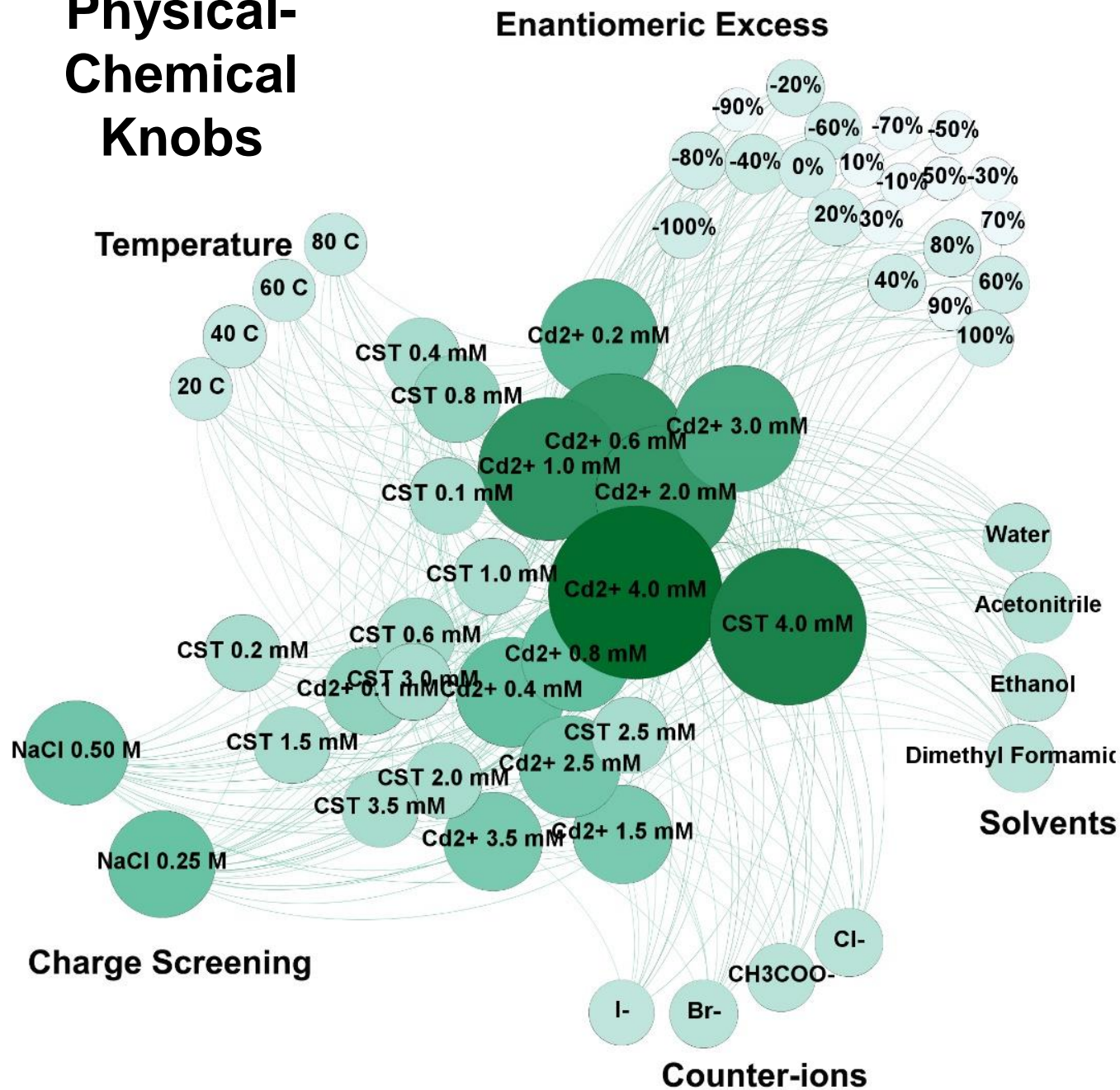


Achiral nanoplatelet



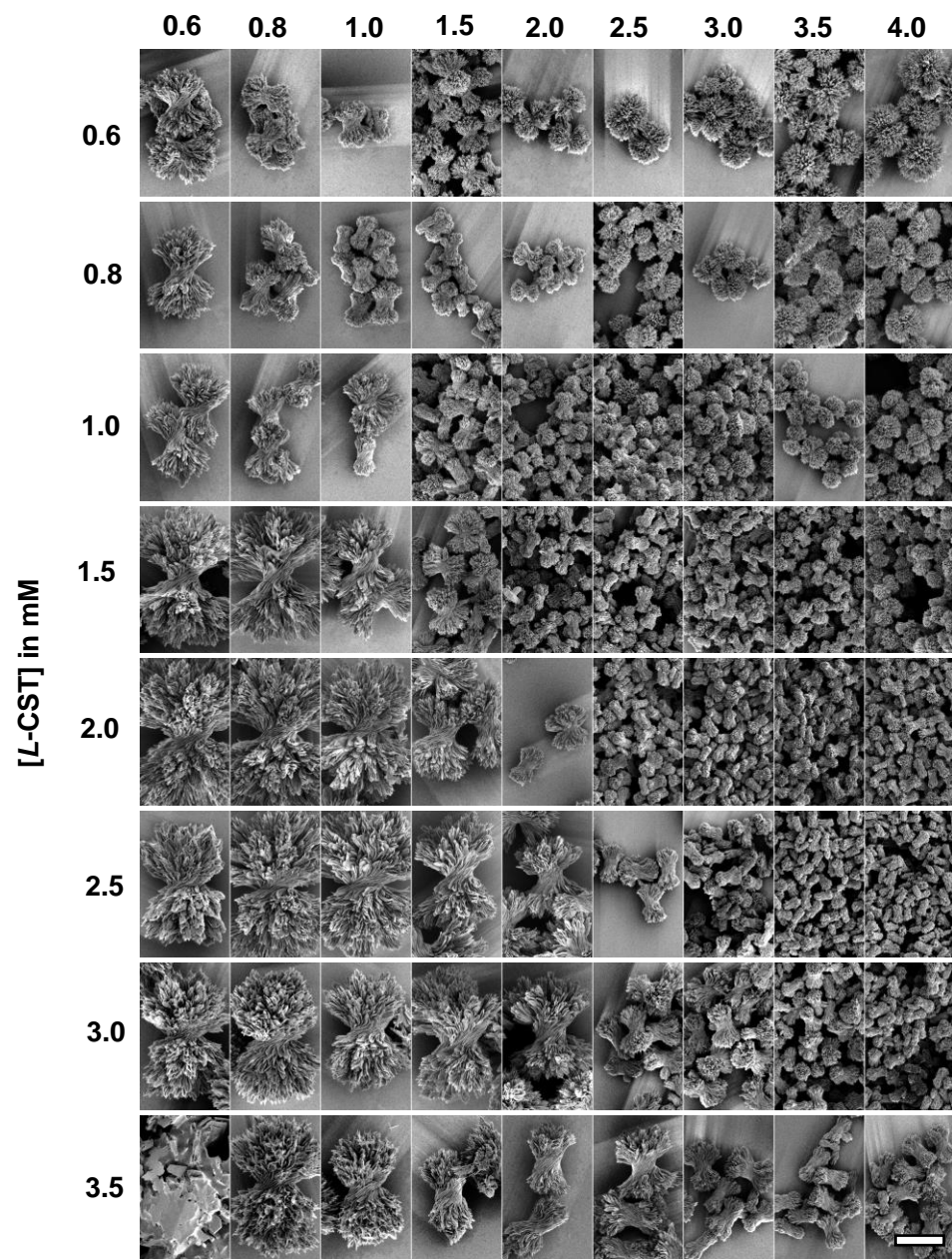
Scale bar is 1 μm

Physical-Chemical Knobs



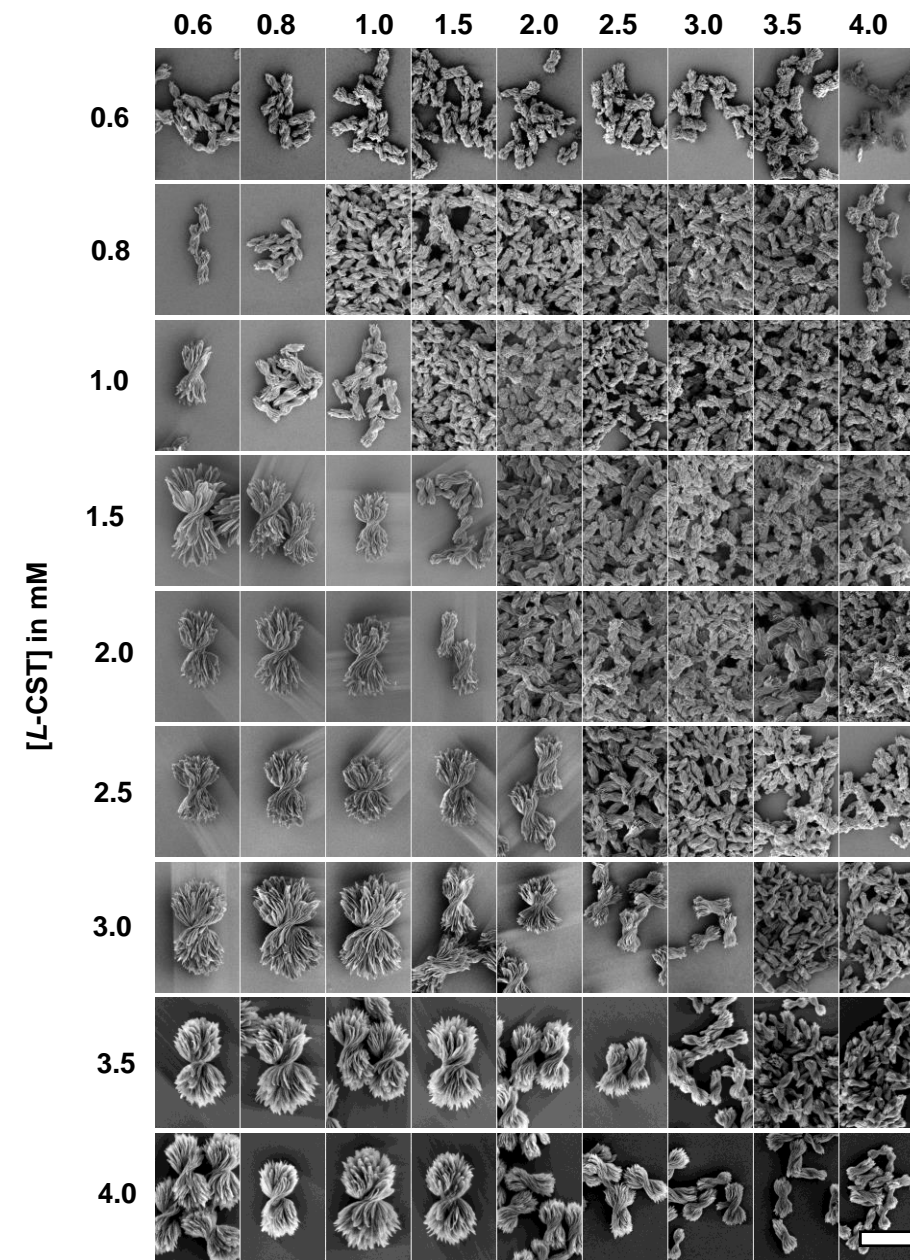
[NaCl] = 0.25 M

[Cd²⁺] in mM

