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# IrAu<sub>12</sub> superatom modified by chiral diphosphines: doping-induced enhancement of chiroptical activity†

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Gold superatoms modified by chiral ligands are a new class of chiroptical nanomaterials, but improvement of their chiroptical properties, such as circular dichroism (CD) and circularly polarized luminescence (CPL), remains a challenge. In this work, we studied the effects of single-atom doping on the chiroptical properties of a representative Au<sub>13</sub> superatom using [Au<sub>13</sub>((R,R)-DIPAMP)<sub>5</sub>Cl<sub>2</sub>]<sup>3+</sup> and [Au<sub>13</sub>((S,S)-DIPAMP)<sub>5</sub>Cl<sub>2</sub>]<sup>3+</sup> (**Au<sub>13</sub>-R/S**; DIPAMP = 1,2-bis((2-methoxyphenyl)phenylphosphino)ethane). We synthesized an enantiomeric pair of superatoms: [IrAu<sub>12</sub>((R,R)-DIPAMP)<sub>5</sub>Cl<sub>2</sub>]<sup>+</sup> and [IrAu<sub>12</sub>((S,S)-DIPAMP)<sub>5</sub>Cl<sub>2</sub>]<sup>+</sup> (**IrAu<sub>12</sub>-R/S**). Single-crystal X-ray diffraction analysis revealed that the icosahedral Ir@Au<sub>12</sub> core of **IrAu<sub>12</sub>-R/S** was more twisted along the Cl–Au–Ir–Au–Cl axis compared with the Au<sub>13</sub> core of **Au<sub>13</sub>-R/S**, leading to a larger absorption anisotropy factor. **IrAu<sub>12</sub>-R/S** exhibited a much higher photoluminescence quantum yield (~70%) compared with **Au<sub>13</sub>-R/S** (15%) due to a larger energy gap between the highest occupied and the lowest unoccupied molecular orbitals. Although Ir doping did not appreciably enhance the photoluminescence anisotropy factors, the brightness of the CPL of **IrAu<sub>12</sub>-R/S** was five times higher than that of **Au<sub>13</sub>-R/S**. This work provides a rational guide for improving the chiroptical activity of Au superatoms *via* the doping-mediated manipulation of the geometric and electronic structures.

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## Introduction

Ligand-protected gold (Au) and silver (Ag) superatoms with chiral structures have attracted growing interest as chiroptical nanomaterials because their atomically-precise structures make them ideal models for elucidating chiral structure–property correlations.<sup>1–4</sup> Since the first preparation of the optically active Au superatom protected by L-glutathione,<sup>5</sup> various enantiomeric superatoms have been synthesized using chiral ligands such as thiolates,<sup>6–9</sup> diphosphines,<sup>10–14</sup> alkynyls,<sup>15</sup> and

N-heterocyclic carbenes.<sup>16</sup> Chiral superatoms also are obtained *via* the asymmetric arrangement of achiral ligands.<sup>17–21</sup> Chiral counterions have often been used for the optical resolution and asymmetric synthesis of such chiral superatoms with achiral ligands.<sup>22–24</sup> These superatoms and assemblies of them exhibit unique chiroptical properties such as circular dichroism (CD) and circularly polarized luminescence (CPL). The CD activity is determined by the absorption anisotropy factor ( $g_{\text{abs}}$ ), whereas the CPL is evaluated by the brightness ( $B_{\text{CPL}}$ ) as given *via* the following equation:<sup>25</sup>

$$B_{\text{CPL}} = \varepsilon \times \Phi_{\text{PL}} \times \frac{g_{\text{PL}}}{2} \quad (1)$$

where  $\varepsilon$ ,  $\Phi_{\text{PL}}$ , and  $g_{\text{PL}}$  are the molar absorption coefficient at the excitation wavelength, the photoluminescence (PL) quantum yield, and the PL anisotropy factor, respectively. For these superatoms, the anisotropy factors ( $g_{\text{abs}}$  and  $g_{\text{PL}}$ ) are typically of the order of  $10^{-3}$ , and the  $\Phi_{\text{PL}}$  is less than 10%. Previous studies on the crystallization, self-assembly,<sup>11,15,19,21</sup> and doping of superatoms<sup>26</sup> have suggested the following strategies for improving these key parameters: (1) the  $g_{\text{abs}}$  value can be enhanced *via* torsion of the superatom<sup>14</sup> and by placing  $\pi$ -electron ligands in the vicinity of the superatom;<sup>10,27</sup> (2) the  $\Phi_{\text{PL}}$  value can be

