

Communication

Site-Selective Coordination Controls Chirality Transfer in an Atomically Precise Au₈ Cluster

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Abstract

Atomically precise metal clusters possess multiple inequivalent coordination sites, enabling site-selective ligand coordination to regulate their structures and chiroptical properties. However, the impact of coordination site on chirality transfer remains poorly understood. Herein, we report the selective functionalization of an Au₈ cluster by installing chiral ligands at two distinct coordination sites, generating two chiral clusters. Coordination of chiral bidentate phosphine ligands at the *core*-Au sites dramatically enhances the chiroptical response, whereas functionalization of the *exo*-Au sites with chiral alkynyl ligands produces only a weak effect. Time-dependent density functional theory calculations show that the *core*-Au coordinated chiral phosphine ligands induce more pronounced distortion of the Au₈ framework than the *exo*-coordinated alkynyl ligands, thus enhancing the intensity of electronic circular dichroism transitions. This work highlights that the coordination site is a key factor in chirality transfer and chiroptical activity in atomically precise metal clusters.

Keywords: chiral metal cluster; circular dichroism; chirality transfer

1. Introduction

Metal clusters have emerged as a unique class of atomically precise nanomaterials that bridge the gap between molecular complexes and plasmonic nanoparticles [1,2]. Owing to their well-defined atomic structures, discrete electronic states, and tunable surface chemistry [3], these clusters provide an ideal platform for establishing precise structure–property relationships. The introduction of chirality further endows these clusters with distinctive chiroptical responses, including circular dichroism (CD) and circularly polarized luminescence (CPL), making them promising candidates for applications in asymmetric catalysis [4,5], enantioselective recognition [6], bioimaging [7], and chiral optoelectronics [8]. Over the past decade, remarkable progress has been achieved in the field of chiral metal nanoclusters, driven by advances in atomically precise synthesis, single-crystal structural determination, and theoretical modeling. These developments have substantially deepened the understanding of the atomic origins of chirality, revealing that chirality can arise from intrinsically chiral metal kernels [9–12], chiral ligands [13,14] and asymmetric arrangements of ligands or metal-ligands motifs [15,16]. Despite these significant advances, current studies have focused on controlling the overall chirality of metal clusters through kernel engineering or ligand design. Whether coordination at different surface sites of the cluster can selectively modulate the cluster structure and chiroptical properties remains largely unexplored.



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In this work, we selectively functionalized two distinct coordination sites of the Au_8 cluster with chiral alkynyl ligands and chiral bidentate phosphine ligands, respectively, generating two different chiral Au_8 clusters. Comparative experimental studies reveal that coordination of chiral phosphine ligands at the *core*-Au coordination sites enhances the CD response of the cluster, whereas modification of the *exo*-Au sites with chiral alkynyl ligands shows only a weak influence on its chiroptical properties. Time-dependent density functional theory (TD-DFT) calculations further suggest that coordination of the chiral phosphine ligands at the *core*-Au site induces greater geometric distortion of the Au_8 framework than the chiral alkynyl ligands, leading to a more efficient chirality transfer. These results demonstrate that the coordination site plays an important role in chirality transfer and chiroptical performance in atomically precise metal clusters.

2. Results

According to previous studies, the [core+exo]-type gold cluster $[\text{Au}_8(\text{dppp})_4]^{2+}$, the kernel of which is composed of a bitetrahedral Au_6 core and two *exo*-Au atoms extended at the opposite edges of the bitetrahedron, can undergo either oxidative modification [17] or ligand exchange [18], enabling selective functionalization at the *exo*-Au or *core*-Au coordination sites, respectively. Inspired by these observations, we sought to elucidate the influence of coordination-site-dependent chirality transfer by selectively installing chiral alkynyl ligands, (R/S)-EPEB ((R/S)-EPEB = 1-ethynyl-2-[(1R/S)-1-phenylethoxy]benzene), at the *exo*-Au sites and chiral bidentate phosphine ligands, (2R,4R)/(2S,4S)-BDPP (BDPP = 2,4-bis(diphenylphosphino)pentane), at the *core*-Au sites, thereby constructing two chiral Au_8 clusters with distinct coordination environments (Figure 1).

