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Insight on chirality encoding from small thiolated molecule to plasmonic Au@Ag and Au@Au nanoparticles

Antonio Carone,¹ Pablo Mariani,¹ Anthony Désert*,¹ Marco Romanelli,^{2,3} Jacopo Marcheselli,^{4,5} Marco Garavelli,⁴ Stefano Corni,^{2,3} Ivan Rivalta,^{1,4} Stephane Parola¹

¹ Université de Lyon, École Normale Supérieure de Lyon, Université Lyon 1, CNRS UMR 5182, Laboratoire de Chimie, 46 allée d'Italie, F-69364 Lyon, France.

² Dipartimento di Scienze Chimiche, Università di Padova, 35131 Padova, Italy.

³ Istituto di Nanoscienze, Consiglio Nazionale delle Ricerche CNR-NANO, 41125 Modena, Italy.

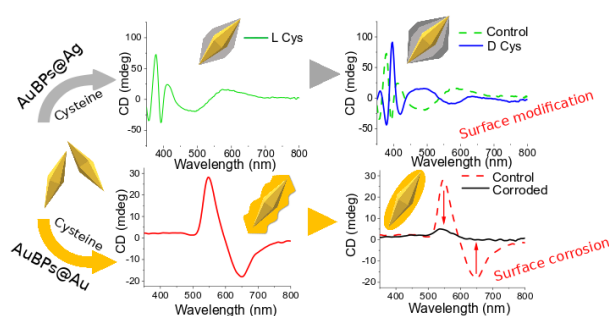
⁴ Dipartimento di Chimica Industriale "Toso Montanari", Università degli Studi di Bologna, Viale del Risorgimento 4, I-40136 Bologna, Italy.

⁵ SISSA—Scuola Internazionale Superiore di Studi Avanzati, Via Bonomea 265, 34136 Trieste, Italy.

*anthony.desert@ens-lyon.fr

ABSTRACT

Chiral plasmonic nanomaterials exhibiting intense optical activity are promising for numerous applications. In order to prepare those nanostructures, one strategy is to grow metallic nanoparticles in the presence of chiral molecules. However, in such approach the origin of the observed chirality remains uncertain. In this work, we expand the range of available chiral plasmonic nanostructures and we propose another vision of the origin of chirality in such colloidal systems. For that purpose, we investigated the synthesis of two core-shell Au@Ag and Au@Au systems built from gold nanobipyramid cores, in presence of cysteine. The obtained nanoparticles possess uniform shape and size and show plasmonic circular dichroism in the visible range, and were characterized by Electron Microscopy, Circular Dichroism and UV-Vis-NIR spectroscopy. Opto-chiral responses were found to be highly dependent on the morphology and the plasmon resonance. It revealed (i) the importance of the anisotropy for Au@Au nanoparticles and (ii) the role of the multipolar modes for Au@Ag nanoparticles on the way to achieve intense plasmonic circular dichroism. The role of cysteine as shaping agent and as chiral encoder was particularly evaluated. Our experimental results, supported by theoretical simulations, contrast the hypothesis that chiral molecules entrapped in the nanoparticles determine the chiral properties, highlighting the key role of the outmost part of the nanoparticles shell on the plasmonic circular dichroism. Along with these results, the impact of enantiomeric ratio of cysteine on the final shape suggested that the presence of a chiral shape or chiral patterns should be considered.



keywords: Chirality, Plasmon, Metal nanoparticles, Bipyramids, Core-shell

If chemists traditionally deal with chirality for organic molecular compounds, the community shows an increasing interest in chiral inorganic nanostructures.¹⁻³ Indeed, in addition to take part in fundamental understanding of chirality concept, studies of chiral inorganic nanostructures lead to unique properties of materials –e.g. high optical activity with circular dichroism (CD) response– with concrete and direct applications in the fields of catalysis, (bio)sensing and photonics. In this context, plasmonic chiral nanostructures appear as excellent objects of investigation as highlighted by recent reviews.⁴⁻⁹ The scientific community often distinguishes intrinsic chirality when the metal nanostructure exhibits a chiral geometry from induced chirality when chiral molecules are coupled to plasmonic NPs.

Thus, top-down and nanofabrication methods have enabled the preparation of plasmonic nanostructures with intrinsic chirality,^{10,11} while the grafting of chiral compounds onto pre-formed plasmonic NPs has shown coupling effects leading to CD response in the plasmon resonance region.^{12,13} Colloidal assemblies of plasmonic nanospheres and nanorods thanks to chiral linkers (like DNA or amino acids) has been also extensively reported to promote both intrinsic and/or induced chirality.¹⁴⁻¹⁷

Another strategy to address chiral plasmonic NPs is to control the growth of metal NPs in presence of chiral molecules. By this way, Ki Tae Nam and coll. have demonstrated for the first time in 2018 the colloidal synthesis of gold NPs with

53 unambiguous chiral geometry by a seed-mediated growth method with cysteine and glutathione.¹⁸ Then, and through several
54 studies and reviews, they have discussed the high potential of their chiral AuNPs (with high *g*-factor values up to 0.2-0.3 in
55 suspension) and the chirality transfer mechanism during the growth of the octahedral seeds.¹⁹⁻²¹ Since then, other seed-
56 mediated growth methods have been reported leading to plasmonic NPs with apparent chiral geometry from gold
57 nanorods,^{22,23} nanooctopods²⁴ or nanoplates.²⁵ However, in such strategy chirality can also be observed even without an
58 obvious chiral shape. In 2007, two possible origins were proposed by Avnir and co-workers²⁶ for the chirality in polycrystalline
59 metal powders doped with chiral biomolecules: (i) the presence of metal cavities and surfaces chirally imprinted (intrinsic
60 chirality); (ii) the interaction between the metal and the entrapped chiral biomolecules (induced chirality). The hypothesis of
61 chiral footprints was later confirmed in palladium nanopowder²⁷ and platinum layer²⁸ retaining chiral properties even after
62 removal of the chiral template molecules.

63 In the case of plasmonic NPs prepared by seed-mediated growth method, induced chirality related to chiral molecules
64 entrapped at the core-shell interface or embedded in the metallic shell is often proposed. For instance, spherical Au@Ag
65 core-shell NPs, entrapping DNA²⁹ or cysteine³⁰ within nanogaps at the Au core-Ag shell interface, have shown large CD signals.
66 The same authors have later reported Au@AuAg yolk-shell nanorods with chiral penicillamine inside the nanogaps.³¹
67 Anisotropic gold cores and entrapped cysteine have been particularly studied for preparing new chiral plasmonic NPs, like
68 Au@Cys@Ag nanorods,³² starfruit-like AuNPs,³³ overgrown Au nanorods with one or two spikes,³⁴ or more recently like Au
69 nanobipyramids coated by silver.³⁵ In these systems, the chirality is induced by strong coupling effect between the plasmonic
70 nanostructures and the chiral molecules through local electromagnetic field enhancement (in nanogaps or “hotspots”).

71 Despite the recent important work devoted to this field, the understanding of the origin of chirality in such systems remains
72 fragile³⁶ and we propose a full investigation to bring a different vision of the origin of chirality in such core-shell systems.
73 Based on our previous work³⁷ describing the synthesis of gold pentatwinned nanostructures with a fine control of the
74 particles' shape, size and plasmonic properties, we propose a strategy through the controlled overgrowth of gold
75 nanobipyramids (AuBPs) into well-defined pentatwinned Au@Ag and Au@Au NPs, in presence of cysteine. Our approach
76 allows high homogeneity in shape and size, which appears to be decisive to obtain strong CD signal and to understand the
77 origin of chirality. We present herein a complete study of the impact of cysteine enantiomers on the morphology and the
78 optical properties (absorption and CD) showing that the CD response is highly dependent on the plasmon resonance modes,
79 as also confirmed by our computational complementary analysis. The synergistic experimental and computational studies
80 allow a deep discussion about the role of cysteine in the origin of chirality in these nanomaterials.

81

82 RESULTS AND DISCUSSION

83 **Preparation and morphology of AuBP@Au and AuBP@Ag nanoparticles.** Pentatwinned gold bipyramids (AuBPs)
84 were employed as core in a seed-mediated growth method in presence of cysteine (Cys) as chiral encoder to obtain
85 AuBP@metal nanoparticles with different shell compositions (Au/Ag), shapes and optical chirality properties. Having highly
86 monodispersed AuBPs was crucial for preparing homogeneous overgrowth NPs with an intense opto-chiral response. To
87 synthesize the AuBPs, a protocol developed recently by our group was used.^{37,38} This method allowed us to obtain highly
88 monodispersed AuBPs, in a high concentration ($[Au^{3+}] = 15 \text{ mM}$), with a shape purity above 95%. Two different sizes of AuBPs
89 were synthesized to be used as core (see [Paragraph S.1](#)).