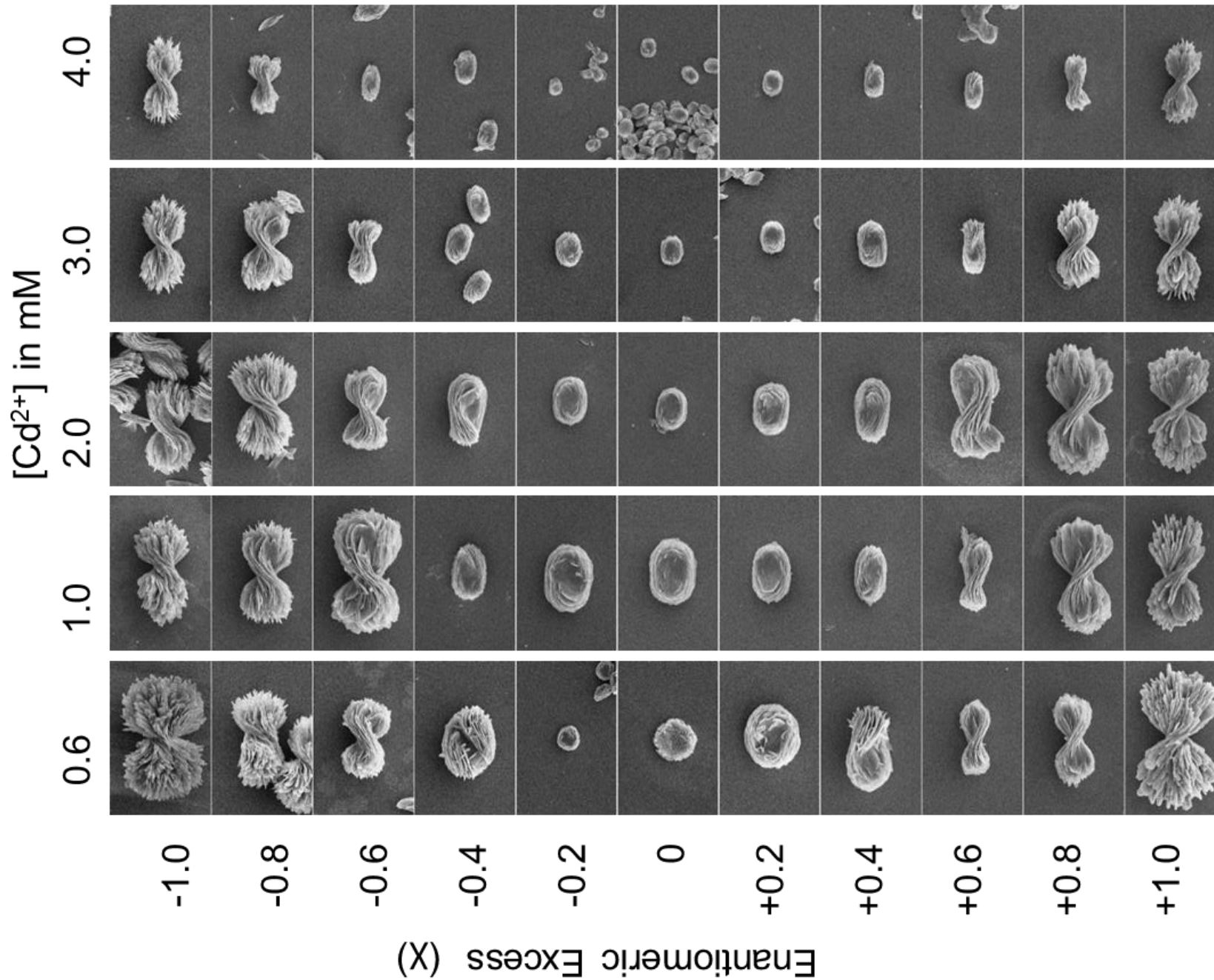


[NaCl] = 0 M

[Cd²⁺] in mM



[L-CST] = 4 mM



Chirality Continuum

Continuous change of twist from left-handed to no twist to right-handed at the micron level has not been observed from direct chirality transfer before

