Peer Review File

Manuscript Title: Photonically Active Bowtie Nanoassemblies with Chirality Continuum

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referees' comments:

Referee #1 (Remarks to the Author):

The authors systematically correlate the geometrical properties of synthesized chiral microstructures with their spectroscopic as well as optical properties. With this aqueous synthesis from hierarchically structured nanoribbons, chiral structures are available in large quantities with tunable chiral properties. Under these important conditions, the authors were able to print the chiral particles on different surfaces where they could observe the chiral effect on large areas. The authors prove the hypothesis with a broad methodology in spite of micrometer-sized structures, low signal intensities for the particles as well as for the surfaces. However, the chain of reasoning is incomplete at one point when the LIDAR method is or should be linked to results of the electromagnetic simulation method. With the LIDAR method the authors observe the CD backscatter signal at an excitation of 1550nm, where a CD difference of 100mdeg (SI Fig 49) is expected. The authors themselves write that there is a small difference in the polarized signal difference (see caption SI Fig 50). This finding makes it even more important to explain the observed results with the simulations. In the simulations in SI Fig 47, the layer model at different polarizations and wavelengths is calculated to account for the differences between the CD signals. Furthermore, the authors change the geometry of the layer structure or change the section. This unnecessarily complicates the understanding of the structure and the effect. The authors must keep the geometry or the cutout section constant and clearly identify the dipolar as well as qudrupolar modes by surface charge calculations. Furthermore, the authors should add the wavelength 1550nm and add a comparison with the LIDAR results. Results should be understandable without video references. Furthermore, a coherent discussion of the simulated modes and the LIDAR results should be added to the revised manuscript.

Referee #2 (Remarks to the Author):

This work describes the development and characterization of multiscale assembled microparticles, in the general shape of bowties, with fully tunable chiral properties. These particles represent the first structures with fully and continuously variable chiral behavior – a true breakthrough in my view, with potential impact on the fields of chiral photonics/materials (including the ability to create and manipulate novel topological and valley properties), biochemical separations, chiral catalysis, and sensing technologies. Their hierarchical physical structuring, which lead to the exciting behavior, are controlled with precision using independent chemical synthetic regulation of their twist pitch, length, size and thickness. The degree of tunability and reproducibility is quantified by the authors. They demonstrate an impressive range of characterization, which highlights the multiscale nature of the structuring and material interplay (and the synthesis achievement!). Further, the accurate, and

predictive, modeling they show is powerful and should enable future developments based in the insights and understanding it affords.

The paper concludes with a demonstration of NIR optical circular dichroism in printed films on glass and cloth. It is a neat demonstration, illustrating a potential application area. Overall, I do think this paper is, for the most part, at the level of Nature. Which brings me to my one critical point: If I am being totally honest, I find myself wanting to see one more application or demonstration of potential utility. More generally, a little more of the type of thing in Figure 4g, and maybe a little less of some of the other details. Those get a little busy, and detract some from the excitement (anything not used can be added to the already thorough SI. Also, one specific figure note: I'm not sure I understand figs. 3d,e. Perhaps some of the labels were cut off? A bit more explanation in the text or figure caption would also be helpful). I do not have a specific application in mind…one possibility could be depositing films of bowties on a 2D semiconductor, and measuring the polarization of the PL that is emitted. Can the bowties lead to circularly polarized PL from the material (signifying the enhancement of valley-specific emission)? Just an idea. As I said, I do find the presented work high quality and compelling, and simply feel a little more emphasis on potential application would further enhance the impact.

Referee #3 (Remarks to the Author):

The authors unveil a nanochemical system that is as rich and complex spectroscopically and intellectually, as it is simple synthetically. Mix cadmium chloride and D/L cysteine. Violà. Bowties, bowties, bowties. Because this system is so easy to reproduce, it is likely that others with equip themselves with bowties in short order, and that the possibility of translational science and extensions to other methods of analysis with be high, especially if this work appears in a high-profile journal. I am fully in support of publication in Nature. There are several places where clarity could be improved but nothing upon which the fate of the study should depend.

There are several comments, small and substantial that I will enumerate in order.

Line 22. In the abstract, the authors say that they form a family of structures with the "same shape". One reads "same", as similar, as in similar triangles, that is, exactly the same shape but just different sizes: small, medium, large. It is really the slight differences in shape about which the whole paper is focused.

Line 24. "size, thickness, and length" should be "width, thickness, and length", as later you specify w, t, and l. This misuse occurs several times. For instance, line 65.

Line 27. Should be either "bowtie nanoassemblies" or "bowtie's nanoassemblies". I prefer the first.