90 The first AuBPs batch, namely AuBP84, presented a L-LSPR centered at 800 nm and a T-LSPR at 511 nm ([Figure S1a](#)) with a
91 ratio between L-LSPR and T-LSPR bands intensities of 7. Transmission electron microscopy (TEM) statistics over 200 particles
92 showed for AuBP84 a length of $84 \pm 6 \text{ nm}$ and a width of $26 \pm 2 \text{ nm}$ (with an aspect ratio of 3.2) ([Table T1](#) in the [Supporting](#)
93 [Information](#)). The second AuBPs batch, namely AuBP140, presented a L-LSPR centered at 940 nm and a T-LSPR at 512 nm
94 ([Figure S1b](#)), with a ratio between L-LSPR and T-LSPR intensities of 8. TEM statistics showed for AuBP140 a length of 140 ± 8
95 nm and a width of $36 \pm 3 \text{ nm}$ (with an aspect ratio of 3.9) ([Table T1](#)). Combining inductively coupled plasma (ICP) and extinction
96 measurements, we experimentally found the molar extinction coefficient at 400 nm for both batches, similarly to what has
97 been done for AuNRs.³⁹ The total surface, volume, and number of AuBPs for a given Au^0 concentration were then calculated
98 with the help of TEM images ([Table T2](#) and [Figure S2](#) in the [Supporting Information](#)).

99 The synthesis route for the AuBP@Ag was adapted from the protocol reported by Zhuo *et al.*, which was initially developed
100 for the preparation of AgNRs starting from AuBPs.⁴⁰ In this reaction Ag(I) chlorine-surfactant complex is reduced using
101 ascorbic acid (AA) in presence of CTAC on the surface of AuBPs core.

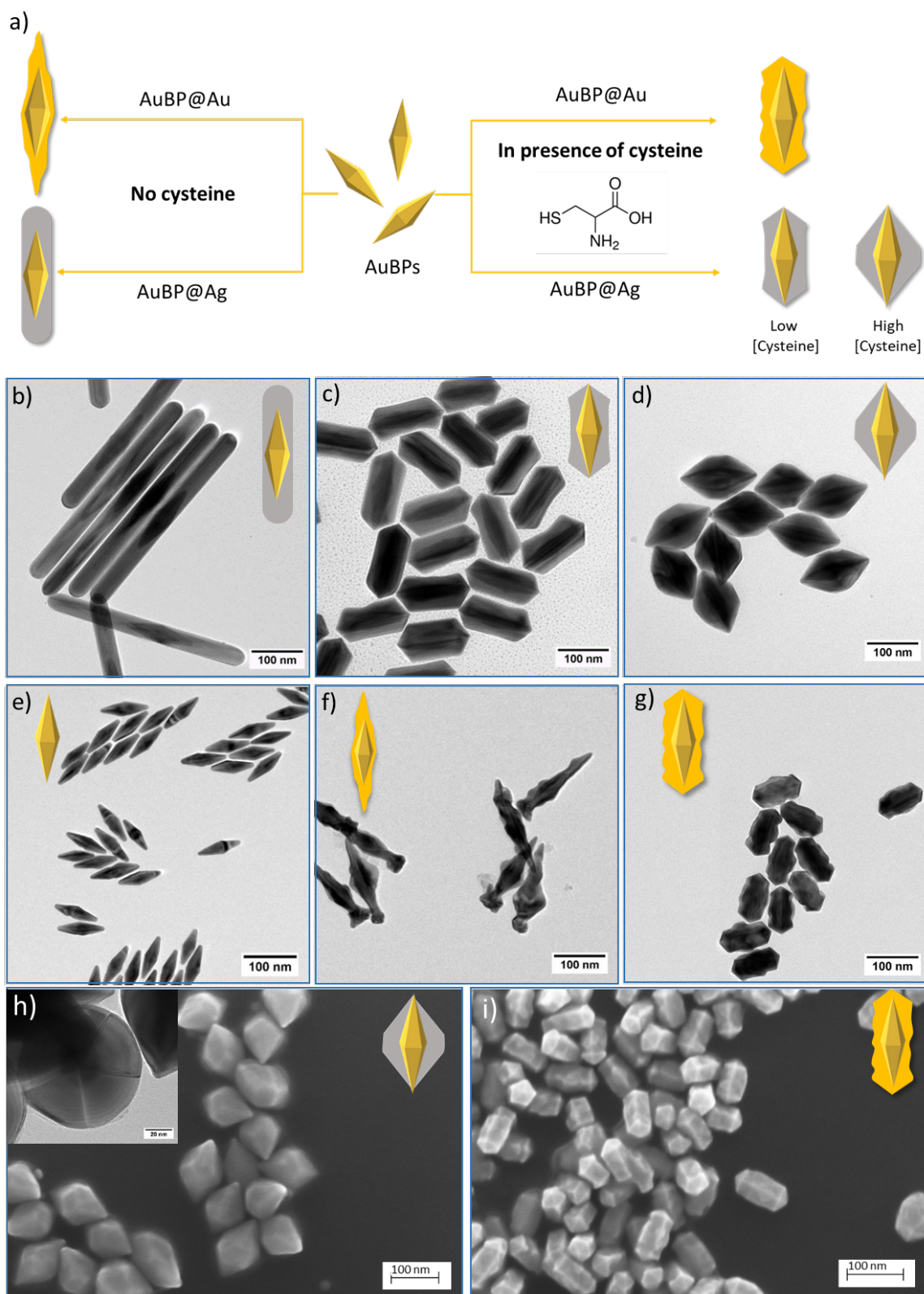


Figure 1. (a) Scheme representing the different strategies used for the preparation of the core-shell NPs, (b-g) TEM images of the obtained nanostructures in each condition. (b) AuBP140@AgNRs synthesized in absence of Cys. (c) AuBP140@Ag synthesized at 1 μM of Cys. (d) AuBP140@Ag synthesized at 5 μM of Cys. (e) Pentatwinned gold bipyramids AuBP84. (f) AuBP84@Au synthesized in absence of Cys. (g) AuBP84@Au synthesized at 10 μM of Cys. (h) SEM image of AuBP140@Ag synthesized at 20 μM. In the inset a TEM image showing the pentatwinned structure of the silver shell. (i) SEM image of AuBP84@Au synthesized at 10 μM of Cys

103 In order to form AuBP@Au we used another protocol that takes inspiration from the synthesis of starfruit-like nanoparticles
104 starting from AuNRs.³³ In this case AA is used to reduce Au(III) in presence of CTAB to form Au(I) bromide-surfactant complex.
105 The Au(I) in the complex is reduced to Au⁰ by the excess of AA on the surface of AuBPs in presence of Ag(I) as a shaping agent.
106 In both cases, Cys was used as chiral encoder due to the ability to easily bind to Au surface through its thiol group.

107 It was observed that the presence of Cys in the reaction mixture led to radical change in the shells morphologies for both
108 AuBP140@Ag and AuBP84@Au. The impact of Cys on the shape was then further studied for both systems (Figure 1a). For
109 AuBP140@Ag system, when no Cys was present in the reaction mixture, some well calibrated AuBP140@AgNRs were formed
110 as expected (Figure 1b). At 1 μM Cys in the reaction mixture, the silver shell growth direction was completely reversed. The
111 analysis of the final length (142 ± 8 nm) in the TEM images (Figure 1c) showed that the silver deposition along the longitudinal
112 axis was completely suppressed in favor of a deposition on the side of the AuBPs (final aspect ratio of 1.9). The nanoparticles
113 showed regular edges on the tips, while a certain degree of irregularity was present on the sides. Increasing Cys concentration
114 ([Cys]) in the reaction mixture led again to a change in the synthesized nanoparticles morphology. While at 1 μM Cys a
115 truncated rod-like structure was formed, at 5 μM Cys the Ag deposition on the side was enhanced as shown in Figure 1d (final
116 aspect ratio of 1.4). TEM analysis confirmed the 5-fold symmetry of the metallic shell (Figure 1h) as observed for the
117 pentatwinned core. Further increase of [Cys], *i.e.* from 5 μM to 100 μM, did not bring any change in the nanoparticles
118 morphology. Similar shaping effect was observed in presence of Cys,^{33,35} using different thiolated molecules⁴¹ or DMSO^{42,43}
119 to control the final morphology of the metallic shell. However, the low [Cys] necessary to provoke a change in morphology (1
120 μM, with [Cys]/[Ag] ≈ 1·10⁻³) lead to the assumption that Cys is playing a role by binding on the Au⁰ surface, rather than
121 influencing other species in solution. We assume that Cys binding through the thiol group to the AuBPs surface is altering the
122 growth kinetics.

