

## Article

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# Chiroptical Activity Enhancement via Structural Control: the Chiral Synthesis and Reversible Interconversion of Two Intrinsically Chiral Gold Nanoclusters

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Supporting Information Placeholder

**ABSTRACT:** We report the synthesis and crystal structure determination of two novel chiral gold nanoclusters. By utilizing BINAP, we isolate atomically precise intrinsically chiral Au nanoclusters  $[Au_9(R- / S-BINAP)_4](CF_3COO)_3$  and  $[Au_{10}(R- / S-BINAP)_4(p-CF_3C_6H_4C\equiv C)](CF_3COO)_3$  in high yield with one-pot synthesis. **Au**<sub>9</sub> has  $C_2$  geometry while **Au**<sub>10</sub> is  $C_1$  symmetric. Interestingly, reversible interconversion between **Au**<sub>9</sub> and **Au**<sub>10</sub> can be realized by the addition or removal of a RC=CAu component. The transformation from **Au**<sub>9</sub> to **Au**<sub>10</sub> leads to significant enhancement of CD signals. The maximum anisotropy factor in the visible region of  $[Au_{10}(BINAP)_4(p-CF_3C_6H_4C\equiv C)]^{3+}$  is the hitherto largest (up to 6.6 \* 10<sup>-3</sup>) among gold nanoclusters, which is approximately twice of that of  $[Au_9(BINAP)_4]^{3+}$ . This work demonstrates that chiroptical activity of gold nanoclusters can be modulated by structural control through the introduction of second ligands.

#### INTRODUCTION

Chiral materials are of great interest for their promising applications in medicine design, biorecognition, enantioselective catalysis, optical devices, holography, chiral sensing and isolation.<sup>1-8</sup> Among chiral nanomaterials, ligand-protected chiral coinage metal nanoclusters with atomic precision attracted recent attention,<sup>9-25</sup> because chiral nanoclusters with well-defined structures are advantages in correlating the chirality with nanocluster size and surface properties.<sup>12-15</sup> The understanding and application of the optical characteristics of chiral gold clusters remains a great challenge due to rare structural evidences of enantiomerically pure Au clusters.<sup>15, 20</sup>

Chiral metal clusters can be sorted into three categories:<sup>17, 18</sup> (i) the structure of the metal skeleton is intrinsically chiral; (ii) an inherently achiral core with a chiral shell generated from the symmetric arrangement of surface-protecting units; (iii) chiral ligands induce chiroptical properties of Au nanoclusters through vicinal effects or through a chiral electrostatic field.<sup>16,</sup> <sup>26-30</sup> For the second category, racemic mixtures are produced, so enantioseparation of Au nanoclusters has been carried out by using chiral HPLC columns  $(Au_{28}^{26} Au_{38}^{31})$  and phase transfer method with chiral ammonium salts  $(Au_{11}^{32} Au_{102}^{33})$ . It is inconvenient and time-consuming to employ chiral HPLC columns to separate the as-prepared racemic mixture into enantiomers. Although an ion-pairing strategy was used for direct asymmetric synthesis of optically active nanoparticles, this method requires the design of chiral counterions and is impractical when the Au nanoclusters are neutral. Thus, chiral ligand induction provides a practical and straightforward protocol for the synthesis of chiral Au nanoclusters.<sup>15, 20, 30, 34-36</sup>



Chart 1. Phosphine ligands employed in the present study.

So far, structural evidences for gold nanoclusters with chiral ligands remain relatively scarce. <sup>15, 36</sup> There are only three examples with determined structures by X-ray diffraction:  $[Au_{11}(R-/S-DIOP)_4Cl_2]Cl$ ,  $[Au_8(R-/S-BINAP)_3(PPh_3)_2](PF_6)_2^{15}$  and  $[Au_{24}L_6Cl_4]Cl_2$  (L = (R,R)- and (S,S)-2,3-bis(diphenylphosphino)butane).<sup>36</sup> In our previous work, we achieved the introduction of alkynyl ligands into the protecting sphere of metal nanoclusters and obtained atomically precise nanol-custers  $[Au_{19}(PhC\equiv C)_9(Hdppa)_3](SbF_6)_2$  (Hdppa = N,N-bis(diphenylphosphino)amine),  $[Au_{23}(PhC\equiv C)_9(PPh_3)_6](SbF_6)_2$ ,  $[Au_{24}(PhC\equiv C)_{14}(PPh_3)_4](SbF_6)_2$ ,