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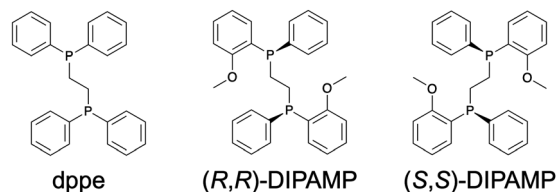


Chart 1 Diphosphine ligands used in this study.

enhanced through rigidification of the superatom and widening of the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).<sup>26</sup>

To test the effectiveness of the above strategies, we herein studied the effects of single-atom doping on the chiroptical properties of a representative Au<sub>13</sub> superatom protected by chiral diphosphine ligands (Chart 1; dppe = 1,2-bis(diphenylphosphino)ethane, DIPAMP = 1,2-bis[(2-methoxyphenyl)phenylphosphino]ethane), *i.e.*, [Au<sub>13</sub>((R,R)-DIPAMP)<sub>5</sub>Cl<sub>2</sub>]<sup>3+</sup> (**Au<sub>13</sub>-R**) and [Au<sub>13</sub>((S,S)-DIPAMP)<sub>5</sub>Cl<sub>2</sub>]<sup>3+</sup> (**Au<sub>13</sub>-S**).<sup>13,14</sup> Single-crystal X-ray diffraction (SCXRD) analysis showed that the icosahedral Au@Au<sub>12</sub> core consisted of a pair of Au<sub>5</sub> rings bridged by five DIPAMP ligands with a linear Cl–Au–Au–Cl axis at their center (Fig. 1a). The degree of structural distortion of the Au@Au<sub>12</sub> core was evaluated *via* the dihedral angle of the two Au<sub>5</sub> rings ( $\theta$ ) (Fig. 1b). The average deviation of  $\theta$  from that of a perfect icosahedron ( $\Delta\theta = |36^\circ - \theta|$ ) was  $1.19 \pm 0.61^\circ$  and  $1.24 \pm 0.59^\circ$  for **Au<sub>13</sub>-R/S**, respectively.<sup>14</sup> The dopant chosen in this study was iridium (Ir), based on the following findings obtained using achiral diphosphine ligands (Chart 1), for [Au<sub>13</sub>(dppe)<sub>5</sub>Cl<sub>2</sub>]<sup>3+</sup> (**Au<sub>13</sub>-dppe**) and [IrAu<sub>12</sub>(dppe)<sub>5</sub>Cl<sub>2</sub>]<sup>+</sup> (**IrAu<sub>12</sub>-dppe**). First, the  $\Delta\theta$  value increased from  $1.03 \pm 0.95^\circ$  for **Au<sub>13</sub>-dppe** to  $1.69 \pm 0.50^\circ$  for **IrAu<sub>12</sub>-dppe**, probably due to the smaller atomic radius of Ir (2.0 Å) compared with that of Au (2.1 Å).<sup>28,29</sup> Second, the  $\Phi_{\text{PL}}$  value increased markedly from 11% for **Au<sub>13</sub>-dppe** to  $\sim 70\%$  for **IrAu<sub>12</sub>-dppe**<sup>26</sup> due to the expansion of the HOMO–LUMO (HL) gap from 1.9 eV for **Au<sub>13</sub>-dppe** to 2.3 eV for **IrAu<sub>12</sub>-dppe**. These results suggest that the chiroptical properties of the Au<sub>13</sub> superatom can be improved through manipulation of the geometric and electronic structures *via* single-atom doping with Ir. To test this hypothesis, we freshly synthesized an enantiomeric pair of Ir@Au<sub>12</sub> superatoms: [IrAu<sub>12</sub>((R,R)-DIPAMP)<sub>5</sub>Cl<sub>2</sub>]<sup>+</sup> (**IrAu<sub>12</sub>-R**) and [IrAu<sub>12</sub>((S,S)-DIPAMP)<sub>5</sub>Cl<sub>2</sub>]<sup>+</sup> (**IrAu<sub>12</sub>-S**). The  $B_{\text{CPL}}$  values of the **IrAu<sub>12</sub>-R/S** enantiomers were five times larger than those of

the non-doped **Au<sub>13</sub>-R/S** enantiomers, mainly due to the enhancement of  $\Phi_{\text{PL}}$  (eqn (1)).