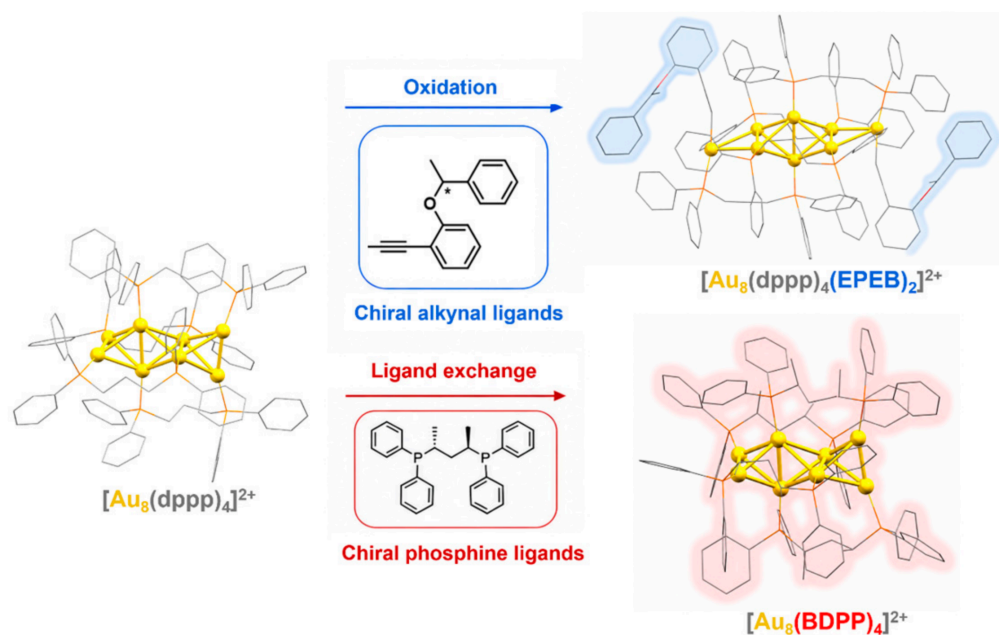


Figure 1. Synthesis of two chiral Au_8 clusters via oxidation and ligand exchange. * = Chiral carbon atom.

The molecular composition of $[\text{Au}_8(\text{dppp})_4(\text{EPEB})_2]^{2+}$ (**1**) was first confirmed by high-resolution electrospray ionization mass spectrometry (HR-ESI-MS). A prominent peak at $m/z = 1833.7647$ agrees well with the simulated isotopic distribution of the doubly charged molecular ion, confirming the molecular composition of **1** in solution (Figure S5). The ^{31}P -NMR spectrum of **1** exhibits four well-resolved resonances at $\delta = 54.9, 52.5, 37.6$, and 33.1 ppm (Figure S6), similar to those reported for analogous $[\text{Au}_8(\text{dppp})_4\text{L}_2]^{2+}$ clusters [17], indicating that the characteristic Au_8 framework is retained.

Single crystals of chiral metal clusters suitable for X-ray diffraction are often difficult to obtain. Among all the crystalline samples obtained, only meso isomer crystals of **1** were suitable for single-crystal X-ray diffraction analysis. The crystal structure of *meso*-**1** reveals that the overall framework and coordination geometry closely resemble those of previously reported Au₈ clusters (Figure 2). The Au₈ framework is composed of six *core*-Au atoms arranged as two edge-sharing tetrahedra, with one *exo*-Au atom (Au1 and Au1') capping each end to afford a centrosymmetric structure (Figure S9). The six *core*-Au atoms exhibit relatively short Au–Au distances from 2.627(9) to 2.861(8) Å, whereas the *exo*-Au atoms display longer Au–Au distances of 3.028(6) and 3.0269(9) Å to their nearest neighboring Au atoms (Table S1), indicating stronger Au–Au metallophilic interactions within the Au₆ core. Each *core*-Au atom is coordinated by a single phosphorus atom from a dppp ligand, while each *exo*-Au atom combines with one phosphorus atom and one alkynyl ligand. Notably, the ortho-substituted phenylalkynyl ligand introduces considerable steric hindrance around the *exo*-Au sites, leading to a remarkable bending of the Au–C≡C linkage. Consequently, the bond angle ∠Au1–C1–C2 is reduced to 162.47°, which is a notable deviation from linear configuration. Packing figures of *meso*-**1** also show that there are weak C–H...π interactions between peripheral phenyl rings (Figure S10).