 in order to induce the formation of chiral pure gold nanoclusters with intrinsic chiral metal cores. We managed to isolate two pairs of chiral gold nanoclusters, namely  $[Au_9(R-/S-BINAP)_4](CF_3COO)_3$  ((**R**)-**Au**<sub>9</sub>/(**S**)-**Au**<sub>9</sub>) and  $[Au_{10}(R-/S-BINAP)_4(p-CF_3C_6H_4C=C)](CF_3COO)_3$  ((**R**)-**Au**<sub>10</sub>/(**S**)-**Au**<sub>10</sub>).<sup>43</sup> Herein, we report their asymmetric synthesis and crystal structures as well as the reversible interconversion between **Au**<sub>9</sub> and **Au**<sub>10</sub>. It is noteworthy that **Au**<sub>10</sub> show a large g value (up to 6.6 \* 10<sup>-3</sup>), which is the largest among reported chiral gold nanoclusters so far.<sup>31</sup>

## RESULT AND DISCUSSION

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**Synthesis and Characterization.** To prepare (**R**)-**Au**<sub>9</sub>, a  $CH_2CI_2$  solution containing o-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C≡CAu and (**R**)-BINA-PAu<sub>2</sub>(CF<sub>3</sub>COO)<sub>2</sub> was reduced by NaBH<sub>4</sub> (Method 1). Similarly, (**S**)-**Au**<sub>9</sub> can be synthesized by using (**S**)-BINAPAu<sub>2</sub>(CF<sub>3</sub>COO)<sub>2</sub>. o-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C≡C ligands were not in the product **Au**<sub>9</sub> due to steric factor. Therefore the reaction was repeated without o-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C≡CAu precursor, i.e. direct reduction of (**R**)- or (**S**)-BINAPAu<sub>2</sub>(CF<sub>3</sub>COO)<sub>2</sub> gave rise to homoleptic phosphine-protected **Au**<sub>9</sub> (Method 2, Figure S1). (**R**)-**Au**<sub>10</sub> and (**S**)-**Au**<sub>10</sub> were prepared from the reduction of p-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C≡CAu and (**R**)- or (**S**)-BINAPAu<sub>2</sub>(CF<sub>3</sub>COO)<sub>2</sub> by NaBH<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>, respectively. Dark red crystals of **Au**<sub>9</sub> and **Au**<sub>10</sub> were grown by layering n-hexane : ether (V : V=1 : 1) onto the filtrate of the reaction mixture. Similar synthetic procedures gave different products.