Line 41. The line that begins "Small chiral molecules…while larger molecules…." should be rewritten. Stereochemical descriptors for configuration have nothing to do with molecular size. I would rewrite it as say: "Descriptors for stereochemical configuration are binary, e.g. D/L, RR/SS, M/P etc. for

enantiomers." I used RR here rather than just R because it indicates that it has a different usage that D/L which is given to the whole rather than individual stereogenic centers.

Line 68. Capitalize the "L" in microliters.

Line 83. Give a reference to where the single crystal structure comes from.

Line 97. Change "neighboring ones" to "neighboring chains"

Line 132. The interpretation of the VCD spectra is the softest spot of the manuscript in my view. VCD is 100 stronger because of "long-range resonant coupling between chains". The 1600 cm-1 is split due to the "asymmetric coordination environment". There isn't much offered to support these interpretations. Perhaps the authors know more than they say. On the other hand, in their favor, I do not know of a single study with ECD, VCD, and TCD spectra of the same chemical system. That is a real achievement. So, when you are carrying the whole EM spectrum in your arms, you can't attend to absolutely everything at the same time.

Line 149. The authors have develop a model for size limited growth which is based on the zeta potential. This seems like a good model. The results are impressive. But I don't know if this is the only factor at play or if it is proxy for some other effect. Local growth generally leads to geometrical frustration. For helicoidal objects, this strain is size-limiting because the frustration grows with each new layer. Perhaps FIB'ing the helicoids longitudinally and seeing how they respond might reveal something of the stress that is stored within. This is sort of like trying to rejoin shattered tempered glass. Each piece relaxes and changes shape. The puzzle can't be put back together. This idea has the same consequences as the zeta potential idea but the motive force is different. Alternatively, as the individually lamellae separate from one another, they appear to become less twisted. It could be that when who chiral lamellae come together, but slightly misoriented, there is a strain that caused them to wrap around one another, like rubber sheets, stretched in non-parallel directions, glue together, and then released. When freed they become like old-fashioned shaving brushing made from individual, untwisted, uncooperative whiskers.

Line 189. As far as I am aware, this is the best use of geometric chirality measures for correlations with pseudoscalar observables. The authors don't say too much in the manuscript itself. Of course, space is limited. The SI is more fulsome. It may also be the case that the authors are afraid of a controversial subject, but this is not so because the first five references take on the virtues and vexations alike of continuous symmetry measures. These results are helping me to rethink this subject in the context of our own work. Bravo.

Author Rebuttals to Initial Comments:

Replies to the Reviewers' Comments.

We would like to thank all the Reviewers for careful analysis of the manuscript, encouragement about the fundamental/technological significance of the work, insightful suggestions and critical comments. We have thoroughly considered all the comments and made the requested changes to fully address them. Please find below our replies (blue font) that follow the corresponding comments given *verbatim* (black font).

REVIEWER #1:

Comment 1-1: The authors systematically correlate the geometrical properties of synthesized chiral microstructures with their spectroscopic as well as optical properties. With this aqueous synthesis from hierarchically structured nanoribbons, chiral structures are available in large quantities with tunable chiral properties. Under these important conditions, the authors were able to print the chiral particles on different surfaces where they could observe the chiral effect on large areas. The authors prove the hypothesis with a broad methodology in spite of micrometer-sized structures, low signal intensities for the particles as well as for the surfaces.

Response 1-1: We would like to thank ***Reviewer 1*** for careful reading of the manuscript and their insightful comments.

Comment 1-2: However, the chain of reasoning is incomplete at one point when the LIDAR method is or should be linked to results of the electromagnetic simulation method. With the LIDAR method the authors observe the CD backscatter signal at an excitation of 1550nm, where a CD difference of 100mdeg (SI Fig 49) is expected. The authors themselves write that there is a small difference in the polarized signal difference (see caption SI Fig 50). This finding makes it even more important to explain the observed results with the simulations. In the simulations in SI Fig

47, the layer model at different polarizations and wavelengths is calculated to account for the differences between the CD signals. Furthermore, the authors change the geometry of the layer structure or change the section. This unnecessarily complicates the understanding of the structure and the effect. The authors must keep the geometry or the cutout section constant and clearly identify the dipolar as well as qudrupolar modes by surface charge calculations.

Response 1-2: The comments from *Reviewer 1* prompted us to go back to our simulations and understand the chiroptical spectra in more detail. We have revisited the values of wavelength-dependent refractive index we used for simulations and found that it was the cause of discrepancy between simulated and experimental CD spectra pointed out by *Reviewer 1*. The atomic structure of bowties (**SI Fig 8b**) is based on CdO nanosheets assembled into twisted stacks. Thus, we repeated our simulations accounting for (**i**) experimentally obtained refractive index of bulk CdO instead of theoretically calculated refractive index of bulk Cd_2(*L*-CST)$_2$ used before (SI Fig 44) and, (**ii**) exact morphology of the bowties obtained from SEM images for different OPD indices (**SI Fig 46,49,50**). We observe a much better agreement between experiment and simulations in terms of both peak P1,P2, and P3 positions, and *g*-factors (~ 0.01). We have updated these results in **Fig 4, SI Fig 49,49,50**. A red shift of ~ 300 nm observed in simulated spectra is attributed to the band gap shift between the optical response of bulk *vs* two-dimensional CdO nanosheets[1,2], which is common for the nanoscale metal oxides[3,4].