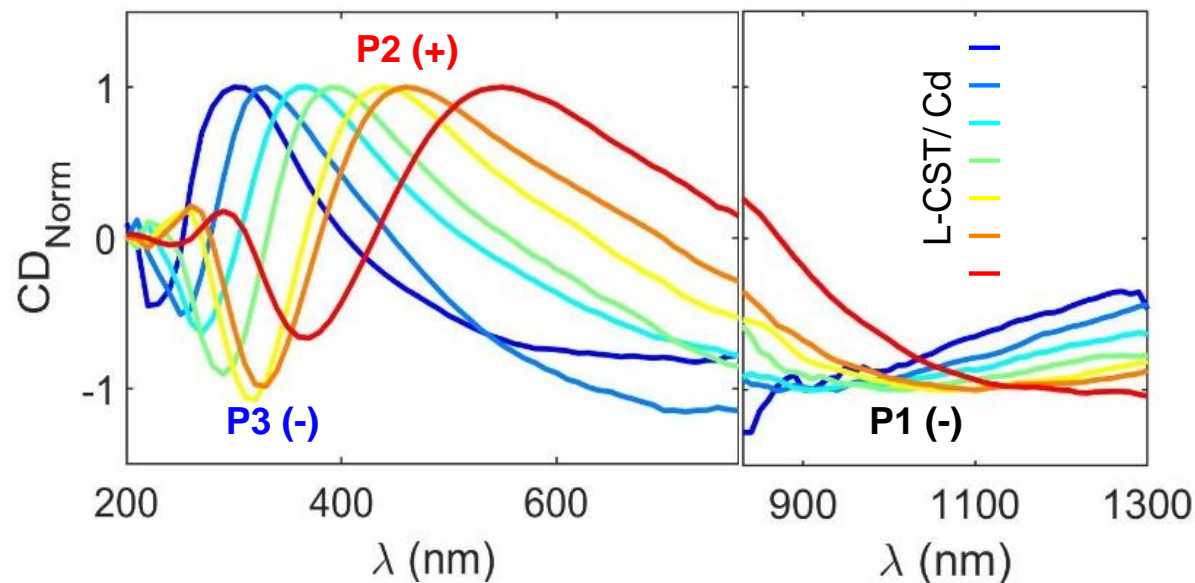
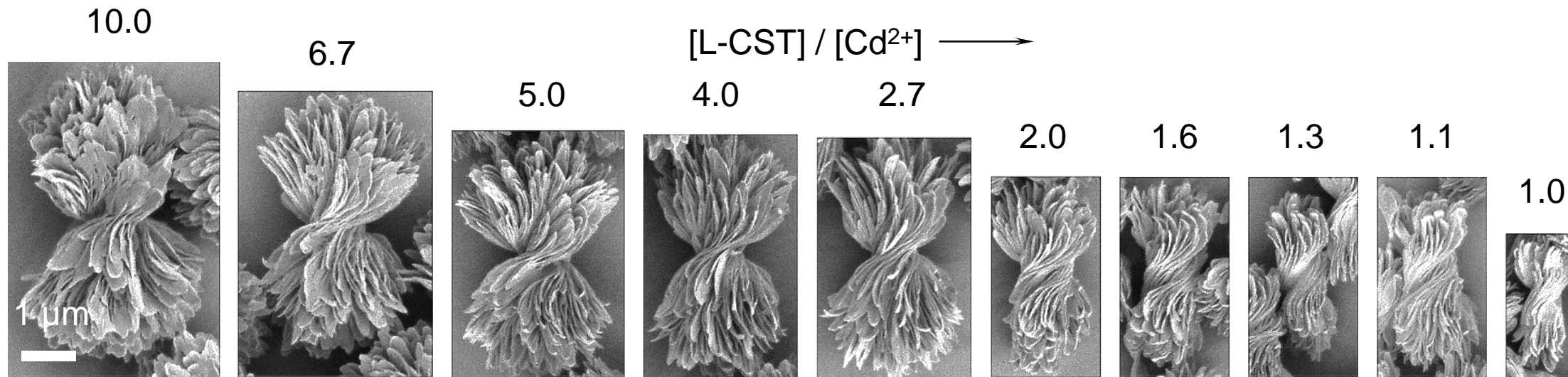
Combine multiple chemical parameters to generate a vast design space for bowtie morphology

Enantiomeric Excess (χ)

$$= \frac{[\text{L-CST}] - [\text{D-CST}]}{[\text{L-CST}] + [\text{D-CST}]}$$

CST : Cystine 24

Structure Property Relationships: Toward Inverse Design



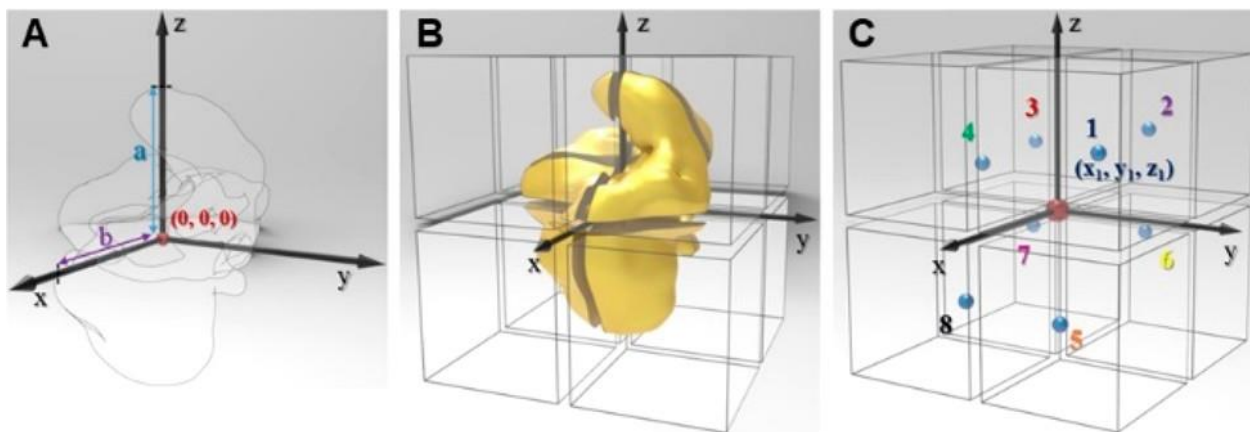
Shape of object \leftrightarrow CD spectra

- Length
- Width
- Thickness
- Twist Angle
- P1 (-)
- P2 (+)
- P3 (-)

Chirality Measures !

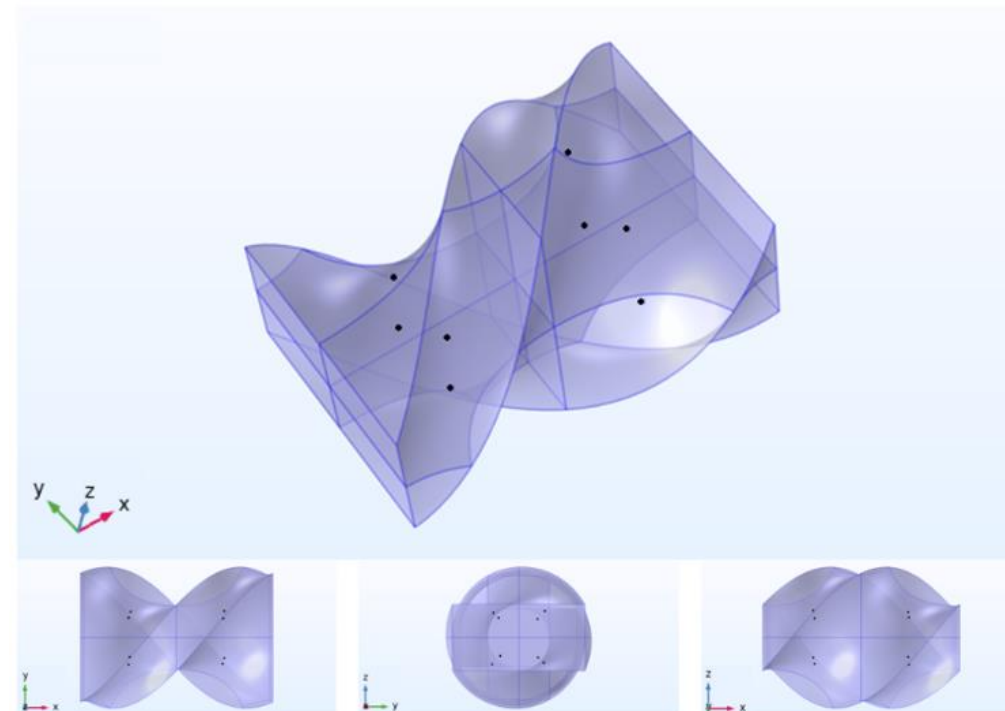
Chirality Measures

OPD – Osipov-Pickup-Dunmur chirality measure, a mathematical descriptor of chirality



