

# Chemical Science

Volume 12  
Number 31  
21 August 2021  
Pages 10399–10674

rsc.li/chemical-science



ISSN 2041-6539



ROYAL SOCIETY  
OF CHEMISTRY

## EDGE ARTICLE

Yoshitaka Aramaki, Takashi Ooi, Masakazu Nambo,  
Cathleen M. Crudden *et al.*  
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Cite this: *Chem. Sci.*, 2021, 12, 10436

All publication charges for this article have been paid for by the Royal Society of Chemistry

## Synthesis and enantioseparation of chiral Au<sub>13</sub> nanoclusters protected by bis-*N*-heterocyclic carbene ligands†

Hong Yi, <sup>‡a</sup> Kimberly M. Osten, <sup>‡a</sup> Tetyana I. Levchenko,<sup>b</sup> Alex J. Veinot, <sup>b</sup> Yoshitaka Aramaki, <sup>\*ac</sup> Takashi Ooi, <sup>\*ac</sup> Masakazu Nambo <sup>\*a</sup> and Cathleen M. Crudden <sup>\*ab</sup>

A series of chiral Au<sub>13</sub> nanoclusters were synthesized *via* the direct reduction of achiral dinuclear Au(I) halide complexes ligated by *ortho*-xylyl-linked bis-*N*-heterocyclic carbene (NHC) ligands. A broad range of functional groups are tolerated as wingtip substituents, allowing for the synthesis of a variety of functionalized chiral Au<sub>13</sub> nanoclusters. Single crystal X-ray crystallography confirmed the molecular formula to be [Au<sub>13</sub>(bisNHC)<sub>5</sub>Cl<sub>2</sub>]Cl<sub>3</sub>, with a chiral helical arrangement of the five bidentate NHC ligands around the icosahedral Au<sub>13</sub> core. This Au<sub>13</sub> nanocluster is highly luminescent, with a quantum yield of 23%. The two enantiomers of the Au<sub>13</sub> clusters can be separated by chiral HPLC, and the isolated enantiomers were characterized by circular dichroism spectroscopy. The clusters show remarkable stability, including configurational stability, opening the door to further investigation of the effect of chirality on these clusters.

Received 2nd June 2021  
Accepted 27th June 2021

DOI: 10.1039/d1sc03076k

rsc.li/chemical-science

The intersection of chirality with nanomaterials has been called “one of the most dynamic areas in modern science”.<sup>1a</sup> Atomically precise nanoclusters are a particularly important class of nanomaterials in this area because of the ability to discern molecular structure with high precision, and the high structural purity obtainable.<sup>1</sup> The unique properties of these nanomaterials opens up applications in chiral sensing,<sup>2</sup> enantioselective nanocatalysis<sup>3</sup> and chiroptics.<sup>4</sup> Chirality in metal nanoclusters can be generated *via* an intrinsically chiral metal core,<sup>5</sup> from an achiral core with chiral organic ligands<sup>6</sup> or from an achiral core with achiral ligands that are arranged in an asymmetric fashion.<sup>7</sup> Although impressive strides have been made in the synthesis of chiral metal clusters, considerable challenges remain with regards to designing chiral nanoclusters with stable chirality that is resistant to racemization and with optimized properties, for example photo-physical properties.

The Bürgi group have been pioneers in the creation of chiral thiolate-stabilized nanoclusters, highlighted by their work with Au<sub>38</sub>(SR)<sub>24</sub>, which is chiral by virtue of the arrangement of thiol staples around the core, and can be separated into its enantiomers by HPLC.<sup>8</sup> Cluster Au<sub>38</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>24</sub> shows high stability at room temperature, with racemization occurring in approximately 30 minutes at 80 °C.<sup>9</sup> Computational work from the Häkkinen group suggests that chiral inversions for Au<sub>38</sub>(SR)<sub>24</sub> and Pd-doped Au<sub>38</sub> can take place through a rotational reconstruction of the metal core without the need for ligand–metal bond cleavage.<sup>10</sup>