Comment 1-3: Furthermore, the authors should add the wavelength 1550nm and add a comparison with the LIDAR results. Results should be understandable without video references.

Response 1-3: To address this comment we have simulated (i) averaged CD spectra from 25 different orientations with respect to light beam, (ii) three-dimensional scattered electric field from LCP and RCP, (iii) dipolar and quadrupolar decomposition of scattered field using a stack of 5

sheets with *l, w, t, θ* as 5.3±0.3 μm, 2.1±0.1 μm, 0.7±0.1 μm, 46±5°, measured from SEM images focusing specifically at the chiroptical properties at 1550 nm. We observe that a maxmium *g*-factor value from simulated CD spectra of -0.024, experimental CD spectra (-0.004), and LIDAR (-0.016) measurements are of the same order of magnitude. By comparing these values at 1550 nm we are able to confidently say that the scattering at 1550 nm is composed of both dipolar and quadrupolar modes.

Comment 1-4: Furthermore, a coherent discussion of the simulated modes and the LIDAR results should be added to the revised manuscript.

Response 1-4: We have simplified and updated our results on the scattering modes in **SI Fig 54d,e**. We find that at 1550 nm, the contributions from dipolar and quadrupolar modes is nearly equal. Previously we had observed for a single twisted sheet that at higher wavelengths the scattering modes were dominated by dipolar scattering. However, in a stack of twisted sheets the scattering modes get more complex due to interference of scattered field between the sheets leading to mixed scattering modes. We observe this from simulations of scattered field in **SI Fig 54f-k**.

REVIEWER #2:

Comment 2-1: This work describes the development and characterization of multiscale assembled microparticles, in the general shape of bowties, with fully tunable chiral properties. These particles represent the first structures with fully and continuously variable chiral behavior – a true breakthrough in my view, with potential impact on the fields of chiral photonics/materials (including the ability to create and manipulate novel topological and valley properties), biochemical separations, chiral catalysis, and sensing technologies. Their hierarchical physical structuring, which lead to the exciting behavior, are controlled with precision using independent

chemical synthetic regulation of their twist pitch, length, size and thickness. The degree of tunability and reproducibility is quantified by the authors. They demonstrate an impressive range of characterization, which highlights the multiscale nature of the structuring and material interplay (and the synthesis achievement!). Further, the accurate, and predictive, modeling they show is powerful and should enable future developments based in the insights and understanding it affords. The paper concludes with a demonstration of NIR optical circular dichroism in printed films on glass and cloth. It is a neat demonstration, illustrating a potential application area. Overall, I do think this paper is, for the most part, at the level of Nature.

Response 2-1: We would like to thank ***Reviewer 2*** for careful reading of the manuscript and their insightful comments.

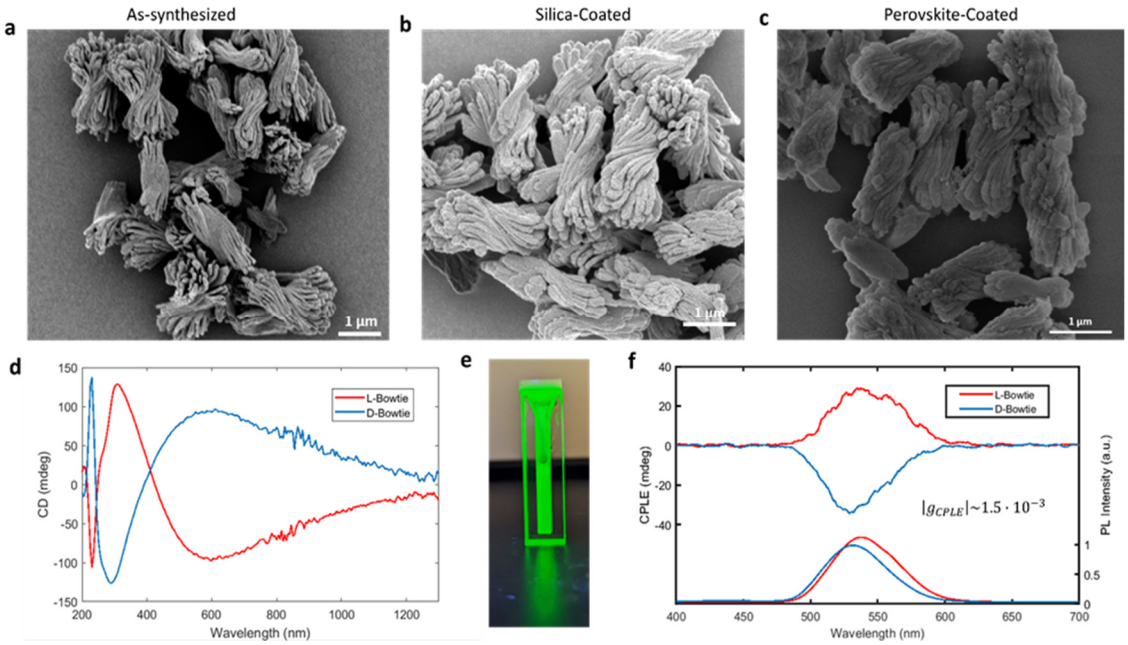
Comment 2-2: Which brings me to my one critical point: If I am being totally honest, I find myself wanting to see one more application or demonstration of potential utility. More generally, a little more of the type of thing in Figure 4g, and maybe a little less of some of the other details. Those get a little busy, and detract some from the excitement (anything not used can be added to the already thorough SI.