123 A similar impact of Cys on the morphology was also observed when a Au shell was deposited around the AuBP84. When
124 no Cys was present in the reaction mixture, the final structure showed a length of 167 ± 27 nm. Compared with the length of
125 the AuBP84 (84 ± 6 nm), a predominant growth along the longitudinal axis is demonstrated. These irregular structures recall
126 the morphology of nails (presence of heads and tips) with evident signs of anarchic growth (Figure 1f). At 10 μM Cys, the
127 deposition of the metal shell was predominant on the side, forming gnocchi-like nanoparticles with a wavy lateral surface
128 and well-shaped facets on the tips (Figure 1g). Electron microscopy analyses (SEM, TEM and HRTEM) also confirmed that in
129 this case the shell preserved the pentatwinned structure of the AuBPs (Figure 1i). Statistical analysis showed a length of 97 ±
130 5 nm, evidencing a few nanometers deposition on the AuBPs tips (final aspect ratio of 1.8). The presence of Cys permitted
131 also to retrieve a uniformity in nanoparticles size and shape. Increasing [Cys] from 5 μM to 20 μM did not lead to appreciable
132 changes in the overall morphology. Similar overgrown nanostructure is obtained by combining different surfactants⁴⁴ or using
133 Cys and glutathione to prevent overgrowth along the longitudinal axis starting from AuNRs.⁴⁵ The formation of a wavy lateral
134 surface observed in our gnocchi-like nanoparticles is similar to the arrow-like nanostructure formed starting from AuNRs.⁴⁶
135 In the same study, it was found by Wang *et al.* that Cys is active on the formation of the wavy lateral surface. The strong Au-
136 S formed on the surface in presence of Cys is slowing the metal deposition rate and thus inducing a thermodynamic controlled
137 growth with formation of more stable prismatic facets on the side. When a different size of AuBPs core was used, the same
138 shaping effect in presence of Cys was found for both AuBP84@Ag and AuBP140@Au (Figure S3).

139
140 **Spectroscopic characterization.** When Cys was employed, a blue-shift of the L-LSPR was recorded in the extinction
141 spectra for both AuBP84@Au and AuBP140@Ag (Figure 2a,b), reflecting the lower aspect ratio observed by microscopy. For
142 AuBP84@Au the L-LSPR was shifted from 800 nm toward 600-630 nm (5 μM to 40 μM Cys) (Figure 2a). In a similar way, in
143 AuBP140@Ag the L-LSPR was shifted from 940 nm toward 580-670 nm (1 μM to 100 μM Cys) (Figure 2b).

144 Along with the changes in the extinction spectra, when Cys was used an intense plasmonic circular dichroism (PCD) was
145 detected for both systems (Figure 2c,d). For AuBP84@Au, at 5 μM Cys abisignate peak appeared (Figure 2c). The positive
146 band between 500 nm and 600 nm was attributed to the T-LSPR, while the negative band between 600 nm and
147 700 nm was attributed to the L-LSPR. Increasing [Cys] to 10 μM provoked a reduction of the g-factor. When 20 μM Cys was
148 used the shift of the negative band between 600 nm and 650 nm was associated to the shifts of L-LSPR in the extinction
149 spectra (Figure 2a). When 40 μM Cys was used, a negative peak appeared at 374 nm. We attributed this peak to a previously
150 reported chiral Cys-Au(I) complex, formed as a result of the excess of Cys able to react with available Au(I) in solution.^{33,47}

151 For AuBP140@Ag, the g-factor spectra (Figure 2d) changed with different [Cys], partly due to the change in the extinction
152 spectra caused by the different morphologies. In the spectrum of AuBP140@Ag (Figure 2d), when 1 μM Cys was employed

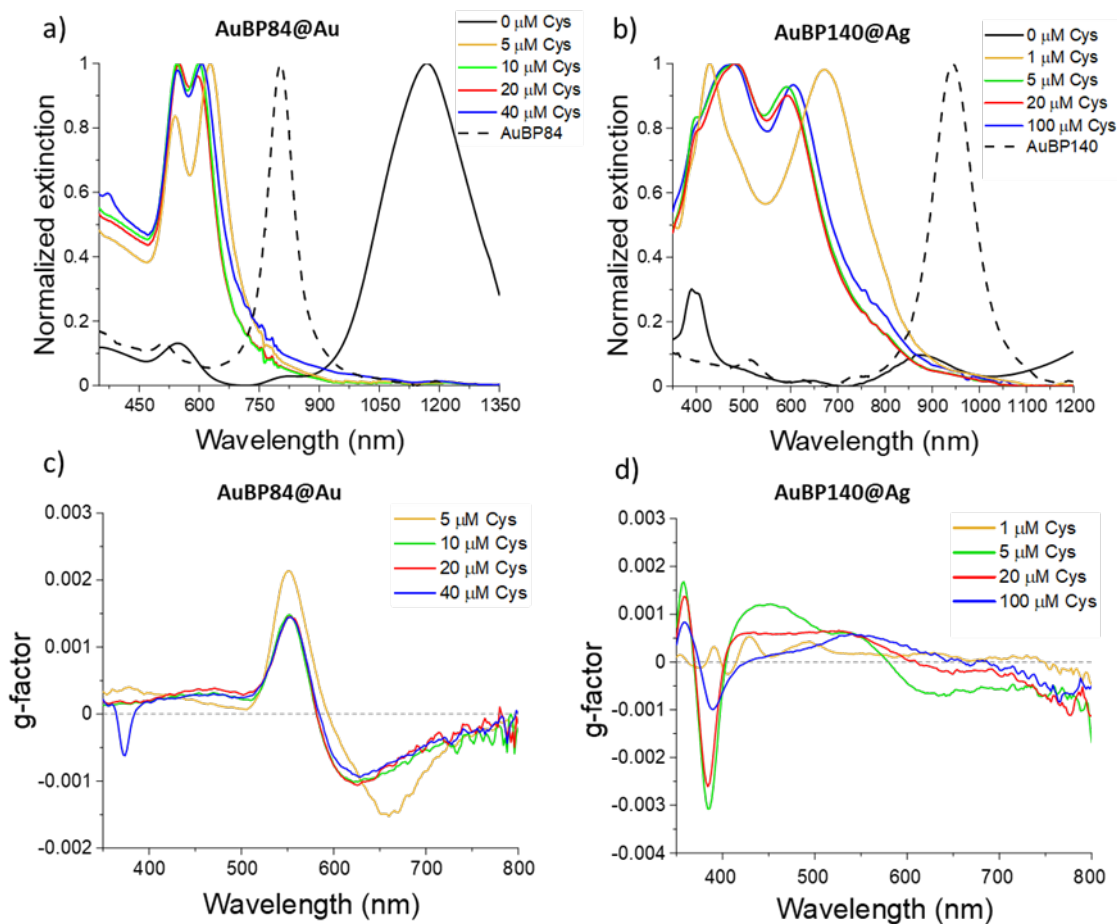


Figure 2. Effect of Cys concentration on the optical response. (a,b) Normalized extinction spectra of (a) AuBP84@Au and (b) AuBP140@Ag obtained at different Cys concentrations. (c,d) Calculated g-factor of (c) AuBP84@Au and (d) AuBP140@Ag obtained using different concentrations of Cys.

153 six broad bands with a relative low intensity were observed. When [Cys] was set from 5 μM to 20 μM , a predominant
 154 contribution in the spectrum appeared at 380 nm. When [Cys] was further increased to 100 μM , even if no relevant changes
 155 appear on the extinction spectra, the g-factor was observed to decrease.

156 For both AuBP140@Ag and AuBP84@Au systems when enantiomeric pure D-Cys or L-Cys (Figure 3a,b) was used, no
 157 difference on the extinction spectra was recorded. The CD spectra, instead, showed a mirror signal depending on the
 158 enantiomer used, confirming the role of Cys as chiral encoder. However, differently from the AuBP84@Au system, where the
 159 two contributions to the CD spectrum were easily attributed to L-LSPR and T-LSPR (Figure 3b), the CD spectra of the
 160 AuBP140@Ag feature a peculiar lineshape (Figure 3a). To identify the different contributions on the CD spectrum, the
 161 extinction spectrum of AuBP140@Ag synthesized at 20 μM Cys was simulated (Figure 3c,d) (see computational details in
 162 methods section). While blue-shifted with respect to experimental data (by <2 eV *i.e.* ~ 35 nm), the simulated spectra feature
 163 three main contributing bands to the extinction spectrum of AuBP140@Ag with the same morphology, *i.e.* those obtained
 164 using a [Cys] from 5 μM . As it is possible to see in Figure 3c,d the absorption peak at the highest wavelength is associated to
 165 a longitudinal plasmon band (L3) while the central peak is due to two transversal absorptions (T2, T3), one of which involves
 166 the tip of the Au core (T2). Moreover, as indicated by the surface charge distribution plots (Figure 3d), these T2, T3 and L3
 167 resonances had dipolar character, in contrast with the lowest wavelength peaks (T1, L1, L2) featuring a multipolar character
 168 for both longitudinal and transversal excitations, with T1 being more intense and showing predominant quadrupolar
 169 contribution. The presence of multipolar resonances in the low wavelength range, *i.e.* around the experimental peak at 400
 170 nm, was further confirmed by simulations of absorption spectra within a quasi-static approximation (Figure S4) and it was in
 171 agreement with other results present for similar systems.^{32,48} Notably, by simulating the absorption spectra of the Ag outer
 172 shell with (and without) the Au core (Figure S5) we observed that optical properties of the AuBP140@Ag objects were
 173 dominated by the outer Ag surface, with spectra being almost identical to those of the Ag particles, thus, with minor effects
 174 induced by the Au core. A similar analysis concerning the extinction spectrum and related surface charge densities for the

