Self-Assembly of Chiral Gold Clusters into Crystalline Nanocubes of Exceptional Optical Activity

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Abstract: Self-assembly of inorganic nanoparticles into ordered structures is of interest in both science and technology because it is expected to generate new properties through collective behavior; however, such nanoparticle assemblies with characteristics distinct from those of individual building blocks are rare. Herein we use atomically precise Au clusters to make ordered assemblies with emerging optical activity. Chiral Au clusters with strong circular dichroism (CD) but free of circularly polarized luminescence (CPL) are synthesized and organized into uniform body-centered cubic (BCC) packing nanocubes. Once the ordered structure is formed, the CD intensity is significantly enhanced and a remarkable CPL response appears. Both experiment and theory calculation disclose that the CPL originates from restricted intramolecular rotation and the ordered stacking of the chiral stabilizers, which are fastened in the crystalline lattices.

Inorganic nanoparticle self-assembly not only offers a feasible route to realize possible application of nanomaterials in the macro world, but also provides an opportunity to produce new physiochemical properties beyond those of their individual building blocks through collective behavior.[1] Generally, the prerequisite of self-assembly is that both the size and shape of the building blocks must be highly uniform.[2] Such a stringent requirement severely limits application of nanoparticles prepared via self-assembly process, because different from molecular synthesis, to prepare monodisperse nanoparticles needs accurate control over nucleation and growth process that is time- and cost-consuming. Another great challenge in the field of nanoparticle assembly is that the reported assemblies seldom exhibit properties or functions greatly different from those of the individual nanoparticles, and therefore the potential advantages of the ordered assemblies are not demonstrated, only the problems associated with self-assembly.[3]

We expect that a specific type of nanoparticles, noble metal clusters with the size of less than 2 nm,[4] would be excellent candidates for assembly building blocks. Thanks to their thermodynamic stability, varied types of noble-metal clusters with magic numbers of atoms have been easily synthesized in large quantities, allowing possible construction of the assemblies at atomic level.[5] However, until now there are only rare reports on self-assembly of noble-metal clusters into ordered colloidal structures,[6] and more importantly, no new function has been achieved with the assembled structures compared with individual building blocks, although the clusters themselves possess many intriguing optical, electrical, magnetic, and catalytic properties.

Herein, we investigate the self-assembly of chiral Au clusters for two reasons. 1) Unlike other nanoparticles, specific chirality can appear in Au clusters, it can arise from the organic ligands, surface staples, or the intrinsic Au atom arrangement, which gives rise to many additional unique features.[7] 2) It is known that chirality and its resulting properties are highly sensitive to the surrounding environment and spatial organization, so the assemblies might generate the novel properties distinct from individual chiral clusters.[8] Based on above idea, we attempt to design and synthesize the smallest chiral Au clusters, the optical activity of which could then be easily influenced after self-assembly into ordered structures.

(R)- or (S)-2,2'-bis(di-p-tolyolphosphino)-1,1'-binaphthyl, (R)- or (S)-Tol-BINAP, were adopted as chiral ligands to synthesize Au clusters (Supporting Information part 1.2).[9] The single-crystal X-ray diffraction (SC-XRD) analysis reveals that the products are Au₃[(R)-Tol-BINAP]Cl and Au₃[(S)-Tol-BINAP]Cl clusters, respectively (Table S1 and S2 in the Supporting Information).[10] and the as-formed crystal structure of both Au₃[(R)-Tol-BINAP]Cl and Au₃[(S)-Tol-BINAP]Cl clusters belongs to a cubic space group, I2₃, which is chiral. In detail, three Au atoms in one cluster connect with each other and form a regular triangle, in which the Au–Au bond lengths are 2.676(2) Å (Figure 1 and Figure S1 b). These Au–Au bond lengths are in the reported range of 2.572(2)–3.216(2) Å, suggesting presence of the attractive aurophilic interaction inside chiral Au clusters.[11] In addition, each Au atom binds with a chiral biphosphate ligand through the P–Au–P bonds with two unequal bond lengths of 2.380(7) Å and 2.397(8) Å. By simply changing the chirality of ligand in synthesis from R to S used the cluster with the opposite chirality can easily be prepared (Figure 1).
The molecular formula of \( \text{Au}_{3}\{[(R)-\text{Tol-BINAP}]\text{Cl}\} \) cluster was further verified by electrospray ionization mass spectrometry (ESI-MS). Figure S2a shows an isotopically resolved peak at \( m/z \) 2626.71987 with a \(+1\) charge, corresponding to a species of the cluster minus one \( \text{Cl}^-\) (calcd: 2626.68411 in Figure S2b). As for the \( \text{Au}_3 \) core, its charge state is determined by measuring the bonding energy of \( \text{Au} \ 4f_{7/2} \) via X-ray photoelectron spectroscopy (XPS). The fitting result manifests that all the \( \text{Au} \) atoms in the cluster are same, characteristic with the bonding energy of \( \text{Au} \ 4f_{7/2} \) at 84.4 eV and \( \text{Au} \ 4f_{7/2} \) at 88.1 eV that locates in the middle of \( \text{Au}^6 \) and \( \text{Au}^4 \) (Figure S3). In regard of the surrounding chiral ligand, its six aromatic rings can be divided into three groups based on the crystal structure (Figure 1): two outward naphthalene rings (yellow double hexagons), two outward \( p\)-tolyl rings (yellow hexagons) and two inward \( p\)-tolyl rings (red hexagon and hollow hexagon, Figure 1). These aromatic rings form left- or right-handed stacking on the surface of \( \text{Au} \) clusters based on the chirality of ligands (Figure 1), endowing the capability to produce the strong optical activity of \( \text{Au} \) clusters.\(^{[12]}\)

