

# Additive-Free Synthesis of (Chiral) Gold Bipyramids from Pentatwinned Nanorods

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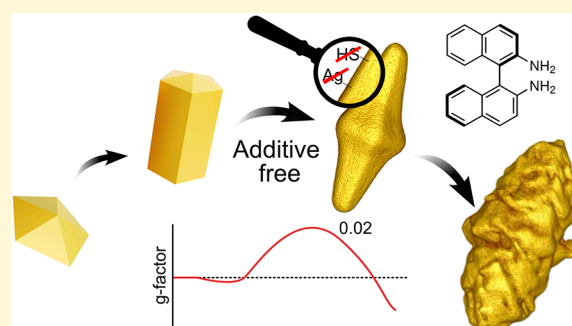
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**ABSTRACT:** The production of colloidal metal nanostructures with complex geometries usually involves shape-directing additives, such as metal ions or thiols, which stabilize high-index facets. These additives may however affect the nanoparticles' surface chemistry, hindering applications, e.g., in biology or catalysis. We report herein the preparation of gold bipyramids with no need for additives and shape yields up to 99%, using pentatwinned Au nanorods as seeds and cetyltrimethylammonium chloride as surfactant. For high-growth solution:seed ratios, the bipyramids exhibit an unusual “belted” structure. Three-dimensional electron microscopy revealed the presence of high-index {117}, {115}, and {113} side facets, with {113} and {112} facets at the belt. Belted bipyramids exhibit strong near-field enhancement and high extinction in the near-infrared, in agreement with electromagnetic simulations. These Ag-free bipyramids were used to seed chiral overgrowth using 1,1'-binaphthyl-2,2'-diamine as a chiral inducer, with *g*-factor up to 0.02, likely the highest reported for bipyramid seeds so far.



Various fabrication methods have enabled the reliable fabrication of both anisotropic and asymmetric (chiral) noble metal nanoparticles, with potential applications in various fields such as sensing,<sup>1,2</sup> imaging,<sup>3,4</sup> and nanomedicine.<sup>5,6</sup> Distinct optical properties arise from localized surface plasmon resonances (LSPRs), which result in high absorption and scattering cross-sections in the visible and near IR (NIR). Such optical properties, including LSPR wavelength and the strength of near-field interactions, depend on nanoparticle composition, shape, and size, as well as on the dielectric environment.<sup>7</sup> Inherently chiral plasmonic nanomaterials offer new opportunities to develop functional materials with strong, tunable, and specific interactions with circularly polarized light, which could be leveraged e.g. for enantioselective catalysis and biosensing.<sup>2</sup> Overall, gold is frequently the preferred choice for many applications because of its higher chemical stability, optical tunability in the visible and NIR, and biocompatibility.

Colloidal seed-mediated nanoparticle synthesis has been shown to direct crystal growth into different geometries, depending on the crystallinity of the seeds and the presence of “shape-directing” species such as metal salts or surfactants.<sup>8</sup> As surfactants are needed for nanoparticle growth and stabilization, we consider “additives” any other chemical species that may be used to affect crystal growth. Seed preparation is therefore a key step, especially for the growth of uniform gold

nanorods (NRs) and bipyramids (BPs).<sup>9–11</sup> Although single crystalline (SC)-NRs are readily prepared from SC Au seeds (in the presence of Ag<sup>+</sup> ions),<sup>10,12</sup> Ag-free Au pentatwinned (PT)-NRs require decahedral seeds presenting five twin planes, which propagate during growth into a pentagonal prism-like morphology. The addition of Ag<sup>+</sup> as a shape-directing reagent is similarly required for the growth of Au PT BPs. Even though the preparation of PT nanoparticles often suffers from contamination with other morphologies (often due to poor twinning yield within the seeds), recent improvements have demonstrated twinning efficiencies up to 98%.<sup>13,14</sup> This significant increase in the yield of PT seeds enables more extensive studies on PT morphologies such as decahedrons, PT-NRs, and BPs.<sup>15,16</sup> Apart from the absence or presence of crystalline defects in SC or PT nanocrystals, they also differ in their surface facet Miller indices. For instance, SC-NRs feature high-index {520} lateral facets and a combination of {100}, {110}, and {111} facets at the tips,<sup>17,18</sup> whereas PT-NRs are enclosed by five {100} lateral facets and ten {111} tip facets.<sup>19</sup>

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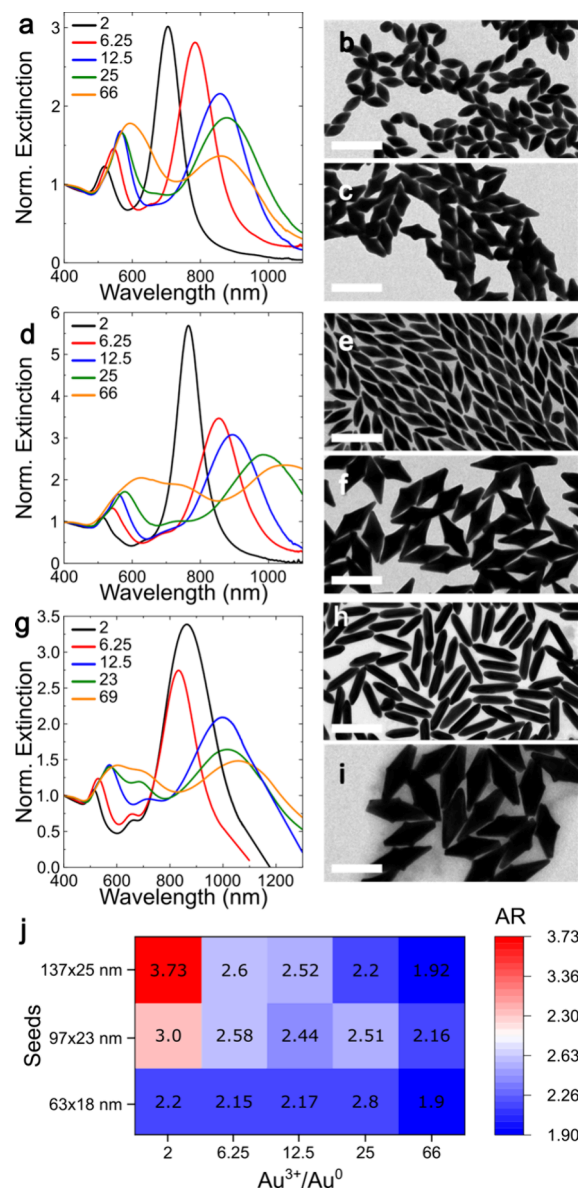
Albeit less popular, Au BPs are attractive alternatives to NRs, capable of exhibiting higher-quality plasmon bands,<sup>20</sup> stronger near-field enhancements,<sup>21</sup> as well as higher sensitivity to refractive index changes in the surrounding medium.<sup>22</sup> The geometry of these particles consists of two elongated pyramids with pentagonal cross-section, joining at a common base plane. PT seeds are decahedral, thus enclosed by ten {111} facets.<sup>23</sup> During growth into bipyramids, the particle is elongated in the  $\langle 110 \rangle$  direction, with the seed staying at the center.<sup>13</sup> Although the role of silver remains unclear, it seems to reduce the growth rate along the {100} and {110} facets, while favoring the development of higher index facets.<sup>24</sup> Most crystallographic studies report indices in the {11n} family, i.e., {115}, {113}<sup>20,25–27</sup> on the side facets, with higher indices less often reported.<sup>20</sup> Lower index {100} and {111} facets are still reported at the center and at the tips, respectively. The presence of high index facets shows potential interest in the development of more efficient catalysts.<sup>28</sup>

Regarding silver content, 3–4 wt % has been reported for Au BPs, mostly localized at/near the surface, thereby modifying their surface chemistry.<sup>29</sup> Silver-free preparation of BPs is also reported in the literature. One example uses salicylate and  $\text{H}_2\text{PdCl}_4$  as additives,<sup>30</sup> whereas a most recent one uses a racemic mixture of *L/D* cysteine.<sup>16</sup> Both preparations show intriguing structures of BPs with unusual rounded structures.<sup>16,30</sup> In general, for BPs above ca. 200 nm, stair-like, rough facets with high indices ({910} and {730}) have also been reported.<sup>13,14,31</sup> Additionally, some studies report the possibility of overgrowing BPs into different geometries such as dumbbell shapes, rods, or larger bipyramids, using different surfactants.<sup>20</sup> For example, concave bipyramids were obtained by the overgrowth of BPs in the presence of cetyltributylammonium bromide and silver nitrate.<sup>32</sup>

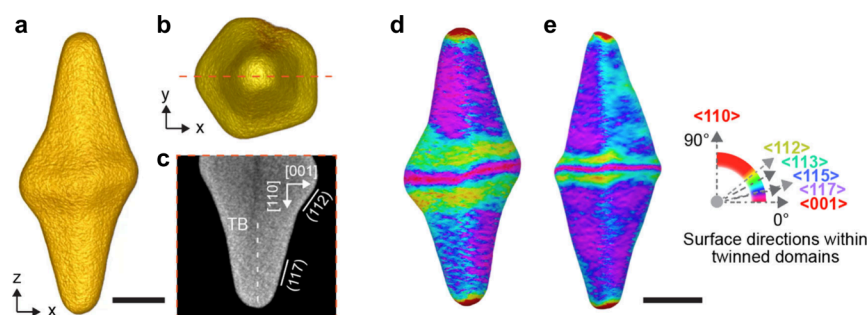
The increased knowledge of the surface chemistry of Au nanoparticles has pushed forward investigations of these materials as seeds for the preparation of chiral nanomaterials. Previous investigations on the preparation of chiral plasmonic particles employed chiral biomolecules, such as cysteine and glutathione, to induce chiral overgrowth on cubes or octahedra.<sup>33</sup> Cysteine was also used for chiral growth on Au SC-NRs, resulting in chiral NRs with interesting 4-fold symmetries.<sup>34</sup> On the other hand, by using the cosurfactant 1,1'-binaphthyl-2,2'-diamine (BINAMINE) as a chirality-inducing agent, Au SC-NRs covered by chiral wrinkled geometries were obtained.<sup>35,36</sup> More recently, PT-NRs, BPs, and decahedra have also been used as seeds, showing different morphological evolution during chiral growth,<sup>37–40</sup> even with inverted handedness resulting from chiral growth on PT- and SC-NRs, while using the same enantiomer of the chiral inducer.<sup>37,38</sup>

We report herein an unusual additive-free overgrowth of Au PT-NRs, which allows the formation of large BPs (up to ca. 330 nm × 170 nm) with smooth facets. Interestingly, in the larger BPs we consistently observe the formation of a pronounced “belt” at the BP central plane. We stress that the synthetic process is entirely free of additives that might ultimately affect the surface chemistry of the BPs (such as other metal ions or thiols/cosurfactants), rendering these particles particularly interesting for various applications (e.g., biomedical, where  $\text{Ag}^+$  can induce cytotoxicity).<sup>41</sup> In the context of chiral overgrowth, silver-free surfaces are also usually preferred.<sup>39,40</sup>

The synthesis protocol comprises three main steps, namely, (i) PT seed formation, followed by (ii) their overgrowth into PT-NRs, and (iii) overgrowth of PT-NRs into PT-BPs, as schematically shown in Supporting Information (SI) Figure S1. The first and second steps are based on our previous report on the synthesis of PT-NRs,<sup>13</sup> including the seed aging and postsynthetic purification of Au PT-NRs by depletion forces (see details and additional characterization in the Supporting Information, Table S1 and Figures S1 and S2). Although the growth of Au BPs from small seeds relies on the use of CTAB as a shape-directing surfactant,<sup>13</sup> the overgrowth of PT-NRs into BPs was found to work best in the presence of the chloride



**Figure 1.** Overgrowth on Au PT-NRs with different sizes and varying  $[\text{Au}^{3+}]/[\text{Au}^0]$  ratios. UV-vis-NIR spectra normalized at 400 nm (a, d, g) and TEM images (b–i) for two selected molar ratios (2 and 12.5) are shown for the overgrowth on small (a–c), medium (d–f), and large (g–i) Au PT-NRs. The  $[\text{Au}^{3+}]/[\text{Au}^0]$  ratios for each spectrum are indicated in the legends. Scale bars in TEM images: 200 nm. (j) Heat map of the aspect ratio (AR) evolution for the various Au PT-NR seeds, depending on the growth ratio.



