



## Digest paper

## Chiral metal cluster and nanocluster complexes and their application in asymmetric catalysis



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## ABSTRACT

Asymmetric catalysis has always been the focus of attention for synthetic chemistry. In this review, we summarize recent advances in the synthesis and asymmetric catalysis application of chiral metal clusters, nanoclusters and nanoparticles.

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## Contents

Introduction.....	310
Chirality introduction in metal clusters and NCs.....	311
Asymmetric arrangement of achiral ligands or metal–ligand motifs.....	311
Intrinsically chiral metallic core.....	311
A chiral environment constructed by chiral ligands.....	313
Application of metal clusters, NCs and NPs in asymmetric catalysis.....	313
Chiral ligand modified metal NPs.....	313
Chiral metal NCs immobilized on support.....	314
Asymmetric catalysis of chiral metal clusters.....	314
Conclusions and perspectives.....	315
Acknowledgment.....	315
References.....	315

## Introduction

Chirality is a fascinating property of molecules in nature. Due to the prevalence of chiral molecules in biological systems and their key role in molecular recognition through chirality-induced specificity, enantioselective synthesis of chemical compounds has become an important research topic not only in chemistry, but also in biology, biomaterial and pharmaceutical sciences.<sup>1</sup> In this regard, asymmetric catalysis is a significant and efficient way to obtain chiral compounds. A plethora of homogeneous catalysts

including coordination complexes and organic molecules have been extensively applied in a broad range of synthetic reactions, showing high efficiency and enantioselectivity.<sup>2</sup> However, the practical application of such homogeneous catalysts in industry remains a formidable challenge due to the recovery problem of catalysts, which is usually the major concern of catalyst cost. Over the past decades, chemists have established a number of immobilization approaches for homogeneous chiral catalysts, including using inert inorganic materials or organic polymers as supports<sup>3</sup> or inventing self-supported catalysts,<sup>4a</sup> in order to achieve both excellent enantioselectivity and recovery efficiency. Recently, chiral metal cluster and nanocluster (NC) complexes have been of great interest because their application in asymmetric

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catalysis may enhance catalytic efficiency through synergetic and cooperative effect of cluster complexes and meanwhile provide an alternative pathway to recover catalysts by simple centrifugal separation.<sup>4b,c</sup>

Chirality studies in nano-objects, especially metal nanoparticles (NPs) and NCs, attracted much recent attention due to their promising application in optical devices,<sup>5</sup> chiral recognition and separation,<sup>6</sup> bio-sensing,<sup>7</sup> polarization-sensitive devices,<sup>8</sup> functional self-assembly,<sup>9</sup> and asymmetric catalysis.<sup>10</sup> Generally, there are three major strategies to generate chirality in metal NCs and NPs: i) to construct an intrinsically chiral metallic core; ii) to make an achiral metallic core inside a chiral environment constructed by chiral ligands; iii) to form an asymmetric arrangement of achiral ligands or metal-ligand motifs over a metallic core.<sup>11</sup> In this review, we summarize several characteristic examples of chiral metal clusters and NCs, especially the ones with well-defined crystal structures, based on the above three strategies. Although there are few systematic investigations on the application of chiral metal clusters and NCs in asymmetric catalysis, we endeavor to present some recent advances in this undeveloped field.