... I do not have a specific application in mind…one possibility could be depositing films of bowties on a 2D semiconductor, and measuring the polarization of the PL that is emitted. Can the bowties lead to circularly polarized PL from the material (signifying the enhancement of valley-specific emission)? Just an idea.

Response 2-2: We do agree that bowtie particles with variable chirality can lead to multiple additional applications, besides LIDARs including the optics, catalysis, and electronics. We are glad to address these comments considering applications complex particles for whom the bowties

can serve as a starting point. Particularly exciting is the possibility of using bowties as templates for other materials that become chiroptically active and spin selective. For example, one can deposit a layer of perovskites on the bowties. Within the constrains of this manuscript, we show that it leads to the circularly polarized light emission (CPLE, **Fig. R1**). Based on prior studies of chirality-induced spin selectivity effect (CISS), we also believe that bowties with perovskite layer will exhibit magnetooptical Kerr effect due to spin-selective current[5,6,7]. Chiral electrocatalysis would also be possible especially when the particles are converted to CdS or using electrochemically stable perovskites.

We are leaning toward a separate publication in line of these applications because there are indeed most interesting optical and electronic effects here related to interplay between the template and



SI Fig. 51. SEM image of **a,** as synthesized bowtie, **b,** silica coated bowtie by Stöber process, **c,** formamidinium lead bromide perovskite nanocrystals coated atop the silica coated bowties. **d,** CD spectra of as-synthesized bowtie shown in panel a. **e,** photograph of a vial containing perovskite coated bowtie displaying green emission at 535 nm when excited with a UV lamp. **f,** Circularly polarized light emission spectra from perovskite coated bowtie with a g-factor of 1.5x 10^{-3}.

the deposited material. With the kind *Reviewer 2* approval, we are happy to include these data in the manuscript as **SI Fig 51**.

Comment 2-3: Also, one specific figure note: I'm not sure I understand figs. 3d,e. Perhaps some of the labels were cut off? A bit more explanation in the text or figure caption would also be helpful).

Response 2-3: Thanks a lot for the comment that we are happy to address. Besides making sure that the figure is reproduced in its entirety in the manuscript, we have updated the figure caption to improve its clarity. Specifically the figure legend now reads *"... **d,** Scatter chart demonstrating the variability of the geometrical parameters (l, w, t) vs pitch (p) for the bowtie assemblies obtained in this study and the same parameters obtained in other studies;*[8–12] *bowties retain their shape over two orders of length scales. **e,** Variation of the morphological parameters with calculated OPD chirality measure show empirical correlations between the l, w, t, p and, OPD."*

Comment 2-5: As I said, I do find the presented work high quality and compelling, and simply feel a little more emphasis on potential application would further enhance the impact.

Response 2-5: We have added a discussion at the end of the manuscript highlighting the possibilities of bowties as pathway to electro-optical and spin-selective materials. The work here also shows a unique effect that bowties can act as electromagnetic field concentrators with exceptionally values of electromagnetic field in the gaps between the nanosheets, which would be valuable for biosensing and asymmetric catalysis. Since our expertise lies primarily in synthetic fundamentals of chiral (biomimetic) nanostructures, we are happy to collaborate with our colleagues with greater expertise in electro-optics, spin-polarization, and electro-catalysis.

