



Supporting Information

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Materials and Methods

Chemicals: $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (99.99% (metals basis)), and *L*-Cystine hydrochloride (*L*-2cys, 98%) were purchased from Alfa Aesar. Ascorbic acid (AA) was purchased from Acros Organics. AgNO_3 (>99.9%) was purchased from Roth. (*R*)-(+)-1,1'-binaphthyl-2,2'-diamine (*R*-BINAMINE, 99%), (*S*)-(–)-1,1'-binaphthyl-2,2'-diamine (*S*-BINAMINE, 99%), cetyltrimetylammonium chloride (CTAC, >98.0%), cetyltrimethylammonium bromide (CTAB; 99%), silver nitrate (AgNO_3 ; $\geq 99.0\%$), *n*-decanol (for synthesis; $\geq 99.0\%$), sodium borohydride (NaBH_4 ; 99%), and ascorbic acid (AA; $\geq 99\%$) were all purchased from Sigma-Aldrich. Hydrochloric acid (HCl; ACS, ISO grade, 3% w/v) was sourced from Scharlau. All reagents were used as received without further purification. Milli Q water was used to prepare solutions.

Synthesis of pentatwinned Au nanorods (PT-Au NRs): Pentatwinned nanorods were synthesized using a method adopted from the literature.^[30] In general, a two-step synthesis involving the preparation of twinned Au seeds and larger rods was implemented. To prepare pentatwinned Au seeds, a 0.05 M HAuCl_4 solution (50 μL) was added to 10 mL of 50 mM CTAC and 5 mM citric acid. After 30 minutes, a solution of a 25 mM NaBH_4 solution (250 μL) was quickly added to the mixture. After a further 2 minutes, the seeds are aged for 90 min at 80 °C with stirring to encourage twinning. For nanorod growth, a 0.05 M HAuCl_4 solution (125 μL) was mixed with 50 mL of 8 mM CTAB. The mixture was stored at 20 °C for at least 15 minutes, to allow for complete complexation between the Au^{3+} and CTAB. After this time, a 0.1 M solution of AA (125 μL) was added, followed by 100 μL of pentatwinned Au seeds ($\text{Au}^{3+}/\text{Au} = 1.25$). The reaction mixture was left undisturbed overnight, and then centrifuged at 3000 rpm for 10 min and washed with 10 mM CTAC thrice.

Synthesis of single-crystalline Au nanorods (SC-Au NRs): Single-crystalline nanorods were synthesized using a method adopted from the literature.^[29] In brief, a three-step synthesis involving the preparation of Au cluster seeds, mini rods, and larger rods was implemented. To prepare the Au cluster seeds, a 0.05 M HAuCl_4 solution (200 μL) and 100 μL of a 0.1 M AA solution were added to 20 mL of a 50 mM CTAB and 13.5 mM *n*-decanol solution, in a 50 mL glass beaker at 25–27 °C. A colorless solution was obtained. After 1–2 min, 800 μL of a freshly prepared 0.02 M NaBH_4 solution was injected under vigorous stirring. Excess borohydride was consumed by aging the seed solution for at least 60 min at 25–27 °C, prior to use. Then Au mini rods were synthesized by the following protocol: 2400 μL of 0.01 M AgNO_3 , 21 mL of 1 M HCl, 3000 μL of 0.05 M HAuCl_4 , and 3900 μL of 0.1 M AA were added to 300 mL of a 50 mM CTAB and 13.5 mM *n*-decanol solution, at 25 °C. Then, 18 mL of the seed solution was added under stirring. The mixture was left undisturbed at 25 °C for at least 4 h. The longitudinal LSPR of the small anisotropic nanocrystals at this point should be located at 725–730 nm. The obtained small anisotropic seeds were centrifuged at 14000–15000 rpm for 45–60 min. After washing, the final Au^0 concentration of Au mini rods was fixed to 4.65 mM ($\text{Abs}_{400\text{nm}}$: 1, optical path of 1 mm). Larger SC-Au NRs were then synthesized by the following steps: 3000 μL of 0.01 M AgNO_3 , 1000 μL of 0.05 M HAuCl_4 , 800 μL of 0.1 M AA, and a certain amount of 1M HCl solution were added to 100 mL of a 50 mM CTAB and 11 mM *n*-decanol solution. After vigorous stirring, 500 μL of the Au mini rods was added into the mixture and stirred. The mixture was then left undisturbed at 35 °C for at least 4 h, and subsequently centrifuged at 8000 rpm for 15 min and washed with 10 mM CTAB solutions.

Chiral growth of PT-Au NRs and SC-Au NRs: The methods were adopted from the literature.^[16,26] The multi-step synthesis protocol is described in the following: the concentration of PT-Au NRs and SC-Au NRs was adjusted to 0.8 mM, according to the optical absorbance at 400 nm. Then 1.9 mL of CTAC solution (40 mM) was poured into a tube, followed by addition of 5 μ L of HAuCl₄ (5 mM) and 0.2 mL of AA (0.1 M). The solution was sonicated for 30s. Then, 30 μ L of L-2cys (2.5 μ M) was added into the PE tube, followed by addition of 10 μ L of seed solution, shaking several times and store in a water bath at 25 °C (this step is called as the first addition). After 50 min, 5 μ L of HAuCl₄ (5 mM) was added into the PE tube. The addition was repeated several times, and the temperature of the water bath could also be tuned according to the growth requirements. After the 6 HAuCl₄ addition steps, the temperature of the water bath was decreased to 16 °C. After 9 additions, the PE tube was centrifuged (6000 rpm, 5 min) and washed twice with H₂O. The obtained particles were dispersed in H₂O. The sizes of the chiral products were significantly different when using different seeds. For the chiral particles obtained from SC-Au NRs we measured an average particle length of 109.2 ± 7.5 nm and average width of $61.4 \text{ nm} \pm 4.7$ nm (for optical characterization) and 154.6 ± 11.5 nm x 77.9 ± 7.8 nm (for electron tomography), which depended on the size of the starting SC-Au NR. On the other hand, an average length was determined of 179.5 ± 20.1 nm for the particles obtained from PT-Au NRs, but we hesitate to indicate accurate values for their width, given their ill-defined lateral morphologies.

For chiral particles prepared using the micelle-directed strategy, single-crystal or pentatwinned achiral seeds were first incubated overnight in a chiral solution of 50 mM CTAC and 1.25 mM *R*- or *S*- BINAMINE. A typical chiral synthesis was prepared in an Eppendorf tube at a total volume of 1 mL, using 500 μ M BINAMINE, 20 mM CTAC, 500 μ M HAuCl₄, 160 mM ascorbic acid, and 31.25 μ M achiral seeds (Au₀). Seeds and ascorbic acid were sequentially added, and the tube was immediately shaken before leaving for 30 minutes at room temperature. Chiral particles were centrifuged at 3000 rpm for 10 minutes and resuspended in MILLIPORE-grade water. This process was repeated twice to separate chiral products from excess reagents and non-chiral reaction byproducts. The optical spectra for both SC and PT products made in this way included a single broad extinction peak around 580 nm, which trailed off into the NIR range. The obtained wrinkled rods had average dimensions of 134.4 ± 8.3 nm x $65.1 \text{ nm} \pm 5.6$ nm for chiral SC-Au NRs, and 182.9 ± 11.2 nm x $76.2 \text{ nm} \pm 2.9$ nm for chiral PT-Au NRs.