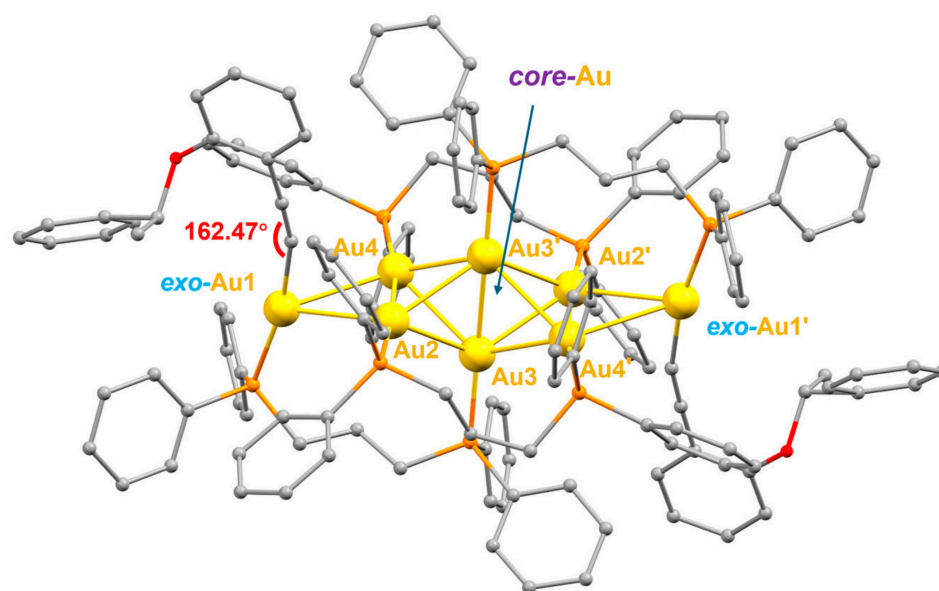


Figure 2. Single crystal structure of *meso*-[Au₈(dppp)₄(EPEB)₂]²⁺ (**1**). Hydrogen atoms are omitted for clarity. Color coding: yellow, Au; gray, C; red, O; orange, P.

The *core*-Au coordination sites were functionalized with chiral bidentate phosphine ligands following a previously reported ligand-exchange strategy [18]. Specifically, the precursor Au₉(PPh₃)₈(NO₃)₃ reacted with the chiral diphosphine ligands (2*R*,4*R*)-BDPP or (2*S*,4*S*)-BDPP, generating the corresponding chiral octanuclear gold clusters [Au₈((2*R*,4*R*)-BDPP)₄](NO₃)₂ ((*R*)-**2**) and [Au₈((2*S*,4*S*)-BDPP)₄](NO₃)₂ ((*S*)-**2**). However, cluster **2** shows lower solution stability than [Au₈(dppp)₄]²⁺. After dissolving in dichloromethane, cluster **2** remains stable in solution for approximately 1 h. With prolonged standing, the initially purple solution gradually changes to fuchsia and eventually becomes pale yellow or colorless, accompanied by the formation of black precipitates, indicating decomposition of the Au₈ cluster. To further probe this process, the solution stability of **2** was monitored by UV–Vis absorption spectroscopy in CH₂Cl₂ (10 μM). A freshly prepared solution of (*S*)-**2** shows two characteristic absorption bands at 515 and 567 nm. Their intensities remained unchanged within 1 h, then decreased continuously and vanished completely after 4 h (Figure S12). The relatively low solution stability of **2** is likely associated with the steric characteristics

of the BDPP ligand from the additional methyl groups, which impose structural strain on the Au₈ kernel. Because cluster **2** exhibits limited solution stability, crystals were rapidly obtained by room-temperature vapor diffusion of diethyl ether into concentrated CH₂Cl₂ solutions of (*R*)-**2** and (*S*)-**2**. Unfortunately, twinning and polycrystallinity prohibited structure solution via single-crystal XRD. Therefore, freshly prepared solutions from crystals of (*R*)-**2** and (*S*)-**2** were used for all subsequent characterizations and all measurements were completed within 30 min to preserve the structural integrity of the cluster.