● **Primary center of mass** ● **Secondary center of masses**

$$G = \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) \rho(\mathbf{r}_3) \rho(\mathbf{r}_4) \times \frac{[(\mathbf{r}_{12} \times \mathbf{r}_{34}) \otimes \mathbf{r}_{14}](\mathbf{r}_{12} \cdot \mathbf{r}_{23})(\mathbf{r}_{23} \cdot \mathbf{r}_{34})}{(r_{12} r_{23} r_{34})^n r_{14}^m},$$

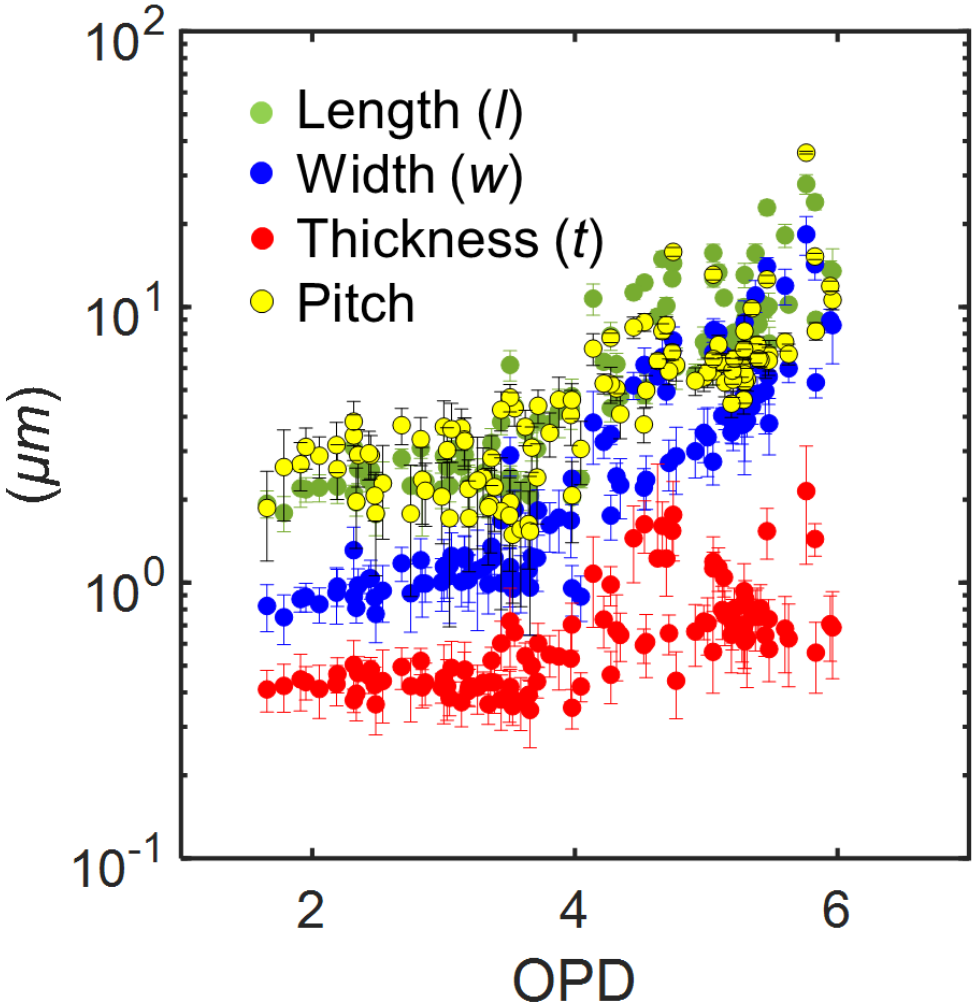
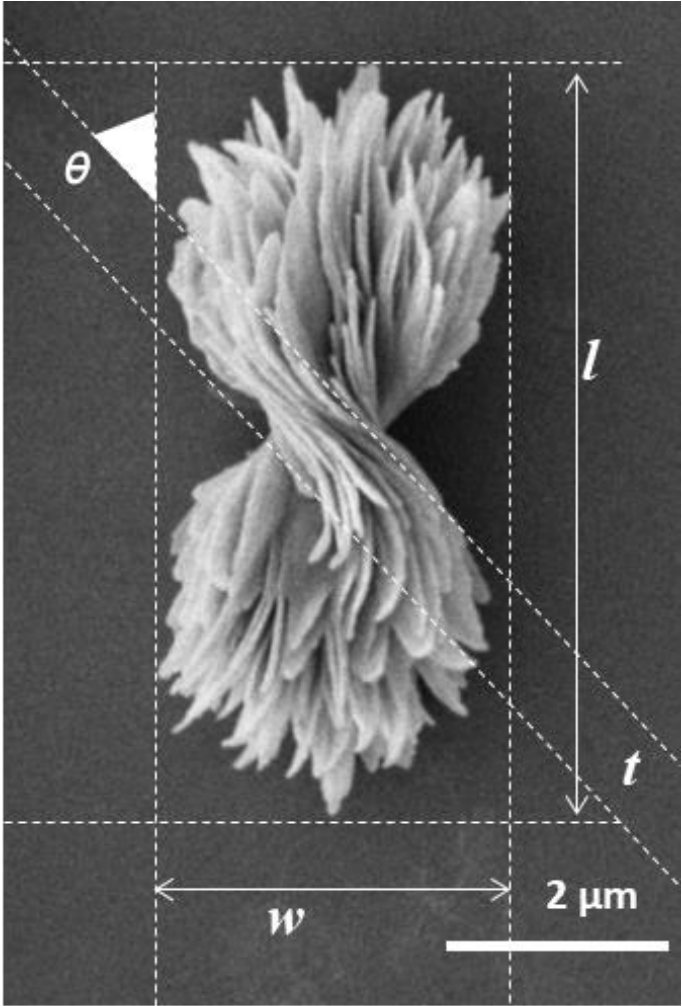


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J. Am. Chem. Soc. 2019, **141**, 30, 11739-11744

Osipov, M. A., Pickup, B. T. & Dunmur, D. A. A new twist to molecular chirality: intrinsic chirality indices. *Molec. Phys.* **84**, 1193–1206 (1995).