REVIEWER #3:

Comment 3-1: The authors unveil a nanochemical system that is as rich and complex spectroscopically and intellectually, as it is simple synthetically. Mix cadmium chloride and D/L cysteine. Violà. Bowties, bowties, bowties. Because this system is so easy to reproduce, it is likely that others with equip themselves with bowties in short order, and that the possibility of translational science and extensions to other methods of analysis with be high, especially if this work appears in a high-profile journal. I am fully in support of publication in Nature.

Response 3-1: We would like to thank ***Reviewer 3*** for careful reading of the manuscript and his/her insightful comments.

Comment 3-2: There are several places where clarity could be improved but nothing upon which the fate of the study should depend. There are several comments, small and substantial that I will enumerate in order.

Line 22. In the abstract, the authors say that they form a family of structures with the "same shape". One reads "same", as similar, as in similar triangles, that is, exactly the same shape but just different sizes: small, medium, large. It is really the slight differences in shape about which the whole paper is focused.

Response 3-2: We thank the reviewer for pointing out the ambiguity of the previous characterization. We agree these shapes are similar and not same. The corresponding change in the main text was made.

Comment 3-3: Line 24. “size, thickness, and length” should be “width, thickness, and length”, as later you specify w, t, and l. This misuse occurs several times. For instance, line 65.

Response 3-3: We agree with *Reviewer 3* that the terminology for description of geometry needs to be precise. We have used “size” at multiple places in the manuscript as an umbrella term for length, width and thickness. However, at places we talk about thickness, length and width, we have removed the term size in the updated version of the manuscript. The suggested change was implemented in the revised version of the manuscript.

Comment 3-4: Line 27. Should be either “bowtie nanoassemblies” or “bowtie’s nanoassemblies”. I prefer the first.

Response 3-4: We agree that *bowtie nanoassemblies* should be the preferred term. We have corrected the main text and the SI to address this comment.

Comment 3-5: Line 41. The line that begins “Small chiral molecules…while larger molecules….” should be rewritten. Stereochemical descriptors for configuration have nothing to do with molecular size. I would rewrite it as say: “Descriptors for stereochemical configuration are binary, e.g. D/L, RR/SS, M/P etc. for enantiomers.” I used RR here rather than just R because it indicates that it has a different usage that D/L which is given to the whole rather than individual stereogenic centers.

Response 3-5: Indeed, the currently used stereochemical descriptors are not related to the size of the molecules. What we wanted to point out here that helical molecules, where *M/P* or notations are applicable, tend to be larger ion molecular weight. Nevertheless, this is a good point because there are no built-in considerations for molecular weight implied in these notations.

The corresponding sentence was changed to "*However, chirality in chemistry commonly manifests as a binary property: chiral molecules are either right-handed or left-handed and the descriptors for stereochemical configurations of enantiomers at molecular scale are correspondingly binary, e.g. D/L, RR/SS, M/P, and Δ/Λ.*"

Comment 3-6: Line 68. Capitalize the "L" in microliters.

Response 3-6: Thank you for pointing out the inconsistency in notation. We have updated the units in the main text and in electron microscopy and vibrational circular dichroism spectroscopy methods section.

Comment 3-7: Line 83. Give a reference to where the single crystal structure comes from.

Response 3-7. We have solved the single crystal structure from synchrotron XRD data and have added the reference to figures, and table **(SI Table 1, SI Fig 6, Fig 1k)** that describe the crystal structure in the main text.

Comment 3-8: Line 97. Change "neighboring ones" to "neighboring chains"

Response 3-8: Done! We have made this change.

Comment 3-9: Line 132. The interpretation of the VCD spectra is the softest spot of the manuscript in my view. VCD is 100 stronger because of "long-range resonant coupling between chains". The 1600 cm-1 is split due to the "asymmetric coordination environment". There isn't much offered to support these interpretations. Perhaps the authors know more than they say. On the other hand, in their favor, I do not know of a single study with ECD, VCD, and TCD spectra of the same chemical system. That is a real achievement. So, when you are carrying the whole EM spectrum in your arms, you can't attend to absolutely everything at the same time.

Response 3-9: We appreciate this critique and happy to deepen the description of vibrational circular dichroism (VCD). To explain the trends observed in the experimental spectra, we collaborated with Prof. Valentin Paul Nicu from the University of Sibiu whom we serendipitously met at one of the recent conferences. Prof. Nicu developed a unique set of DFT codes that enable identification of specific modes in the VCD spectra[13]. He has performed a series of DFT calculations for (**a**) the lowest conformer of the isolated cystine molecule, (**b**) a complex formed between 1 Cd atom and 4 cysteine ligands and (**c**) a complex formed between 5 Cd atoms and 16 cysteine ligands. He found that two carbonyl stretching modes (**Fig R2a**), an out-of-phase mode at 1768 cm^{-1} and an in-phase mode at 1771 cm^{-1}, are associated with oscillating dipoles of large magnitude. Unfortunately they are nearly degenerate and result in polarization rotation in opposite directions, their VCD intensities cancel each other to a large degree. So, the resulting VCD bands are not very intense (blue spectrum in SI Fig. 9).