Characterization: A JEOL 2200FS HRTEM operated at 200 kV, was used to perform bright field and high-angle annular-dark-field (HAADF) scanning TEM (STEM). Atomic resolution HAADF-STEM images were acquired using a probe-corrected Titan Themis microscope operated at 300 kV. Tilt-series for tomography were acquired typically over $\pm 75^\circ$ in 3° or 2° increments for atomic resolution electron tomography measurements or conventional tomography measurements, respectively. A Cary 50 UV-Visible Spectrophotometer from Agilent Technologies, and a JASCO J-815 Circular Dichroism (CD) spectropolarimeter were used for UV-Vis and CD spectroscopy, respectively.

Electron tomography reconstructions: The tilt-series were aligned with a combination of in-house Matlab code to perform cross-correlation and using the cSAXS Matlab package to perform vertical-mass fluctuation and projection-matching alignments with sub-pixel accuracy.^[35] 3D reconstructions were computed with an in-house method using a constrained version of the SIRT algorithm,^[34] or with the standard expected maximization (EM) algorithm using the Astra toolbox 2.1 for Matlab.^[37,38]

Helicity calculation: Helicities and helicity plots were calculated using previously established definitions and methods.^[27,39] The surface of the NR was extracted by manually segmenting the tomographic reconstructions. The normal vector of the surface elements was then used to calculate the orientation (or inclination) of each element with respect to the major axis of the NR. For each NR, helicity functions $H(\alpha, \rho)$ and total helicity H_{tot} were calculated, whereby helicity is defined as the integral of orientation angles over the NR surface. We attribute a positive helicity value to surfaces with dominantly right-handed orientations and a negative helicity to surfaces with dominantly left-handed orientations. The helicity function $H(\alpha, \rho)$ is a distribution mapping a helicity value for a cylindrical section at radius ρ and surface elements of orientation α . H_{tot} integrates the entire surface at all possible orientations, resulting in a scalar value where -1 corresponds to a perfect left handed helix, +1 corresponds to a perfect right-handed helix and 0 indicates no helical character and thus no dominant orientation of the surface elements.

Dominant wrinkle orientation: To track the dominant wrinkle orientation, the 3D reconstructions were sliced to obtain tomograms going through the wrinkled corona, typically 20-30 nm away from the center of the NRs, for a range of rotation angles (see the schematized pipeline in **Figure S13**). The OrientationJ plugin for ImageJ/FIJI was then used to calculate the dominant orientation in a central subarea of these rotational tomograms. Details about the plugin can be found elsewhere.^[40,41] Briefly, the dominant orientation is calculated as the angle of the first eigenvector of the gradient structure tensor matrix.^[42]

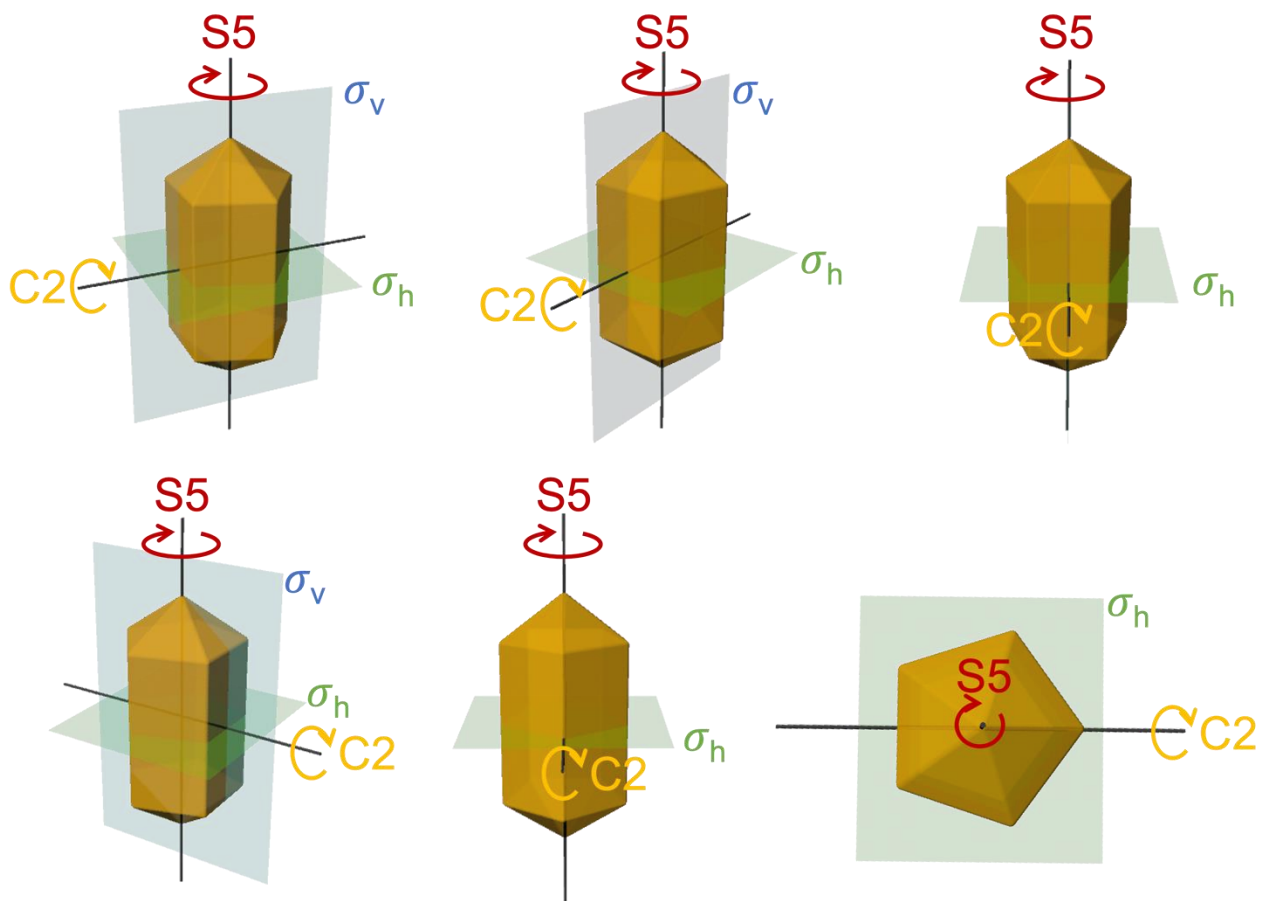


Figure S1. Main symmetry elements of a PT-Au NR along different observation angles.

Due to the existence of five twin planes, the symmetry of PT-Au NR can be very different to that in single-crystalline fcc lattices, i.e., not a subset of the $\frac{4}{m}\bar{3}\frac{2}{m}$ symmetry. The symmetry elements of a PT-Au NR contain a S5 main improper rotation axis (marked in red) with 5 perpendicular C2 axes (marked in orange), 5 vertical mirror planes (σ_v , marked in blue), and one horizontal mirror plane (σ_h , marked in green). Only one C2 axis and one vertical mirror plane (σ_v) are shown here for simplicity, the rest 4 C2 axes and 4 vertical mirror planes can be constructed according to the S5 axis. Hence, the structure belongs to the D5h point group, according to the Schoenflies notation, which is equivalent to the $(\bar{10})m2$ symmetry in the Hermann–Mauguin notation.