## Chirality introduction in metal clusters and NCs

### Asymmetric arrangement of achiral ligands or metal–ligand motifs

Arrangement of coordinative ligands in a chiral pattern to introduce chirality has been frequently observed in coordination chemistry.<sup>12</sup> It is therefore envisioned that chirality can also be generated in metal clusters and NCs by the same protocol. To date, asymmetric arrangement of achiral ligands or metal–ligand motifs on the cluster surface has been often observed in chiral metal NCs. Kornberg and co-workers once successfully accomplished the crystallization and X-ray structure determination of  $\text{Au}_{102}(\text{p-MBA})_{44}$  (*p-MBA* = *para*-mercaptobenzoic acid), in which chirality was derived from chiral arrangement of monomeric RS–Au–SR staples on the cluster surface.<sup>13</sup> Similarly, such chiral arrangement of RS–Au–SR staples on cluster surface was also found in many other gold NC examples such as  $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$  (Fig. 1a–b),<sup>14</sup>  $\text{Au}_{30}\text{S}(\text{S-}t\text{-Bu})_{18}$ ,<sup>15</sup>  $\text{Au}_{28}(\text{TBBT})_{20}$  (TBBT = 4-*tert*-butylbenzenethiolate),<sup>16</sup>  $\text{Au}_{130}(\text{p-MBT})_{50}$  (*p-MBT* = 4-methylbenzenethiolate),<sup>17</sup>  $\text{Au}_{133}(\text{SR})_{52}$  (SR = SPh-*p*-Bu<sup>t</sup>),<sup>18</sup>  $\text{Au}_{40}(\text{o-MBT})_{24}$  (*o-MBT* = 2-methylbenzenethiolate).<sup>19</sup>

In addition to only one kind of staple structure in thiolate-protected gold NCs, asymmetric arrangement of two different metal RS motifs (e.g.,  $\text{Ag}_2\text{AuSR}$  and  $\text{Ag}_4\text{SR}$ ) were also found in a heteronuclear chiral NC  $[\text{Ag}_{46}\text{Au}_{24}(\text{S}^t\text{Bu})_{32}](\text{BPh}_4)_2$ .<sup>20</sup> Furthermore, recent studies have explored that  $\pi \cdots \pi$  interaction between benzene rings of thiolate ligands helps lock the arrangement of surface

ligands and therefore facilitates the construction of stable heteronuclear chiral NC  $[\text{MAG}_{24}(\text{SR})_{18}]^{2-}$  (M = Pd, Pt; SR = 2,4-SPhCl<sub>2</sub>) (Fig. 1c).<sup>21</sup>

It is worth noting that abovementioned chiral metal NCs generated by asymmetric arrangement of achiral ligands or metal–ligand motifs are racemic. Enantiopure chiral metal clusters and NCs have to be isolated by other techniques such as chiral HPLC.<sup>14c</sup>

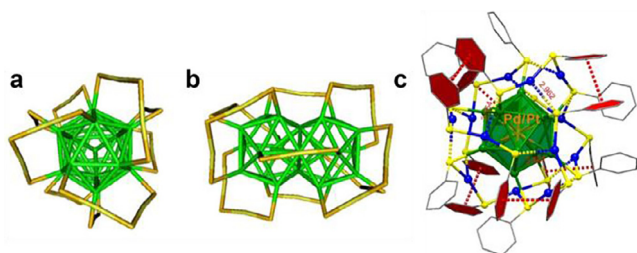
### Intrinsically chiral metallic core

Intuitively, the synthesis of chiral clusters based on chiral ligands is the most common method. In fact, various chiral ligands have been employed to induce structural deformation of metal cores, which often lead to intrinsic chirality of metal clusters and NCs. Tsukuda and co-workers once utilized achiral triphenylphosphine (TPP) and chiral 2,2'-bis(diphenyl-phosphino)-1,1'-binaphthyl (BINAP) to synthesize different ligand-protected  $[\text{Au}_{11}]^{3+}$  clusters.<sup>22</sup> Only chiral BINAP-capped  $[\text{Au}_{11}]^{3+}$  cluster showed circular dichroism (CD) response. The authors conjectured that the CD response might arise from the deformation of the gold core caused by chiral BINAP ligands. This assumption was recently evidenced by Zhao and co-workers.<sup>23</sup> They prepared a series of enantiopure  $\text{Au}_6$  clusters  $[(\text{AuPPh}_3)_6(\text{L}^n)](\text{BF}_4)_2$  (*n* = 1, 2 and 3) by using chiral diamine ligands (Fig. 2). Such chiral gold clusters exhibited strong CD response, which is finally attributed to asymmetric arrangement of six gold atoms based on structural comparison and theoretical modeling.