24 Single-crystal structural analysis revealed that (R)-Au<sub>9</sub>/(S)-25 Au<sub>9</sub> and (R)-Au<sub>10</sub> / (S)-Au<sub>10</sub> comprise tricationic clusters  $[Au_9(R-/S-BINAP)_4]^{3+}$ and  $[Au_{10}(R-/S-BINAP)_4(p-$ 26  $CF_3C_6H_4C\equiv C)$ <sup>3+</sup>, respectively (Figure 1). For better under-27 standing the structures, the anatomy illustration is shown in Fig-28 ure 2. The core of (R)-Au<sub>9</sub> or (S)-Au<sub>9</sub> is composed of two Au<sub>4</sub> 29 tetrahedra sharing a common Au atom, and two additional Au 30 atoms are attached from the opposite side (Figure 2a). The Au<sub>9</sub> 31 core has a  $C_2$  symmetry with a twofold axis passing through 32 Au9 and the middle point between Au1 and Au2. The skeleton 33 is different from the reported butterfly  $[Au_9(PPh_3)_8]^{3+}$  with  $D_{2h}$ 34 symmetry.44 However, the Au<sub>9</sub> core can be viewed as a distorted 35 crown structure, which is somewhat similar to the crown  $[Au_9{P(C_6H_4OMe-p)_3}_8]^{3+}$  with  $D_{4d}$  symmetry. <sup>45, 46</sup> Au<sub>10</sub> has an 36 exterior Au atom attaching on one of the corner of a tetrahedron 37 with the Au-Au distance of 2.953 Å, which leads to a very low 38 symmetry  $(C_1)$ . It is also interesting to compare the 39  $[Au_{10}(BINAP)_4(p-CF_3C_6H_4C\equiv C)]^{3+}$ cluster with a very different 40 from  $[Au_{10}(C_6F_5)_4(PPh_3)_5],^{47}$ Au10 structure 41  $[Au_{10}(PPh_3)_7 \{S_2C_2(CN)_2\}_2]$ ,<sup>48</sup>  $[Au_{10}Cl_3(PCy_2Ph)_6](NO_3)^{49}$  and 42 K[Au(AuCl)(AuPPh<sub>3</sub>)<sub>8</sub>)](PF<sub>6</sub>)<sub>2</sub>.<sup>50</sup> The Au-Au distances from 43 the Au atoms of the kernels are different between Au<sub>9</sub> and Au<sub>10</sub>. 44 In the kernel of Au<sub>9</sub>, the Au-Au distances are in the range of 45 2.6544(16)–2.9560(17) Å. The Au–Au distances from the Au 46 atoms of Au<sub>10</sub> are in the range of 2.632(3) - 3.3860(39) Å. As illustrated in Figure 2b, the addition of the RC=CAu component 47 causes the increase of the distances of Au1-Au3 (from 48 2.9244(16) to 3.3026(66)) and Au2-Au4 (from 2.9560(17) to 49 3.3860(39)). The P^P-Au-C=CR staple is different from the 50 previous staple motif previously reported (Figure 2c).<sup>37-42</sup> The 51 P^P-Au-C=CR motif has a linear pattern where the RC=C-52 ligands are almost in line with the Au-P bonds. 53

In solution, the <sup>31</sup>P NMR of **Au**<sub>9</sub> displays four peaks at  $\delta = 53.29, 54.27, 56.25$  and 74.93 ppm in a 1 : 1 : 1 : 1 ratio, which is in accordance with its two fold symmetry (*C*<sub>2</sub>) (Supporting Information, Figure S2). In **Au**<sub>10</sub>, the symmetry is lowered compared to **Au**<sub>9</sub> due to the asymmetrically addition of the *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C=CAu unit. Consequently, the <sup>31</sup>P NMR of **Au**<sub>10</sub>

should display 8 peaks at the same ratio based on the number of atoms of each type. Experimentally, eight peaks at  $\delta = 29.23$ , 48.02, 50.84, 52.13, 57.51, 64.45 and 69.73 ppm were observed in a ratio of 1:1:1:1:1:2 (Supporting Information, Figure S3). The peak at  $\delta = 69.73$  ppm with two fold abundance indicates that phosphorous donors (types G and H) are linked to two types of Au atoms with similar coordination environments (Figure 2b). The <sup>31</sup>P NMR spectra provide strong evidence for supporting that the symmetry and structures of Au<sub>9</sub> and Au<sub>10</sub> are retained in solution (Figure 2b). It is noteworthy that P^P-Au-C=CR motif is formed in Au<sub>10</sub> due to the involvement of the binding of RC=C, and this motif can be viewed as a semi-staple, which is different from the previous reported staple motif RC=C-Au-C=CR.<sup>37-41</sup>



Figure 1. Total X-ray crystal structure of the tricationic cluster (R)-Au<sub>9</sub>/(S)-Au<sub>9</sub> and Au<sub>10</sub>/(S)-Au<sub>10</sub>. Au, orange; P, pink; C, grey. All hydrogen atoms and  $-CF_3$  units are omitted for clarity.