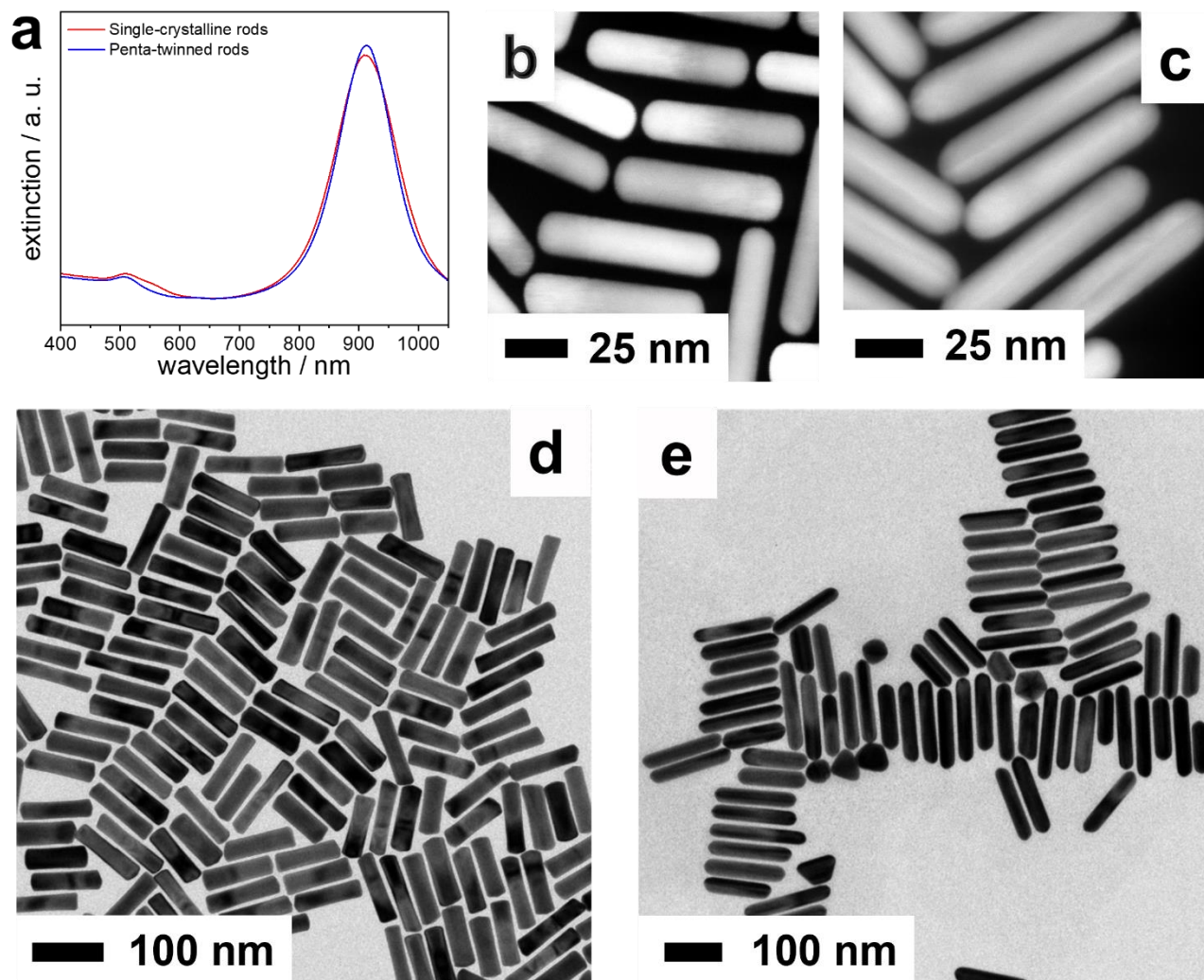


Figure S2. (a) Extinction spectra of SC- and PT-Au NR seeds used in the chemically-induced protocol; (b, c) HAADF-STEM images of SC- and PT-Au NR seeds, respectively.

The SC-Au NRs were 75.4 ± 6.3 nm long and 15.6 ± 1.6 nm wide ($AR \sim 4.8$), whereas PT-Au NRs had dimensions of 90.9 ± 4.2 nm in length and 19.3 ± 1.3 nm in width ($AR \sim 4.7$). (200 particles were measured, error bars indicate the standard deviation)

(d,e) TEM images of SC-Au (a) and PT-Au (b) NR seeds, respectively, used in the chiral micelle growth protocol. The SC-Au NRs were 101 ± 17.3 nm long and 29.0 ± 5.3 nm wide ($AR \sim 3.5$), whereas PT-Au NRs had dimensions of 122 ± 30.4 nm in length and 31.3 ± 6.5 nm in width ($AR \sim 3.9$).

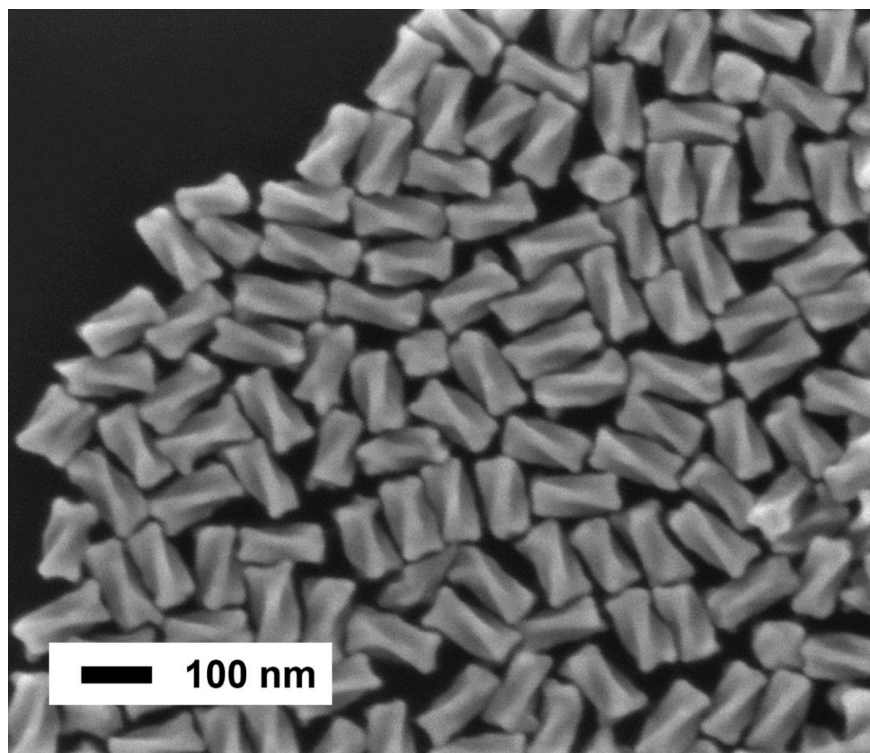


Figure S3. Representative scanning electron microscopy (SEM) image of chiral products obtained by a multi-step growth of SC-Au NRs, in the presence of *L*-2Cys. A right-handed helical structure can be easily identified.

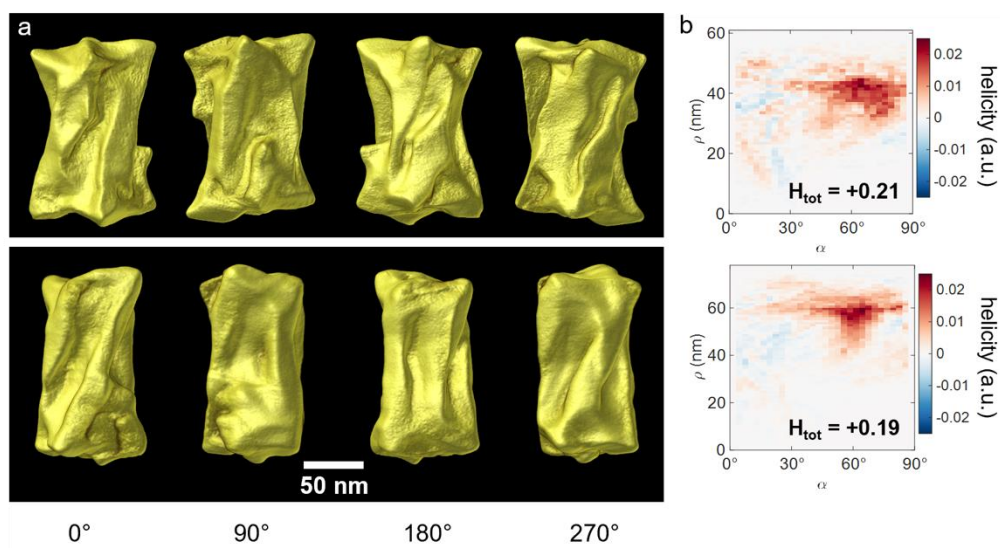


Figure S4. Electron tomography analysis of SC-Au NRs obtained by multi-step growth, in the presence of *L*-2Cys. (a) isosurface rendering of the reconstructed NRs viewed at different angles, revealing a 4-fold symmetry. (c) Helicity plot of the particles. The dominance of right-handed features is visualized by a cluster of positive helicities (red pixels).