**Figure 2.** Structural characterization of “belted” bipyramids. (a, b) Isosurface rendering of an electron tomography reconstruction of a bipyramid prepared from medium Au PT-NRs, with a growth ratio of  $[\text{Au}^{3+}]/[\text{Au}^0] = 6.25$ . An animation is provided as Supporting Information Movie S1. (c) Orthoslice through the 3D reconstruction, extracted along the dotted line in panel b, showing the central twin boundary (TB) as a darker line. This enables identification of the crystal directions within twinned domains and indexing of the lateral and belt facets based on their angles with the vertical axis. (d, e) Surface analysis of particles prepared from medium NRs, with growth ratios of  $[\text{Au}^{3+}]/[\text{Au}^0] = 6.25$  (d) and  $[\text{Au}^{3+}]/[\text{Au}^0] = 12.5$  (e). Color coding corresponds to the angle of the surface normal vectors with respect to the vertical  $\langle 110 \rangle$  axis, which can be related to crystal directions within twinned domains. Scale bars are 30 nm (a–d) and 50 nm (e).

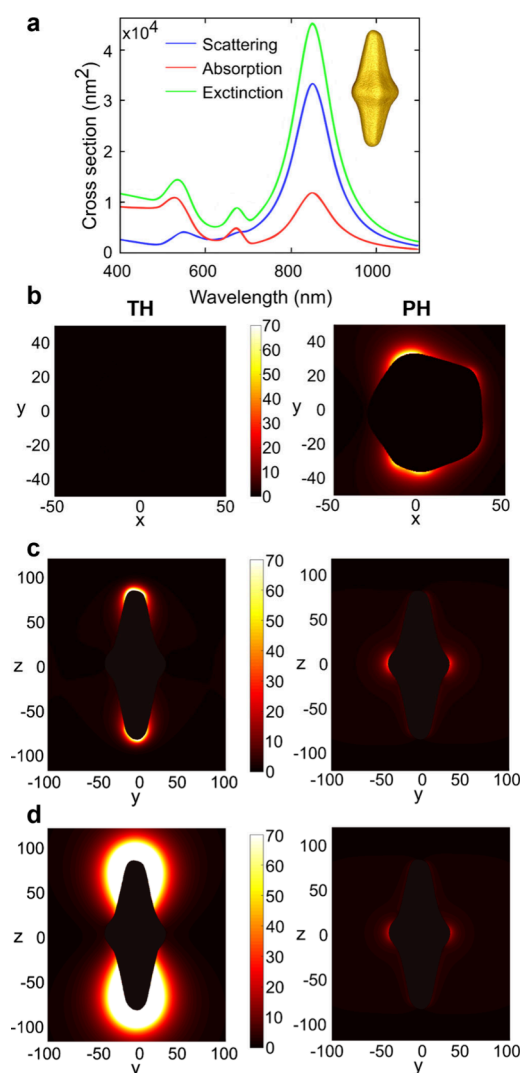
counterpart (CTAC). In a typical preparation, BP overgrowth involves adding the gold precursor to a mixture of ascorbic acid (AA), Au PT-NR seeds, and CTAC, at 30 °C. Compared to CTAB, CTAC exhibits weaker adsorption on the gold surface,<sup>24</sup> and therefore is often used to prepare isotropic geometries such as larger spheres.<sup>42</sup>

We thus expected that CTAC would facilitate uniform NP growth, i.e., similar growth rate along all crystallographic directions.<sup>24,42</sup> Although no significant effects could be observed by varying the AA/Au<sup>3+</sup> molar ratio, the BP morphology appeared less well-defined at high ratios (e.g., AA/Au<sup>3+</sup> = 10, Figure S3). We did observe a strong influence of CTAC concentration and temperature, with wide morphology variations in the ranges of 25–100 mM CTAC and 15–45 °C (Figure S4). Optimal bipyramidal shapes were obtained at 25 mM CTAC and 30 °C. Even though for a more efficient analysis of the synthesis process we chose to work with 10 mL aliquots, the same process can be scaled-up to at least 100 mL with no loss of shape yield (Figure S5).

The generality of the process was explored by using Au PT-NRs of three different sizes and different molar ratios between the growth solution and Au PT-NR seeds:  $[\text{Au}^{3+}]/[\text{Au}^0]$ . The initial Au PT-NR seeds were defined according to their dimensions as small (63 nm × 18 nm), medium (97 nm × 23 nm), and large (137 nm × 25 nm); representative transmission electron microscopy (TEM) images and UV–vis–NIR spectra are shown in Figure S1. As described in the Materials and Methods section (Supporting Information), the concentration of seeds was estimated from the absorbance at 400 nm, which relates to the concentration of Au<sup>0</sup>.<sup>43</sup> It should be noted, however, that this approach is not accurate for large Au NPs due to increased light scattering, but was considered sufficient to identify common features among various syntheses. Overall, BPs of different sizes and aspect ratios were obtained, with smaller seeds producing smaller BPs with lower aspect ratios, and *vice versa* (Figure 1; Table S2). For each seed size,  $[\text{Au}^{3+}]/[\text{Au}^0]$  ratios between 2 and 66 were applied for overgrowth. In all three series, redshift and broadening of the LSPR bands were observed as  $[\text{Au}^{3+}]/[\text{Au}^0]$  was increased (Figure 1a,d,g; Table S2). For a low  $[\text{Au}^{3+}]/[\text{Au}^0]$  ratio of 2, the recorded LSPR maxima (700–860 nm) were blue-shifted with respect to those of the corresponding Au PT-NR seeds, in agreement with the decrease of aspect ratio measured by TEM (see Tables S1 and S2). TEM characterization for this ratio

additionally revealed the formation of elongated BPs with pointy tips, but with a rounded body, featuring less defined edges (Figure 1b,e,h). This effect is more evident when using large PT-NR seeds (Figure 1h). However, when increasing the  $[\text{Au}^{3+}]/[\text{Au}^0]$  ratio, the LSPR red-shifted accordingly (Figure 1a,d,g). For higher growth ratios above *ca.* 6, the BPs exhibited better defined edges and a “belt” structure around the center of the particle (Figures 1c,f,i and S6 and S7). SEM characterization confirmed that particles are uniform in their shape and belted structure (Figures S8 and S9). In general, the aspect ratio decreases at high growth ratios, as illustrated by a heat map in Figure 1j, showing convergence into values close to 2. This result means that BPs of different dimensions but with similar aspect ratios can be prepared. Overall, yields of BP morphology up to ~99% were measured for  $[\text{Au}^{3+}]/[\text{Au}^0] \leq 25$ , but decreased to ~80% for excessive overgrowth. This lower yield at high ratios is accompanied by extensive tip truncation, likely due to favored growth on the lateral BP facets. Tip truncation is more obvious for longer PT-NR seeds (e.g.,  $[\text{Au}^{3+}]/[\text{Au}^0] = 12.5$ , Figure 1i), whereas it only occurs at higher  $[\text{Au}^{3+}]/[\text{Au}^0]$  values for shorter seeds (e.g.,  $[\text{Au}^{3+}]/[\text{Au}^0] > 25$ , Figure S6d,e).

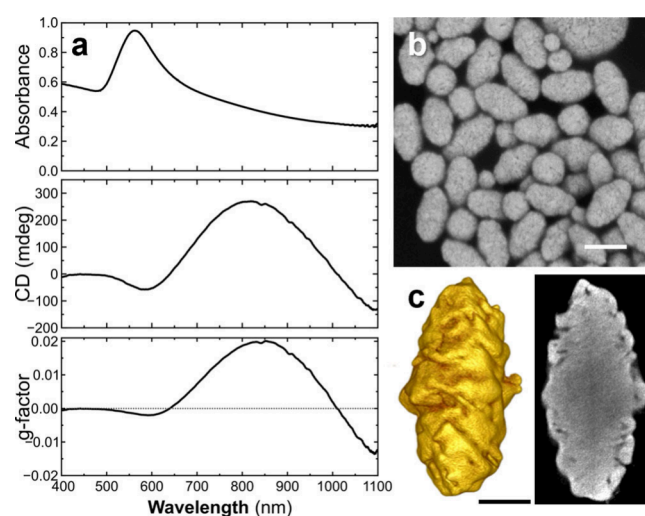
For a detailed characterization of this unusual, belted structure, we employed electron tomography based on tilt series of high-angle annular dark field scanning TEM (HAADF-STEM) images.<sup>44</sup> Panels a and b of Figure 2 show two orientations of a three-dimensional (3D) isosurface rendering of an electron tomography reconstruction, for a representative BP prepared from medium (97 nm × 23 nm) Au PT-NRs with  $[\text{Au}^{3+}]/[\text{Au}^0] = 6.25$ . Viewed along the long axis, the reconstruction confirmed that the 5-fold symmetry and therefore the pentatwinned structure is preserved in the final particles (Figure 2b). Additionally, the 3D reconstruction of the particles allowed us to identify the nature of the various facets, as well as internal lattice defects (central twin boundary, TB, Figure 2c). By measuring the surface angles with respect to the central twinning axis, crystallographic indices can be proposed for the different surface facets within twinned domains (see SI Materials and Methods and Figure 2c–e). Although similar angle dependence measurements are commonly used for the identification of different facets using 2D NP projections,<sup>16,26</sup> the use of a 3D reconstruction allows us to visualize the different facets in space. Interestingly, high-index facets of type  $\{11n\}$  were identified. The pyramidal sides



**Figure 3.** Electromagnetic simulation using as a model the electron tomography reconstruction of the belted BP shown in [Figure 2](#). (a) Simulated scattering (blue), absorption (red), and extinction (green) cross-sections. The inset shows the tomography reconstruction of the particle used for the simulations. (b–d) Near-field enhancement maps for the same belted particle, illuminated at different wavelengths of 525 (b), 675 (c), and 850 nm (d). Left panels show the  $x,y$ -plane; right panels show the  $y,z$ -plane; Light polarization is in the transverse direction (TH) and parallel direction (PH), respectively.

are typically flat and dominated by one of  $\{113\}$ ,  $\{115\}$ , or  $\{117\}$  facets ([Figure 2d,e](#)). The central belt comprises a combination of  $\{112\}$  and  $\{113\}$  facets, and the tips are typically rounded or with facets close to  $\{111\}$ . Similar results were observed at higher  $[\text{Au}^{3+}]/[\text{Au}^0] = 12.5$  ([Figure 2e](#)). Remarkably, despite the lack of silver as a shape-directing agent, we obtained similar crystallographic facets as those typically reported for Ag-assisted syntheses.<sup>20,27</sup> The absence of Ag in the final particles was confirmed by energy dispersion X-ray spectroscopy (EDS), as shown in [Figure S10](#). It should also be mentioned that similar belted BPs were recently reported, but always requiring the addition of additives, such as  $\text{H}_2\text{PdCl}_4$ , salicylate or cysteine.<sup>16,30</sup>