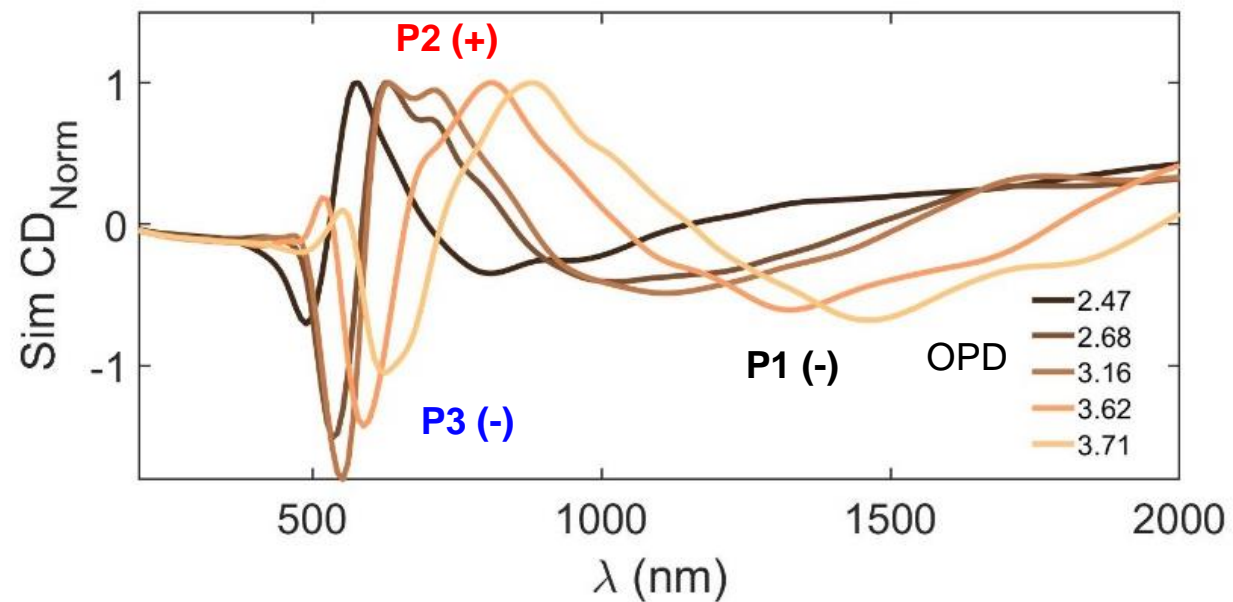
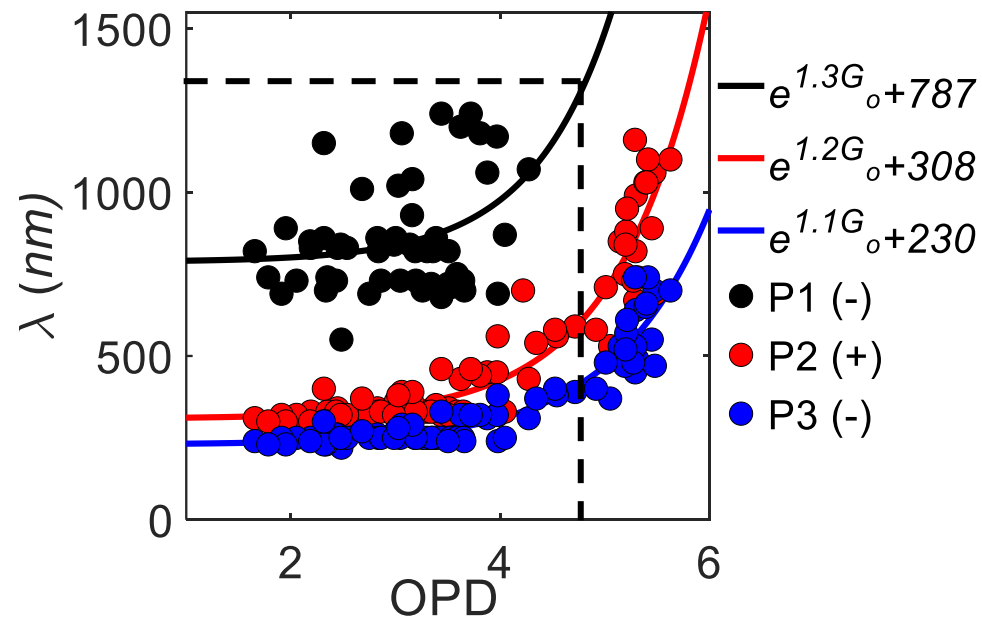
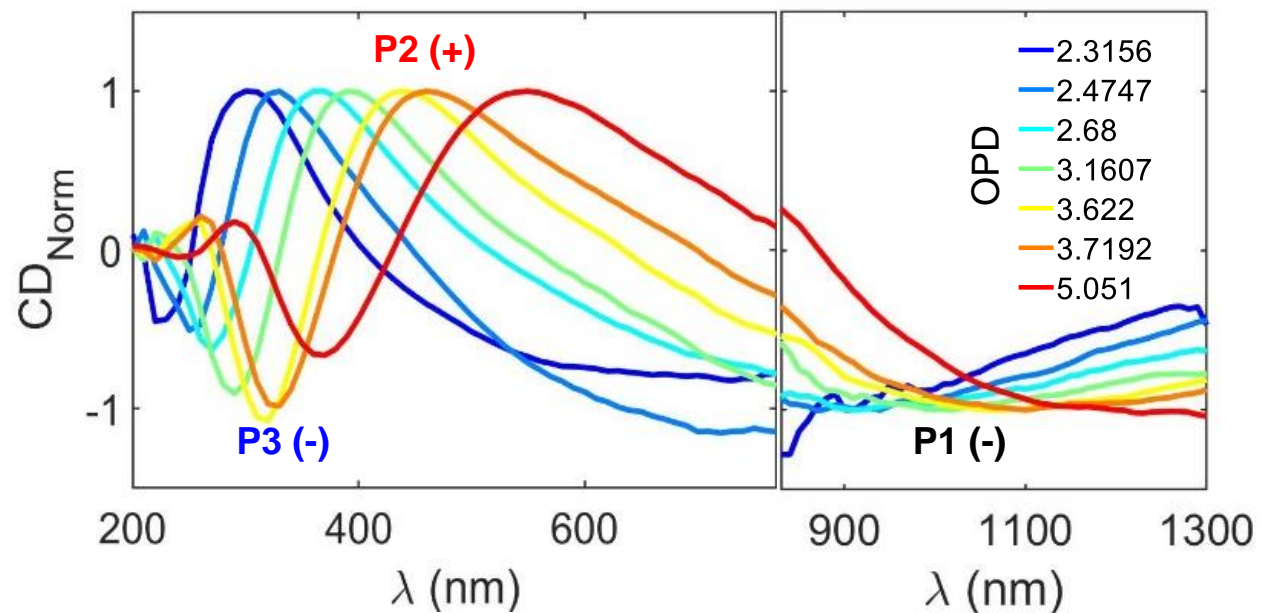
Quantifying the morphology – Spans a large range



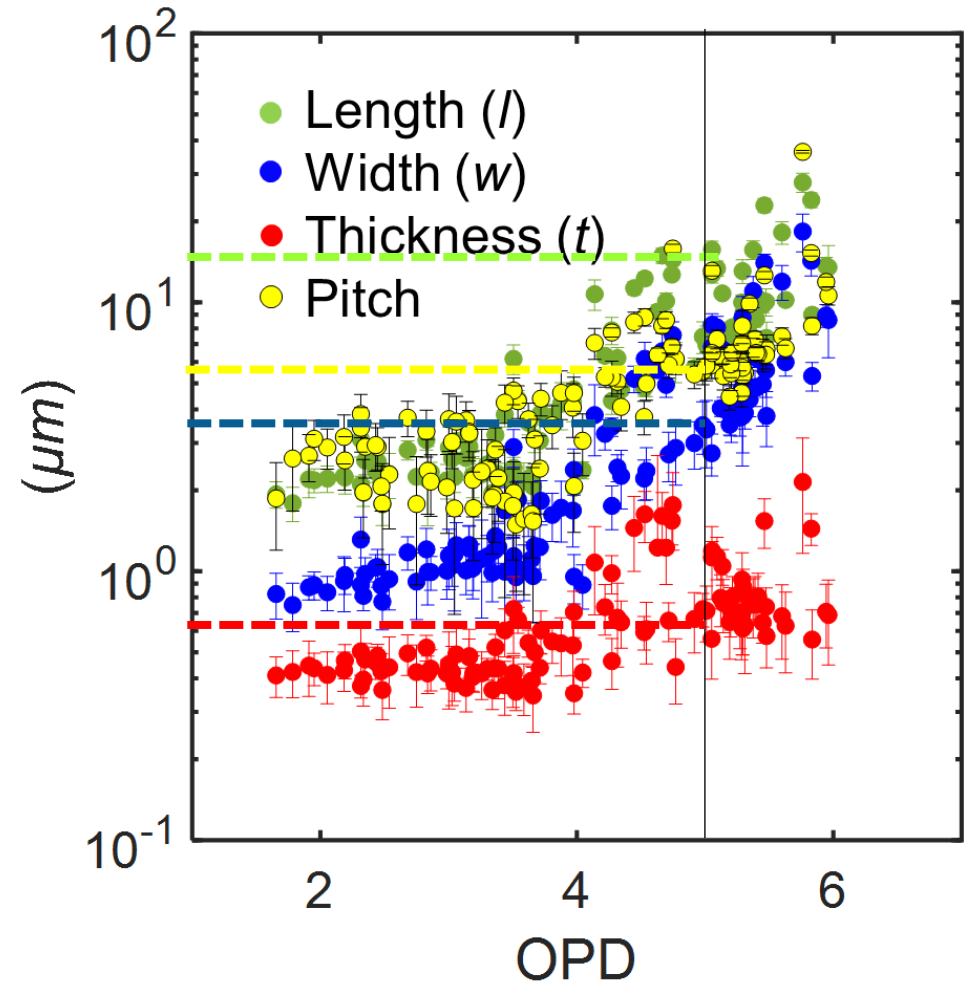
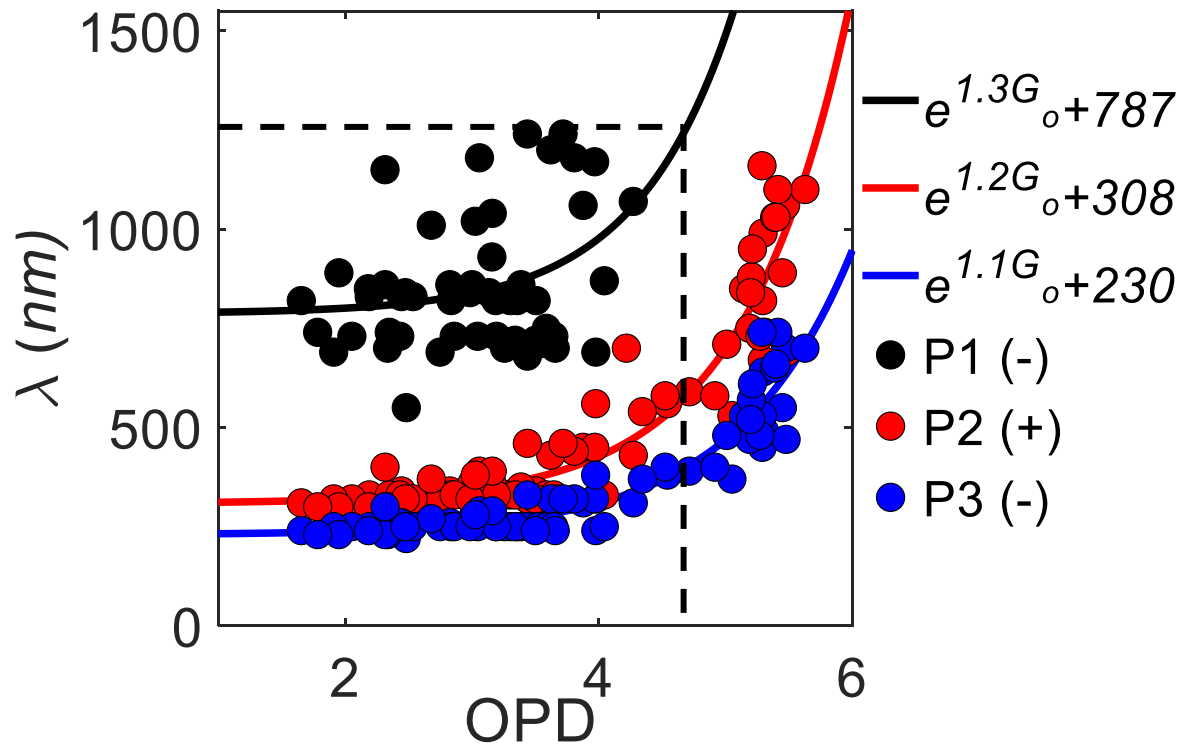
OPD –
Osipov-Pickup-Dunmur
chirality measure, a
mathematical descriptor of
chirality