The situation changes for Cd-cystine nanoribbons made of four cistine ligands bound to one Cd atom. Two of these ligands bind to the Cd atom via one O atom and one N atom, while the other two via only one O atom. For this reason, the four O atoms bonded to a given Cd atom are not equivalent. The carbonyl stretching modes are no longer degenerate. Also, their frequencies are red-shifted. Interestingly enough, this shift causes them to couple with NH_2 scissoring modes. As a result, the more intense VCD bands between 1600 and 1700 cm^{-1} are observed (see black spectrum in **SI Fig. 9**, **Fig R2b**). Finally, the extended structure with 5 Cd atoms shows even larger red-shifts pointing to the vibrational resonance between the equivalent carbonyl bonds of four different Cd atoms. As the red spectrum in **SI Fig 9** shows, this collective mode results in significantly increase of intensity in VCD signals **(Fig R2c)**.

Extending these observations to semi-infinite nanoribbons, this collective phonon mode leads to the very intense VCD peaks observed experimentally at ca 1615 cm^{-1}.

The corresponding data and explanations were added to the main text and ESI together with figure **SI Fig. 9,10** (see also the **Fig R2** below). Prof. Nicu also kindly agreed to be a co-author of this manuscript.

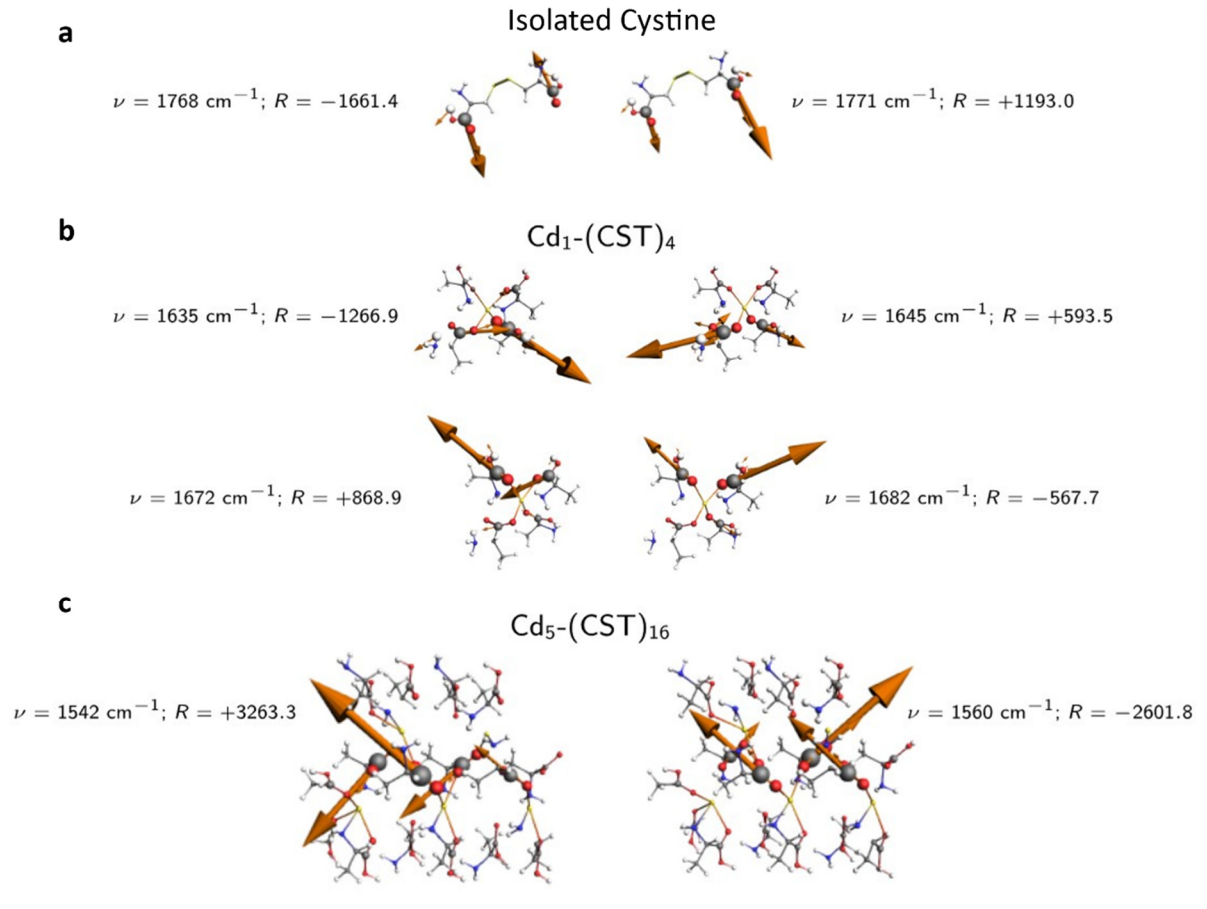


Fig R2. VCD oscillator modes in **a,** isolated cystine, **b,** Cd_1-$(CST)_4$ and **c,** Cd_5-$(CST)_{16}$ structures. The magnitude of the atomic radius indicates the magnitude of the associated nuclear displacement vector, while the orange arrows represent the electric dipole transition moments that couple through space yielding the large VCD intensities. Unit of the rotational strengths (R): 10^{-44} esu^2cm^2.

Comment 3-10: Line 149. The authors have develop a model for size limited growth which is based on the zeta potential. This seems like a good model. The results are impressive. But I don't know if this is the only factor at play or if it is proxy for some other effect. Local growth generally leads to geometrical frustration. For helicoidal objects, this strain is size-limiting because the frustration grows with each new layer.