**Figure 2.** (a) **Au**<sub>9</sub> and **Au**<sub>10</sub> cores. (b) The arrangement of BINAP ligands in (**R**)-**Au**<sub>9</sub>/(**S**)-**Au**<sub>9</sub> and (**R**)-**Au**<sub>10</sub>/(**S**)-**Au**<sub>10</sub>. (c) Reported staple motifs in gold–alkynyl or gold–alkynyl-phosphine systems. Au, orange; P, pink; C, grey. Blue curve: binaphthy unit. All hydrogen atoms, -CF<sub>3</sub> unit and some benzene rings are omitted for clarity.

The samples were further characterized by an ESI-TOF mass spectrometer with an electrospray ionization source in positive mode (Figure 3). Intense peak at m/z = 1420.83 in Figure 3a corresponds to the molecular ion  $[Au_9(BINAP)_4]^{3+}$ . The observed isotopic patterns of  $[Au_9(BINAP)_4CI]^{2+}$  and  $[Au_9(BINAP)_4CF_3COO]^{2+}$  are in perfect agreement with the simulated (Figure 3b), and CF\_3COO<sup>-</sup> counteranions could be confirmed in negative mode (Figure S4). The mass spectrum of  $Au_{10}$  shows two prominent peaks at m/z = 1542.8 and 2371.2, corresponding to the molecular ion  $[Au_{10}(BINAP)_4(p-CF_3C_6H_4C=C)]^{3+}$  and dicationic ion  $[Au_{10}(BINAP)_4(p-CF_3C_6H_4C=C)(CF_3COO)]^{2+}$  (Figure 3c and 3d), respectively. The isotopic distribution patterns are in perfect agreement with the simulated.



**Figure 3.** (a) Mass spectrum of the Au<sub>9</sub> cluster. Inset: The measured (black trace) and simulated (red trace) isotopic patterns of [Au<sub>9</sub>(BINAP)4]<sup>3+</sup>. (b) The measured (black trace) and simulated (red trace) isotopic patterns of [Au<sub>9</sub>(BINAP)4(Cl)]<sup>2+</sup> and [Au<sub>9</sub>(BINAP)4 (CF<sub>3</sub>COO)]<sup>2+</sup>. (c) Mass spectrum of the Au<sub>10</sub> cluster. Inset: The measured (black trace) and simulated (red trace) isotopic patterns of [Au<sub>10</sub>(BINAP)4(*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C=C)]<sup>3+</sup>. (d) The measured (black trace) and simulated (red trace) of [Au<sub>10</sub>(BINAP)4(*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C=C)]<sup>3+</sup>. (d) The measured (black trace) and simulated (red trace) isotopic patterns of [Au<sub>10</sub>(BINAP)4(*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C=C)]<sup>3+</sup>.

As shown in Figure 4, both clusters in  $CH_2Cl_2$  show one prominent absorption band at 426 nm, and a broad band around 500 nm tailing to 626 nm. **Au<sub>9</sub>** has a peak at 320 nm, while **Au<sub>10</sub>** exhibits an absorption at 340 nm. And **Au<sub>9</sub>** shows a shoulder peak at 444 nm while **Au<sub>10</sub>** displays a characteristic peak at 467

nm attributed to the presence of the P^P-Au-C=CR motif, which can be used to differentiate it from Au<sub>9</sub>. The molar absorption coefficient at 426 nm of Au<sub>9</sub> were calculated to be 2.1 \* $10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  and is approximately 1.5 times of that in Au<sub>10</sub>. The absorptions with wavelength larger than 400 nm are associated with the metal cluster cores, because the BINAP ligands and Au(I) precursors [(BINAP)Au<sub>2</sub>]Cl<sub>2</sub> show no absorption in the region of 350-700 nm (Figure S5). The thermal and photo stability of Au<sub>9</sub> and Au<sub>10</sub> were monitored by UV-vis spectroscopy. No decomposition was observed after Au<sub>9</sub> and Au<sub>10</sub> had been stored under ambient light for one week in dichloromethane, which shows their excellent photo-stability (Figure S6). A CH<sub>3</sub>CN solution of Au<sub>9</sub> was kept at 20 °C, 40 °C, 60 °C, 80 °C for 10 min, respectively, then its UV-vis spectra were measured (Figure S7). No obvious changes of UV-vis absorption spectra were observed, which indicates that Au<sub>9</sub> has good thermal stability. However, it was observed that  $Au_{10}$  was converted to Au<sub>9</sub> at elevated temperature such as 40°C (Figure S7).