Regarding the optical properties, it was interesting to note that, whereas BPs were produced in high shape yield ( $\sim 99\%$ ), the ratio between the extinction of longitudinal and transverse



**Figure 4.** (a) UV-vis, CD, and  $g$ -factor spectra for chiral particles grown from medium BPs (see text for details), with an  $[\text{Au}^{3+}]/[\text{Au}^0]$  ratio of 3. (b) Representative SEM image of the wrinkled BPs. Scale bar is 200 nm. (c) Electron tomography reconstruction (left) and central orthoslice (right) of a selected chiral BP, scale bar is 50 nm. An animation is provided as Supporting Information [Movie S6](#).

bands is lower than typical values for silver-assisted BPs ([Table S2](#)).<sup>13</sup> To understand this unusual result, electromagnetic simulations were carried out using the method of moments (MoM).<sup>35,45</sup> This methodology is particularly accurate for solving scattering problems because it uses Green's functions and its derivatives. Greater accuracy is obtained because we use a 3D reconstruction from electron tomography as the input model in the simulations. The calculated extinction, absorption, and scattering cross-section spectra ([Figure 3a](#)) clearly show that the longitudinal band is dominated by scattering, whereas the major contribution to other modes is absorption. Although the position of the longitudinal band is not strongly influenced by the presence of the belt, a small blue-shift is observed due to the belt, compared to "ideal" BPs with similar dimensions ([Figure S11](#)). The belted bipyramids are observed to have a more intense transverse band and a reduced longitudinal intensity, leading to the observed lower ratio. Electromagnetic simulations also allowed us to identify the nature of the various plasmon modes ([Figure 3b–d](#)). Under irradiation at 525 nm ([Figure 3b](#); [SI Movie S2](#)) a transverse dipolar feature is clearly observed. Interestingly, when compared to a nonbelted bipyramid, the enhancement is observed to be more distributed over the whole belt ([SI Figure S12](#) and [Movie S3](#)). However, for the lower intensity band at 675 nm we can see ([Figure 3c](#); [SI Movie S4](#)) enhancement both at the belt and the tips, depending on the polarization of incident light, which we identify as corresponding to a multipolar mode. Finally, for the mode at 850 nm ([Figure 3d](#); [SI Movie S5](#)), a dipolar longitudinal character is clearly observed, as usual for Au BPs, with strong near-field enhancement at the tips. One can note that the enhancement under transverse polarized light is strongly localized at the tips for belted particles, whereas the enhancement is more distributed on the sides when the belt is not present.

We finally explored one of the benefits of growing Ag-free BPs, related to their potential use as seeds for further chiral growth. Even though chiral growth on both Au SC-NRs and

BPs has been reported,<sup>38–40</sup> the results indicate that the presence of Ag on the surface was detrimental to chiral growth. This is the case for the growth of chiral wrinkles in the presence of BINAMINE.<sup>35</sup> We thus tested S-BINAMINE-induced chiral growth on our Ag-free BPs. We selected BPs prepared from medium PT-NRs with  $[\text{Au}^{3+}]/[\text{Au}^0] = 6.25$ , to which an appropriate growth solution was added,<sup>35</sup> with  $[\text{Au}^{3+}]/[\text{Au}^0]$  ratios ranging from 1 to 5 (additional information about these samples can be found in SI Figure S13). Summarized in Figure 4a is the optical and morphological characterization of the particles resulting from chiral overgrowth of medium BPs, with  $[\text{Au}^{3+}]/[\text{Au}^0] = 3$ . The UV–vis–NIR spectrum shows maximum absorbance at 563 nm and a tail over the whole range up to 1100 nm, resembling the usual results for wrinkled Au NRs. Both circular dichroism (CD) and *g*-factor spectra in Figure 4a display a broad positive band around 820 nm, with a second negative feature at higher (NIR) wavelengths that could not be recorded in our instrument. This result is in agreement with a previous report for S-BINAMINE-induced chiral PT-NRs, showing inverted handedness compared to SC-NR seeds.<sup>38</sup> In this sample, a maximum *g*-factor of 0.02 was obtained, which is below the best values for other chiral NRs, but still significantly higher (by one order of magnitude) than the values reported for cysteine and glutathione-induced chiral BPs.<sup>39,40</sup> Both SEM and electron tomography (Figure 4b,c) confirmed the presence of wrinkled features around a central BP. Although some secondary nucleation could be observed in this sample, most of the particles maintain the elongated shape dictated by the BP seeds. The high resolution provided by electron tomography evidence the formation of thin, tilted wrinkles (Figure 4c) and preservation of the 5-fold symmetry during the growth (Figure S14). These results enable further opportunities to tune the overall size and the fine details of chiral features on Au BPs, with the corresponding optimization of the chiroptical response. A control experiment for chiral overgrowth on Au BPs prepared in the presence of silver (Figure S15),<sup>13</sup> evidenced hindered chiral overgrowth using similar conditions, with poor optical response and moderate or even no wrinkling (Figure S16).

In summary, we have introduced an efficient synthesis route toward the preparation of Ag-free Au bipyramids. This synthesis has the advantage of not requiring the use of any additives that might affect the surface chemistry and applications of Au BPs. The method offers wide flexibility in terms of particle size and aspect ratio, which can be tuned through the dimensions of the PT-NR seeds and the concentration of the growth solution. The stabilization of high-index facets in the absence of silver challenges some of the currently proposed growth mechanisms and offers possibilities for catalysis or sensing. Finally, we also demonstrated efficient and simple chiral overgrowth in the presence of BINAMINE/CTAC, which is also facilitated by the absence of Ag on the BP surface. Wide opportunities arise for optimization of chiral morphologies and for reaching higher *g*-factors, either with the same or other chiral inducers, such as amino acids or peptides.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmaterialslett.4c01605>.

Materials and methods; additional microscopy and spectroscopy characterization data; additional simulation results (PDF)

Movie S1 showing visualization of a 3D belted bipyramid reconstruction (MPG)

Movie S2 showing electric field enhancement calculated for belted bipyramid shown in Figure 2 (illumination wavelength, 525 nm) (MP4)

Movie S3 showing electric field enhancement calculated for ideal (nonbelted) bipyramid (MP4)

Movie S4 showing electric field enhancement calculated for belted bipyramid shown in Figure 2 (illumination wavelength, 675 nm) (MP4)

Movie S5 showing electric field enhancement calculated for belted bipyramid shown in Figure 2 (illumination wavelength, 850 nm) (MP4)

Movie S5 showing Visualization of a 3D reconstruction of a chiral particle grown from a medium BP (MPG)

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## Author Contributions

F.B., J.H., and L.M.L.-M. conceptually designed the project. F.B. performed nanoparticle synthesis and analysis; K.V.G. collaborated on chiral synthesis and characterization; R.G. and S.B. performed and interpreted electron tomography measurements. V.F.M., M.O.-L. and J.M.T. performed and interpreted electromagnetic simulations. All authors contributed to writing the manuscript. CRediT: **Francisco BEVILACQUA** data curation, formal analysis, methodology, writing - original draft; **Robin Girod** data curation, formal analysis, visualization, writing - review & editing; **Victor F Martin** data curation, formal analysis, software, writing - review & editing; **Manuel Obelleiro-Liz** data curation, formal analysis, software, writing - review & editing; **Gail Anne Vinnacombe-Willson** data curation, visualization, writing - review & editing; **Kyle Van Gordon** methodology, writing - review & editing; **Johan Hofkens** conceptualization, resources, writing - review & editing; **Jose M Taboada** formal analysis, methodology, resources, software, writing - review & editing; **Sara Bals** formal analysis, funding acquisition, resources, supervision, writing - review & editing; **Luis M. Liz-Marzán** conceptualization, formal analysis, funding acquisition, methodology, project administration, resources, supervision, validation, writing - review & editing.

## Notes

The authors declare no competing financial interest.

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## **Supporting Information for:**

# **Additive-Free Synthesis of (Chiral) Gold Bipyramids from Pentatwinned Nanorods**

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## Materials and Methods

### Materials:

Analytical grade reagents, silver nitrate ( $\text{AgNO}_3$ ;  $\geq 99.9\%$ ),  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  ( $\geq 99.9\%$ ), L-ascorbic acid (99%), cetyltrimethylammonium bromide (CTAB,  $\geq 96.0\%$ ), cetyltrimethylammonium chloride (CTAC, 25 wt% in  $\text{H}_2\text{O}$ ), citric acid ( $\geq 99.5\%$ ), sodium borohydride ( $\geq 99.0\%$ ), hydrochloric acid (37%), and (S)-(-)-1,1'-binaphthyl-2,2'-diamine (BINAMINE,  $\geq 99\%$ ), were all purchased from Merck.

### Preparation of pentatwinned seeds:

Pentatwinned Au seeds were prepared following a previously reported protocol.<sup>1</sup> Typically, 5 mL of 100 mM CTAC were first mixed with 0.5 mL of 100 mM citric acid and 4.2 mL of water. Subsequently, 50  $\mu\text{L}$  of 50 mM  $\text{HAuCl}_4$  was added under stirring. The solution was left under mild magnetic stirring (200 – 300 rpm) for 30 minutes to ensure homogeneous mixing. After this time, 250  $\mu\text{L}$  of a freshly prepared ice-cold 25 mM  $\text{NaBH}_4$  solution was quickly added under vigorous stirring ( $>1000$  rpm) the color turned from light yellow to light brown. At this stage, a UV-vis spectrum was recorded to verify gold salt reduction through the absorbance at 400 nm (the value should be close to 0.6 for an optical pathlength of 1 cm). After borohydride addition, the solution was kept at room temperature for 15 minutes to ensure borohydride decomposition, followed by a heat treatment at 80 °C for 90 minutes, during which the color of the solution turned red. A larger amount of borohydride might result in extensive overgrowth during the heat treatment and thus a lower yield of twinning.

### Growth of Au pentatwinned nanorods:

The preparation of PT-NRs was based on the protocol reported in the same study as the pentatwinned seeds.<sup>1</sup> Typically, a 100 mL solution of 8 mM CTAB was prepared, to which 250  $\mu\text{L}$  of 50 mM  $\text{HAuCl}_4$  was added. The solution was left for 15 minutes under mild magnetic stirring to ensure the formation of  $[\text{Br} - \text{Au} - \text{Br}]^-$  complexes,<sup>2</sup> before being left for 15 more minutes in a water bath at 20 °C. Thereafter, 250  $\mu\text{L}$  of 100 mM ascorbic acid solution and a selected amount of PT seeds (for small, medium and large Au PT-NRs) were added under vigorous stirring. The solution was subsequently stored at 20 °C overnight without stirring.