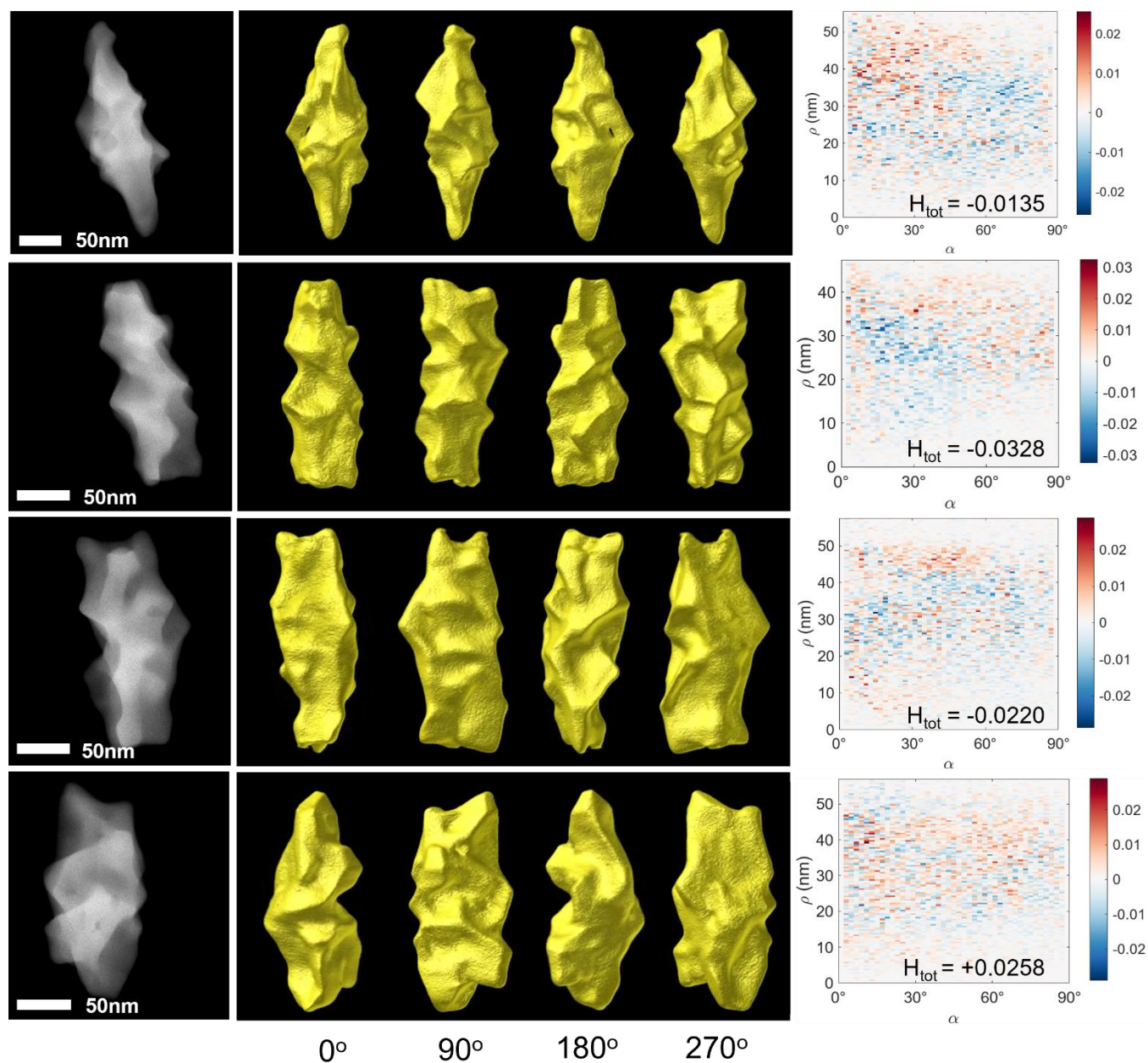


Figure S5. Isosurface visualizations of 3D reconstructions for several Au nanoparticles obtained through multi-step chiral growth. All four particles were obtained from the same synthesis batch. It can be seen that the overall morphologies differ significantly, even though all particles contain rough surfaces and tilted ridges. The corresponding helicity analysis showed both left- (blue pixels) and right-handed (red pixels) surfaces. Total helicity calculations yielded an overall left-handed helicity for most of the particles (negative H_{tot}).

Results of single-step seeded growth in the presence of *L*-2cys

Single-step growth in the presence of *L*-2Cys also resulted in remarkably different morphologies for PT- or SC-Au NRs. Whereas SC-Au NRs evolved into helical cuboid-like structures with obvious tip protrusions, PT-Au NRs evolved into complex structures. The linear optical response for both SC and PT products included an extinction peak around 580 nm (usually assigned to a transverse localized surface plasmon resonance – LSPR), whereas the second (longitudinal) LSPR band was significantly redshifted for chiral PT-Au NRs, compared to chiral SC-Au NRs, in agreement with a larger average aspect ratio for the former (PT chiral NRs: 199.8 ± 6.3 nm x 68.1 nm ± 4.0 nm; SC chiral NRs = 118.5 ± 8.6 nm x 47.0 nm ± 3.7 nm). More remarkable differences were observed in the corresponding circular dichroism (CD) spectra, which showed a negative peak at 595 nm and a positive plateau at the NIR region for chiral SC-Au NRs, whereas twisted PT-Au NRs featured a positive peak at 563 nm and a negative plateau at the NIR region.