Scaling of different
morphological parameters
with OPD

Structure Property Relationships: Toward Inverse Design

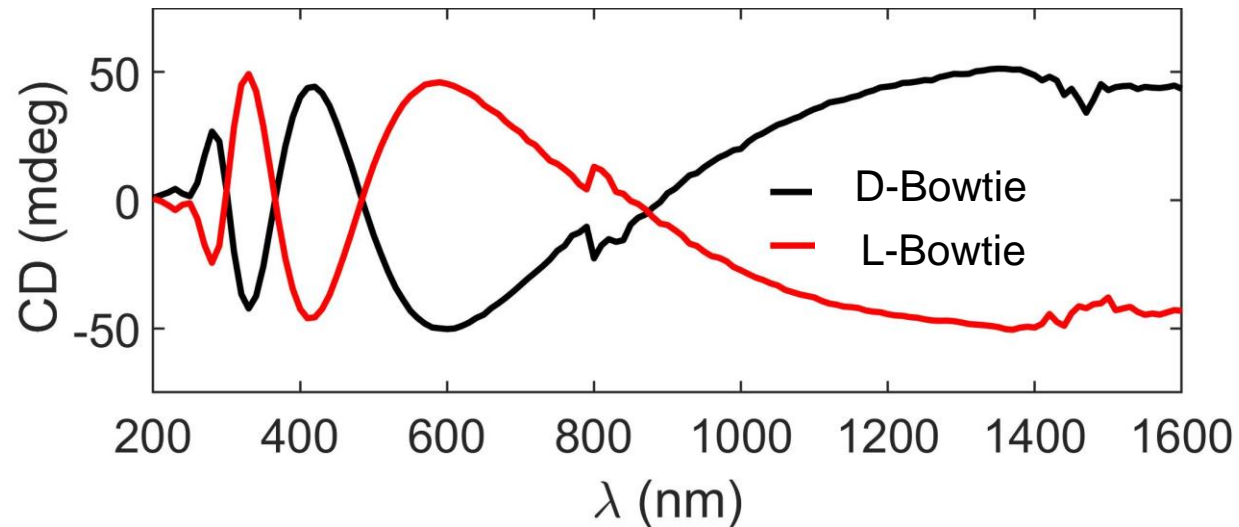
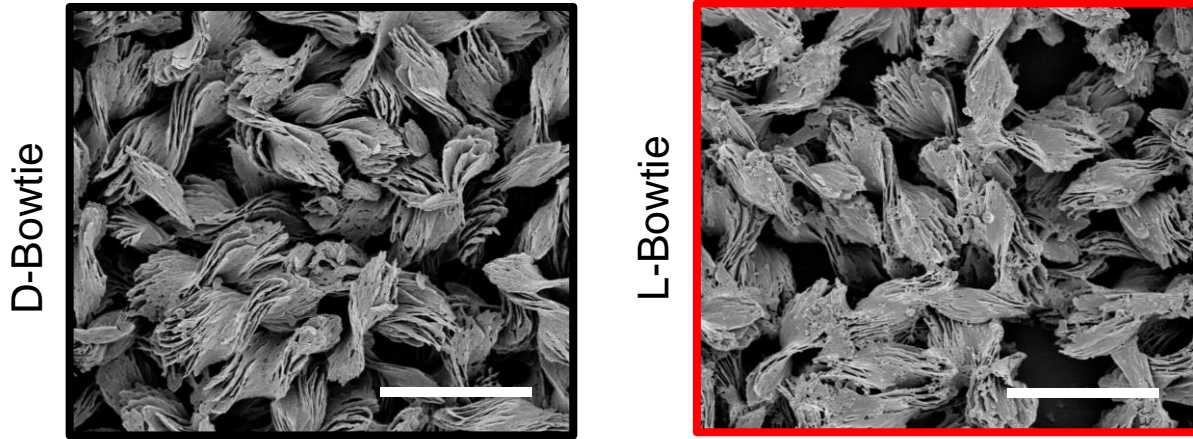


Structure Property Relationships: Toward Inverse Design



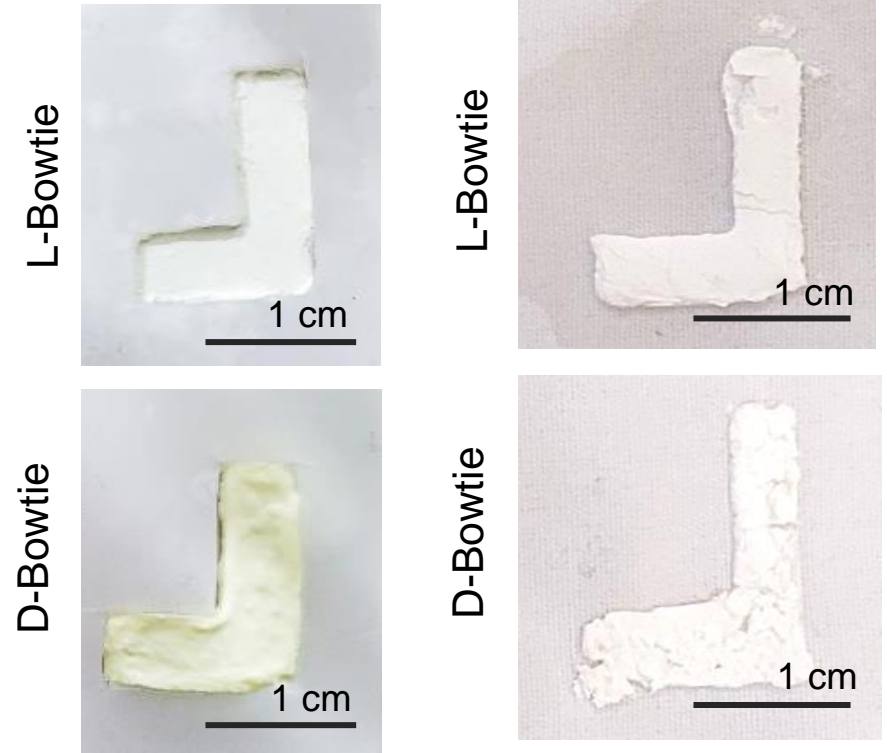
What can we do with the inverse design?