175 AuBP84@Au system is reported in Figure S17, showing a good agreement with experimental data and confirming the
 176 assignment of the L- and T-LSPR bands (see Figure 3b).
 177

178 The CD signals for AuBP140@Ag were then attributed according to the simulated extinction spectrum. The Figure 3a
 179 showed the superposition of the extinction and CD spectra along with the different attributions for AuBP140@Ag synthesized
 180 at 20 μ M Cys. The band centered at 630 nm in the CD spectrum was attributed to the L-LSPR (L3) while the broad band going
 181 from 400 nm to 580 nm to T2 and T3. The intense sharp peak at 380 nm was attributed to the multipolar resonances (T1, L1

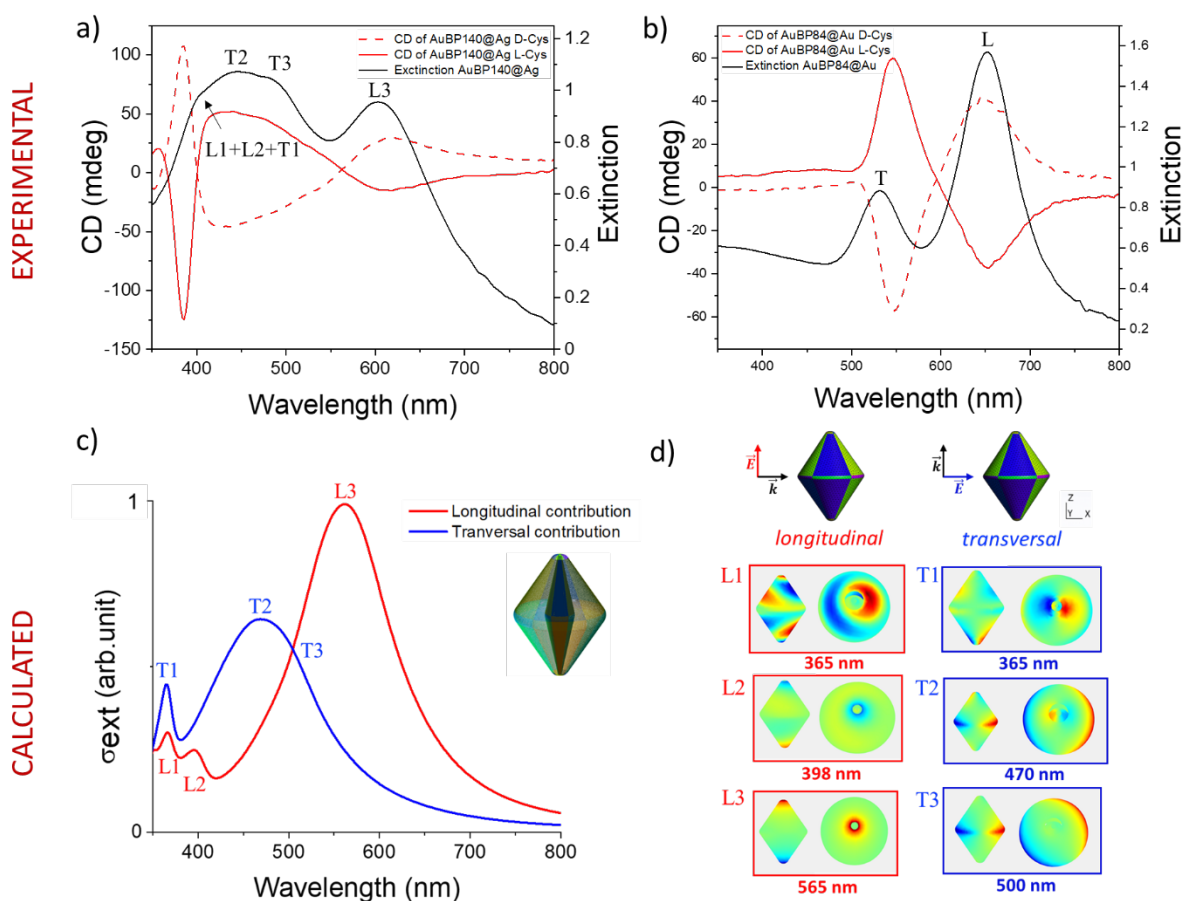


Figure 3. (a,b) Superposition of experimental extinction and circular dichroism spectra obtained in presence of L-Cys or D-Cys for (a) AuBP140@Ag and (b) AuBP84@Au. (c) Simulated extinction spectra of the AuBP140@Ag model structure due to an incident electric field oriented along either the transversal (blue curve) or longitudinal direction (red curve). The labels refer to the corresponding surface charges shown in panel d). (d) Color-scale representation of surface charge distributions induced by the EM field at selected wavelengths.

182 and L2) according to our theoretical calculations. The use of multipolar resonance was already suggested to be a viable way
 183 to obtain materials exhibiting a strong PCD and our results match with what predicted in the literature.⁴⁹⁻⁵¹

184 In order to better study the correlation between the CD and the extinction spectra we tried to vary the thickness of the
 185 metal shell for both systems (Figure 4). Thus, the initial concentration of AuBPs was varied (the concentration expressed in
 186 $[Au^0]$ and $[NPs]$ can be found in the Table T2 in the Supporting Information). For instance, reducing the initial number of
 187 AuBPs resulted in a redistribution of metal atoms available to form the shell among a smaller number of AuBPs, and thus in
 188 a thicker shell. For both systems, we noted that increasing the metal shell thickness led to more isotropic particles. This was
 189 because the metal shell deposition is predominant on the lateral side of the AuBPs for both systems.

190 For AuBP@Au, when 80 μ L was used, statistical analysis on TEM showed a length of 95 ± 5 nm and a width of 43 ± 5 nm
 191 that can be compared with the initial AuBP84 (84 ± 6 nm long and 26 ± 2 nm wide) (Figure 4c). It was also noted the
 192 appearance of a wavy surface on the lateral side along with facets formation on the tips. When 50 μ L was used, the previously
 193 observed gnocchi-like nanoparticles were formed. Well-shaped facets along the tips as well as an evident wavy surface on

194 the side were observed. A measured length of 97 ± 5 nm and a width of 53 ± 3 nm evidenced how the metal deposition, once
 195 tips were formed, was continued on the sides. The wavy surface on the lateral side is less pronounced when $30 \mu\text{L}$ was used
 196 and almost disappeared when $20 \mu\text{L}$ was used. The TEM measurements of the objects formed at $20 \mu\text{L}$, 99 ± 5 nm long and
 197 79 ± 5 nm wide, showed an almost isotropic structure. Thanks to the more symmetric geometry of the object, the preferred
 198 orientation on the TEM grid was no more on the flat side and it was possible to observe the pentagonal symmetry of the
 199 nanostructure formed (Figure 4c).

200 The superposition of the various extinction spectra confirmed this trend (Figure 4a). With $80 \mu\text{L}$ being used the L-LSPR was
 201 located at 678 nm and when the number of AuBPs was decreased, the peak progressively blue shifted and merged with the
 202 T-LSPR to form one single peak located at 567 nm. The maximum of the peaks in the superposition of the various CD spectra,
 203 followed faithfully the extinction spectra (Figure 4a). The broad negative peaks between 600 nm and 700 nm moved according
 204 to the L-LSPR while the positive peaks between 500 nm and 600 nm moved along with the T-LSPR. Interestingly, when $30 \mu\text{L}$
 205 of AuBPs was used, the intensity of the CD diminished considerably and was almost totally suppressed at $20 \mu\text{L}$, condition
 206 that caused the L-LSPR and T-LSPR to merge in the extinction spectrum. The simulation carried out by Govorov *et al.*⁵² showed
 207 the importance of anisotropy in the interaction between a molecule and plasmonic nanoparticles for PCD. Annulation of PCD
 208 signal due to increasing symmetry was also already observed experimentally.³³ Being the CD peaks of opposite signs when L-
 209 LSPR and T-LSPR get closer due to the reduction of aspect ratio, they merged to one peak and the final CD was completely
 210 suppressed.