Figure 4. UV-vis absorption spectrum of Au<sub>9</sub> (black), Au<sub>10</sub> (red). Inset: Photographs of cluster Au<sub>9</sub> and Au<sub>10</sub> in dichloromethane.

The Reversible Interconversion. It was found that Au<sub>9</sub> and Au<sub>10</sub> could be interconverted (Figure 5a). The interconversion is associated with the addition or removal of a RC=CAu component. As shown in Figure 5 b, after the addition of equivalent amount of BINAP to the CH<sub>2</sub>Cl<sub>2</sub> solution of Au<sub>10</sub>, the absorption at 467 nm decreases and the absorption at 426 nm increases, which is indicative of that Au<sub>10</sub> is converted to Au<sub>9</sub>. Interestingly, Au<sub>10</sub> can be recovered by adding RC=CAu to the solution of Au<sub>9</sub>. C<sub>6</sub>H<sub>11</sub>C=CAu was used in the conversion, because its good solubility is helpful for monitoring with UV-vis spectroscopy (Figure 5 c). This Au<sub>10</sub> can be converted reversibly to Au<sub>9</sub> again by adding BINAP to strip off the C<sub>6</sub>H<sub>11</sub>C=CAu component. The interconversion process was completed in about 30 min, and the transformation was confirmed by mass spectrometry (Figure S8).



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(b)



**Figure 5.** (a) Schematic illustration of interconversion between **Au**<sub>9</sub> and **Au**<sub>10</sub> Blue curve: binaphthy unit. Some benzene rings are omitted for clarity. Response of UV-vis absorption spectra at room temperature: (b) The conversion from  $[Au_{10}(BINAP)_4(p-CF_3C_6H_4C=C)](CF_3COO)_3$  to  $[Au_9(BINAP)_4]$  (CF<sub>3</sub>COO)<sub>3</sub>. (c) The interconversion between  $[Au_9(BINAP)_4]$  (CF<sub>3</sub>COO)<sub>3</sub> and  $[Au_{10}(BINAP)_4(C_6H_{11}C=C)](CF_3COO)_3$  in dichloromethane.

The CD Spectrum and the anisotropy factors. The chirality of Au<sub>9</sub> and Au<sub>10</sub> has been confirmed by CD spectroscopy as shown in Figures 6 and 7. The CD curves of (R)-Au<sub>9</sub> and (S)-Au<sub>9</sub> are mirror images to each other, indicating they are a pair of enantiomers (Figure 6a). (R)-Au<sub>10</sub> and (S)-Au<sub>10</sub> are in a like manner (Figure 7a). The chirality of Au<sub>9</sub> or Au<sub>10</sub> depends on the handness of BINAP, i.e. the chirality of BINAP is transferred to the nanoclusters. Consequently, CD signal enhancement was observed as shown in Figure S9a. It is worth noting that apart from the CD features of the ligands and BINA-PAu<sub>2</sub>Cl<sub>2</sub>, the CD spectra of gold clusters exhibit new features in the visible wavelength region, similar to the previous observation by Schaaff et al.<sup>28</sup> We ascribe the optical activity in the visible region to ligand-to-metal charge transfer (LMCT) because the ligands themselves do not show optical activity in the visible region. The anisotropy factors of (R)-Au<sub>9</sub>/(S)-Au<sub>9</sub> and (R)-Au<sub>10</sub>/(S)-Au<sub>10</sub> in the 250-350 nm range are very low (Figure S9b), suggesting that  $\pi$ - $\pi$ \* transitions of (R)- and (S)- BINAP contribute little to the optical activity of gold clusters. But previous studies by Tsukuda et al. revealed that enhancement of the optical activity of gold clusters may be caused by diffusion of  $\pi$ -electron of binaphthalene unit in vicinity to the Au core.<sup>15</sup> The CD spectra of (S)-Au<sub>10</sub>(BINAP)<sub>4</sub>( $C_6H_{11}C \equiv C$ ) (black trace) and (S)-Au<sub>10</sub>(BINAP)<sub>4</sub>(p-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C=C) are almost identical to each other, which indicates that the types of alkynyl ligands affect slightly the chiroptical signals (Figure S10).