## Experimental section

### Synthesis and characterization of IrAu<sub>12</sub>-R/S·(PF<sub>6</sub>)

The PF<sub>6</sub>-salt of **IrAu<sub>12</sub>-R/S** was synthesized according to the synthesis method for **IrAu<sub>12</sub>-dppe**.<sup>26</sup> The **Au<sub>13</sub>-R/S** enantiomers were also synthesized as a reference according to the method in ref. 14. Single crystals of **IrAu<sub>12</sub>-R/S**·(PF<sub>6</sub>) suitable for SCXRD measurements were obtained *via* recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/cyclopentyl methyl ether. Details of the synthesis and the characterization of **IrAu<sub>12</sub>-R/S** are provided in the ESI.†

### Optical and chiroptical measurements

The UV–Vis absorption spectra and CD spectra were recorded using a Jasco V-670 spectrometer and a JASCO J-725 spectropolarimeter, respectively. The  $g_{\text{abs}}$  values were calculated using the equation  $g_{\text{abs}} = \theta \text{ [mdeg]} / (32980 \cdot \text{Abs})$  using the CD ( $\theta$ : ellipticity) and absorbance (Abs) data. PL spectra were recorded using a Jasco FP-8500 spectrofluorometer. The absolute value of  $\Phi_{\text{PL}}$  was measured at ambient temperature using a Hamamatsu Photonics CC9920-02G assembly with an integration sphere. The PL lifetime measurements were carried out using a C4780 streak camera. The excitation source was generated using a Nd:YVO<sub>4</sub> laser (Verdi, Coherent) pumped Ti:sapphire laser system (Mira-900, Coherent) equipped with a cavity dumper (Pulse Switch, Coherent), which delivers 100 fs pulse trains at 800 nm. After doubling the frequency with a LiB<sub>3</sub>O<sub>5</sub> crystal, the incident pulses were focused onto the samples (excitation wavelength = 400 nm). The PL decay curves were extracted from the 2D streak images in the range of 95 nm centered at the PL peak of each temperature. CPL spectra were recorded using a homemade CPL spectroscopy system equipped with a UV laser diode (375 nm) as the excitation source.<sup>30</sup> The  $g_{\text{PL}}$  values were calculated using the equation  $g_{\text{PL}} = 2(I_{\text{L}} - I_{\text{R}}) / (I_{\text{L}} + I_{\text{R}})$ , where  $I_{\text{L}}$  and  $I_{\text{R}}$  are the PL intensity of the left and right circularly polarized light, respectively. An Ar-saturated solution was used for the PL and CPL measurements. The temperature for the PL and PL lifetime measurements was controlled in the range of 80–300 K using an Oxford Instruments OptistatDN liquid N<sub>2</sub> cryostat. For variable-temperature (VT) UV-Vis, CD, and CPL studies, the temperature of the samples was controlled in the range of 200–300 K using a Unisoku CoolSpeK cryogenic cell holder.

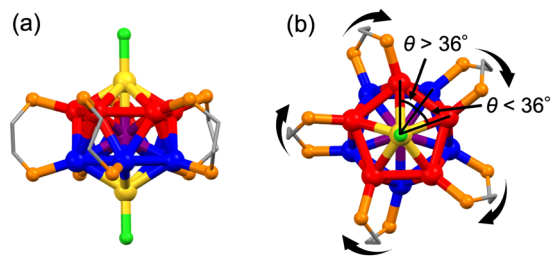


Fig. 1 (a) Side and (b) top view of the chiral structure of **MAu<sub>12</sub>-dppe** (M = Ir, Au). Color code: yellow, Au on the Cl–Au–M–Au–Cl axis; red and blue, Au in the Au<sub>5</sub> rings; purple, M; orange, P; light green, Cl; gray, C.

## Results and discussion

### Geometric structure

Isotopically resolved electrospray ionization (ESI) mass spectra of the **IrAu<sub>12</sub>-R/S** samples confirmed the composition and charge state of [IrAu<sub>12</sub>(DIPAMP)<sub>5</sub>Cl<sub>2</sub>]<sup>+</sup> (Fig. S1, ESI†). The mass spectra also exhibited small peaks at  $m/z \approx 4963$ , assigned to [IrAu<sub>12</sub>(DIPAMP)<sub>5</sub>ClBr]<sup>+</sup> (**IrAu<sub>12</sub>-Br**) that originated from impurities in the chemicals used during the synthesis. Ratios of the