Response 3-10: We greatly appreciate this comment. Mechanical strain and geometric frustration in general, is indeed a part of the growth process that results in the twist of the ribbons. We have updated our growth model to account for the mechanical strain. In brief, the new model incorporates the competition between electrostatic and van-der-Waals forces during the formation of a single nanoribbon, while the self-limited assembly of ribbons into a stack of twisted sheets is observed due to a critical strain that the ribbons can withstand before mechanical failure. Details of this model are added in SI section. The combined model inclusive of geometric frustration and the energy of mechanical strain, indeed displayed a better match with the experimental data.

Comment 3-11: Perhaps FIB'ing the helicoids longitudinally and seeing how they respond might reveal something of the stress that is stored within. This is sort of like trying to rejoin shattered tempered glass. Each piece relaxes and changes shape. The puzzle can't be put back together. This idea has the same consequences as the zeta potential idea but the motive force is different. Alternatively, as the individually lamellae separate from one another, they appear to become less twisted. It could be that when who chiral lamellae come together, but slightly misoriented, there is a strain that caused them to wrap around one another, like rubber sheets, stretched in non-parallel directions, glue together, and then released. When freed they become like old-fashioned shaving brushing made from individual, untwisted, uncooperative whiskers.

Response 3-11: We thank the reviewer for these practical and insightful suggestions. We imaged bowties following their longitudinal FIB. However, due to the beam sensitivity of the Cd-CST ribbons, it was impossible to cut a section without confining the structure inside a protective layer of platinum (**Fig R4**). While we agree with the reviewer's suggestion that the unfolding of bowtie into individual lamellae would release strain, it is difficult to get this information from the cross-sectioned bowtie particles.

Nevertheless, we had success in disassembling the bowtie by judicious adjustment of the media pH. By careful titration with HCl, we were able to break the bowties apart into single lamellae that appear to be nearly flat indicating the elastic relaxation of the twisted ribbons (**Fig R3**). More experiments to quantify the strain would need to be done in the future, through a combination of in-situ and ex-situ mechanical compression.

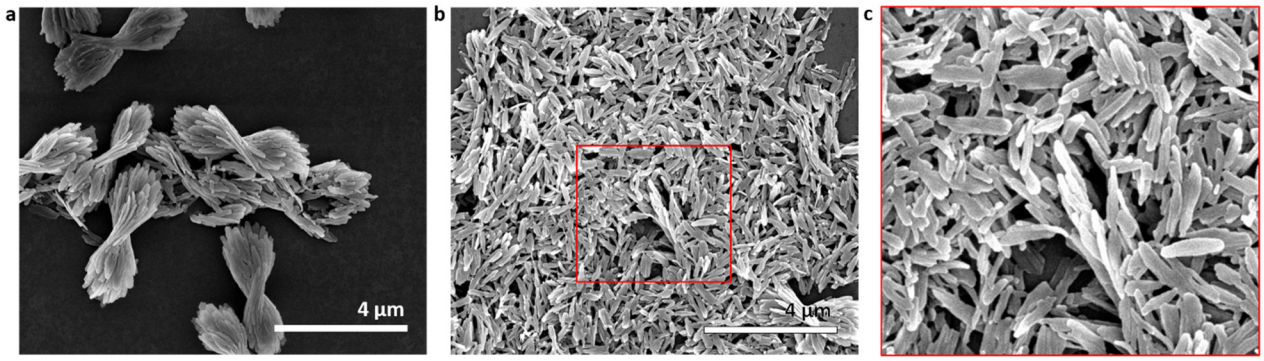


Fig R3. SEM image of **a,** bowtie structure and its **b-c,** disassembled counterpart into individual lamellae. While the bowties have a pronounced twist the individual sheets are less twisted as compared to the fully formed structure.