Smaller Au<sub>13</sub> nanoclusters can also be prepared with achiral phosphine ligands depending on their orientation around the core. Shichibu and Konishi described this situation for [Au<sub>13</sub>(-dppe)<sub>5</sub>Cl<sub>5</sub>]<sup>3+</sup> (dppe = 1,2-bis(diphenylphosphino)ethane),<sup>11</sup> in which the five dppe ligands take up a propeller-like arrangement.<sup>12</sup> However, successful resolution of the individual enantiomers by chiral HPLC was not achieved, possibly due to fast racemization of these clusters in solution. The only examples of resolvable chiral Au clusters stabilized by phosphine ligands require the use of inherently chiral ligands.<sup>13</sup>

*N*-Heterocyclic carbenes (NHCs) have recently emerged as valuable alternatives to thiols or phosphines for the stabilization of metal surfaces, nanoparticles, and clusters.<sup>14</sup> The neutral, electron-rich NHCs form a strong covalent bond with the metal,<sup>15</sup> which is important in providing stability to metal nanoclusters.<sup>16</sup> Our group recently described the utility of NHCs in protecting gold nanoclusters, reporting the first examples of

<sup>a</sup>Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University Furo, Chikusa, Nagoya 464-8602, Japan. E-mail: aramaki@chembio.nagoya-u.ac.jp; tooi@chembio.nagoya-u.ac.jp; mnambo@itbm.nagoya-u.ac.jp; cruddenc@chem.queensu.ca

<sup>b</sup>Department of Chemistry, Queen's University, Chernoﬀ Hall, Kingston, Ontario K7L 3N6, Canada

<sup>c</sup>Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8601, Japan

† Electronic supplementary information (ESI) available. CCDC 2067324. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1sc03076k

‡ Hong Yi and Kimberly M. Osten contributed equally to this work.



NHC-containing Au<sub>11</sub> and Au<sub>13</sub> clusters.<sup>17,18</sup> Zheng *et al.* have also described the synthesis of Au<sub>13</sub>,<sup>19</sup> Au<sub>25</sub> (ref. 20a) and Au<sub>44</sub> (ref. 20b) nanoclusters, and Tsukuda has prepared Au<sub>23</sub> clusters,<sup>21</sup> illustrating the potential of NHCs as stabilizing ligands for a range of gold nanocluster architectures. Very recently, Zang *et al.* reported the synthesis of Au<sub>11</sub> and Au<sub>13</sub> nanoclusters protected by *m*-phenylene-bridged *N*-heterocyclic carbene ligands that result in different clusters based on subtle changes in *N*-substituents.<sup>22</sup>

Herein we report the synthesis of chiral Au<sub>13</sub> nanoclusters prepared with achiral bidentate NHC ligands. The nanoclusters derive their chirality from a helical arrangement of the achiral ligand (Fig. 1). The stability introduced by the NHC ligand permits the separation of the nanocluster into its constituent enantiomers by chiral HPLC. Each enantiomer was characterized by circular dichroism. The clusters display impressive thermal stability and record-setting photoluminescent quantum yields.

Inspired by the work of Zheng, who showed that bisNHC ligands linked by a simple propyl chain can provide stable Au<sub>13</sub> nanoclusters,<sup>19</sup> we set out to examine bis-benzimidazolylidene ligands with aromatic linkers, designed to take advantage of the multitude of CH- $\pi$  interactions observed in other Au<sub>13</sub> clusters.<sup>18</sup> Bis-benzimidazolium salts (**1a–g**) prepared by simple S<sub>N</sub>2 reactions were converted into the corresponding Au complexes (bisNHC)Au<sub>2</sub>X<sub>2</sub> (**2a–g**) by reaction with Au(SMe<sub>2</sub>)Cl in the presence of K<sub>2</sub>CO<sub>3</sub> (see ESI† for full details and characterization).<sup>23</sup> Cluster synthesis was accomplished by reduction of complex **2a** with NaBH<sub>4</sub> followed by etching with HCl. This procedure afforded cluster [3a]Cl<sub>3</sub> in 43% isolated yield based on Au, after purification by column chromatography (Fig. 2A).