211 For AuBP140@Ag when $50 \mu\text{L}$ of AuBP140 was used, a predominant deposition on the side of the AuBPs was observed
 212 (Figure 4d). The different contrast between Au and Ag on TEM allowed us to distinguish the tips of the AuBP core protruding
 213 outside the silver shell. Anyway, our simulations suggested that whether the inner AuBP was protruding outside the outer

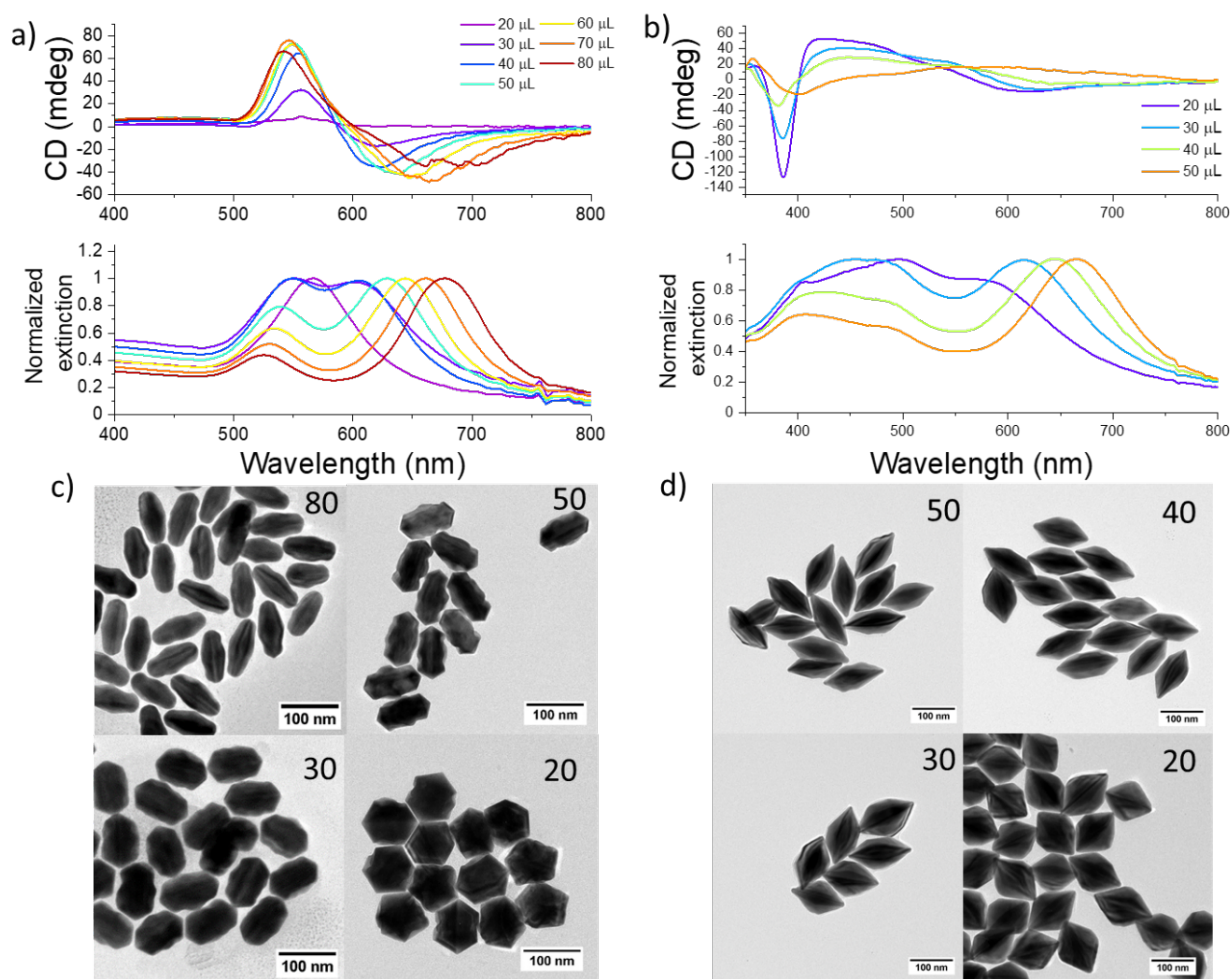


Figure 4. (a,b) Circular dichroism and extinction spectra of (a) AuBP84@Au and (b) AuBP140@Ag nanoparticles obtained by varying the volume of AuBPs suspension. (c,d) Corresponding TEM images of (c) AuBP84@Au and (d) AuBP140@Ag. The number in the upper right corner refers to the added volume in μL of AuBPs.

214 shell or completely included in the silver layer, did not affect the optical response of the overall system (Figure S6). When 50
215 μL , 40 μL , 30 μL and 20 μL of AuBPs was used, the width of the structures changed from 58 ± 3 nm, 66 ± 4 nm, 77 ± 5 nm to
216 94 ± 5 nm, respectively. The length, as expected, remained equal to the length of the AuBPs used as core (140 ± 8 nm). As a
217 consequence, the L3 was blue shifted when a minor number of AuBPs was used, moving from 650 nm (50 μL used) to 578 nm
218 (20 μL used) (Figure 4b). Moreover, at 20 μL , the T1 peak appeared at 400 nm as a shoulder of the broad band formed by
219 merging T2 and T3 resonances.

220 Simulated extinction spectra of AuBP@Ag with variable aspect ratios pointed out that the decrease of aspect ratio induces
221 a blue shift of L-LSPR and a red-shift of T-LSPR (Figure S7). Notably, the spectral position of the multipolar theoretical signal
222 remained invariant, in agreement with the experimental trends. In the superposition of the CD spectra, the band between
223 600 nm and 700 nm moved accordingly to L-LSPR. Differently to AuBP@Au, for AuBP@Ag a more isotropic structure did not
224 result in a total suppression of the CD. This was due to the apparition of a new contribution in the CD spectrum, deriving
225 mostly from the T1 and L1 peaks. The relative high intensity of this CD peak is thus due to his multipolar character. The use
226 of multipolar resonance was already suggested to be a viable way to obtain materials exhibiting a strong PCD⁴⁹⁻⁵¹ and it is
227 strongly confirmed here.

228

229 **Towards the origin of chirality.** The dipole-plasmon coupling effect between chiral molecules grafted on the surface of
230 the nanoparticles is a common accepted mechanism leading to PCD for plasmonic nanoparticles.^{12,13}

231 Moreover, Hou *et al.* advanced the hypothesis that for some core-shell systems, chiral molecules entrapped inside the NPs
232 could be also contributing to the PCD.³² In another study of the same group, AuNR@Au starfruit-like nanoparticles obtained
233 in presence of Cys showed no change in PCD when the L-Cys on surface was exchanged with D-Cys. Starting from this
234 evidence, it was suggested that either Cys entrapped at the interface in-between the Au-Au core-shell, as well as the Cys
235 distributed inside the lattice hotspots of the Au shell, could be the origin of PCD.³³ In a recently published paper,³⁵ the same
236 idea was taken up for a AuBP@Ag system showing PCD, where the presence of sulfur atoms inside the NPs was showed by
237 Energy Dispersive X-ray Spectrometry (EDS). Indeed, the presence of organic molecules inside metal core-shell nanoparticles
238 is discussed in literature.^{53,54}

239 In our case, the lack of clear chiral shapes and the *g*-factor values around 0.002-0.003 (Figure 2c,d) for AuBP@Au and
240 AuBP@Ag NPs, suggest that PCD response could result from electromagnetic coupling effect between Cys molecules and
241 plasmonic nanostructure. In order to explore this hypothesis, the effect on PCD of Cys molecule on the surface of the NPs
242 was evaluated. The exchange L-Cys with D-Cys on the surface was achieved but no change in the PCD was recorded (Figure
243 S8). To corroborate this result, Cys was removed from the surface by reductive desorption reaction in presence on NaBH_4
244 (Paragraph S.2 in the Supporting Information).⁵⁵ Also in this case the PCD response was still present after the NaBH_4 treatment
245 (Figure S9). The quantity of Cys released from the surface was then carefully quantified using a thiol-selective dye method
246 already employed in literature to determine Cys on AuNPs (Figure S10).¹⁸ The quantified amounts of Cys on the surface were
247 9.71 ± 0.65 pmol for AuBP84@Au and 10.94 ± 0.65 pmol for AuBP140@Ag. The Cys surface density for AuBP84@Au and
248 AuBP140@Ag was 0.0021 nmol/cm² and 0.0049 nmol/cm², respectively (Table T3 in the Supporting Information). According
249 to these results, we can affirm that Cys grafted on the surface is not responsible of the PCD.

250 The role of possible Cys entrapped inside the NPs on the PCD was evaluated. However, our attempts to localize the Cys
251 inside the NPs by NMR and EDS did not bring any significant evidence. The presence of molecules inside the nanoparticles is
252 usually evidenced by nanogaps directly observed in the TEM images. Here, HRTEM showed a continuous core-shell structure
253 (Figure S11, S12) without gap.