The enantiomers of \( \text{Au} \) clusters that are well dispersed in dichloromethane (DCM) exhibit intense CD response with an excellent mirror image in the wavelength range of 220 nm–500 nm (Figure 2a), and thus we select \( \text{Au}_{3}\{[(R)-\text{Tol-BINAP}]\text{Cl}\} \) clusters as the representative for following study. The CD spectrum of \( \text{Au}_{3}\{[(R)-\text{Tol-BINAP}]\text{Cl}\} \) has four distinct peaks at 239 nm, 267 nm, 288 nm, and 366 nm, respectively, which is largely different to the CD features of the pure chiral ligands (Figure S4). Impressively, the maximum absorption anisotropy factor (\( g_{\text{max}} \) factor) of \( \text{Au}_{3}\{[(R)-\text{Tol-BINAP}]\text{Cl}\} \) clusters in DCM with various \( n\)-hexane contents, arrows show direction of change with increasing \( n\)-hexane content (cluster concentration: \( 5 \times 10^{-3}\ \text{M}\); optical path length: 1 mm).

A striking discovery regarding the optical properties is that upon self-assembly, the non-luminescent \( \text{Au} \) clusters progressively become highly luminescent (Figure 3a and Figure S6). An orange emission band centered at 583 nm appears for \( \text{Au}_{3}\{[(R)-\text{Tol-BINAP}]\text{Cl}\} \) clusters when the fraction of \( n\)-hexane is increased to 40 %, and displays further enhancement with increase of \( n\)-hexane fraction. When the fraction value of \( n\)-hexane gets to 70 %, the photoluminescence (PL) intensity reaches the highest value with a quantum yield (QY) of 3.6 % (calibrated with luminescent Rhodamine 6G; Figure 3b). The PL intensity shows a clear decrease when the fraction of \( n\)-hexane exceeds 70 %, because of the formation of large aggregates with poor crystallinity.\(^{[16]}\) A similar change is found by analyzing the PL decay profiles. The dominant PL decay time also follows the order: 50 % \( n\)-hexane (0.59 ps) < 60 % \( n\)-hexane (0.69 ps) < 70 % \( n\)-hexane (0.79 ps) > 80 % \( n\)-hexane (0.75 ps) > 90 % \( n\)-hexane (0.68 ps) (Figure S7). The microsecond PL decay time and the large
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More intriguingly, these factor (d) of Au is acquired in 70% n-hexane. The dashed fluctuations in (c) are the original collected data, while the solid curves are the smoothed ones (cluster concentration: 5 × 10⁻⁵ M; optical path length: 1 mm).

Figure 3. a) PL spectra of Au[R]-Tol-BINAP]Cl clusters in DCM with various n-hexane contents (inset: digital photos of samples with 0 or 70% n-hexane under irradiation of 365 nm UV light). b) Relative PL intensity against composition of the mixed solvent. c,d) CPL spectra (c) and corresponding g_CPL factor (d) of Au[R]-Tol-BINAP]Cl (blue curve) and Au[2(S)-Tol-BINAP]Cl (red curve) assemblies in 70% n-hexane. The maximum g_CPL factor of about ± 7 × 10⁻³ is acquired in 70% n-hexane (Figure 3d).

What is the reason for the significant change in both CD and CPL activity upon tuning the n-hexane fraction of the solvent mixture? To answer this question, we characterized the morphology and structure of as-assembled products. As revealed by dynamic light scattering (DLS) measurement, Au[R]-Tol-BINAP]Cl clusters are well dispersed in the solvent with a n-hexane fraction of less than 40%; whereas the cluster aggregates appear when the n-hexane fraction exceeds 40% and their sizes gradually grow from hundred nanometers to several micrometers along with increase of poor solvent fraction (Figure S10). Transmission electron microscopy (TEM) imaging and corresponding selected area electron diffraction (SAED) survey further indicate that the cluster aggregates are irregular and amorphous when the fraction of n-hexane is less than 60%, while well-defined nanocubes of sharp edges start to appear in the mixed solvent of 60% hexane (Figure S11). Significantly, cluster assemblies become very uniform when the fraction of n-hexane reaches 70%, which exhibit a cubic morphology with an average edge length of 366 nm (Figure 4a,c and Figure S12). With further increase of the fraction of n-hexane, the grain sizes of the Au cluster aggregates begin to decrease and their shapes become irregular (Figure S13), which is a result of too quick aggregation of Au clusters in poor solvent. We then focused the structure investigation on the uniform nanocubes obtained in 70% hexane (Figure 4). Notably, all the diffraction peaks in the powder X-ray diffraction (PXRD) pattern of nanocubes are well assigned to the simulated BCC packing pattern based on the single-crystal structure of Au[R]-Tol-BINAP]Cl clusters (Figure 4b). Such an ordered BCC packing structure is also verified by SAED observation on single nanocube (Figure 4c,d), where sharp diffraction spots corresponding to (200) and (020) reflections are clearly discerned along the [001] direction. The calculated interplanar spacing along (200) from SAED (1.41 nm) is very close to the value acquired by SC-XRD (1.44 nm), which further confirms the crystalline BCC packing pattern inside nanocubes.