The effect of HCl on the synthetic protocol was examined by UV-vis spectroscopy and electrospray ionization mass spectrometry (ESI-MS). The absorbance spectra of the cluster were significantly sharper after HCl etching, consistent with the size-focusing effect observed in other systems (Fig. S1†).<sup>14,18</sup> The molecular formula of the cluster [3a]Cl<sub>3</sub> was confirmed by ESI-MS, which showed a dominant molecular ion peak at 1741.26 *m/z* corresponding to [Au<sub>13</sub>(bisNHC<sup>Bn</sup>)<sub>5</sub>Cl<sub>2</sub>]<sup>3+</sup> (Fig. 2B). Good agreement was observed between the experimental and theoretical isotopic distribution patterns. A minor peak at 2629.89 *m/z* was also observed, corresponding to the divalent ion [Au<sub>13</sub>(bisNHC<sup>Bn</sup>)<sub>5</sub>Cl<sub>2</sub>]<sup>2+</sup> derived from incomplete ionization of the parent cluster.

The UV-vis spectrum of [3a]Cl<sub>3</sub> in dichloromethane shows distinct absorption bands at 324, 409, 456, and 511 nm (Fig. 2C,



Fig. 2 (A) Preparation of [Au<sub>13</sub>(bisNHC)<sub>5</sub>X<sub>2</sub>]<sub>3</sub> nanoclusters [3a–e]<sub>3</sub> (B) ESI-MS of [3a]Cl<sub>3</sub>; (C) UV-vis absorbance (red), photoluminescence excitation (black) and emission (green) spectra of [3a]Cl<sub>3</sub> in dichloromethane.

red), which are in line with previously reported Au<sub>13</sub> clusters.<sup>18</sup> Solutions of [3a]Cl<sub>3</sub> in dichloromethane show bright red-orange emission. Photoluminescence quantum yields measured by two independent methods is 23%, a value considerably higher than most superatom gold clusters, including our previous report of 16% for an NHC-protected Au<sub>13</sub> cluster.<sup>18</sup> The spectrum produced by excitation at 784 nm (Fig. 2C, black) is in good agreement with the UV-vis spectrum, supporting the conclusion that the measured quantum yield was not affected by contamination with other emissive species. Although the precise reason for the high quantum yield is currently under investigation, the rigid shell provided by the NHC with multiple  $\pi$ - $\pi$  stacking interactions likely contributes.

Halide counterions had little effect on cluster formation, with bromide complex **2b** affording 27% yield of [Au<sub>13</sub>(bisNHC<sup>Bn</sup>)<sub>5</sub>Br<sub>2</sub>]<sub>3</sub> ([3b]Br<sub>3</sub>) after purification. The nature of the linking unit was found to be critically important, with *meta*- and *para*-xylyl linked ligands (**1f** and **1g** respectively) giving no observable Au<sub>13</sub> clusters (see Fig. S2†). However, wingtip aromatic substituents were readily interchangeable, with complexes **2c–e** all affording Au<sub>13</sub> nanoclusters (see ESI† for full characterization).

Single crystals of [3a]Cl<sub>3</sub> suitable for X-ray crystallography were grown from layering hexane onto a dichloromethane solution of the pure cluster. The structure features an icosahedral Au<sub>13</sub> core with Au–Cl bonds capping the top and bottom of the core and the five bis-NHC ligands bound to the two twisted Au<sub>5</sub> pentagons of the core (Fig. 3). The average Au–C bond length is 2.05(2) Å, similar to other NHC-stabilized nanoclusters.<sup>18</sup> The average Au centre–Au peripheral bond distance of the icosahedral core is 2.7655(12) Å, and the average Au–Cl bond length of the terminal chloride ligands is 2.332(6) Å. A distinct structural characteristic is the face-to-face arrangement



Fig. 1 Synthesis of chiral Au<sub>13</sub> clusters.







Fig. 5 Enantioseparation and characterization of chiral Au<sub>13</sub> nano-clusters: (A) chromatogram showing the enantioseparation of *rac*-**3a** by chiral HPLC using UV-vis detection at 350 nm; (B) CD spectra of the two chiral enantiomers separated by HPLC and *rac*-**3a** for comparison.

chiral HPLC. The enantiomeric excess (ee) of the two collected fractions was determined by chiral HPLC and found to be 88% for **3a-en1** and 95% for **3a-en2**. The UV-vis, NMR and mass spectra of the separated enantiomers were consistent with the starting racemic mixture, illustrating the stability of the Au<sub>13</sub> structure under the separation conditions, although the ESI-MS and NMR spectra suggest that anion exchange with trifluoroacetate anion had occurred (Fig. S3–S5†).