The CD spectra of Au<sub>9</sub> and Au<sub>10</sub> share a minimum at 568 nm and a maximum at 342 nm as well as less intense signals at 380 nm, while some differences are evident. A shoulder at 363 nm was observed with Au<sub>9</sub> (Figure 8a) but not in Au<sub>10</sub>. (**R**)-Au<sub>10</sub> has a negative peak at 265 nm and a strong and broad positive peak at 467 nm (Figure 7a), while the negative peak of (**R**)-Au<sub>9</sub> complex occurs at about 310 nm and the broad positive peak is positioned at 426 nm (Figure 6a). The two systems both exhibit intense and mirror-image Cotton effects in their CD spectra and the peaks of their CD spectra are much more distinct than those of the optical absorption spectra. The presence of P^P-Au-

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C=CR staple has both a structural and electronic impact on the system. The interconversion between  $Au_9$  and  $Au_{10}$  was also monitored by CD spectroscopy (Figure S11), which shows a trend similar to that of UV-vis absorption (Figure 5b and 5c).

The intensity of CD spectra should be correlated with the concentration of the sample, while the anisotropy factors is concentration-independent and  $g = \Delta \epsilon / \epsilon = \Delta A / A = \theta [mdeg] / (32980)$  $\times$  A) ( $\Delta \varepsilon$ : the molar circular dichroism;  $\varepsilon$ : the molar absorption coefficient) were calculated in the wavelength range of 250-620 nm (Figure 7). The maximum anisotropy factor  $(g_{max})$  of Au<sub>10</sub> is up to  $6.6 \times 10^{-3}$  at 473 nm and is around 7 times higher than that at 267 nm (Figure 7b). To the best of our knowledge, this is the highest maximum anisotropy factor of gold nanoclusters reported so far (Table S1). Similar to the trend in anisotropy factors, the value around 450 nm of Au<sub>9</sub> is calculated 3.7 \* 10<sup>-</sup> <sup>3</sup>, which is much higher than that around 317 nm (Figure 6b). The result indicates that ligand-to-metal charge transfer (LMCT) may play a key role in optical activity, whereas the contribution of  $\pi$ - $\pi$ \* transitions of the ligands to the chiroptical properties is relatively small. Notably, the highest anisotropy factors of Au<sub>10</sub> is almost two times of that in Au<sub>9</sub> (Figure 8b). The formation of P^P-Au-C=CR staple has influences on both the geometric and electronic structures, which led to the enhancement of the g value.



**Figure 6.** (a) The CD spectra of enantiomers (**R**)-**Au**<sub>9</sub> (black trace), (**S**)-**Au**<sub>9</sub> (red trace) (y-axis ( $\theta$ ) is in units of mdeg). And UV–vis spectrum of (**R**)-**Au**<sub>9</sub> (dotted line) in dichloromethane. For CD analysis, samples were diluted to 1.3 × 10<sup>-5</sup> mmol/mL. (b) Corresponding anisotropy factors of (**R**)-**Au**<sub>9</sub>.