Postclustering modification (PCM) by chiral compounds was another novel method to introduce chirality to metal NCs. Wang and co-workers utilized dynamic covalent imine bonds between chiral monoamines and aldehydes to transfer chirality from chiral amines to the resulting metal clusters.<sup>24</sup> In the synthesis of bicapped octahedral clusters  $[\text{Au}_6\text{M}_2(\text{C})(\text{dppy})_6](\text{BF}_4)_4$  (M = Ag/Cu) (dppy = diphenylphosphino-2-pyridine), they selected a unique dppy ligand bearing an aldehyde group for PCM with chiral amines. The introduction of chiral amines disrupted any center or plane of symmetry in cluster, consequently determining the chirality of the resulting metal clusters by absolute configuration of chiral amine ligands.

Besides the synthesis of chiral metal clusters for group 11 metals, which have strong potential to form metallophilic interaction between metal atoms, the introduction of chiral ligands also facilitates the preparation of O- or S-bridged chiral metal clusters. For example, (*S/R*)-binaphthols (BINOL) was previously used to synthesize  $[\text{Ti}_4(\mu\text{-}(\text{S/R})\text{-BINOL})_6(\mu_3\text{-OH})_4]$  cluster, which can act as an efficient Lewis acid catalyst.<sup>25</sup> Holm and co-workers once prepared a cubane-type  $[\text{Fe}_4\text{S}_4(\text{SR}^*)_4]^{2-}$  cluster by using chiral thiolate ligands ( $\text{R}^* = \text{CH}(\text{Me})\text{Ph}$ ,  $\text{CH}_2\text{CH}(\text{Me})\text{Et}$ , and  $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ ).<sup>26</sup> They found that the acquired cluster enantiomers produced opposite CD signals. Similarly, a pair of enantiopure cubane-like copper(II) clusters  $\text{Cu}_4^{\text{II}}\text{L}_4\cdot 4\text{MeOH}$  (L = (*R* or *S*)-2-[(2-hydroxy-1-phenylethylimino)methyl]-phenol) were synthesized (Fig. 3),<sup>27</sup> in which a distorted square-pyramidal  $\text{Cu}_4\text{O}_4$  cluster core was in a chiral fashion. Llugar and co-workers employed two enantiomers ((*R,R*)-Me-BPE) or ((*S,S*)-Me-BPE) of a chiral phosphine ligand 1,2-bis[2,5-(dimethylphospholan-1-yl)]ethane to prepared a trinuclear cluster  $[\text{Mo}_3\text{S}_4\{(\text{R,R})/(\text{S,S})\text{-Me-BPE}\}_3\text{Cl}_3]^+$  and a heteronuclear cubane-type cluster  $[\text{Mo}_3\text{CuS}_4\{(\text{R,R})/(\text{S,S})\text{-Me-BPE}\}_3\text{Cl}_4]^+$ .<sup>28</sup> These clusters can be used as efficient catalysts to catalyze intramolecular cyclopropanation of  $\alpha$ -diazoketone and intermolecular cyclopropanation of alkenes with ethyl diazoacetate but with a rather low enantioselectivity.

In addition to chiral ligands, achiral multidentate ligands have also been applied in the synthesis of intrinsically chiral metal clusters although they are racemic. Wang and co-workers obtained the first structural evidence on a gold NC with an intrinsic chiral core by using a tetradentate phosphine ligand tris(2-(diphenylphosphino)



**Fig. 1.** Top view (a) and side-view (b) of the left-handed enantiomer of  $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$  cluster. For clarity, the  $-\text{C}_2\text{H}_4\text{Ph}$  units are removed. Color coding: yellow, Au in staple; green, Au in core; orange, S. Reprinted with permission from Ref. 14c. Copyright 2012 Nature Publishing Group. (c)  $\pi \cdots \pi$  Stacking interaction in the crystal structure of  $[\text{PdAg}_{24}(\text{SR})_{18}]^{2-}$  cluster. Color coding: green and blue spheres, Ag; orange sphere, Pd; yellow sphere, S. Reprinted with permission from Ref. 21. Copyright 2015 American Chemical Society.

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