peak area of **IrAu<sub>12</sub>-Br** to **IrAu<sub>12</sub>-R/S** were 0.05 and 0.04, respectively, indicating that the purity of **IrAu<sub>12</sub>-R/S** was ~95 mol%. The purities of the **IrAu<sub>12</sub>-R/S** samples were further confirmed using <sup>1</sup>H NMR and elemental analysis. The <sup>1</sup>H NMR charts of the **IrAu<sub>12</sub>-R/S** samples showed signals only for the DIPAMP ligands and the cyclopentyl methyl ether (CPME) used for crystallization (Fig. S2, ESI<sup>†</sup>). The ratio of the integrated signals indicated that the samples contained two equivalents of CPME to **IrAu<sub>12</sub>-R/S**. The elemental analysis demonstrated that **IrAu<sub>12</sub>-R/S** contained 1.31 wt% of Cl, which was reproduced by considering that the samples consisted of 95 mol% of **IrAu<sub>12</sub>-R/S**·(PF<sub>6</sub>)·(CPME)<sub>2</sub> and 5 mol% **IrAu<sub>12</sub>-Br**·(PF<sub>6</sub>)·(CPME)<sub>2</sub>. Nevertheless, based on a previous report that the optical absorption profile and  $\Phi_{\text{PL}}$  value of **Au<sub>13</sub>-dppe** were hardly changed by replacing the Cl ligands with Br,<sup>31</sup> we concluded that the effect of the **IrAu<sub>12</sub>-Br** impurity on the optical and chiroptical measurements was negligible.

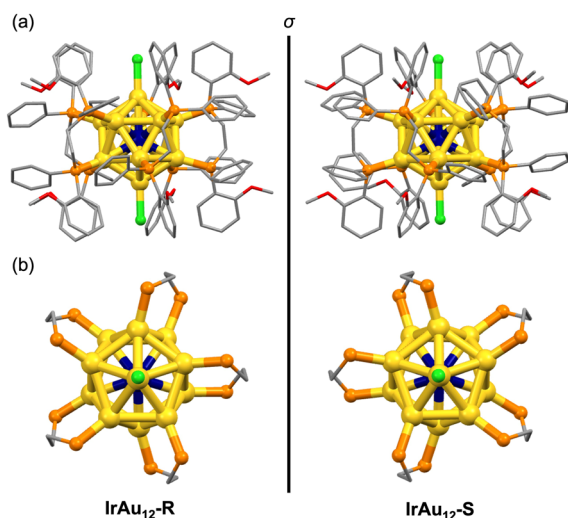
The geometric structures of **IrAu<sub>12</sub>-R/S** were solved *via* SCXRD analysis. The unit cell contained a single **IrAu<sub>12</sub>-R/S** molecule and a PF<sub>6</sub> anion, supporting the monovalent charge state for **IrAu<sub>12</sub>-R/S** as determined *via* ESI mass spectrometry. As shown in Fig. 2a, the **IrAu<sub>12</sub>-R/S** enantiomers have an icosahedral IrAu<sub>12</sub> core ligated by five DIPAMP ligands and two Cl ligands. The position of the Ir atom could not be determined *via* SCXRD analysis due to the inability of distinguishing the electron density of Ir from Au. <sup>31</sup>P{<sup>1</sup>H} NMR analysis was performed to reveal the location of Ir in the IrAu<sub>12</sub> core (Fig. S3, ESI<sup>†</sup>). The single peak in the <sup>31</sup>P{<sup>1</sup>H} NMR charts of **IrAu<sub>12</sub>-R/S** indicated that all ten phosphorus nuclei of the DIPAMP ligands were equivalent on the NMR time scale. Thus, the Ir atom was located at the center of the icosahedral core. The metal–metal bond lengths of **IrAu<sub>12</sub>-R/S** and **Au<sub>13</sub>-R/S** are

summarized in Fig. S4 and Table S1 (ESI<sup>†</sup>). The average lengths of the Ir–Au bonds in **IrAu<sub>12</sub>-R/S** were 2.726 ± 0.012 Å and 2.729 ± 0.017 Å, respectively, which were shorter than those of the corresponding radial Au–Au bonds in **Au<sub>13</sub>-R/S** (2.761 ± 0.033 Å and 2.761 ± 0.034 Å, respectively).<sup>14</sup> The average lengths of the peripheral Au–Au bonds of **IrAu<sub>12</sub>-R/S** (2.866 ± 0.026 Å and 2.870 ± 0.034 Å, respectively) were also shorter than those of **Au<sub>13</sub>-R/S** (2.904 ± 0.030 Å and 2.903 ± 0.032 Å, respectively).<sup>14</sup> The contraction of the Ir@Au<sub>12</sub> core with respect to Au@Au<sub>12</sub> is due to the smaller van der Waals radius of Ir (2.0 Å) compared with that of Au (2.1 Å).<sup>32</sup> The torsion of the Ir@Au<sub>12</sub> core was quantified using the average value of  $\Delta\theta$  (Fig. 2b). The values were 1.47 ± 0.30° and 1.89 ± 0.67° for **IrAu<sub>12</sub>-R/S**, respectively, which were larger than those of **Au<sub>13</sub>-R/S** (1.19 ± 0.61° and 1.24 ± 0.59°, respectively).<sup>14</sup> These results indicated that the Au<sub>5</sub> rings of the Ir@Au<sub>12</sub> core were more twisted around the Cl–Au–Ir–Au–Cl axis compared with those of the Au<sub>13</sub> core. In conclusion, the introduction of a smaller Ir atom to the Au<sub>13</sub> core induced further distortion.