**Table S1:** Preparation of Au PT-NRs, quantity of seeds, and data

Name	$V_{\text{seeds}}$ ( $\mu\text{L}$ )	Gold ratio ( $[\text{Au}^{3+}]/[\text{Au}^0]$ )	Length (nm)	Width (nm)	Aspect ratio	LSPR (nm)	Figure
Small	500	50	$63 \pm 5$	$18 \pm 2.5$	$3.6 \pm 0.5$	745	S1a
Medium	250	100	$97 \pm 4.7$	$23 \pm 1.6$	$4.5 \pm 0.4$	856	S1b
Large	125	200	$137 \pm 15$	$25 \pm 1.4$	$5.5 \pm 0.7$	1033	S1c

### Purification of pentatwinned nanorods:

Despite a relatively high yield in seed twinning, the yield of prepared PT rods does not typically exceed 85%. For further use, PT-NRs and BPs were purified using depletion forces, as previously described.<sup>3,4</sup> Typically, for Small PT-NRs, the solution was separated into ten 10 mL centrifuge tubes, and centrifuged at 8,500 rpm for 15 minutes. After discarding the supernatant, the particles were redispersed in 10 mL of 300 mM CTAC. The solutions were then left to deplete for 72 hours. The formation of a dark precipitate at the bottom of the tubes indicated successful depletion. The pinkish supernatant was then discarded and the particles were redispersed in 5 mL of milli-Q water. Small modifications were required to ensure appropriate purification of PT-NRs of different dimensions. Medium PT-NRs were transferred into ten 10 mL tubes, then centrifuged at 7,500 rpm for 15 minutes redispersed in 200 mM

CTAC and left for 72 hours. After a black precipitate was formed, the supernatant was discarded and particles were redispersed in 2 mL milli-Q water. For Large PT-NRs, centrifugation was carried out at 7,000 rpm for 15 min and depletion was performed with 100 mM CTAC overnight. For this sample, it was important to discard the pinkish supernatant and redisperse the PT-NRs in 5 mL of milli-Q water after the overnight waiting period for optimal purification. The concentration of the sample was then estimated using the absorbance at 400 nm. The samples would then exhibit a purity  $\geq 98\%$  and be ready for further use.

*Synthesis of Ag-free bipyramids:*

After dispersion of PT-NRs in water, the gold concentration was determined by measuring the absorbance at 400 nm. Typically, after purification the absorbance at 400 nm was around 1.7 for an optical pathlength of 1 cm, corresponding to concentrations around 0.7 mM. In a 20 mL scintillation vial, 10 mL of a 25 mM CTAC solution was mixed with 20  $\mu$ L of 100 mM ascorbic acid, to which a selected amount of seeds (for different  $[\text{Au}^{3+}]/[\text{Au}^0]$  ratios) was added. The medium was left at 30 °C for 15 minutes under mild stirring (200 – 300 rpm) to ensure homogeneous temperature and dispersion. After this time, 20  $\mu$ L of 50 mM  $\text{HAuCl}_4$  was added under vigorous stirring ( $>800$  rpm). The vial was then closed, and the reaction was kept at 30 °C under mild stirring for 1.5 hour. After the reaction, the dispersion was transferred to a 10 mL centrifuge tube and centrifuged at 4,000 rpm for the smallest, down to 2,500 rpm for 15 minutes for the largest BPs. The dispersions were stored at room temperature.

**Table S2:** Parameters used for the preparation of silver-free bipyramids and associated figures.

Seeds ( $[\text{Au}^0]$ )	$V_{\text{seeds}}$ ( $\mu\text{L}$ )	Gold ratio( $[\text{Au}^{3+}]/[\text{Au}^0]$ )	Length (nm)	Width (nm)	Aspect ratio	LSPR (nm)	Abs( $\lambda_{\text{long}}$ ) /Abs( $\lambda_{\text{trans}}$ )	Figure
Rods <sub>3.6</sub> (0.68 mM)	740	2	$89 \pm 5$	$41 \pm 2.6$	$2.2 \pm 0.2$	705	2.44	1d, SI 6a
	234	6.25	$141 \pm 10$	$66 \pm 4.4$	$2.15 \pm 0.22$	784	1.93	SI 6b
	117	12.5	$172 \pm 16$	$81 \pm 5$	$2.17 \pm 0.24$	858	1.28	1e, SI 6c
	59.5	25	$203 \pm 17$	$93 \pm 6.3$	$2.18 \pm 0.24$	877	1.12	SI 6d
	22.2	66.6	$210 \pm 18$	$112 \pm 8.2$	$1.9 \pm 0.2$	859	0.76	SI 6e
Rods <sub>4.5</sub> (0.74 mM)	674	2	$118 \pm 8$	$40 \pm 4$	$3 \pm 0.5$	764	4.97	1f, SI 6f
	200	6.25	$166 \pm 12$	$65 \pm 5$	$2.58 \pm 0.3$	856	2.64	SI 6g
	100	12.5	$201 \pm 15$	$83 \pm 5.7$	$2.44 \pm 0.24$	894	1.86	1g, SI 6h
	50	25	$244 \pm 24$	$100 \pm 9$	$2.5 \pm 0.3$	982	1.51	SI 6i
	20	66.6	$303 \pm 24$	$141 \pm 13$	$2.16 \pm 0.3$	1048	1.14	SI 6j
Rods <sub>5.5</sub> (0.73 mM)	700	2	$168 \pm 19$	$45 \pm 4.3$	$3.73 \pm 0.7$	864	3.09	1h, SI 6k
	220	6.25	$182 \pm 13$	$69 \pm 4.7$	$2.6 \pm 0.26$	833	2.23	SI 6l
	110	12.5	$255 \pm 22$	$102 \pm 8.6$	$2.52 \pm 0.32$	1000	1.46	1i, SI 6m
	60	23	$269 \pm 24$	$122 \pm 12$	$2.2 \pm 0.33$	1017	1.17	SI 6n
	20	69	$329 \pm 27$	$172 \pm 15$	$1.92 \pm 0.21$	1057	1.04	SI 6o

*Silver-assisted synthesis of bipyramids:*

Gold bipyramids were prepared by means of a previously reported protocol, using  $\text{AgNO}_3$ , CTAB and  $\text{HCl}$ .<sup>1</sup> In a 20 mL scintillation vial, 100  $\mu$ L of 50 mM  $\text{HAuCl}_4$ , 100  $\mu$ L of 10 mM  $\text{AgNO}_3$ , and 200  $\mu$ L of 1M  $\text{HCl}$  were added to a 10 mL 100 mM CTAB solution. The mixed solution was left for 15 min at 30 °C, and then 80  $\mu$ L of 100 mM AA solution, followed by 38  $\mu$ L of PT AuNR seeds. The reaction was

run for 2h. The resulting articles were then centrifuged and redispersed for chiral growth. TEM showed dimensions of  $144 \pm 5.5$  nm by  $41 \pm 2.5$  nm, with an aspect ratio of  $3.48 \pm 0.2$ .

#### *Chiral Growth:*

Chiral overgrowth on BPs was performed by adapting a previously established method,<sup>5</sup> using the S-enantiomer of BINAMINE. Typically, a batch of BPs prepared with a ratio of  $[\text{Au}^{3+}]/[\text{Au}^0] = 6.25$  was incubated in a solution of S-BINAMINE (2.5 mM) and CTAC (100 mM) for 72 hours. To prepare the incubation solution, BINAMINE and solid CTAC were mixed in water and left under mild stirring at 60 °C for 4h to 6h, to ensure complete solubilization of BINAMINE. The first step consists of washing the particles twice with the incubation solution: 500  $\mu\text{L}$  of particles was centrifuged a 4,000 rpm for 8 min and then redispersed in 250  $\mu\text{L}$  of milli-Q water and 250  $\mu\text{L}$  of the incubation solution (process repeated 2 times). The particles were finally redispersed in a solution of 250  $\mu\text{L}$  of milli-Q water and 250  $\mu\text{L}$  of BINAMINE solution for 72 hours. The absorbance at 400 nm was used to estimate  $\text{Au}^0$  concentration. For chiral overgrowth, a growth solution containing 200  $\mu\text{L}$  of the BINAMINE + CTAC solution and 600  $\mu\text{L}$  of milli-Q water was prepared in a 2 mL Eppendorf tube. To this solution, 10  $\mu\text{L}$  of  $\text{HAuCl}_4$  (50 mM) was added after 5 min, the solution turned brown, then, 200  $\mu\text{L}$  of 0.8 M ascorbic acid solution was added quickly, immediately followed by rapid addition of the BP seeds and vigorously shaken. In our case, the BP concentration was 7.27 mM, thus the studied series corresponds to volumes of 68.7, 34.4, 22.9, 17.2, and 13.7  $\mu\text{L}$ , corresponding to  $[\text{Au}^{3+}]/[\text{Au}^0]$  ratios of 1, 2, 3, 4, and 5, respectively. After 30 minutes, the tubes were centrifuged at 3,000 rpm for 6 minutes, and the yellowish supernatant replaced with milli-Q water, twice. The particles were characterized without any further treatment. Chiral growth of Ag-assisted bipyramids was carried out under the same conditions, for an  $[\text{Au}^{3+}]/[\text{Au}^0]$  ratio of 3.

#### *Optical characterization:*

Spectroscopic characterization was conducted with an Agilent 8453 UV-vis-NIR diode array spectrophotometer in the 400-1100 nm wavelength range. A UV-vis-NIR Cary 5000 Varian spectrophotometer was used for optical characterization at higher wavelengths (up to 1500 nm). Typically, after synthesis, the particles were centrifuged (from 3,500 rpm to 2,000 rpm, for the smallest to the largest BPs, respectively) then redispersed in milliQ water and placed in a polystyrene macro cuvette for analysis. For analysis in the NIR, the particles were centrifuged and redispersed in  $\text{D}_2\text{O}$  and measured in a cuvette from Hellma Analytics in special optical glass (100-OS) with a light pathlength of 10 mm.

Circular dichroism measurements were performed with a spectropolarimeter Jasco J-1500, with a 150 W Xe excitation lamp, air cooled with a detector EXPML-535, offering a detection range from 400-1250 nm. The cuvettes used were 100-OS from Hellma Analytics and the CD extinction of the particles was measured first, followed by standard extinction measurements. To compare samples and assess chiroptical activity, *g*-factor was calculated using the following equation:

$$g - factor = \frac{1}{32980} \times \frac{CD(\text{mdeg})}{\text{Extinction}}$$

#### *Electron microscopy characterization:*

Transmission electron microscopy (TEM) images were captured with a JEOL JEM-1400PLUS transmission electron microscope operating at 120 kV. Scanning electron microscopy (SEM) images were acquired using a JSM-IT800HL from JEOL (Tokyo, Japan) equipped with a top-view backscatter electron detector (BSE detector, scintillator-photomultiplier detector design) using 3–5 kV, under a high vacuum. Energy dispersive X-ray spectroscopy (EDS) was performed on a ThermoFisher Scientific Titan operated in scanning transmission electron microscopy (STEM) mode at 300 kV, 0.4 nA probe current, 50  $\mu\text{m}$  condenser aperture, and equipped with a SuperX detector system with 0.9 sr. collection