Made in 50-50 mixture of acetonitrile and water



Coating on glass

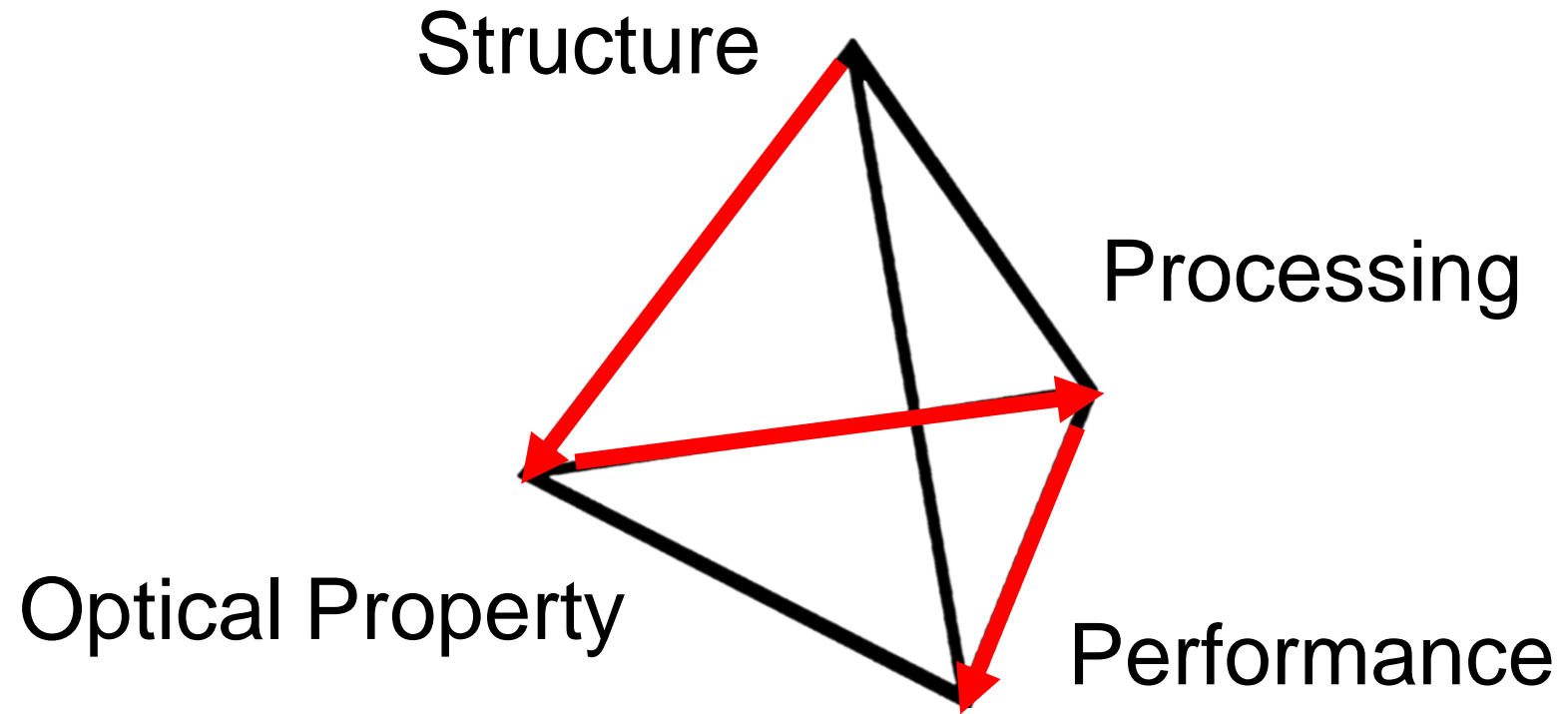
Coating on cloth



Freeze dried bowtie powder mixed with Polyacrylic acid (PAA)

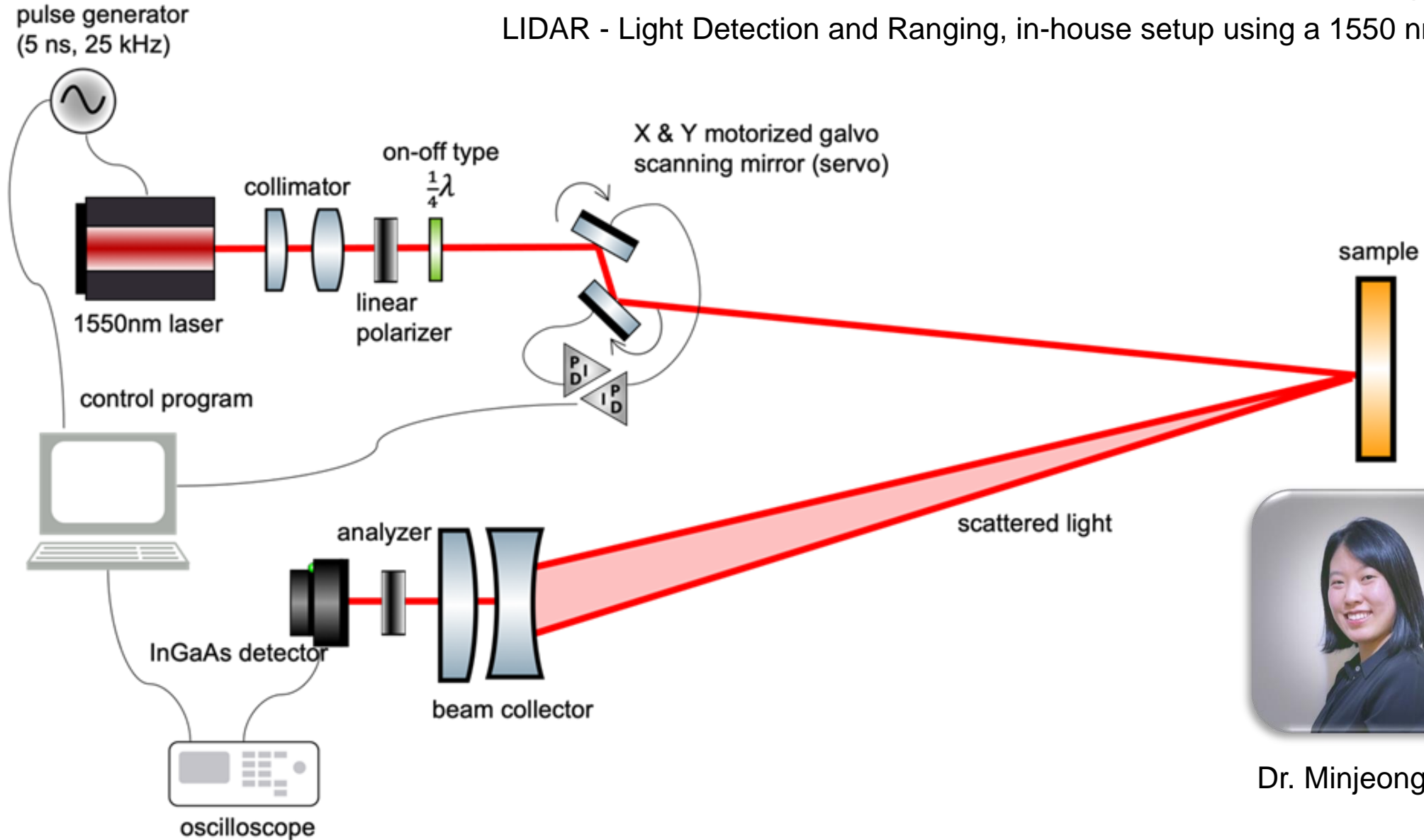
Remember the Mantis Shrimp?