The molecular composition of **2** was verified by HR-ESI-MS, which exhibits a dominant signal at $m/z = 1668.7296$, in agreement with the calculated isotope pattern for the target cluster (Figure S7). The ³¹P-NMR spectrum of **2** showed two peaks at $\delta = 56.9$ and 46.2 ppm (Figure S8), indicating the presence of two kinds of phosphorus atoms with distinct chemical environments, which matched well with the spectrum of [Au₈(dppp)₄]²⁺ reported previously [18]. Moreover, the characteristic dual absorption bands at around 510 nm and 570 nm in the UV–Vis spectrum also match well with that of [Au₈(dppp)₄]²⁺. Geometric rearrangement of the Au₈ kernel would significantly alter the chemical environment of the peripheral phosphorus atoms and alter the electronic structure of the cluster, which would lead to pronounced variations in the UV–Vis spectrum. Therefore, we propose that the structure of [Au₈(BDPP)₄]²⁺ is highly analogous to [Au₈(dppp)₄]²⁺ on the basis of MS, NMR and UV–Vis characterizations.

3. Discussion

To elucidate the influence of ligand coordination site on chirality transfer in Au₈ clusters, we monitored the chiroptical properties of clusters **1** and **2** by circular dichroism (CD) spectroscopy. Despite both clusters bearing chiral ligands, they exhibit markedly different CD responses. For cluster **1**, in which the chiral alkynyl ligands are coordinated to the *exo*-Au sites, the two enantiomers display mirror-image CD spectra with weak Cotton effects at 306 and 336 nm (Figure 3b). The corresponding absorption anisotropy factors (g_{abs}) are all below 2.0×10^{-4} , indicating a weak overall chiroptical response. Notably, these CD bands coincide with the absorption features of the free (*R/S*)-EPEB ligands, suggesting that they originate from the ligand-centered electronic transitions. In contrast, no CD signal is observed at approximately 510 nm, the characteristic absorption band of the Au₈ framework (Figure 3a). These results indicate that coordination of chiral alkynyl ligands at the *exo*-Au sites is insufficient to induce significant chirality in the metal core. The inefficient chirality transfer is likely a consequence of the relatively large spatial separation between the stereogenic centers of the alkynyl ligands and the Au₈ framework.

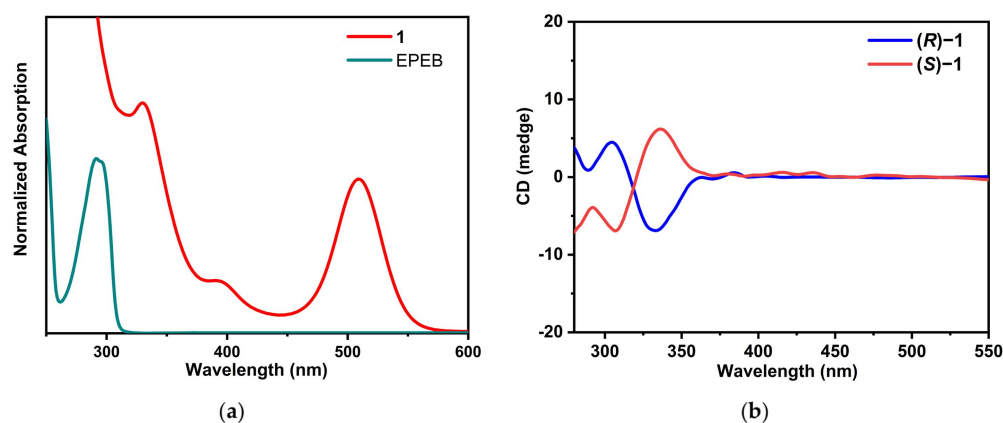


Figure 3. Cont.