To understand the influence of cluster assembly on the optical activity, theoretical calculations on individual clusters were carried out. Note that the simulated UV/Vis absorption and CD spectra of the enantiomers match very well with the measured ones regardless of the peak sign or the peak position, demonstrating the validity of our calculation (Figure S14a). The HOMO of Au[2(R)-Tol-BINAP]Cl and Au-[2(S)-Tol-BINAP]Cl clusters mainly lies on the Au and P
atoms, while the transition-related doubly degenerate LUMO and LUMO + 1 mostly locate on the naphthalene rings of (R)- or (S)-Tol-BINAP ligands (Figure S14b). All the excited states are composed by metal-to-ligand charge transfer (MLCT) and ligand-to-ligand charge transfer (LLCT), so the conformation of chiral ligands on Au cluster surfaces is crucial in determining their optical activity (for detailed analysis, see Figure S14–S25).

The extremely enhanced optical activity via self-assembly of the chiral Au clusters can be understood based on crystal-structure analysis. In the nanocube with an ordered chiral \( I_2 \) \( 3 \) packing structure, each Au cluster contacts six nearby Au clusters, which are divided into two groups because the cluster assembly has a local chiral \( C_2 \) symmetry (Supporting Movie). Three adjacent Au clusters form CH/\( \pi \) interactions with the central one via both outward-facing pairs of naphthalene rings (Figure S26) and the inward p-tolyl ring pairs (Figure S27). Meanwhile, the other three adjacent Au clusters form CH/\( \pi \) interactions with the central one through an outward naphthalene ring and an inward p-tolyl ring (Figure S28). Note that the attraction energy of the CH/\( \pi \) interactions is in the range of \(-1.5\) to \(-2.5\) kcal mol\(^{-1}\) \footnote{[18]} which is much larger than the molecular thermal energy at room temperature (0.57 kcal mol\(^{-1}\)). Once the Au clusters are assembled, the strong intermolecular CH/\( \pi \) interactions would largely restrict the intramolecular rotation of the inward p-tolyl rings, which is confirmed by temperature- or concentration-dependent \(^1\)H NMR spectroscopy (Figures S29–S33). Subsequently, ordered left- or right-handed stacking patterns are formed on the surface of \( R/S \)-Au\(_3\) clusters (red arrows in Figure 1), which are responsible for enhancement of CD intensity. Such strong intermolecular CH/\( \pi \) interactions between chiral ligands further result in red shift of the peaks in both UV/Vis absorption and CD spectra (Figure 2h,c), which is reasonable considering that all the peaks originating from MLCT or LLCT process are largely contributed by chiral ligands (Figure S14 and Tables S4 and S5). More importantly, the restricted intramolecular rotation of inward p-tolyl rings efficiently blocks the non-radiative relaxation channel of the excited state and populates its radiative decay pathway\footnote{[19]} which finally facilitates generation of PL and CPL responses from \( ^1\)LMCT or \( ^1\)MMCT excited state. The corresponding luminescence mechanism is as follows: the singlet state formed via the MLCT or LLCT process relaxes to a triplet state through fast intersystem crossing with aid of the large spin-orbit coupling of the heavy gold atoms\footnote{[20]} followed by PL and CPL generation via \(^3\)LMCT or \(^3\)MMCT process. Note that as for the exceptional case of nanocubes with ordered BCC packing structure (Figure 4), every inward p-tolyl ring on the Au cluster surfaces is fully fixed via intermolecular CH/\( \pi \) interactions, and thus both PL intensity and \( g_{\text{sum}} \) factor reach the highest values (Figure 3a,b).

In summary, chiral Au\(_3\) clusters with a record-high optical absorption activity have been synthesized and used as building blocks for spontaneous organization into nanocubes of well-defined BCC arrangement. Thanks to the strong intermolecular CH/\( \pi \) interactions, the rotation of the chiral ligands are drastically restricted, and therefore the optical absorption activity of the as-assembled products is red-shifted and further enhanced. Unlike the individual clusters which are free of luminescence, the chiral Au cluster assemblies become highly emissive and the strongest CPL response is acquired with the ordered structure. It is expected that design and application of clusters, which have accurate atomic structure and specific optical, magnetic, or catalytic properties, will open a new era in the self-assembly field beyond conventional molecules and nanoparticles.

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Conflict of interest

The authors declare no conflict of interest.

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[10] CCDC 1491313 (Au(3(R)-Tol-BINAP)3Cl), 1491314 (Au(3(S)-Tol-BINAP)3Cl) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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