254 Regardless of the presence of Cys or not inside the NPs, since common explanations for core-shell systems on PCD origin
255 could be rather incomplete, we proceeded to study its role on PCD using some conceptually simple experiments.

256 AuBP140@Ag nanoparticles were synthesized taking care to deposit the silver shell in two steps. A first incomplete shell
257 was deposited in presence of L-Cys. Then, the shell deposition was completed in presence of D-Cys to form
258 AuBP140@AgL@AgD (Figure 5a). More in detail, 30 μL of AuBPs was employed to synthesize AuBP140@Ag-L, in standard
259 conditions, in presence of L-Cys. Such incomplete structures are the same ones observed using 30 μL of AuBPs in Figure 4.
260 The so-synthesized NPs were then washed three times by centrifugation, to remove the excess of L-Cys still present in the
261 growth solution, and re-dispersed in CTAC. Then, the silver shell deposition was completed using the same conditions as
262 before but this time introducing D-Cys. TEM images (Figure 5c) as well as extinction spectra (Figure S13) confirmed the correct
263 formation of the core-shell nanostructures. The CD spectrum recorded for AuBP140@AgL@AgD (Figure 5b) was almost mirror
264 to the AuBP140@AgL@AgL (synthesized using L-Cys in both steps and used as control). The small discrepancies, like position
265 and broadness of the peaks, were attributed to a slightly different position of the peaks in the extinction spectrum (Figure

266 S13). This evidence permitted to highlight the major role of the external part of the shell with respect to the inner part of the
 267 particle on the PCD properties.

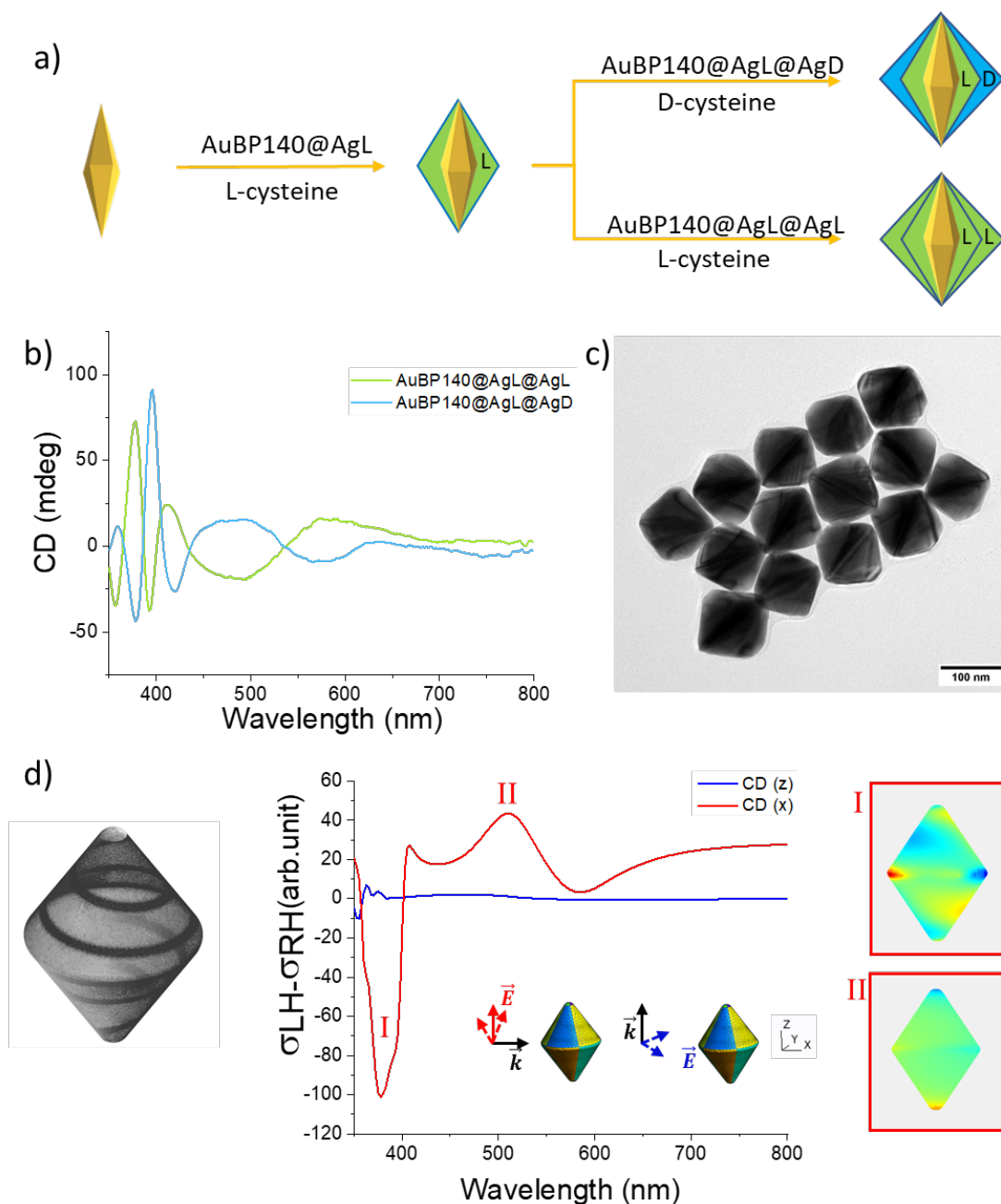


Figure 5. (a) Scheme representing the two steps synthesis with the inversion of the Cys enantiomers during the formation of the outer shell. (b) Circular dichroism spectra of the nano-objects obtained. (c) TEM image of AuBP140@AgL@AgD. (d) Simulated CD response of the chiral AuBP140@Ag model structure obtained by introducing a spiral motif on the Ag surface (shown on the left) and corresponding surface charges.

268 We can exclude that L-Cys entrapped in between Au core and Ag shell is at the origin of PCD as previously proposed in a
 269 similar system.³² If this was the case, the final CD spectrum of AuBP140@AgL@AgD should have shown a similar trend as
 270 AuBP140@AgL@AgL, when L-Cys was used in both steps. Moreover, a similar argumentation can be extended to exclude the
 271 possible contribution of the L-Cys entrapped inside the crystal lattice of the first silver shell, with a mechanism similar to what
 272 proposed for this system.³⁵ If the Cys entrapped inside the hotspots of the Ag crystal lattice was responsible for the PCD,
 273 having half of the silver shell formed in presence of L-Cys and the other half with D-Cys should have shown a strong impact
 274 on the final CD spectrum. From this result we can suggest that: (i) only the Cys present in hotspots near the surface contributes
 275 to PCD or (ii) a chiral shape of the particles or chiral surface patterns, difficult to visualize with routine TEM or SEM analysis,

276 were present. In order to evaluate the latter hypothesis from a theoretical point of view, we built a AuBP140@Ag model with
 277 a chiral surface pattern obtained numerically by thickening the external surface mesh around a spiral pattern along the
 278 longitudinal axis (Figure 5d).

279 As shown in Figure 5d, the simulated CD spectrum of the AuBP140@Ag model with pattern features one main peak below
 280 400 nm (when the light electric field rotates in the z-y plane while the wave is travelling along x, see cartesian reference frame
 281 in Figure 5d) that had a multipolar character, as indicated by the charge distribution, in agreement with the multipolar signal
 282 observed experimentally (see Figure 4b). A signal with opposite sign with respect to the multipolar one is found around 500
 283 nm, possessing a dipolar character, while transversal CD signals are absent. The simulated CD spectra, despite the crude chiral
 284 surface modeling, are in qualitative agreement with the experimental data for AuBP140@Ag particles obtained (see Figure
 285 4b), indicating that chiral patterns present on the external Ag surface could provide PCD signals such as those obtained
 286 experimentally. Additional AuBP140Ag model structures, whose dimensions were chosen from the extreme tails of TEM