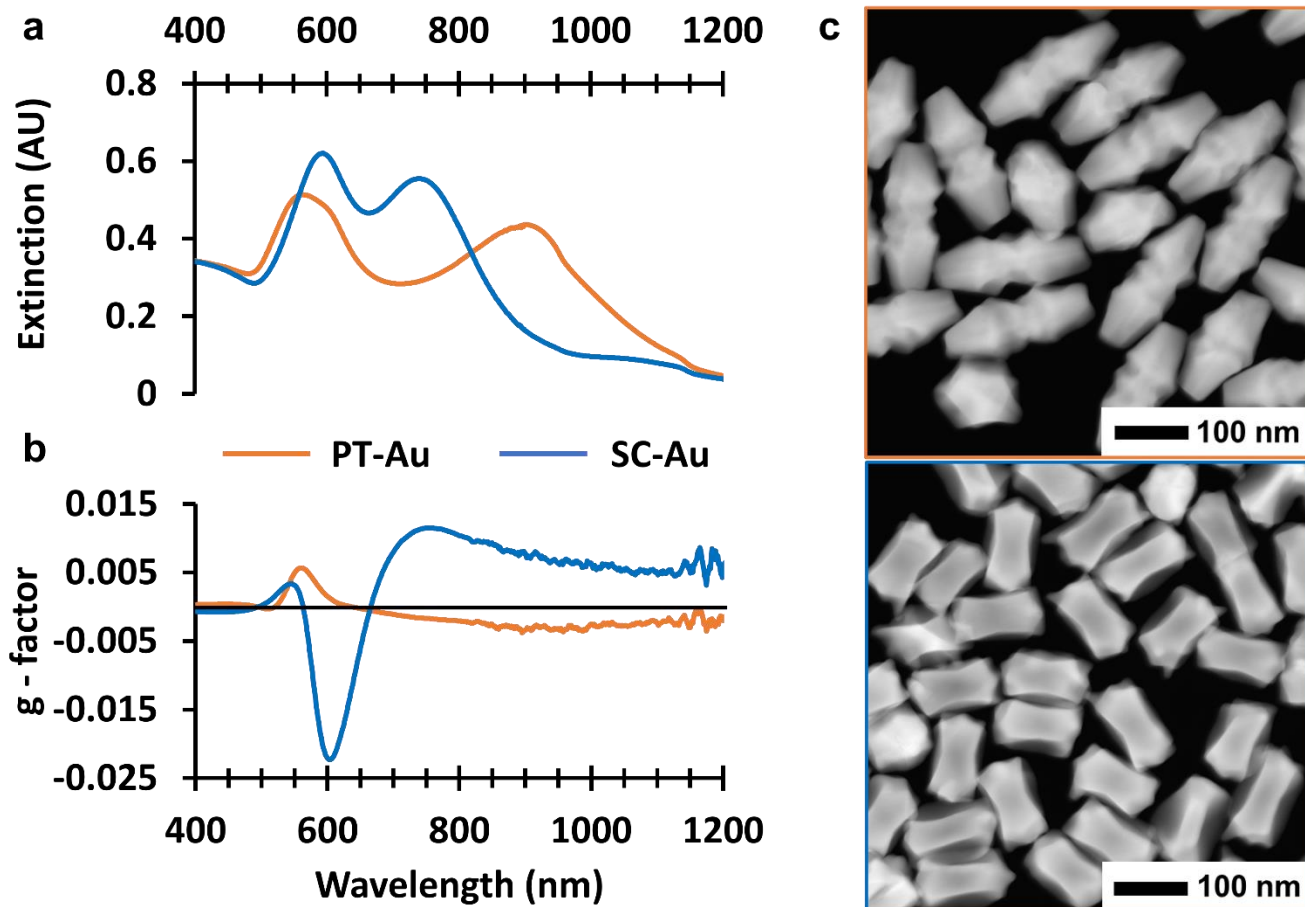


Figure S6. Extinction (a) and chiroptical spectra (b) for particles synthesized by a single-step growth protocol, using *L*-2cys and PT- or SC-NR seeds, as labeled. HAADF-STEM characterization of chiral products (c), image outlines are color-coded to match legend of plot.

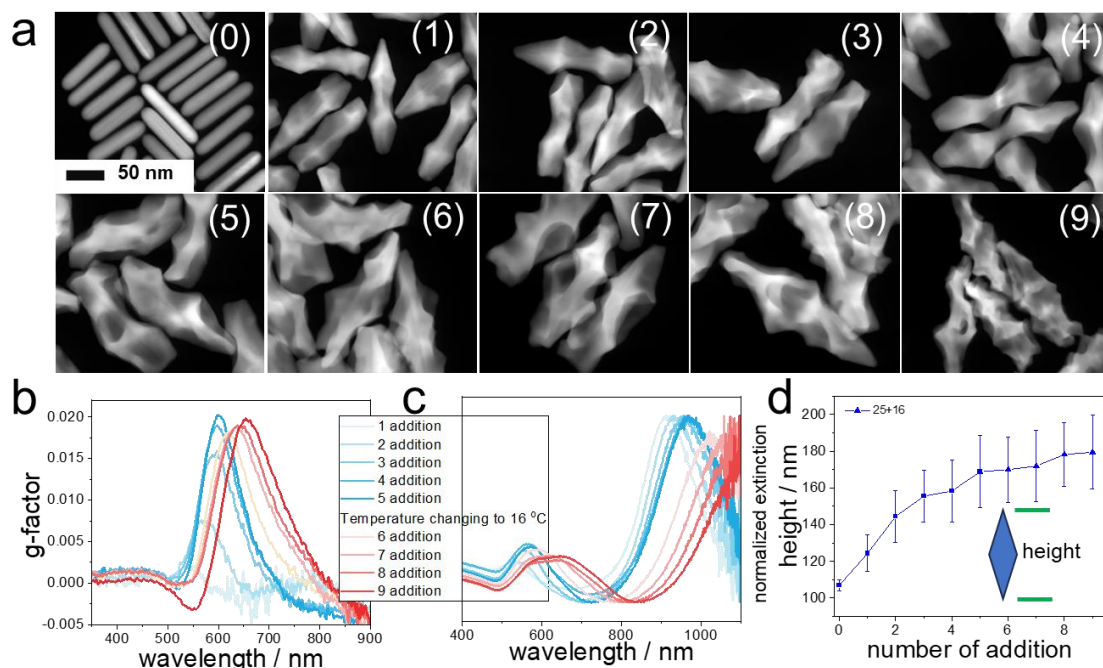


Figure S7. (a) Representative STEM images of the products obtained after different number of HAuCl₄ additions on PT-AuNRs (as labeled), in the presence of *L*-2cys. The scale bar applies to all images. (b,c) Corresponding *g*-factor and extinction spectra during the various growth steps. (d) Particle height (as defined in the inset) as a function of the number of HAuCl₄ additions. The particle length was measured on 300 nanoparticles, from which the average and standard deviation were calculated accordingly. Standard deviation values are plotted as error bars.