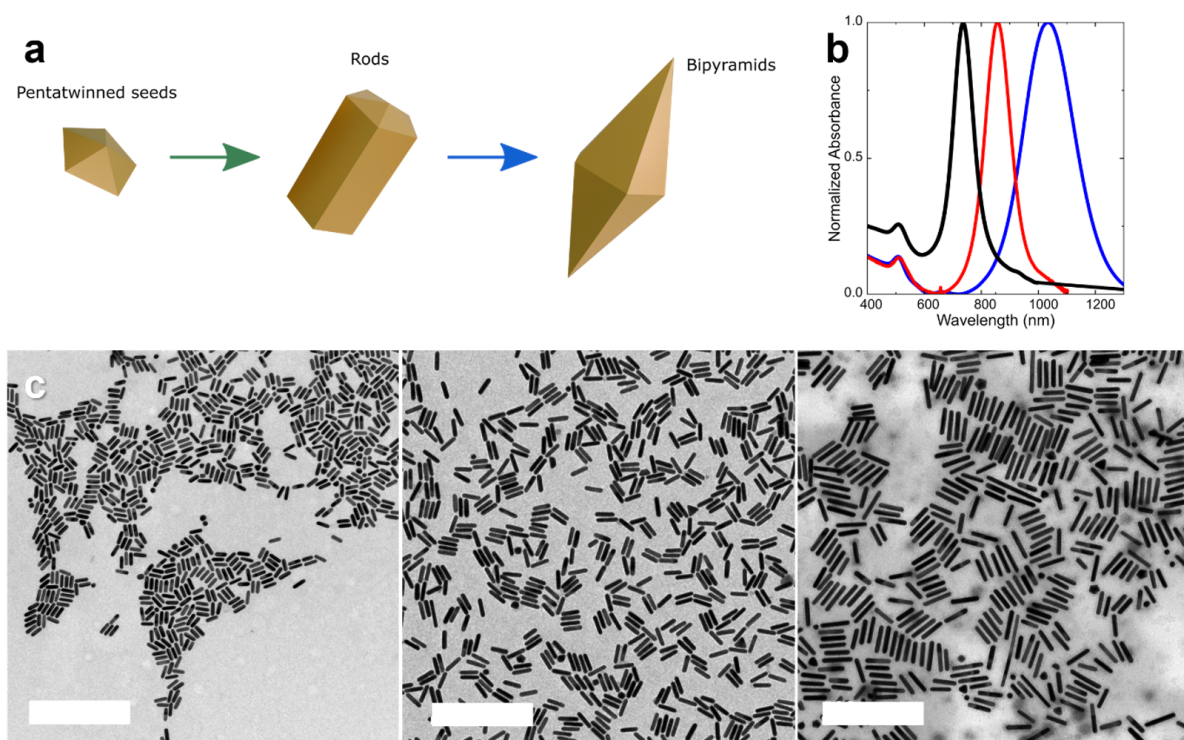
solid angle. Analysis and quantification was performed using the k-factor method in Velox (ThermoFisher Scientific). Electron tomography (ET) was performed in high angle annular dark field (HAADF) STEM mode on a ThermoFisher Scientific Osiris operated at 200 kV with 50 pA probe current, a 70  $\mu\text{m}$  condenser aperture, and 115 mm camera length. Tilt-series were acquired typically over  $\pm 75^\circ$  in  $3^\circ$  increments using a Fischione 2020 single-tilt tomography holder. The tilt-series were aligned with cross-correlation using an in-house Matlab code and 3D reconstructions were computed with the standard expected maximization (EM) algorithm using the Astra toolbox 2.1 for Matlab.<sup>6,7</sup> Isosurface renderings were performed with Amira (v5.4.0).

For surface facet analysis, each reconstruction was binarized with a manual threshold and its surface mesh was extracted by triangulation using the built-in Amira module. The mesh was aligned to have the long axis of the nanorod, corresponding to  $\langle 110 \rangle$  crystal directions, vertical. We modified our existing helicity Matlab toolbox<sup>8</sup> to calculate, for each surface element of the mesh, the orientation of the normal vector with respect to the long axis of the particle (angle  $\beta$  in **Figure S17a**). The orientation was remapped between 0 and  $90^\circ$  with  $90^\circ$  assigned to the  $\langle 110 \rangle$  directions along the long (central twinning) axis. This angle was color-coded for each surface element and exported in a .obj file with the Matlab toolbox “Save Wavefront .obj”<sup>9</sup> then visualized with Blender (v4.0). Within the twinned domains of the BP, this angle can be directly related to one of the  $\langle 111 \rangle$  crystal directions (**Figure S17b**).

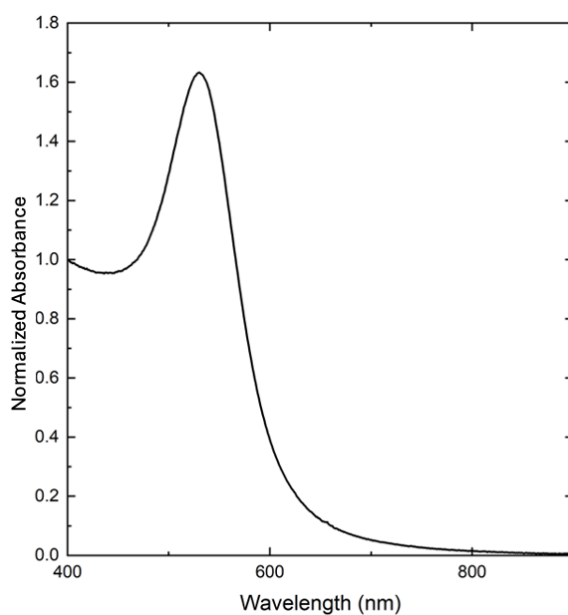
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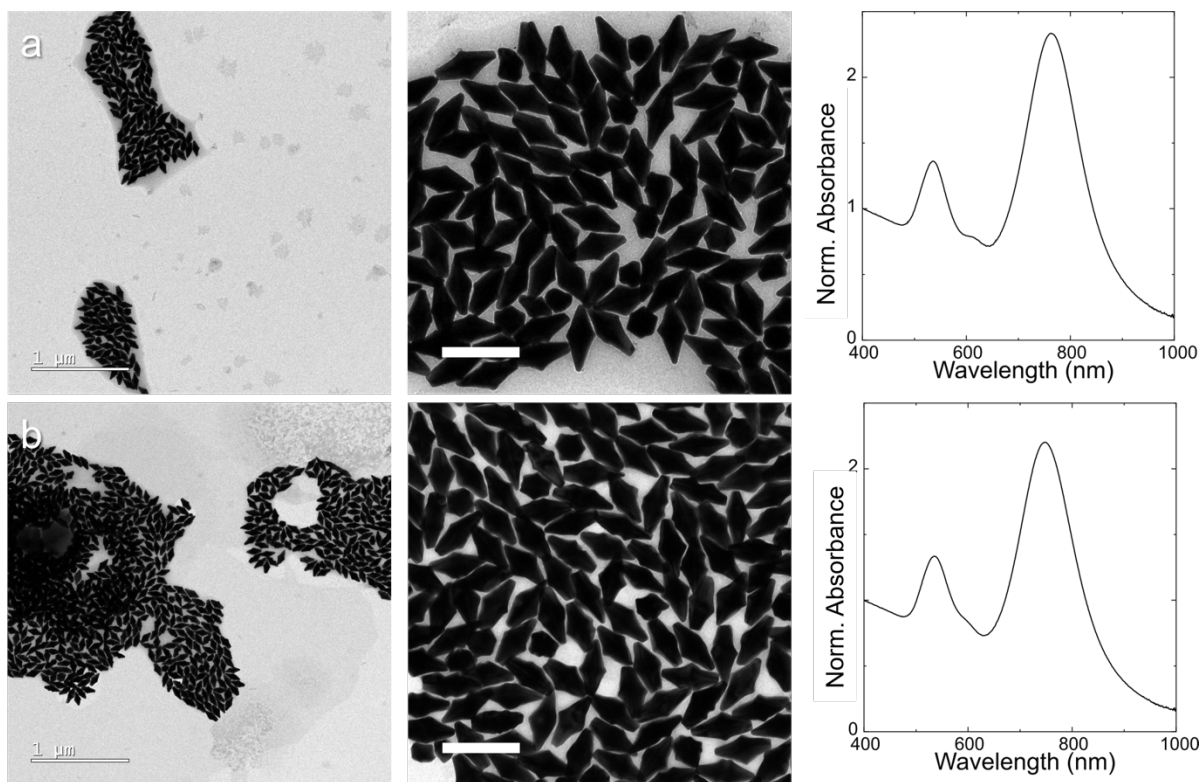
## Supporting Figures:



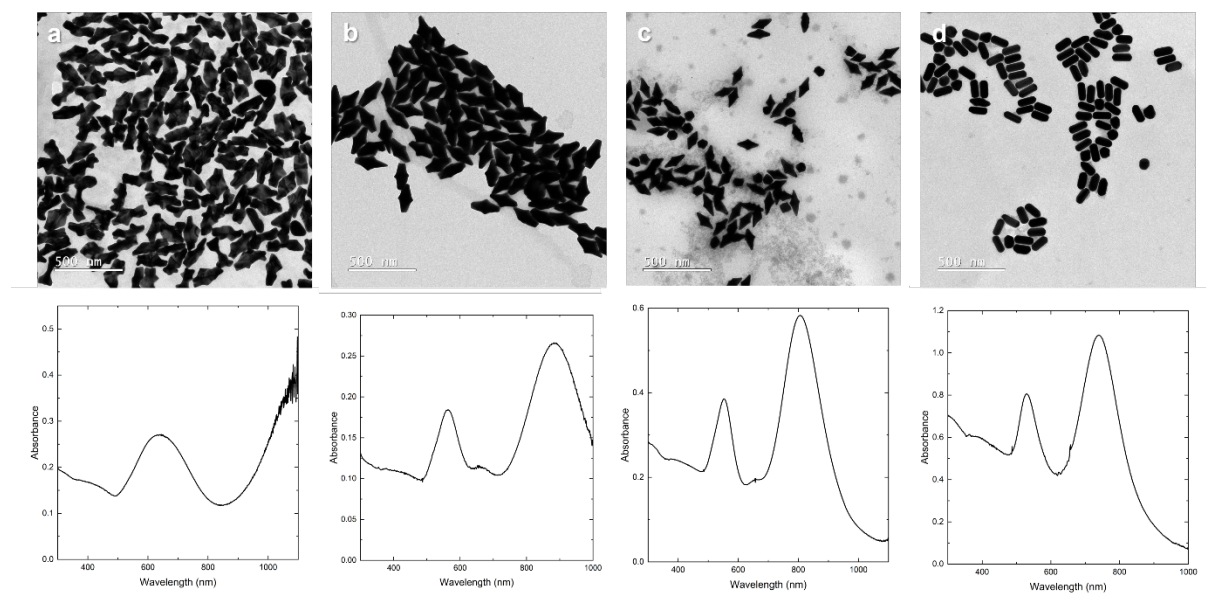
**Figure S1.** (a) Schematic representation of the three-step seed-mediated synthesis of silver-free bipyramids. (b) Extinction spectra (normalized at the maximum) for Small (black), Medium (red), and Large (blue) Au PT-NRs. (c) Representative TEM micrographs of Au PT-NRs of different sizes used as seeds: Small: 63 nm × 18 nm; Medium: 97 nm × 23 nm; and Large: 137 nm × 25 nm, from left to right. Scale bars are 500 nm.