**Figure 7.** (a) The CD spectra of enantiomers (**R**)-**Au**<sub>10</sub> (black trace), (**S**)-**Au**<sub>10</sub> (red trace) (y-axis ( $\theta$ ) is in units of mdeg). And UV–vis spectrum of (**R**)-**Au**<sub>10</sub> (dotted line) in dichloromethane. For CD analysis, the solution was diluted to  $1.3 \times 10^{-5}$  mmol/mL. (b) Corresponding anisotropy factors of (**R**)-**Au**<sub>10</sub>/(**S**)-**Au**<sub>10</sub>.



**Figure 8.** (a) Comparison of the CD signal of (**R**)-**Au**<sub>9</sub> (black trace), (**R**)-**Au**<sub>10</sub> (red trace) in dichloromethane (y-axis ( $\theta$ ) is in units of mdeg). For CD analysis, samples were diluted to  $1.3 \times 10^{-5}$  mmol/mL. (b) Comparison of the anisotropy factor of (**R**)-**Au**<sub>9</sub> (black trace), (**R**)-**Au**<sub>10</sub> (red trace).

**Computational Results.** The correlation between the optical activity and geometrical structure of the two clusters was studied by DFT calculations. Cluster  $Au_9$  and  $Au_{10}$  are ideal models for studying the origin of chiroptical properties of nanoclusters because of the comparability between the two well-defined structures.

As shown in Figure 9a, the calculated electronic absorption spectrum of Au<sub>10</sub> is in good agreement with the experimental. The peaks at 573 nm, 467 nm, 426 nm and 340 nm, are well reproduced. Simulated CD spectra of (R)-Au<sub>10</sub>/(S)-Au<sub>10</sub> are also presented in Figure 9b. One can see that Au<sub>10</sub> exhibits five peaks distinct from 250 nm to 600 nm, which closely match experiment. As shown in Figure S12a, the first calculated CD band 1 at 508 nm of (R)-Au<sub>10</sub>/(S)-Au<sub>10</sub> correspond to shoulder peak I in the theoretical absorption spectrum at 502 nm ( $\lambda_{exp}$  = 573 nm), which arises primarily from the HOMO→LUMO transition (Table S2). According to the frontier molecular orbital diagrams (Figure S13), the HOMO is located over BINAP, while the LUMO is on the metal core. The second CD peak at 450 nm is related to the absorption peak II at 450 nm, which is ascribed to HOMO-2→LUMO, HOMO-2→LUMO+1 and HOMO-4→LUMO transitions. Notably, the HOMO-2 is mostly contributed by the P^P-Au-C=CR motif (Table S3). Therefore, the introduction of alkynyl ligands is crucial for the CD band at 450nm ( $\lambda_{exp} = 467$  nm). Moreover, the CD band 3 at 426 nm matches the absorption peak III ( $\lambda_{exp}$ = 426 nm), which corresponds to the deep occupied orbitals to LUMO/LUMO+1 transitions.

We also calculated the UV-Vis and CD spectra of (R)-Au<sub>9</sub>/(S)-Au<sub>9</sub> (Figure S12b, S14). We found that a weak CD peak at 521 nm is related to the absorption peak I ( $\lambda_{exp} = 553$ nm), and an indistinctive CD peak at 462 nm can be associated with absorption shoulder peak II ( $\lambda_{exp} = 444$  nm). These two absorption bands arise primarily from HOMO-JLUMO transition and HOMO→LUMO+2 transition, respectively. Despite a blue-shift, a primary absorption band at 426 nm from the experiment is well reproduced in the simulated spectrum (Figure S14). This absorption peak accounts for the CD band III (Figure S12b), which mainly represents HOMO-9→LUMO transition. It is worth noting that the absorption peak at 426 nm is related to the transition of the phosphine ligand to the metal core, similar to that of the Au<sub>10</sub>. However, there is no "P^P-Au-C $\equiv$ CR" motif in cluster Au<sub>9</sub>, so the absorption peak at 467 nm is missing. Consequently, the theoretical calculations confirm that the optical properties in the visible spectral region are dominated by electronic transitions from the ligands to the chiral core.

(a)







Figure 9. (a) Experimental (black) and calculated (red) UV-vis absorption spectrum of Au<sub>10</sub>. (b) Experimental (solid line) and calculated (dotted line) CD spectrum of (**R**)-Au<sub>10</sub>/(**S**)-Au<sub>10</sub>.