What can we do with the inverse design?

LIDAR - Light Detection and Ranging, in-house setup using a 1550 nm laser



Dr. Minjeong Cha

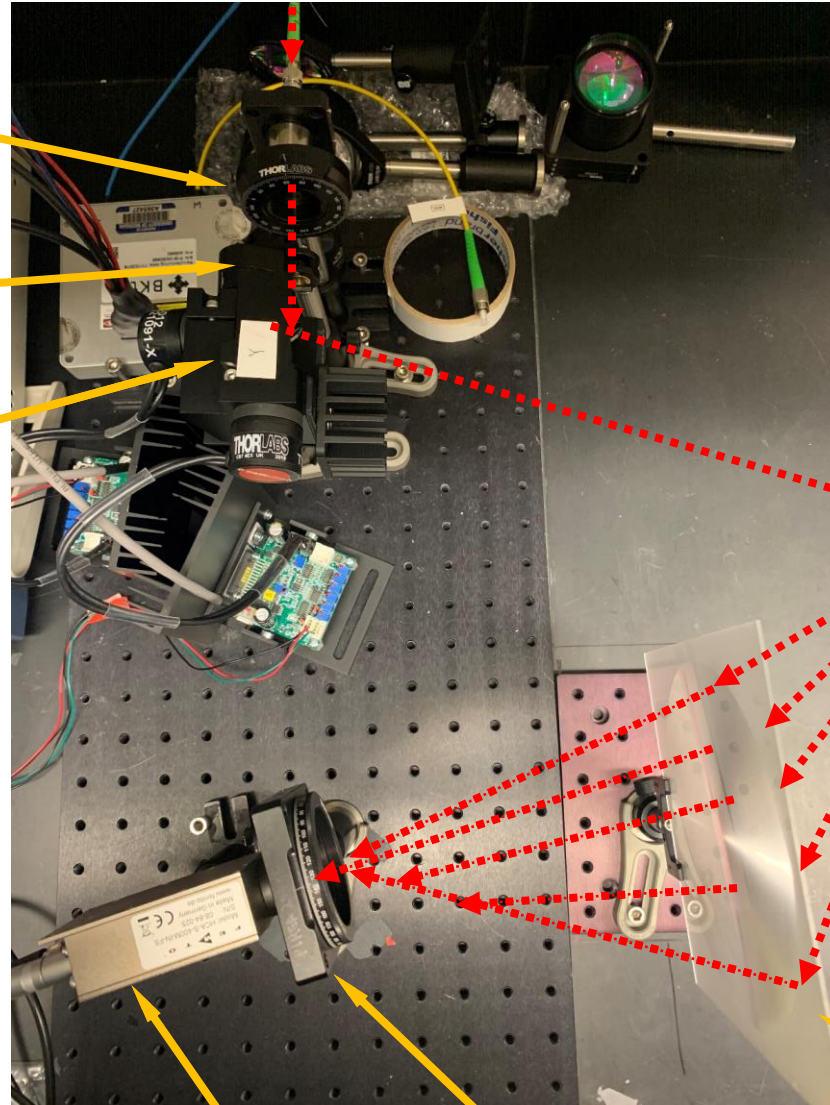
Top view

1550nm pulsed laser

Linear Polarizer

Quarter wave plate
On/off

Beam Steerer



Object

Detector

Analyzer

Beam collector

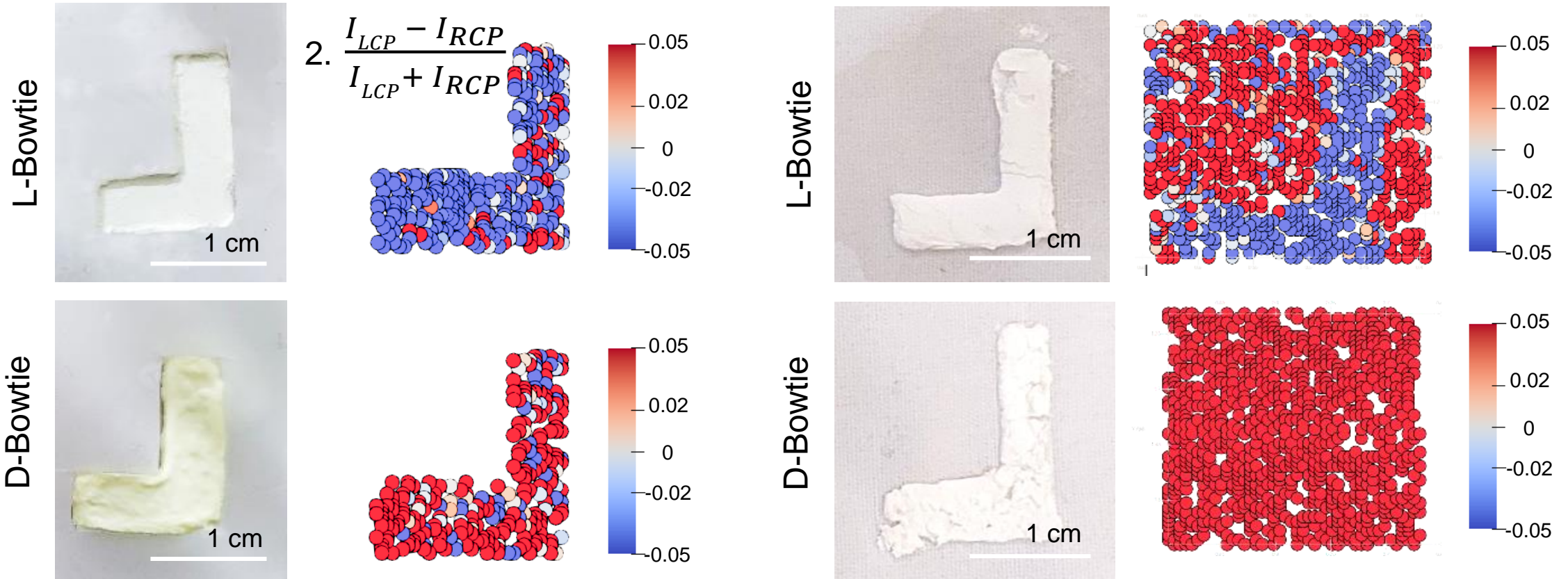
What can we do with the inverse design?

LIDAR - Light Detection and Ranging, in-house setup using a 1550 nm laser



Dr. Minjeong Cha

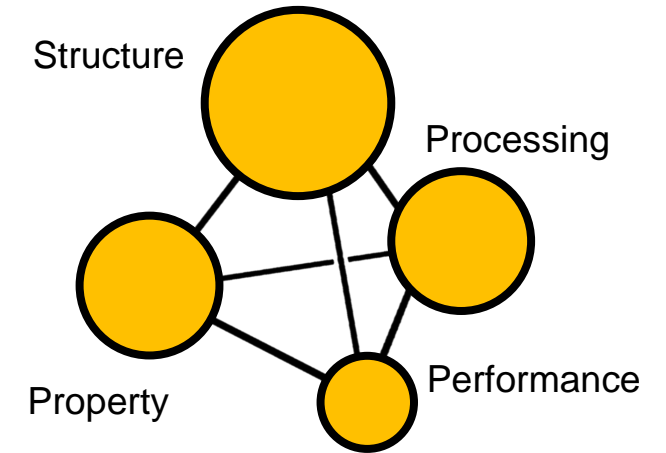
Friend or foe using bowties as coatings



Summary

- Designed a tunable bowtie metamaterial
- Created a tunable structure: 500 nm to 4 um size
- Developed structure – property correlation
- “Slightly” better than the mantis shrimp

Kumar, P., Vo, T., Cha, M. *et al.* Photonically active bowtie nanoassemblies with chirality continuum.
Nature **615**, 418–424 (2023).



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- Kotov group members
- Glotzer group members
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Q&A

WITH PRASHANT KUMAR, PhD



Kumar, P., Vo, T., Cha, M. et al. Photonically active bowtie nanoassemblies with chirality continuum. *Nature* 615, 418–424 (2023).



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