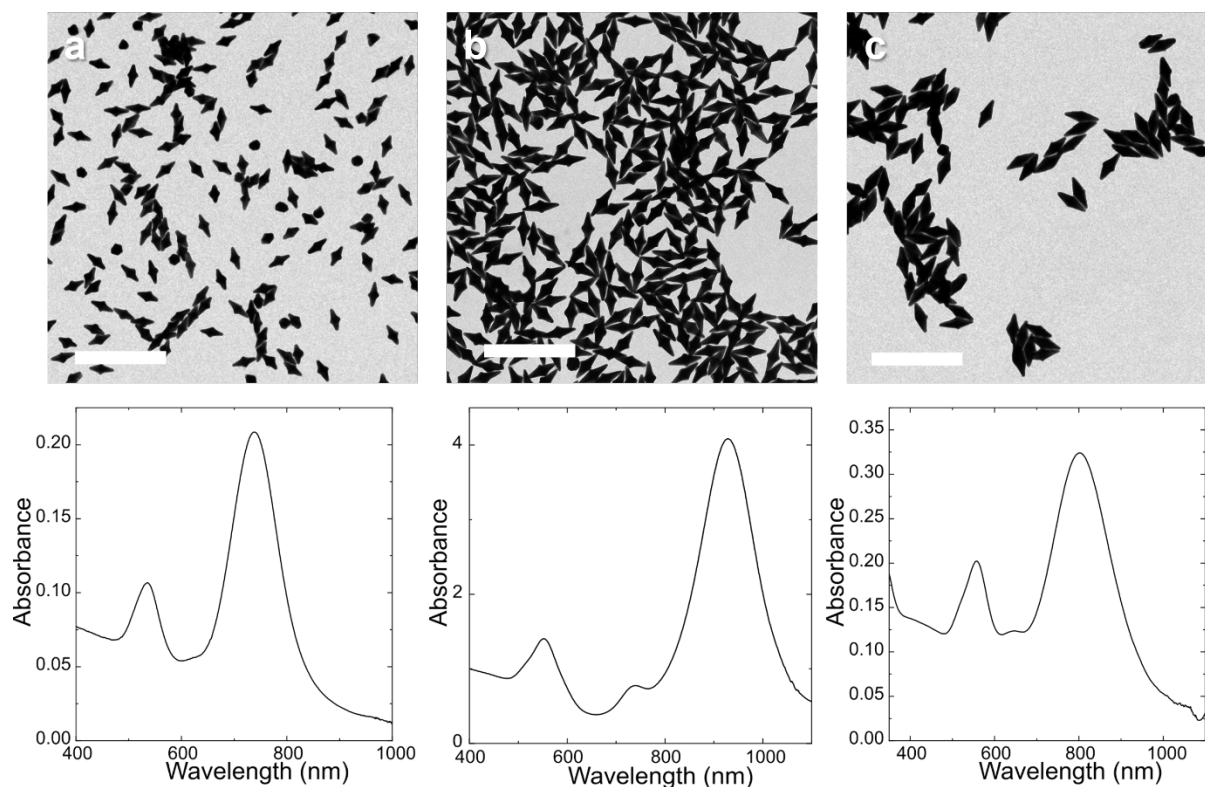
**Figure S2.** UV-vis absorbance spectrum (normalized at 400 nm) of heat-treated pentatwinned Au seeds.



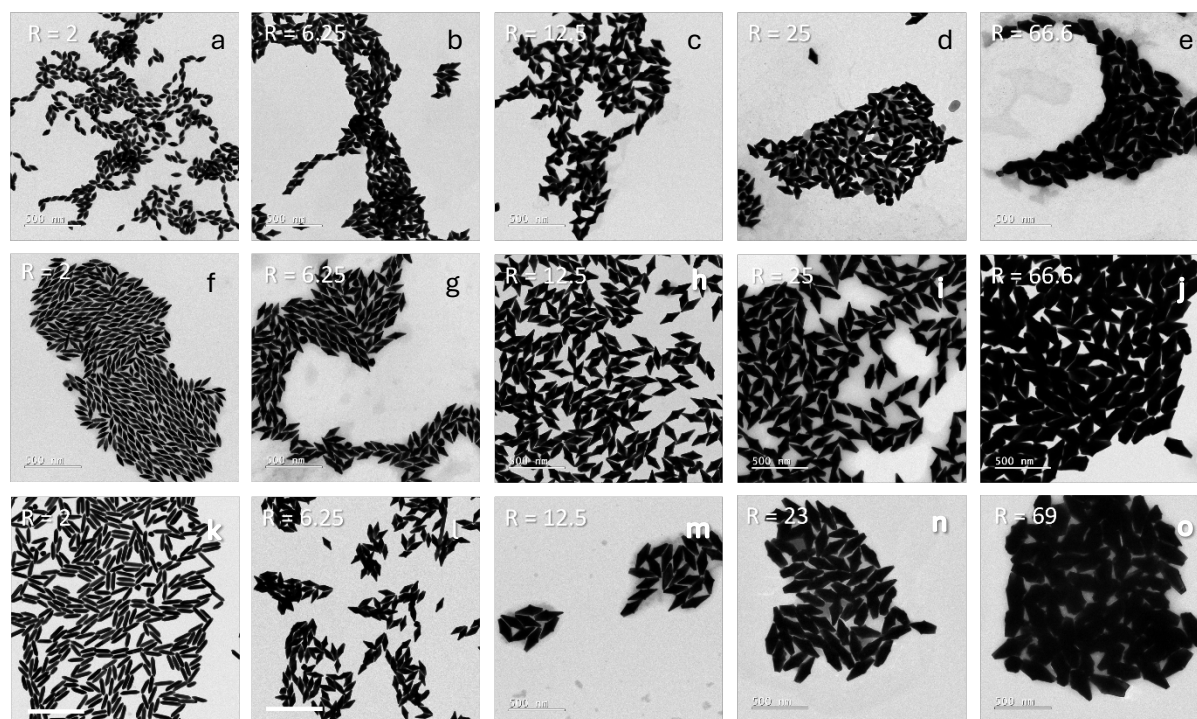
**Figure S3.** (a) Bipyramids prepared from Small Au PT-NRs with a  $[\text{Au}^{3+}]/[\text{Au}^0]$  ratio of 12.5 and low concentration of ascorbic acid:  $[\text{AA}]/[\text{Au}^{3+}] = 4$ . Left low magnification image, middle scale bar is 200 nm, right UV-Vis spectrum. (b) Bipyramids prepared from Medium Au PT-NRs with a  $[\text{Au}^{3+}]/[\text{Au}^0]$  ratio of 12.5 and high concentration of ascorbic acid:  $[\text{AA}]/[\text{Au}^{3+}] = 10$ . Scale bars are 1000 nm (left panels) and 200 nm (middle panels). UV-vis spectra shown in right panels.



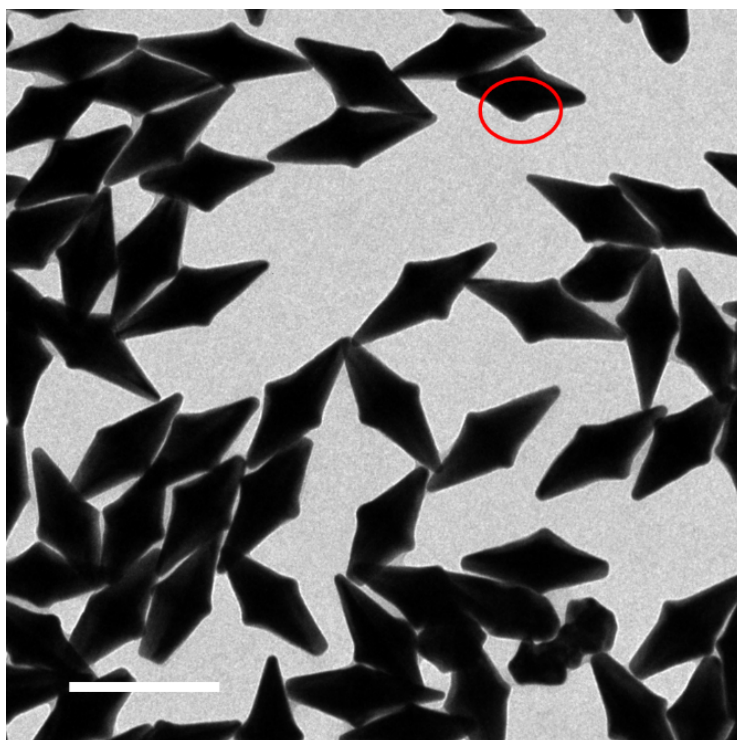
**Figure S4.** Standard overgrowth conditions from Medium Au PT-NRs, with  $[\text{Au}^{3+}]/[\text{Au}^0] = 12.5$  and  $[\text{CTAC}] = 25$  mM, at different temperatures: 16 °C (a) and 45 °C (b). Standard overgrowth conditions from Medium Au PT-NRs, with  $[\text{Au}^{3+}]/[\text{Au}^0] = 12.5$  at 30 °C, varying CTAC concentration: 50 mM (c); 100 mM (d).



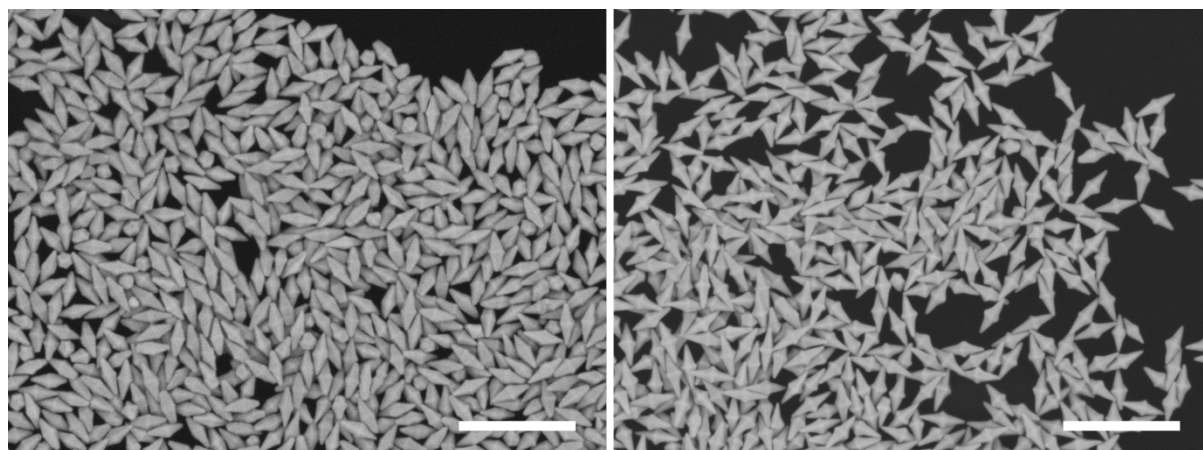
**Figure S5.** Representative TEM images and UV-vis-NIR spectra for upscaled (100 mL) BP growth from Small (a), Medium (b), and Large (c) Au PT-NRs, at  $[Au^{3+}]/[Au^0] = 6.25$ . Scale bars are 500 nm.



**Figure S6.** TEM micrographs of bipyramids prepared varying the  $[Au^{3+}]/[Au^0]$  ratio (R) from Small (a-e), Medium (f-j), and Large (k-o) Au PT-NRs. Scale bars are 500 nm.

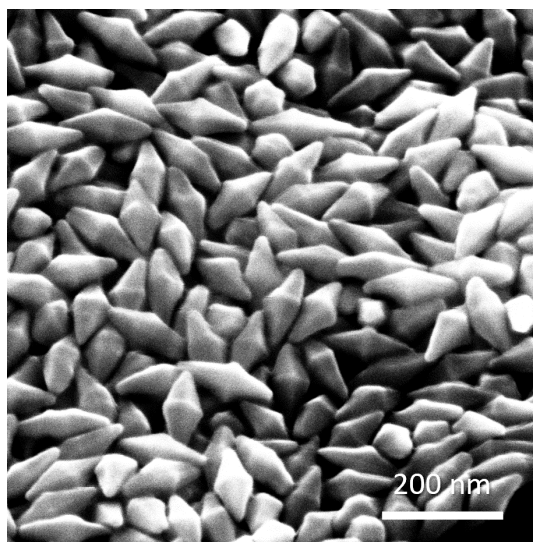


**Figure S7.** TEM image of bipyramids prepared from Medium Au PT-NRs, with  $[\text{Au}^{3+}]/[\text{Au}^0] = 12.5$ . The equatorial belt is highlighted with a red circle. The scale bar is 200 nm.