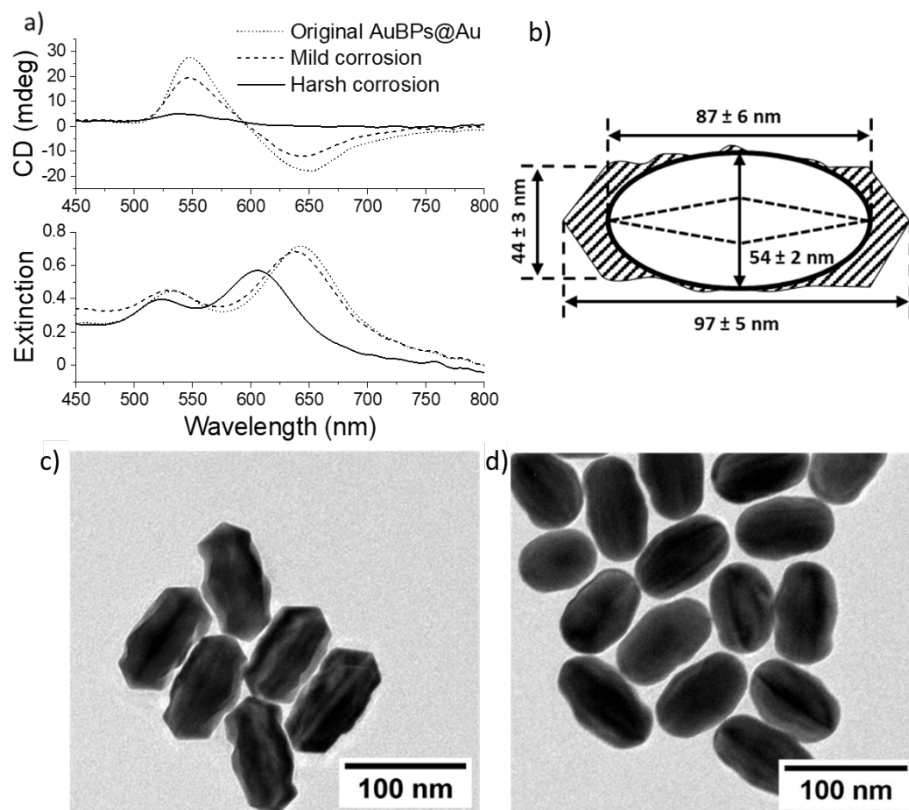


Figure 6. (a) Circular Dichroism and Extinction spectra for different corrosion conditions. (b) Schema reporting the corroded area of gold from the original AuBP84@Au. The dimensions of the inner AuBP (dashed line) and the particles after harsh corrosion (solid line) are also represented. (c,d) TEM images of (c) AuBP84@Au and (d) AuBP84@Au after harsh corrosion.

287 statistical distribution previously mentioned and featuring a similar spiral motif to that of Figure 5d, were considered for
 288 further calculations. The results, shown in Figure S16 in the SI, clearly indicate that the different structures present similar CD
 289 responses.

290
 291 In order to corroborate this claim, the importance of the external part of the metallic shell to PCD was further investigated
 292 experimentally also in AuBP84@Au systems (Figure 6). AuBP84@Au were partially corroded to study the impact on PCD by
 293 removing the superficial Au shell. In addition, the corrosion of the surface brought inner layers of metallic shell to the surface,
 294 allowing us to study their contribution to PCD by removing the contribution of the uppermost surface. We chose
 295 tetrachloroauric acid as oxidizing agent, which is commonly employed in etching methods for smoothing gold
 296 nanoparticles.^{56,57}

297 Tuning the Au³⁺ quantity introduced in the reaction allowed us to have a very good control over the etching process. A first
 298 mild etching was made by adding 2.5% of Au³⁺/Au⁰_{shell}, at room temperature. A second harsh etching was made adding 10%
 299 of Au³⁺/Au⁰_{shell} at 45 °C. As shown in Figure 6a, the mild etching resulted in a shift in the extinction spectrum of the L-LSPR

300 from 644 nm to 638 nm. In the CD spectrum the impact was significant with a loss of 30% of the signal intensity. When harsh
301 conditions were used, the extinction spectrum showed a more pronounced shift of the L-LSPR from 644 nm to 604 nm
302 followed by almost total suppression of the PCD bisignate signal.

303 TEM images before and after etching (Figure 6c,d) showed that the surface asperities were corroded to generate smooth
304 structures. From statistical analysis of the lengths (see Figure 6b) it was possible to observe that the majority of the gold shell
305 deposited was still present in the structure. The strong PCD variation intensity, when the surface was corroded, confirmed
306 the importance of the external structured layers in the PCD. Moreover, this result suggested that Cys entrapped deep inside
307 the metal shell hotspots, as well as Cys at the interface, was not participating to PCD. Since most part of the metal shell was
308 still present, removing few nanometers of the surface should not have played such a significant role on the observed spectra.
309 The importance of the superficial part of the shell on PCD led us to investigate a possible different role of Cys.

310 To bring in additive evidence that Cys could have an impact on the final shape, AuBP84@Ag were synthesized in presence
311 of a racemic mixture of L-Cys and D-Cys. As expected, the CD spectrum showed the suppression of the PCD (Figure S14). More
312 interesting and not expected was the difference in the extinction spectra when the racemic mixture was used. The NPs
313 synthesized using pure L-Cys or D-Cys possessed nearly identical extinction spectra (Figure 7a). while when racemic Cys was
314 used, an evident difference was present in the extinction spectrum. The TEM observation confirmed that a different shape
315 was present depending if an enantiomeric pure Cys was used or not (Figure 7b,c). When enantiomeric pure L or D-Cys
316 was used, the formed objects were similar to the nanoparticles described above with well-defined facets, while using racemic Cys
317 led to the formation of more spherical particles. To the best of our knowledge the difference in reactivity was not observed
318 elsewhere for this kind of systems and clearly bring in evidence that contribution of a chiral shape of the particles to PCD
319 should not be excluded.

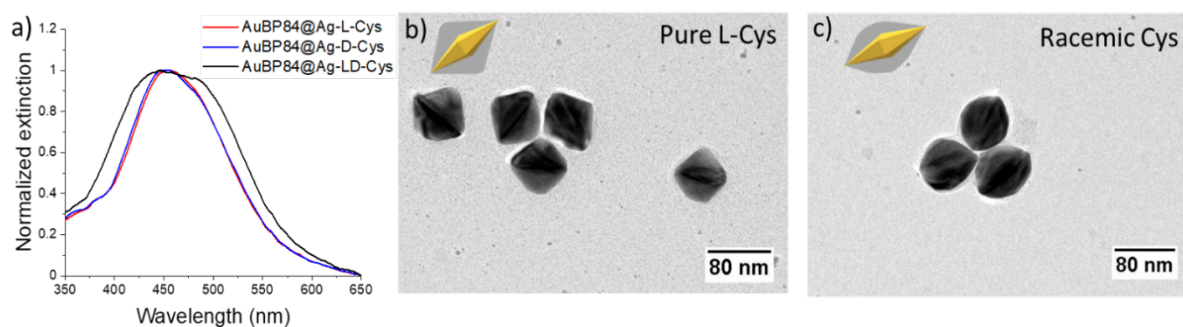


Figure 7. (a) Extinction spectra of AuBP84@Ag obtained with L, D or racemic Cys. (b,c) TEM images of AuBP84@Ag obtained with (b) pure L-cys and (c) a racemic mixture of Cys.

320

321 CONCLUSIONS

322 In this work we present AuBP@Au and AuBP@Ag nanoparticles with opto-chiral response obtained using gold bipyramids
323 as core. Cysteine, a small thiolated molecule, is used as shaping agent and chiral encoder during the deposition of the Ag or
324 Au metal shell. Cysteine is found to have a strong impact on the morphology in both AuBP@Au and AuBP@Ag systems,
325 preventing the growth of the Ag or Au shell along the longitudinal direction. Moreover, plasmonic circular dichroism is
326 observed for both AuBP@Ag and AuBP@Au systems. The presence of multipolar resonance for AuBPs@Ag suggests that
327 silver is a promising candidate to obtain a strong plasmonic circular dichroism response. Moreover, resonance modes,
328 anisotropy and monodispersity seem relevant conditions to achieve a strong circular dichroism. Concerning the role of
329 cysteine in plasmonic circular dichroism, the crucial importance of the superficial part of the metal shell suggests that the
330 common hypothesis presents in literature could be incomplete. In our system the cysteine entrapped in the interface
331 between the AuBPs and the metal shell, as well as the one encapsulated in the inner metal shell lattice, is not contributing to
332 the plasmonic circular dichroism. These results, supported by theoretical simulations, along with the observed impact of
333 enantiomeric ratio on the final shape, prove that a chiral shape or chiral patterns induced by cysteine during the synthesis in
334 this kind of systems should be taken in consideration. Further investigation will focus on the detailed nanostructure (HRTEM,
335 Electron Tomography), the single object spectroscopy and the localization of the cysteine in the external part of the metal
336 shell.