## CONCLUSION

We explore a facile synthetic strategy of homoleptic phosphineprotected or mixed ligand-stabilized chiral nanoclusters. The CD spectra give perfect mirror images and the identified peaks of the experimental spectra are in good agreement with those computed for the spectral range from 250 to 600 nm. The P^P-Au-C=CR staple in Au<sub>10</sub> not only causes the reduction of chiral symmetry from  $C_2$  to  $C_1$ , but also has a strong effect on electronic system. These results reveal that using mixed ligands may be an effective strategy to lower symmetry of chiral nanoclusters. Intriguingly, we can realize reversible interconversion between  $Au_9$  and  $Au_{10}$  by the addition of BINAP or RC=CAu. Furthermore, insights from the tunable chiroptical activity could provide a new platform to control the chiro-optical properties of metal nanoclusters and find their potential applications in chiroptical functional materials. Rational design of ligand shell structures may be an effective way for controlling the optical response of chiral nanostructures and aiding in the research of reconfigurable switching of nanomaterials.

## ASSOCIATED CONTENT

#### Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Physical measurements and computational details, synthesis and characterization data (PDF)

Detailed crystallographic structure and data for (R)-Au<sub>9</sub>, (S)-Au<sub>9</sub>, (R)-Au<sub>10</sub> and (S)-Au<sub>10</sub> (CIF).

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#### Notes

The authors declare no competing financial interests.

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54	space group $P_{21}$ , $Z = 4$ , $T = 100$ K, 261387 reflections measured 64802	
55	unique ( $R_{int} = 0.0840$ ), final $R_1 = 0.0976$ , $wR_2 = 0.2581$ for 59231 ob-	
50	served reflections $[I > 2\sigma(I)]$ . Flack factor = 0.013(5). (b) Crystal data	
5/	for (S)-Au <sub>9</sub> : $a = 17.4001(3)$ , $b = 35.5243(5)$ , $c = 30.5610(6)$ Å, $\alpha =$	
58	90.00, $\beta = 98.414(2)$ , $\gamma = 90.00$ °, $V = 18687.2(6)$ Å <sup>3</sup> , space group $P2_1$ ,	
59		

*Z* = 4, *T* = 100 K, 176380 reflections measured, 57490 unique ( $R_{int}$  = 0.0980), final  $R_1$  = 0.1441,  $wR_2$  = 0.3511 for 51849 observed reflections [*I* > 2 $\sigma$ (I)]. Flack factor = 0.108(7). (c) Crystal data for (**R**)-**Au**<sub>10</sub>: *a* = 19.3620(3), *b* = 19.3620(3), *c* = 92.9191(11) Å, *a* = 90.00, *β* = 90.00, *γ* = 120.00 °, *V* = 30167.3(8) Å<sup>3</sup>, space group *P*6<sub>5</sub>, *Z* = 6, *T* = 100 K, 64850 reflections measured, 29115 unique ( $R_{int}$  = 0.0785), final  $R_1$  = 0.1133,  $wR_2$  = 0.2591 for 27471 observed reflections [*I* > 2 $\sigma$ (I)]. Flack factor = 0.034(14). (d) Crystal data for (**S**)-**Au**<sub>10</sub>: *a* = 19.4670(3), *b* = 19.4670(3), *c* = 92.8172(14) Å, *a* = 90.00, *β* = 90.00, *γ* = 120.00 °, *V* = 30167.3(8) Å<sup>3</sup>, space group *P*6<sub>1</sub>, *Z* = 6, *T* = 100 K, 158112 reflections measured, 30549 unique ( $R_{int}$  = 0.1339), final  $R_1$  = 0.1120,  $wR_2$  = 0.2514 for 26574 observed reflections [*I* > 2 $\sigma$ (I)]. Flack factor = 0.038(13). (44) Wen, F.; Englert, U.; Gutrath, B.; Simon, U. Crystal Structure,

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