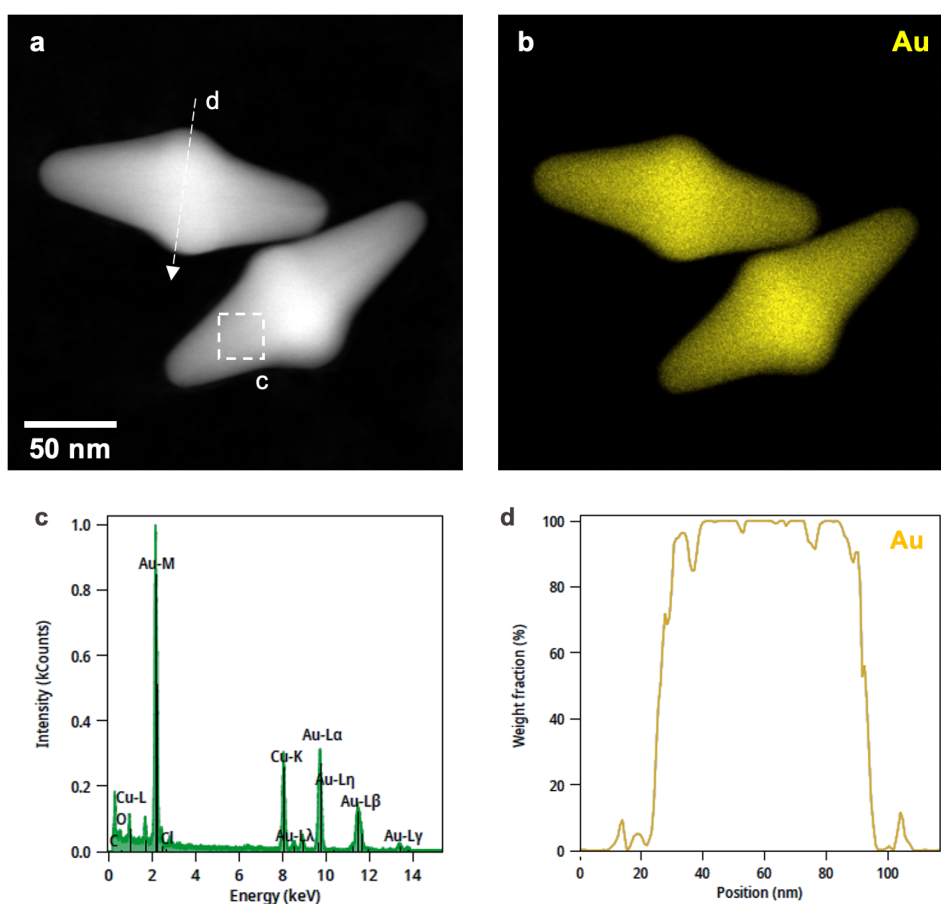


**Figure S8.** SEM images of BPs prepared from Medium Au PT-NRs, with  $\text{Au}^{3+}/\text{Au}^0 = 6.25$  (left) and  $[\text{Au}^{3+}]/[\text{Au}^0] = 12.5$  (right). Scale bars are 500 nm.

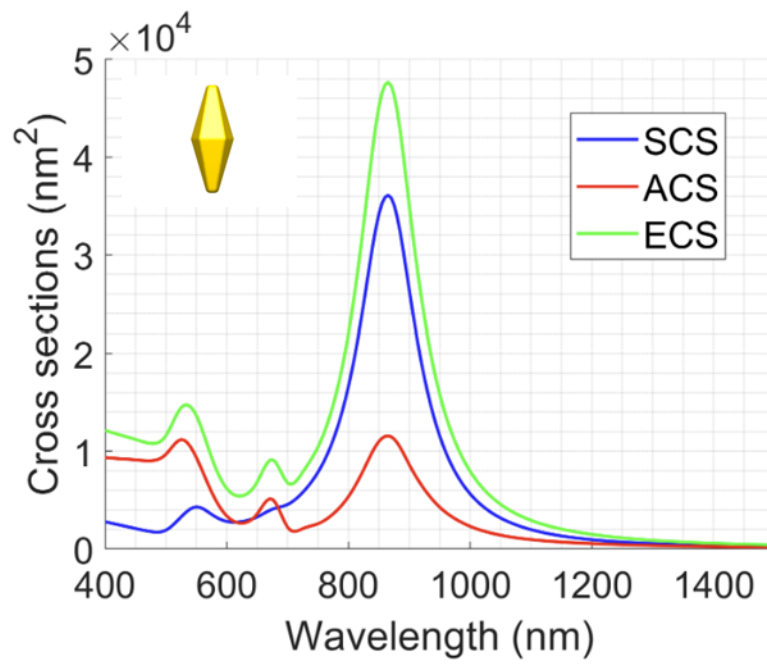




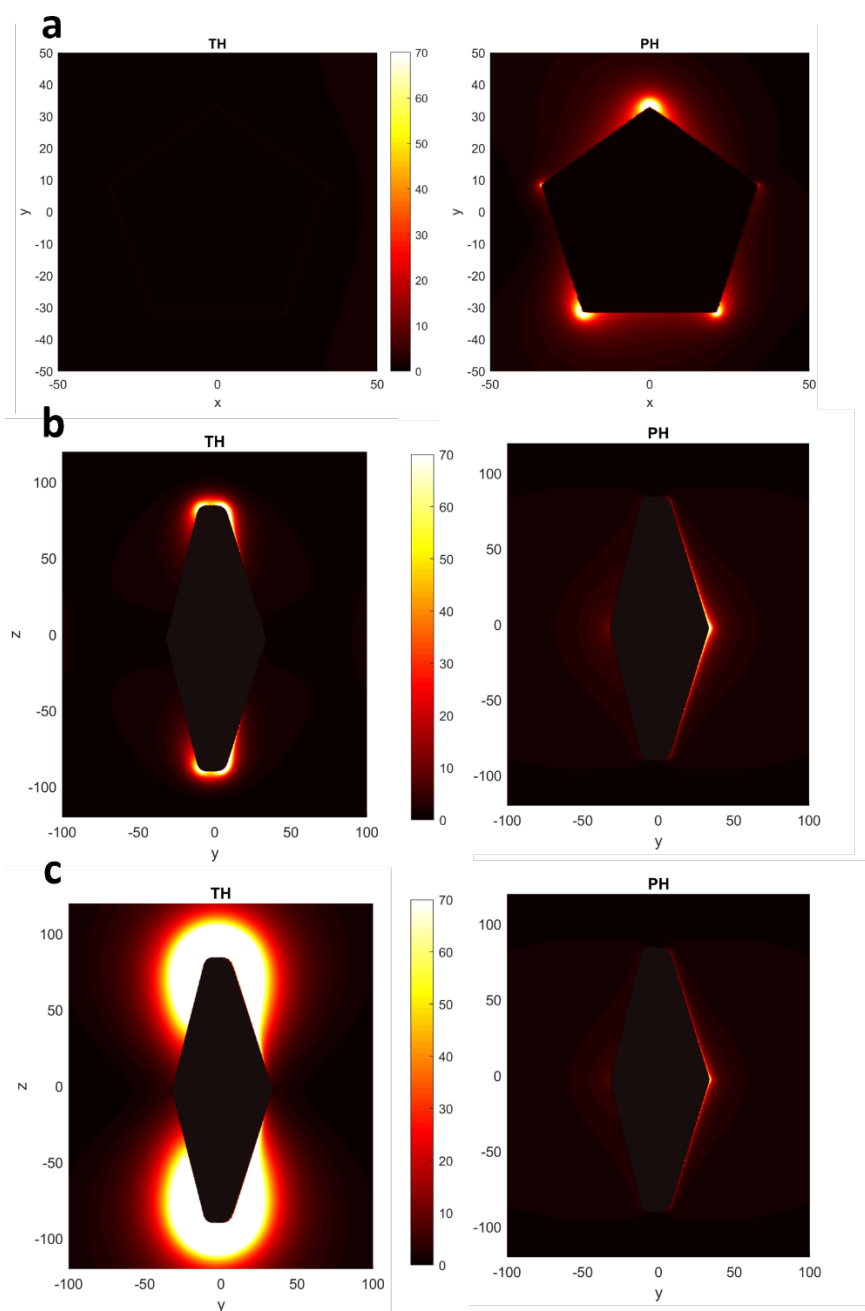
**Figure S9.** High magnification SEM image of particles prepared from Medium Au PR-NRs, with  $[\text{Au}^{3+}]/[\text{Au}^0] = 6.25$ .



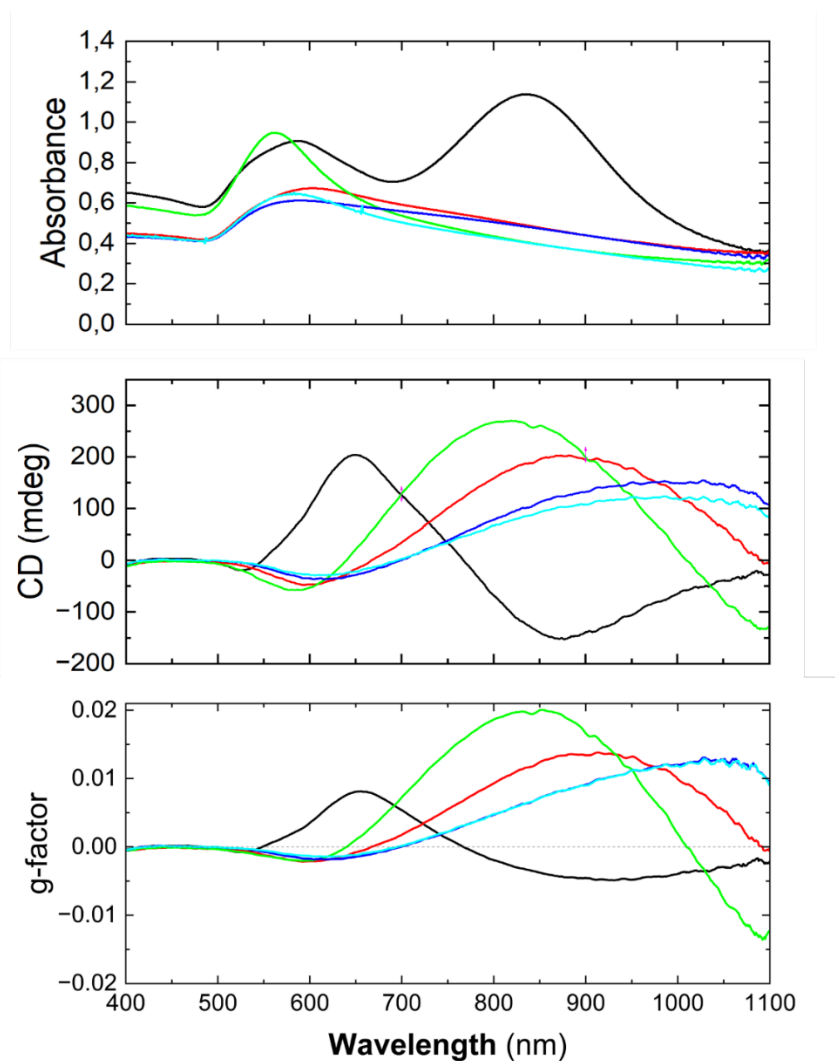
**Figure S10:** EDS characterization of belted bipyramids prepared from medium Au PT-NRs, with a growth ratio of  $[\text{Au}^{3+}]/[\text{Au}^0] = 6.25$ . (a) STEM-HAADF image and (b) corresponding EDS map of the Au M and L counts. (c) Region-averaged spectra of the dashed area in a, showing strong Au signal, C, O and Cu elements from the TEM grid, and trace Cl from the synthesis. (d) Quantification result and weight fraction profile along the line in a.