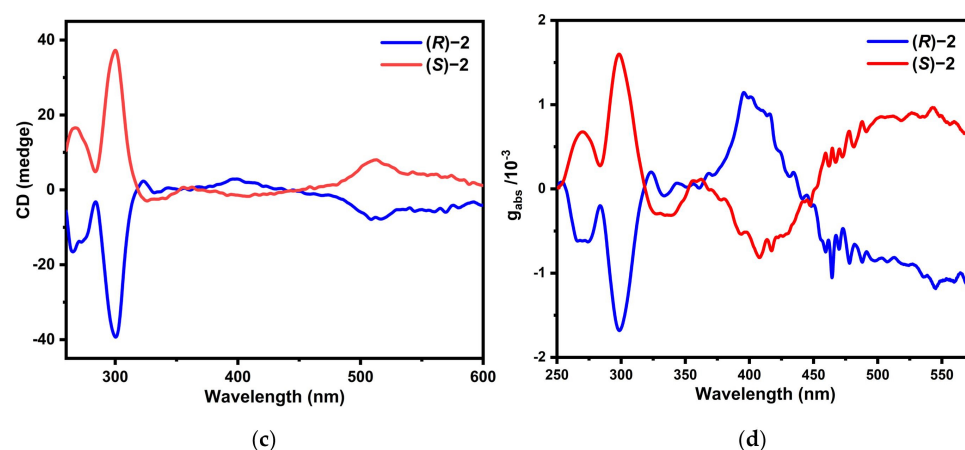


Figure 3. (a) UV-Vis absorption spectra of EPEB and $[\text{Au}_8(\text{dppp})_4(\text{EPEB})_2]^{2+}$ (**1**) and (b) CD spectra of (*R*)-**1** and (*S*)-**1** in dichloromethane; (c) CD spectra and (d) absorption dissymmetry factor (g_{abs}) of (*R*)-**2** and (*S*)-**2**.

A different chiroptical behavior is observed for cluster **2**, in which chiral BDPP ligands directly coordinate to the *core*-Au sites. The enantiomers (*R*)-**2** and (*S*)-**2** exhibit nearly mirror-image CD spectra with well-defined Cotton effects at 275, 295, 400, and 510 nm (Figure 3c). While the high-energy signals at 275 and 295 nm can be assigned primarily to ligand-involved electronic transitions, the CD signals at around 510 nm to 600 nm, which correspond to the characteristic absorption of the Au_8 kernel, suggest the efficient chirality transfer from the BDPP ligands to the Au_8 kernel. Cluster **2** also exhibits a maximum g_{abs} value of approximately 1.7×10^{-3} (Figure 3d), nearly one order of magnitude larger than that of cluster **1**. These results clearly indicate that the coordination site of the chiral ligand plays an important role in the efficiency of chirality transfer in Au_8 clusters. Notably, neither solutions nor thin films of clusters **1** and **2** exhibit obvious CPL signals, which may originate from the absence of intermolecular assembly and ordered stacking.

To investigate the mechanism of chirality transfer in Au_8 clusters, TD-DFT calculations were performed for (*S*)-**1** and (*S*)-**2**. The results showed that the lowest-energy transition of (*S*)-**1** is calculated at 479.2 nm and is dominated by the HOMO→LUMO excitation (Table S3). This transition corresponds to Au_8 kernel-centered excitation with a large oscillator strength ($f = 0.400$), but it gives only a weak CD response (Figure 4b). Natural transition orbital (NTO) analysis shows that the hole and electron are largely co-localized within the Au_8 kernel (Figure S13), resulting in limited transition-density asymmetry and inefficient electric–magnetic dipole coupling due to the nearly symmetric Au_8 kernel. The intense CD features in the 309–340 nm region arise from multi-configurational Au_8 kernel to the peripheral ligand shell excitations (Figure S13). These results indicate that the chirality of (*S*)-**1** is not associated with an individual ligand chromophore. In contrast, it originates from the cooperative electronic coupling between the Au_8 kernel and the asymmetric ligand environment. The relatively weak overall CD response of (*S*)-**1** is attributed to its modest kernel distortion, which limits the spatial asymmetry of the low-energy kernel-centered excitation.

Since we assume that the crystal structure of cluster **2** is highly analogous to $[\text{Au}_8(\text{dppp})_4]^{2+}$, we added eight extra methyl groups to the crystal structure of $[\text{Au}_8(\text{dppp})_4]^{2+}$ for ground-state optimization followed by subsequent TD-DFT calculations. For (*S*)-**2**, TD-DFT calculations combined with NTO analyses reveal that the strong chiroptical response originates from the cooperative electronic coupling between the distorted Au_8 kernel and the chiral diphosphine shell (Figure S13). The low-energy S_2 state is dominated by HOMO→LUMO/LUMO+1 excitations and represents an Au_8 kernel-centered transition (Figure 5c). Although the hole and electron are largely co-localized, the asymmetric Au_8

framework enables efficient electric–magnetic dipole coupling, inducing a positive CD response (Figure 5b). The relatively high g_{abs} factor near 400 nm is assigned to S_{14} , which is HOMO→LUMO + 13 excitation involving transition-density reorganization from the Au_8 kernel toward the asymmetric ligand shell (Figure 5c). This metal-to-ligand excitation combines a moderate magnetic transition moment with a relatively weak electric-dipole contribution (Table S2), thereby displaying a relatively high g_{abs} value. The strongest positive Cotton effect near 300 nm (Figure 5b) arises from the multi-configurational S_{54} state, in which several Au_8 kernel to Au–ligand interface transition channels coherently reinforce the positive rotational strength (Figure S14). In contrast, the weak CD response between 325 and 340 nm results from partial cancelation among closely spaced states with opposite Cotton effects (Figure S14).