The as-separated enantiomers were characterized by circular dichroism (CD) spectroscopy (Fig. 5B). As expected, the CD spectra of the two enantiomers are mirror images and show distinct bands between 250 and 800 nm (main peaks: 259, 271, 296, 317, 333 nm, weak peaks at 376, 425 nm, and a broad peak at 500 nm). No CD signal was observed for the racemic mixture.

The thermal stability of cluster [**3a**]Cl<sub>3</sub> was investigated by UV-vis spectroscopy. The UV-vis spectrum showed no discernible change after 3 days of heating at 60 °C in acetonitrile (Fig. 6A). Emission spectra were also identical within error after this time (Fig. S7†). The configurational stability of **3a** was investigated by monitoring the change in enantiopurity upon heating to different temperatures. Samples of **3a-en1** (88% initial ee) were heated in MeOH at a variety of temperatures for 1 h. At 60 °C, there was no discernible change, but a slight drop to 81% ee was observed when the cluster was heated to 80 °C, and at 100 °C the ee further decreased to 72% (Fig. 6B). Changes in enantiomeric ratios were documented by HPLC (Fig. S8†) and CD (Fig. S9†). Work to clarify the mechanism of racemization is underway in our lab.



Fig. 6 (A) Thermal stability of *rac*-**3a** at 60 °C in acetonitrile monitored by UV-vis spectroscopy; (B) chiral stability of **3a-en-1** in methanol after treatment at different temperatures for 1 h. The enantiomeric purity after heating was examined by chiral HPLC.

## Conclusions

In conclusion, we have described the synthesis and structural characterization of a new chiral *ortho*-xylyl linked bisNHC-stabilized Au<sub>13</sub> cluster [Au<sub>13</sub>(bisNHC<sup>Bnn</sup>)<sub>5</sub>Cl<sub>2</sub>]Cl<sub>3</sub> (**[3a]**Cl<sub>3</sub>) and its bromide derivative [**3b**]Br<sub>3</sub>. These clusters have a similar icosahedral structure to previously reported Au<sub>13</sub> clusters, including those ligated by monodentate,<sup>18</sup> bis-NHC<sup>19</sup> and bis-phosphine ligands.<sup>11</sup> A variety of wingtip groups were compatible with nanocluster formation, allowing for the isolation of clusters incorporating diverse functionality (**3c–e**). The chirality of cluster **3a** in the solid-state was investigated by X-ray crystallography, where it was discerned that chirality results from a helical arrangement of the surface ligands that is dictated by the choice of a bidentate ligand. The two enantiomers were separated by chiral HPLC and characterized by CD spectra. The clusters show high thermal stability and stability against racemization, which may facilitate their future applications in chiral catalysis and sensing.

## Data availability

The experimental data is included in the ESI.

## Author contributions

C. C. and M. N. conceived the project. H. Y. and K. O. carried out the synthesis, purification and characterization of the Au<sub>13</sub> nanoclusters. T. L. performed the quantum yield of Au<sub>13</sub> nanocluster. A. V., Y. A., and T. O. analysed the X-ray crystal of the cluster [**3a**]Cl<sub>3</sub>. All the authors wrote the paper, supplementary methods, and related materials.

## Conflicts of interest

The authors declare no competing financial interests.

## Acknowledgements

This work was supported by KAKENHI from JSPS (17H03030 to C. M. C.). H. Y. and K. M. O. thank JSPS for funding through the JSPS International Research Fellow program. M. N. thanks the support from The Mazda foundation. A. J. V. thanks NSERC for a Vanier Scholarship and the Walter C. Sumner foundation for additional scholarship support. T. I. L. thanks NSERC for a postdoctoral fellowship. We thank DAICEL corporation for the assistance of separation of enantiomers. JSPS and NU are acknowledged for funding of this research through The World Premier International Research Centre Initiative (WPI) program. NSERC and the Canada Foundation for Innovation (CFI) are thanked for financial support of this work in terms of operating and equipment grants to C. M. C. The authors thank Dr Kevin Stamplecoskie (Queen's University) for access to UV-vis absorbance and fluorescence spectrometers and for useful advice on fluorescence quantum yield measurements.



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