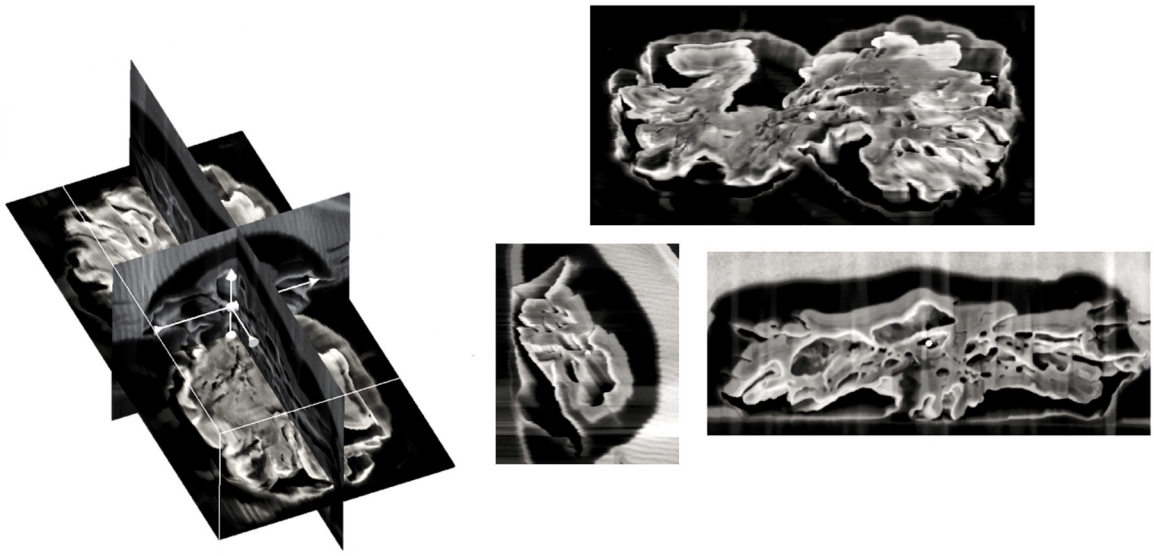


Fig R4. Cross-section of the reconstructed bowtie structure obtained by FIB cross-sectioning in the longitudinal direction. The material has to be confined by platinum layers to avoid Ga-ion beam damage.

Comment 3-12: Line 189. As far as I am aware, this is the best use of geometric chirality measures for correlations with pseudoscalar observables. The authors don't say too much in the manuscript itself. Of course, space is limited. The SI is more fulsome. It may also be the case that the authors are afraid of a controversial subject, but this is not so because the first five references take on the virtues and vexations alike of continuous symmetry measures. These results are helping me to rethink this subject in the context of our own work. Bravo.

Response 3-12: We are glad that *Reviewer 3* appreciates our effort to find these correlations. It is indeed controversial subject. With great respect to our predecessors, we are adding in conclusions a point about the origin of the vivid correlation between OPD and the spectra. I believe they originate from the fact that for bowties the transition between the chiral and achiral state is a simple twisting around a single axis that must proceed through the achiral flat state. Under these circumstances the 'false zeros' do not occur and pseudoscalar chirality measures work well

because of this geometrical restriction. Perhaps, in the future a weighted combination of OPD, Hausdorff, continuous chirality measures and perhaps newer ones using graph/information theory can be used to develop a more comprehensive chirality-property functions, which would be intellectually exciting.

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Reviewer Reports on the First Revision:

Referees' comments:

Referee #1 (Remarks to the Author):

Due to the thorough revision, the authors could address all issues. Furthermore, the manuscript has gained significantly in quality and is now recommended for publication.

Referee #2 (Remarks to the Author):

In their revised manuscript and SI, the authors have, in my view, put forth major efforts to address the previous reviewer comments. This has further improved manuscript clarity, and provided new insights with the addition of new modeling, simulation, and experiment. I appreciate the updated EM simulations, and particularly the use of experimentally measured refractive indices rather than calculated values, which appears to result in better agreement with the observed dichroism properties. Likewise, I found the new theoretical modeling of VCD behavior to add nice mechanistic insight, which can guide future application-driven design efforts. Speaking of applications: the authors state that they would prefer to put more application demonstrations in a future manuscript. I certainly understand this sentiment and recognize the additional collaborations that may be required, so am supportive of it. Within this context, I think the additional language in the conclusion on this point further highlights future potential. I therefore feel the authors have satisfied my concerns, and recommend publication in Nature.

Referee #3 (Remarks to the Author):

I was supportive of this paper at the outset.
I continue to be. The response to the referees was comprehensive and thoughtful. Time to publish.