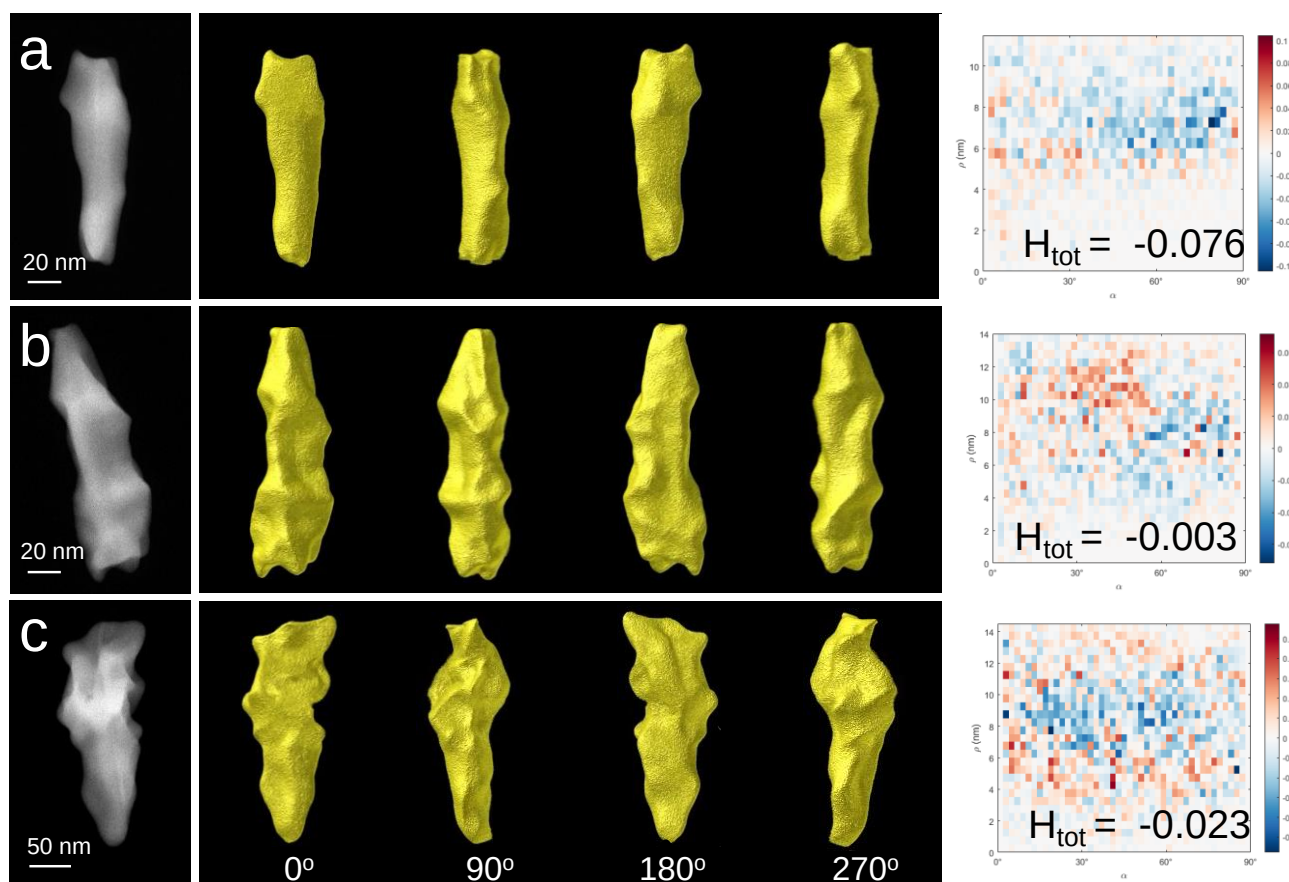


Figure S8. Morphology evolution of PT seeds during multistep growth and the corresponding helicity calculations. (a) Products obtained with reduced HAuCl_4 feeding (1/5 compared to the standard condition) after 1 chiral growth step; (Method: 1.9 mL of CTAC (40mM) was put into a tube, which was followed by adding 1 μL of HAuCl_4 (5 mM) (not 5 μL as that in the standard synthesis) and 0.2 mL of ascorbic acid (0.1 M) into the solution. Then 30 μL of L-2cys (2.5 μM) was added into the PE tube, followed by 10 μL of seed solution. (b) product obtained after 1 standard chiral growth step; (c) product obtained after 9 chiral growth steps.

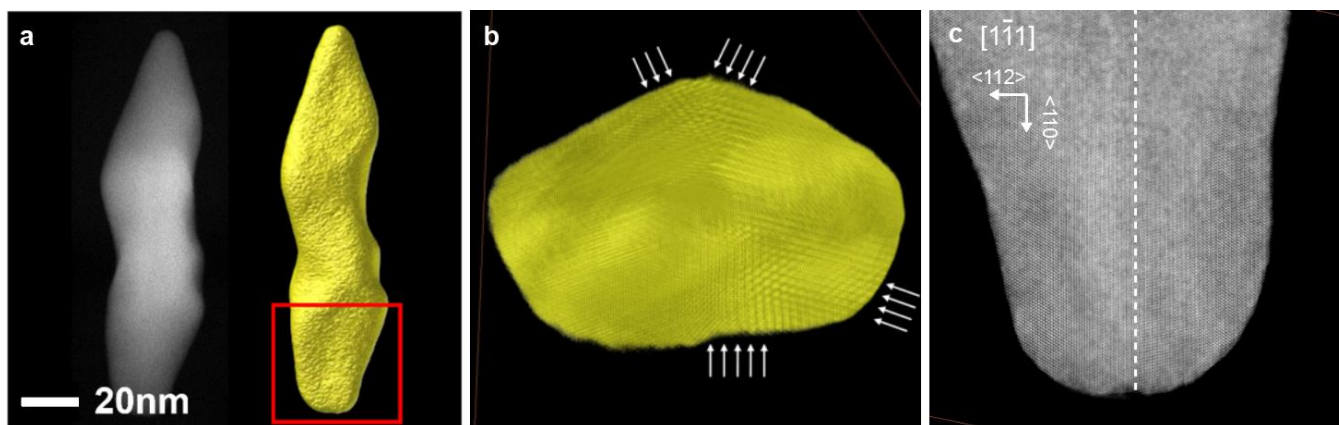


Figure S9. Detail of a PT-Au NR after one growth step. (a) HAADF image of the particle and its electron tomography (ET) results. The red square marks the area for atomic resolution ET measurement. (b) atomic-resolution ET reconstruction of the particle viewed from the bottom. The white arrows indicate the twin-boundaries. (c) Orthoslice through the 3D reconstruction viewed along the $[1\bar{1}1]$ zone axis. Note that the crystallographic orientations are indicated for one side of the twin boundary (dashed line).