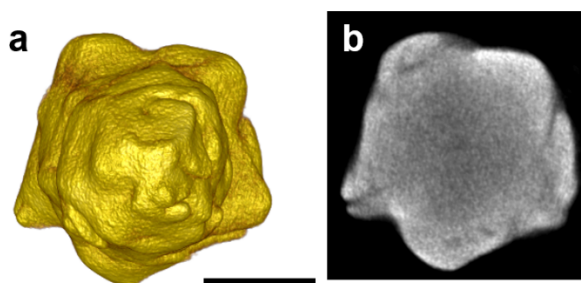
**Figure S11.** Simulated scattering (blue), absorption (red), and extinction (green) cross-sections for a non-belted BP with dimensions of  $180 \times 80$  nm (see model in the inset).



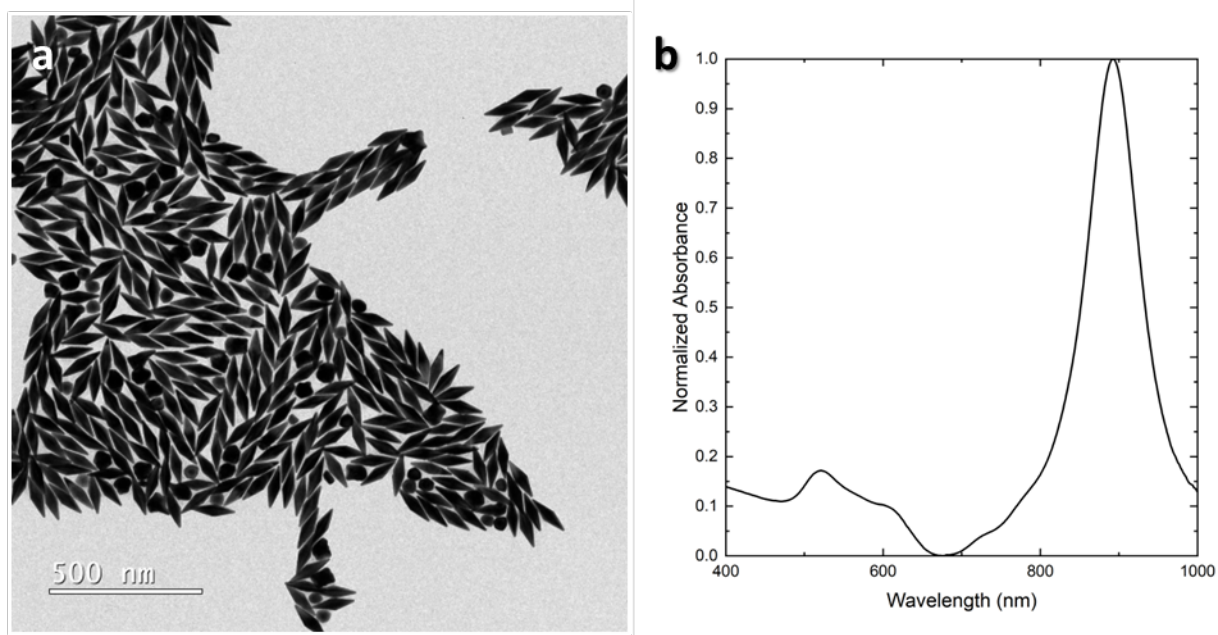
**Figure S12.** Near-field enhancement simulation maps for non-belted ideal particles with dimensions of 180 x 80 nm, illuminated at different wavelengths: 525 nm (a), 675 nm (b), and 850 nm (c). On the left panels, the XY plane is shown; YZ planes shown on right panels. Light was polarized in the transverse (TH) and parallel (PH) directions, respectively.



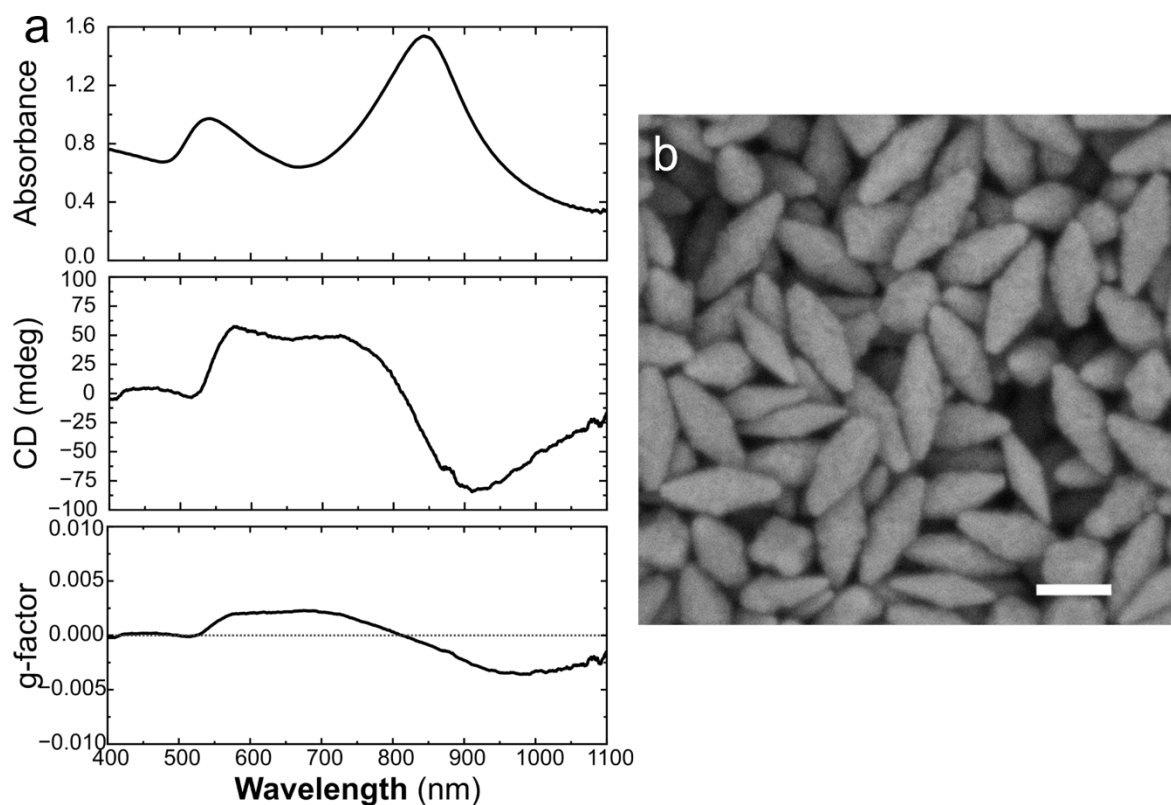
**Figure S13.** UV-Vis, CD, and  $g$ -factor spectra recorded during  $g$ -factor optimization for chiral BPs, with  $[\text{Au}^{3+}]/[\text{Au}^0]$  overgrowth ratios of 1 (black lines), 2 (red lines), 3 (green lines), 4 (blue lines), and 5 (cyan lines).



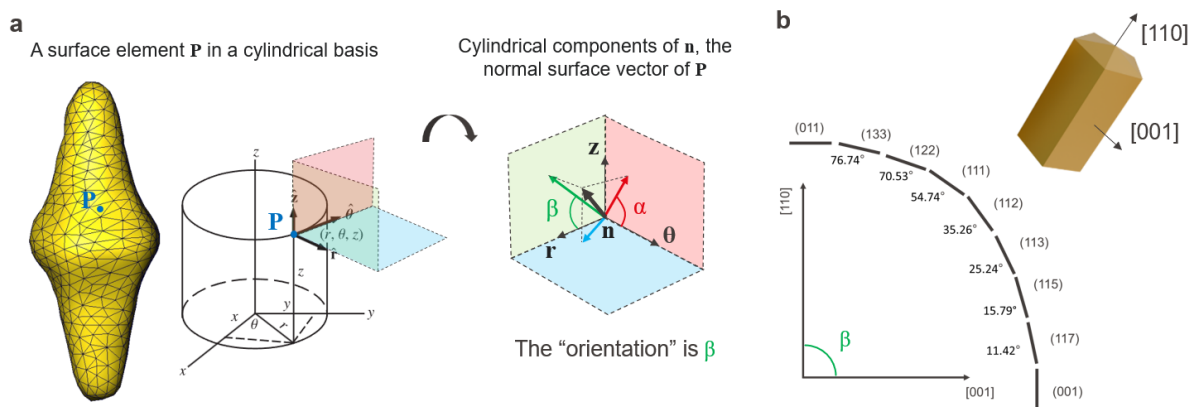
**Figure S14.** Electron tomography 3D reconstruction of the chiral BP in Figure 4 (main text). (a) Surface rendering viewed along the major axis and (b) central orthoslice, showing the conservation of 5-fold symmetry. Scale bar is 50 nm.



**Figure S15:** Bipyramids prepared from PT seeds in the presence of silver. (a) TEM micrograph and (b) the corresponding UV-vis-NIR spectrum.



**Figure S16:** Chiral growth of Ag-assisted Au BPs, with  $[Au^{3+}]/[Au^0] = 3$ . (a) Optical characterization: UV-vis-NIR spectrum (top), CD spectrum (middle), and g-factor spectrum (bottom). (b) Representative SEM image, scale bar is 100 nm.



**Figure S17.** (a) Definition of the orientation angle used to visualize surface facets in Figure 2 of the main text. (b) Relationship to [111] crystal directions between [001] (faces of a pentatwinned nanorod) and [110] (long axis of a pentatwinned nanorod).

### Description of Supporting Movies:

**Supporting Movie S1.** Visualization of a 3D reconstruction of a belted bipyramid grown medium Au PT-NRs, with a growth ratio of  $[\text{Au}^{3+}]/[\text{Au}^0] = 6.25$ . The reconstruction was obtained by HAADF-STEM tomography.

**Supporting Movie S2.** Electric field enhancement calculated for the belted bipyramid shown in Figure 2 (main text), under illumination at a wavelength of 525 nm. Two polarizations are shown next to each other. Illumination is from the bottom.

**Supporting Movie S3.** Electric field enhancement calculated for an ideal (non-belted) bipyramid with dimensions similar to the real (belted) bipyramid (180 nm  $\times$  80 nm) under illumination at a wavelength of 550 nm. Two polarizations are shown next to each other. Illumination is from the bottom.

**Supporting Movie S4.** Electric field enhancement calculated for the belted bipyramid shown in Figure 2 (main text), under illumination at a wavelength of 675 nm. Two polarizations are shown next to each other. Illumination is from the bottom.

**Supporting Movie S5.** Electric field enhancement calculated for the belted bipyramid shown in Figure 2 (main text), under illumination at a wavelength of 850 nm. Two polarizations are shown next to each other. Illumination is from the bottom.

**Supporting Movie S6.** Visualization of a 3D reconstruction of a chiral particle grown from a medium BP (see main text for details), with an  $[\text{Au}^{3+}]/[\text{Au}^0]$  ratio of 3. The reconstruction was obtained by HAADF-STEM tomography.