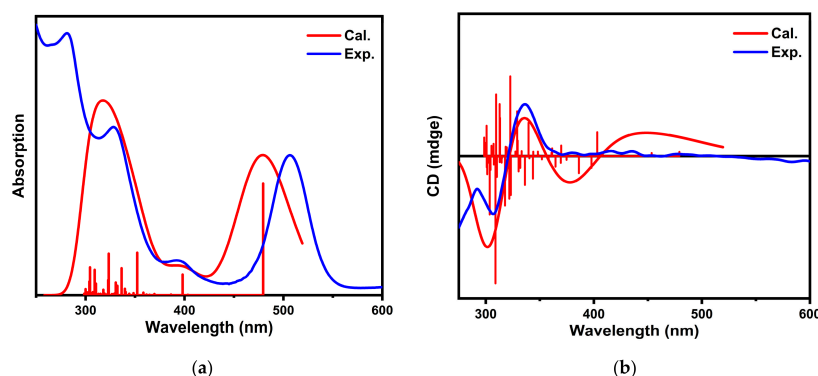


Figure 4. Comparison of calculated and experimental spectra of (a) UV-Vis and (b) CD of (S)-1.

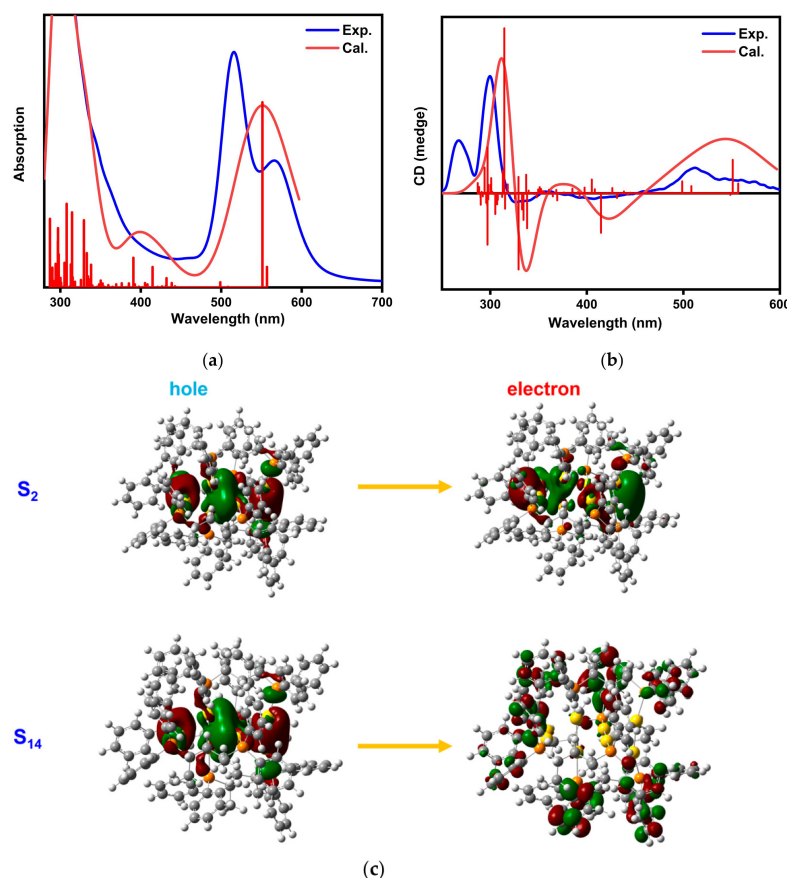


Figure 5. Comparison of calculated and experimental spectra of (a) UV-Vis and (b) CD of (S)-2; (c) NTO analysis for key excited states of (S)-2.