337

338 METHODS

339 Hexadecyltrimethylammonium bromide (CTAB, 98%, ref. 10146269), tetrachloroauric acid hydrate ($\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$, 99.9%),
340 silver nitrate (AgNO_3 , 99.9995%), and 1,1,3,3-tetramethylguanidine (99%) were purchased from Alfa Aesar. Powder
341 hexadecyltrimethylammonium chloride (CTAC, 98%), sodium borohydride (NaBH_4 , 98%), 8-hydroxyquinoline (99%), catechol
342 (98%), L-ascorbic acid (AA, 99%) from Sigma-Aldrich. Citric acid monohydrate (99.5%) was purchased from Merck. L-cysteine
343 (L-Cys, 98%) was purchased from Acros Organics. D-cysteine (D-Cys, 98%) was purchased from ChemCruz. Sodium hydroxide
344 (NaOH , 97%) and absolute ethanol were purchased from Carlo Erba. All aqueous solutions were prepared in Milli-Q distilled
345 water (18.2 $\text{M}\Omega\cdot\text{cm}$)
346

347 **Characterization.** TEM images were acquired using a JEOL 2100F equipped with a Gatan ultrascan 1000 camera operating
348 at 200 kV while scanning electron microscopy images (SEM) on a MERLIN Compact VP microscope (ZEISS). TEM statistics were
349 acquired measuring over 200 objects with the help of ImageJ software. High-resolution TEM (HRTEM) was performed on a
350 JEOL 2200FS with a point-to-point resolution of 0.23 nm. The extinction spectra were recorded with a PerkinElmer UV-vis-
351 NIR Lambda 750 spectrometer using 1 cm PMMA cuvette for measurements between 350 nm and 1350 nm and quartz 1 mm
352 cuvette for measurements above 1400 nm. Simultaneous measurements of extinction and circular dichroism (CD) spectra
353 were recorded using a J-1700 CD spectrophotometer (JASCO) using 1 cm path PMMA or quartz cuvette. Kuhn's dissymmetry
354 factor (*g*-factor) was calculated according to the following equation:
355

$$g\text{-factor} = \frac{CD}{32980 \cdot Ext}$$

356
357
358 With *CD* in mdeg and *Ext* the extinction intensities. Dissymmetry *g*-factor is dimensionless and permits to compare
359 chiroptical activity between different chiral systems.
360

361 **Synthesis of AuBPs.** The AuBPs used as core were prepared according to a protocol fully described by Chateau *et al.*^{37,38}
362 Two main batches of AuBPs were synthesized, AuBP84 and AuBP140 (see [Supporting Information](#) for synthetic details of the
363 AuBPs core).
364

365 **Synthesis of AuBP@Ag.** In a typical synthesis, 20 μL ($[\text{Au}^0] = 0.5 \text{ g/L}$) of AuBP84 or AuBP140 was added in a 4 mL vial
366 containing 1 mL of 30 mM CTAC. Then, 2 μL of L-Cys (10 mM) was added, followed by 100 μL of AgNO_3 (5 mM) and 100 μL of
367 AA (20 mM) and mixed manually to homogenize the mixture. Due to the instability of Cys and AA in diluted aqueous solution,
368 these solutions were prepared and used the same day to improve reproducibility. The mixture was then heated for 30 min in
369 a water bath at 75°C. The color of final suspension was red with an intense yellow scattering. The obtained AuBP@Ag NPs
370 were then washed with water by centrifugation at 8k rpm for 5 min. A final redispersion was done in 1 mM CTAC. To store
371 the NPs, they can be left in the raw reaction mixture and purified when necessary. The particles stored in this condition are
372 stable at least one month after the synthesis.
373

374 **Synthesis of AuBP@Au.** In a 4 mL vial a seed solution was prepared by adding 50 μL ($[\text{Au}^0] = 0.5 \text{ g/L}$) of AuBP140 or
375 AuBP84 to 1 mL aqueous solution of 100 mM CTAB followed by 2 μL of L-Cys (10 mM). In a different vial, the growth solution
376 was prepared adding in the following order, 20 μL of HAuCl_4 (25 mM), 20 μL of AgNO_3 (5 mM) and finally 50 μL of AA (20 mM)
377 to an aqueous solution of 1 mL of 100 mM CTAB at room temperature and mixed manually to homogenize the mixture. Due
378 to the instability of Cys and AA in diluted aqueous solution, these solutions were prepared and used the same day to improve
379 reproducibility. When AA was added, the color of the solution changed from orange/yellow to totally transparent. Then, 1
380 mL of the growth solution was incorporated in the seed suspension and mixed manually. The mixture was then heated in a
381 water bath for 1 h at 70°C to start the reaction. The color of the final suspension was violet with an intense red scattering.
382 The obtained AuBP@Au NPs were then purified by centrifugation at 8k rpm for 5 min twice and redispersed in 1 mL of 5 mM
383 CTAB. The particles remained stable at least during one month after purification.
384

385 **Synthesis of AuBP140@AgL@AgD.** A volume of 30 μL of AuBP140 ($[\text{Au}^0] = 0.5 \text{ g/L}$) was added in a 4 mL vial containing
386 1 mL of 30 mM CTAC. Then, 2 μL of L-Cys (10 mM) was added, followed by 100 μL of AgNO_3 (5 mM) and 100 μL of AA (20 mM)
387 at room temperature and mixed manually to homogenize the mixture. The mixture was then heated in a water bath for 30
388 min at 75°C. The obtained AuBP140@AgL were then washed by centrifugation (8k rpm, 5 min) three times to remove all the
389 excess of L-Cys still present in the solution and finally redispersed in 1 mL of 30 mM CTAC. Then, 2 μL of D-Cys (10 mM) was

390 added, followed by 100 μL of AgNO_3 (5 mM) and 100 μL of AA (20 mM). The obtained AuBP140@AgL@AgD NPs were then
391 purified by centrifugation and redispersed in 1 mM CTAC.

392

393 **AuBP84@Au etching.** After the synthesis in the conditions described above, AuBP84@Au were purified by centrifugation
394 and redispersed in 2 ml of CTAB (5 mM). To etch them, 1 mL of the suspension was introduced in a 4 mL vial containing 1 mL
395 of CTAB (5 mM) and 2 μL HAuCl_4 (6.25 mM) and incubated for 10 minutes at room temperature (mild conditions). The CD and
396 extinction spectra were then measured. 15 min after the first HAuCl_4 addition, 6 μL of HAuCl_4 was added and the mixture was
397 heated in an oven for 10 min at 45°C (harsh conditions). The CD and extinction spectra were then acquired.

398

399 **Computational details.** Computations were performed using the MNPBEM toolbox of Matlab,⁵⁸ an implementation of
400 the Boundary Element Method (BEM) developed specifically for metal nanoparticles.⁵⁹ This approach, employing classical
401 electrodynamics, has been proven very effective for simulation of AuBPs (obtained from pentatwinned seeds) optical
402 properties, as demonstrated in a previous work.⁶⁰ Here, our previous modeling strategy is extended to model the
403 AuBP140@Ag nanoparticles with 5-fold symmetry bipyramidal outer Ag shell, *i.e.* nano-objects obtained for [Cys] ranging
404 from 5 μM to 100 μM . We used two nested surface meshes: an inner surface representing the Au pentatwinned core and an
405 outer surface representing the silver shell. The surface tip of the outer shell is cut off to leave an Au-exposed tip, as indicated
406 by TEM images of these objects, in such a way that the inner and outer surface meshes are distant enough to avoid numerical
407 errors due to diverging matrix elements. Regarding this last point, we also tested how the tips geometrical features affect the
408 optical response of the overall system and it turned out that they do not significantly affect it (Figure S6). The dielectric
409 functions of Au and Ag are taken from P. B. Johnson and R. W. Christy⁶¹ and the refractive index of the surrounding medium
410 was set to 1.33 (bulk water). The geometrical data of the AuBP140@Ag model structure have been extracted from one
411 measured reference particle observed on the TEM image of the samples with [Cys] of 20 μM and 20 μL of AuBPs. The height
412 of the NPs was set at 134 nm, while the width of the outer shell and inner core at 99 and 32 nm respectively. Starting from
413 this reference model, analogous models have been constructed to simulate the effect of aspect ratio change (with various
414 base sizes at constant length, as documented in the Supporting Information, Figure S7). The quantities computed are the
415 extinction cross-sections to simulate the extinction spectra and the surface charge distributions at given energies, allowing
416 visualization of the excitation character. Additional structures, whose dimensions were chosen to account for the whole
417 statistical distribution in TEM images of the 20 μL sample (Figure 4d), were tested as well (Figure S15) and they showed no
418 significant deviations.

419 A similar modelling strategy has been adopted for AuBP84Au, where the detailed geometrical parameters of the
420 inner/outer structures can be found in Figure 6b and the related simulations are reported in Figure S17.

421

422 In order to perform a qualitative test of the role of surface chirality, a chiral asymmetry is induced artificially, thickening
423 the mesh density around a spiral pattern onto the surface of the object (Figure 5d). This is not geometrical chirality, but it
424 allows to introduce it regardless of the symmetrical features of the model. The simulated CD spectra have been computed
425 using the difference in extinction cross-sections of left-handed and right-handed circularly polarized light. The additional
426 structures based on TEM statistical analysis previously mentioned were also tested for surface chirality (Figure S16).

427

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434

435 SUPPORTING INFORMATION AVAILABLE

436 Supporting Information: Additional experimental details, including electron microscopy images, methods and spectra.

437

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