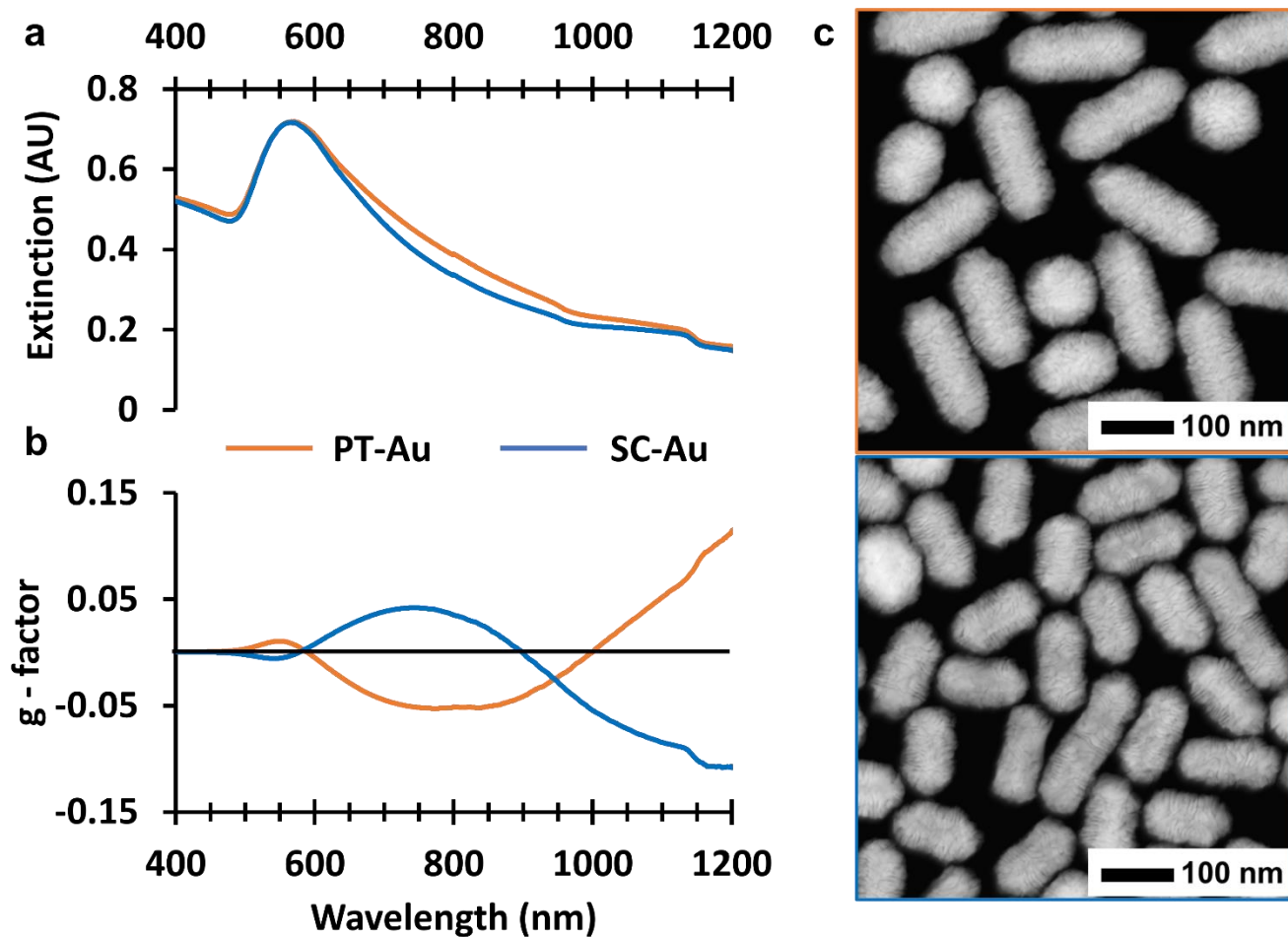


Figure S10. Extinction spectra (a) and chiroptical spectra (b) for chiral particles synthesized using *R*-BINAMINE and PT- or SC-Au NR seeds, as labeled. Right: HAADF STEM characterization of chiral products, image outlines are color-coded to match legend of plot.

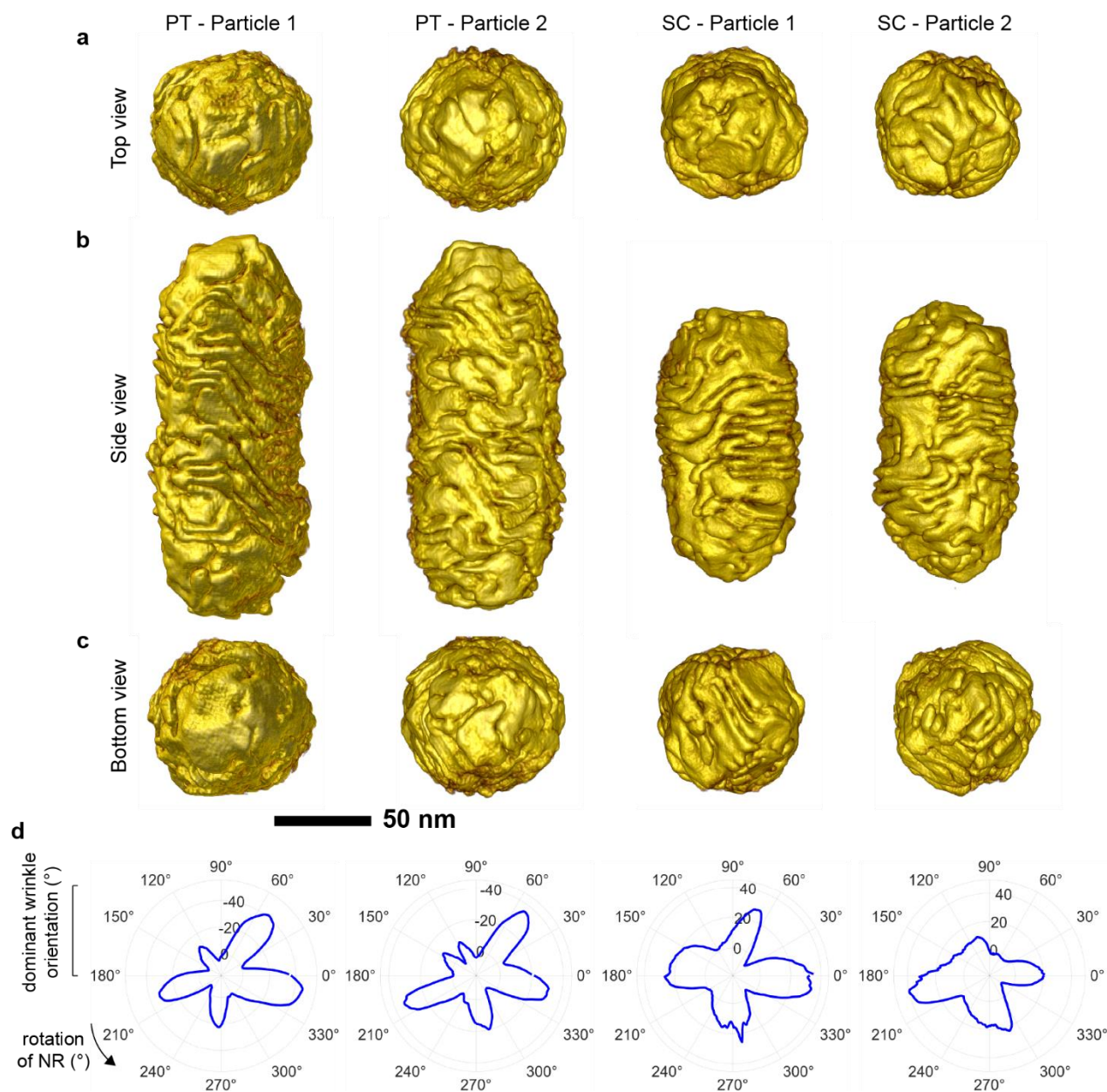


Figure S11. Overview of wrinkled chiral particles obtained from micelle-directed synthesis with *S*-BINANIME and PT or SC seeds as labeled on top. Surface views from (a) the top, (b) the side, (c) the bottom of the particles demonstrating the difference in wrinkle orientation and tip morphology. Note the typically wrinkled tips on SC particles. The scale bar is valid for all views and particles. (d) corresponding plots of the dominant wrinkle orientation as a function of the particle's rotation demonstrating a typically 5-fold rotational symmetry in PT particles and a 4-fold one in SC particles. Note that the radial axis is inverted for PT particles to show increasing magnitude outwards.

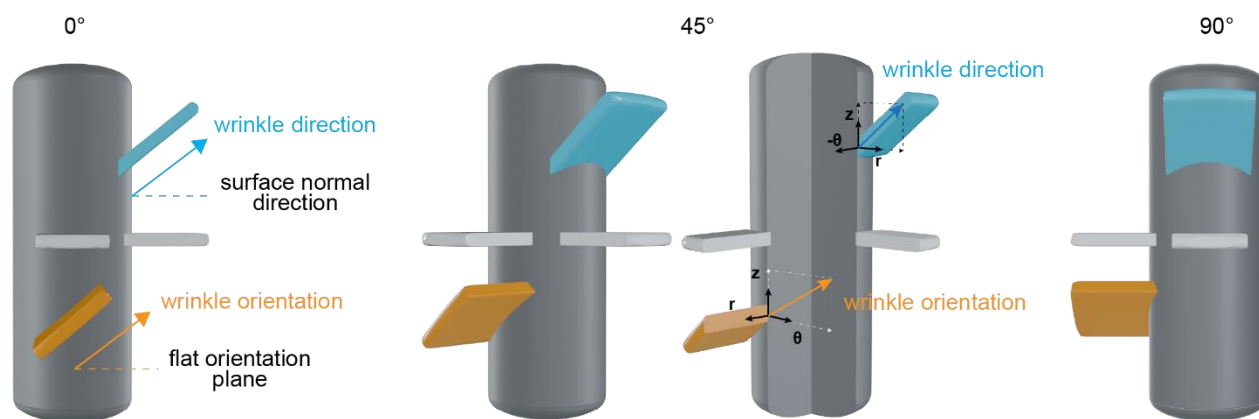


Figure S12. Geometry of wrinkle growth. Two angles are necessary to fully describe Au wrinkles on Au NRs: we define the angle of wrinkle direction with respect to the surface normal when seen in cross section; the wrinkle orientation is the angle with respect to the horizontal plane when NRs are seen from the front with their major axis vertical. Here, the blue wrinkle has a positive direction but 0° orientation, the orange wrinkle has a positive orientation but a 0° direction, the grey wrinkles have neither.