These results reveal that the strong chirality of (**S**)-**2** may arise from the distorted Au₈ kernel and the asymmetric phosphine shell. The effective transmission of ligand chirality into the metal-centered electronic manifold is therefore responsible for the large CD and g-factor responses.

4. Materials and Methods

Synthesis of (*R/S*)-[Au₈(dppp)₄(EPEB)₂](NO₃)₂ ((*R/S*)-**1**) and meso-**1**

The initial cluster [Au₈(dppp)₄](NO₃)₂ was synthesized following the reported procedure [18]. MeONa (90.7 mg, 1.68 mmol), 1-ethynyl-2-[(1*R/S*)-1-phenylethoxy]benzene ((*R/S*)-EPEB, 5.0 mg, 22.4 μmol) and 30 mL MeOH were added into a 100 mL flask. Then 2 mL MeOH solution of [Au₈(dppp)₄](NO₃)₂ (18.8 mg, 5.6 μmol) were added into the flask and the solution was stirred for 24 h at 310 K. The solution turned from purple to red after 24 h. 50 mL H₂O was added into the solution and the mixture was extracted with CH₂Cl₂ (10 mL × 3). The crude product was collected by adding diethyl ether into the concentrated CH₂Cl₂ solution. Red crystals of (**R/S**)-**1** were obtained by slow diffusion of diethyl ether into the concentrated CH₂Cl₂/MeOH (*v/v* = 1:1) mixed solution of (**R/S**)-**1**. The *meso*-**1** product and its single crystals were also obtained via the same synthetic route using racemic EPEB ligand. The crystal yields of (**R**)-**1**, (**S**)-**1**, and *meso*-**1** are 35%, 38% and 40%, respectively. All subsequent measurements and characterizations were performed using the crystals or solutions prepared by dissolving the crystals.

Synthesis of (*R/S*)-[Au₈(BDPP)₄](NO₃)₂ ((*R/S*)-**2**)

The initial cluster Au₉(PPh₃)₈(NO₃)₃ was synthesized according to the reported method [19]. Au₉(PPh₃)₈(NO₃)₃ (20.0 mg, 5 μmol) was dissolved in dichloromethane (3 mL), while (2*R,4R*)-BDPP or (2*S,4S*)-BDPP (13.2 mg, 0.03 mmol) was dissolved in dichloromethane (2 mL). The solution of (2*R,4R*)-BDPP or (2*S,4S*)-BDPP was added dropwise to the Au₉ cluster solution under continuous stirring. The reaction mixture was stirred for an additional 5 min, during which the solution color gradually changed from yellowish brown to dark brown and finally to deep purple. Diethyl ether (25 mL) was then added to the reaction mixture to precipitate the crude product as a purple solid, which was collected by filtration. Purple crystals of (**R**)-**2** or (**S**)-**2** were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the crude product. The crystal yields of (**R**)-**2** and (**S**)-**2** are 56%. All measurements were carried out on freshly prepared solutions from crystals of **2** within 30 min to maintain the structural integrity of **2** in solution throughout measurements.

Theoretical calculations

Theoretical calculations of model clusters were performed using the Gaussian 16 program [20]. The structure of (**S**)-**1** for ground state optimization was established on the basis of single-crystal structures of *meso*-**1** by modifying the configuration of the EPEB ligand. The geometry of (**S**)-**2** for ground-state optimization was built by adding eight additional methyl groups to the analogous [Au₈(dppp)₄]²⁺ crystal structure. The Becke three-parameter hybrid functional accompanied by the Lee–Yang–Parr correlation functional (B3LYP) [21,22] was employed in optimizations and TD-DFT calculations without any symmetry constraints on molecular structures. The basis sets of def2-DZVP [23] and def2-SVP [24] were applied for gold and all remaining atoms respectively. Eighty singlet states (*n*_{state} = 80, singlet) were included in the calculations of the UV-Vis absorption of clusters (**S**)-**1** and (**S**)-**2**. The root is set to 1 in all of the TD-DFT calculations. Solvent contributions were neglected in optimization and TD-DFT calculations. NTO analysis was performed on the basis of optimized ground-state geometries at the same level and processed with Multiwfn software [25,26]. The theoretically simulated UV-Vis and CD

spectra were plotted using Multiwfn software, with broadening parameters set to 0.3 eV for both spectra.