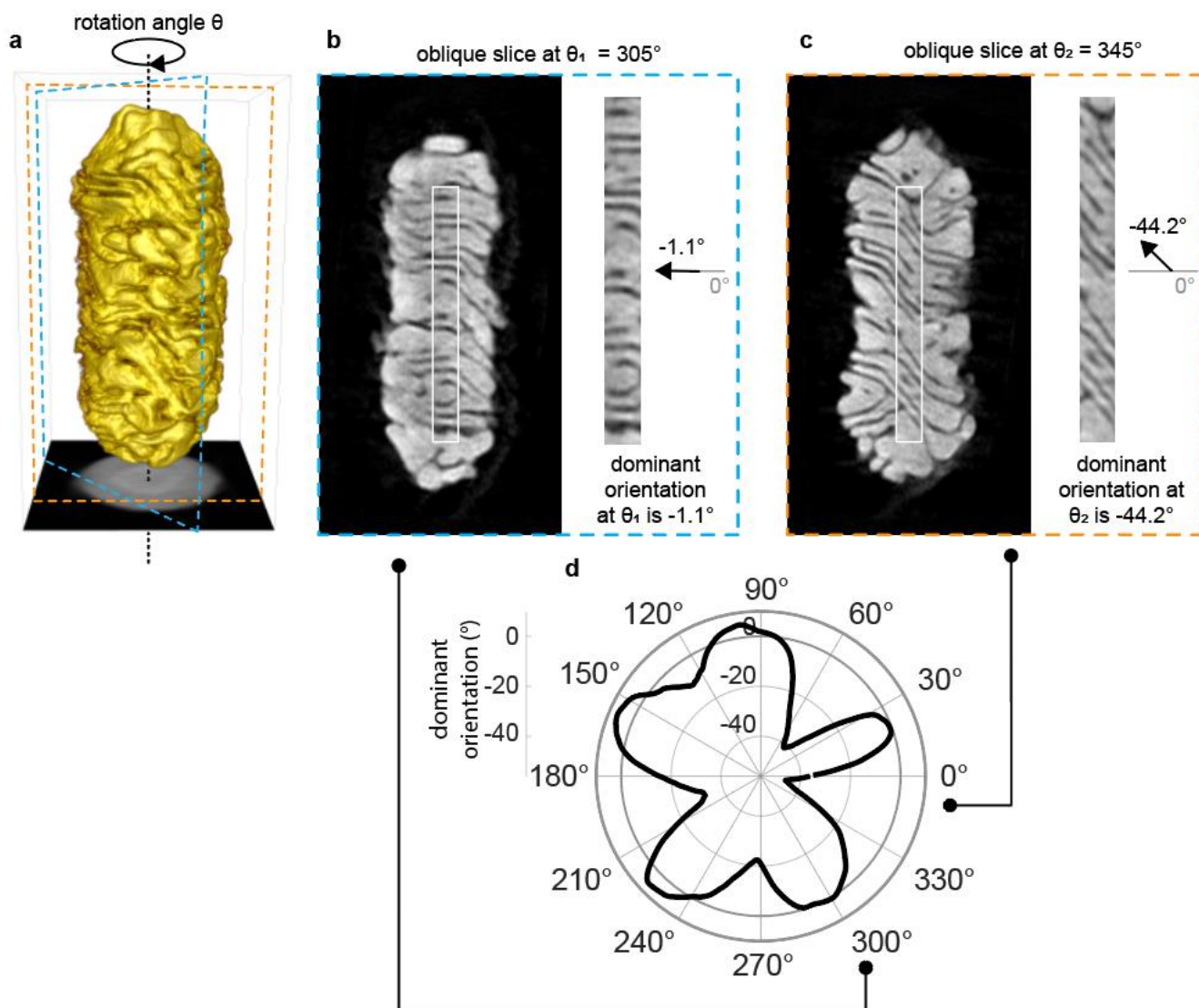


Figure S13. Method for tracking the dominant orientation of the wrinkles. The 3D reconstruction (a) is sliced through the wrinkle corona, 20-30 nm away from the center, for 360 rotation angles θ . The orange and blue dashed lines demonstrate two examples at (b) $\theta_1 = 305^\circ$ and (c) $\theta_2 = 345^\circ$. The dominant orientation is then computed in central areas (white rectangles in (b) and (c)) to prevent bias from the edges of the particle and ensure the metric is specific to a given rotation angle. Assembling the results for all 360 rotational slices yields the polar plots in (d).

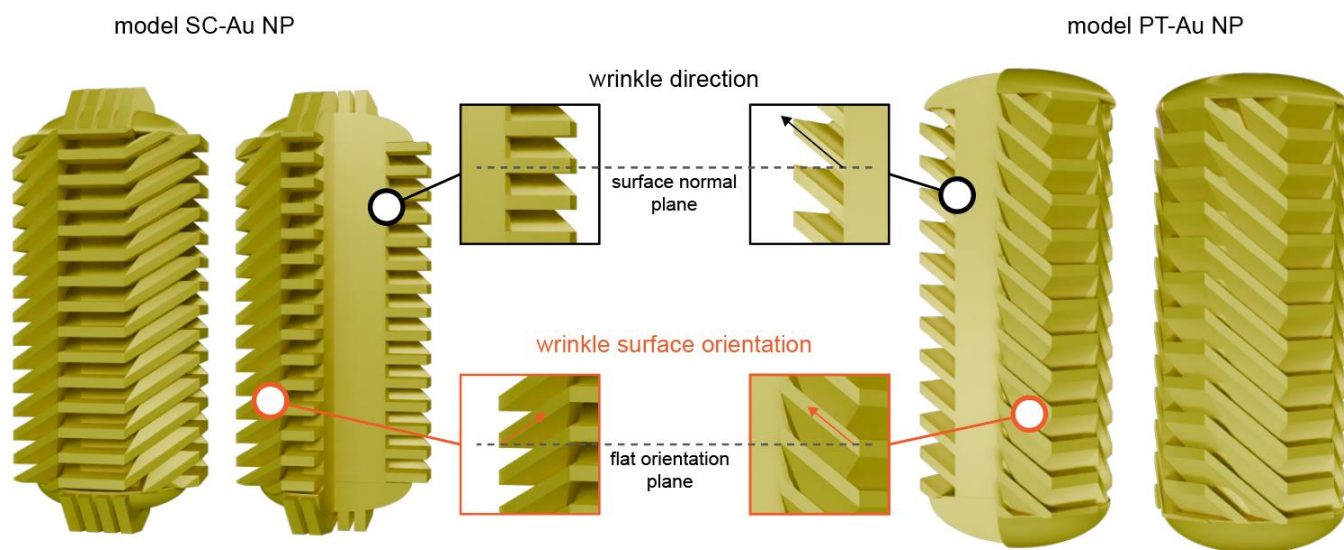


Figure S14. Idealized models of the micelle-templated growth results and example of wrinkle growth direction and wrinkle orientation according to the definitions used herein.