5. Conclusions

In summary, two atomically precise chiral Au₈ clusters were successfully synthesized by decorating chiral ligands at distinct *exo*-Au and *core*-Au coordination sites. Decoration of chiral alkynyl ligands at the *exo*-Au sites affords only weak ligand-centered chiroptical responses, whereas coordination of chiral diphosphine ligands to the *core*-Au sites generates intense CD signals and enhanced absorption dissymmetry factors. TD-DFT and NTO analyses show that *exo*-Au site functionalization induces limited perturbation of the Au₈-centered low-energy excited states. In contrast, coordination of chiral diphosphine ligands at the *core*-Au sites generates an asymmetric phosphine environment and may induce greater distortion of the Au₈ kernel, thereby promoting chirality transfer from the ligand shell to the metal framework. These results indicate that site-specific coordination is an effective strategy for controlling chirality transfer and amplifying the chiroptical properties of metal clusters.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/inorganics14080220/s1>, Figure S1: Synthesis of R/S-EPEB; Figure S2: ¹H-NMR spectrum of **b** (400 MHz, CDCl₃, 20 °C; δ/ppm: 7.80 (dd, J = 7.6, 1.6 Hz, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.29 (t, J = 7.2 Hz, 1H), 7.14 (ddd, J = 8.0, 7.2, 1.6 Hz, 1H), 6.68 (dd, J = 8.0, 1.6 Hz, 1H), 6.65 (dd, J = 7.6, 1.6 Hz, 1H), 5.39 (q, J = 6.4 Hz, 1H), 1.74 (d, J = 6.4 Hz, 3H)); Figure S3: ¹H-NMR spectrum of **c** (400 MHz, CDCl₃, 20 °C; δ/ppm: 7.45 (d, J = 7.2 Hz, 2H), 7.43 (dd, J = 7.6, 1.6 Hz, 1H), 7.35 (t, J = 7.2 Hz, 2H), 7.27 (t, J = 7.2 Hz, 1H), 7.13 (ddd, J = 8.4, 7.2, 1.6 Hz, 1H), 6.84 (td, J = 7.6, 0.8 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 5.41 (q, J = 6.4 Hz, 1H), 1.67 (d, J = 6.4 Hz, 3H), 0.32 (s, 9H)); Figure S4: ¹³C-NMR spectrum of **c** (100 MHz, CDCl₃, 20 °C; δ/ppm: 159.2, 143.2, 133.7, 129.7, 128.6, 127.6, 125.8, 120.8, 115.0, 114.1, 101.8, 98.6, 24.3, 0.2); Figure S5: HR-ESI-MS spectrum of [Au₈(dppp)₄(EPEB)₂]²⁺ (**1**); Figure S6: ³¹P-NMR spectrum of **1** (162 MHz, CD₂Cl₂, 20 °C; δ/ppm: 54.9, 52.5, 37.6 and 33.1); Figure S7: HR-ESI-MS spectrum of [Au₈(BDPP)₄]²⁺ (**2**); Figure S8: ³¹P-NMR spectrum of **2** (162 MHz, CD₂Cl₂, 20 °C; δ/ppm: 56.86 and 46.24); Figure S9: Stereopair diagrams of (a) the complete molecule (hydrogen atoms omitted for clarity) and (b) the Au₈ core of *meso*-**1**; Figure S10: Packing figures of single crystal of *meso*-**1**; Figure S11: Stereopair diagrams of (a) the complete molecule (hydrogen atoms omitted for clarity) and (b) the Au₈ core of [Au₈(dppp)₄]²⁺; Figure S12: UV-vis spectra of (S)-**2** in CH₂Cl₂ (10 μM) within 4h; Figure S13: NTO analysis of S₁, S₃₁ and S₄₆ excited state of cluster (S)-**1**; Figure S14: NTO analysis of S₄₉ and S₅₄ excited state of cluster (S)-**2**; Figure S15: Asymmetric distortion of (R)-**2** and (S)-**2** based on optimized structures; Table S1: Crystal data of *meso*-[Au₈(dppp)₄(EPEB)₂](NO₃)₂; Table S2: Key bond length and bond angle in crystal structure of *meso*-**1**; Table S3: TD-DFT results of key excited states of cluster (S)-**1**; Table S4: TD-DFT results of key excited states of cluster (S)-**2**.

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Conflicts of Interest: The authors declare no conflicts of interest.

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