### UV-Vis absorption and CD properties

The UV-Vis absorption spectra of **IrAu<sub>12</sub>-R/S** (Fig. 3a) exhibited a distinct peak at 418 nm with an  $\epsilon$  value of 2.08 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup> and 2.01 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>, respectively. These  $\epsilon$  values were larger than those of **Au<sub>13</sub>-R/S** at 495 nm (1.61 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup> and 1.76 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>, respectively) (Fig. 3b).<sup>14</sup> The onsets of the spectra revealed that the HL gaps of **IrAu<sub>12</sub>-R/S** were 2.3 eV, which are larger than those of **Au<sub>13</sub>-R/S** (1.9 eV) (insets of Fig. 3).<sup>14</sup> These results indicated the expansion of the HL gap upon Ir doping, as observed in **IrAu<sub>12</sub>-dppe** and **Au<sub>13</sub>-dppe** (Table 1).<sup>26</sup> Fig. S5 (ESI<sup>†</sup>) shows the VT UV-Vis spectra of **IrAu<sub>12</sub>-R/S** in 2-methyltetrahydrofuran (MeTHF) recorded at 300 and 200 K. The spectrum at 200 K exhibited a sharper profile than that of the spectrum at 300 K because the hot band transition was suppressed at the lower temperature.<sup>33–35</sup> As a result, the two peaks at 420 and 470 nm became more pronounced and a new shoulder structure appeared at ~520 nm (the insets of Fig. S5, ESI<sup>†</sup>).

The VT CD spectra of **IrAu<sub>12</sub>-R/S** are shown in Fig. 4a. The spectral profiles of the enantiomeric pair show a mirror image relationship, indicating the enantiopurity of the samples. The peak positions in the CD spectra at ~310, 340, 370, 400, 470,



**Fig. 2** (a) SCXRD structures of **IrAu<sub>12</sub>-R** (left) and **IrAu<sub>12</sub>-S** (right). Phenyl rings, ethylene bridges, and methoxy groups are depicted as sticks and hydrogen atoms are omitted for simplicity. (b) Top view of the core structures of **IrAu<sub>12</sub>-R** (left) and **IrAu<sub>12</sub>-S** (right). Phenyl rings and methoxy groups are omitted for simplicity. Color code: yellow, Au; dark blue, Ir; orange, P; light green, Cl; red, O; gray, C.



**Fig. 3** UV-Vis absorption spectra of (a) **IrAu<sub>12</sub>-R** (red) and **IrAu<sub>12</sub>-S** (blue) in MeTHF and (b) **Au<sub>13</sub>-R** (red) and **Au<sub>13</sub>-S** (blue) in acetonitrile at ambient temperature. Arrows indicate the HL gaps estimated from the spectral onsets. Insets show the expanded spectra in the energy scale.



Table 1 Optical and chiroptical properties of **IrAu<sub>12</sub>-S** and **Au<sub>13</sub>-S**

Superatom	HL gap (eV)	$\epsilon$ ( $\times 10^4$ M <sup>-1</sup> cm <sup>-1</sup> )	$ g_{\text{abs}} $ ( $\times 10^{-3}$ )	$\lambda_{\text{PL}}$ (nm)	$\Phi_{\text{PL}}$ (%)	$\tau_{\text{PL}}$ ( $\mu\text{s}$ )	$\lambda_{\text{CPL}}$ (nm)	$ g_{\text{PL}} $ ( $\times 10^{-3}$ )	Ref.
<b>IrAu<sub>12</sub>-S</b>	2.3	2.01 (418 nm)	$\sim 4$ (475 nm, 300 K) $\sim 5$ (475 nm, 200 K)	$\sim 609$ (400 nm)	65.9	5.87	$\sim 600$	$\sim 2$ (600 nm, 300 K) $\sim 4$ (600 nm, 200 K)	
<b>Au<sub>13</sub>-S</b>	1.9	1.76 (495 nm)	$\sim 2$ (400 nm, 300 K) $\sim 3$ (400 nm, 200 K)	$\sim 792$	15	3.19	$\sim 760$	$\sim 2$ (760 nm, 300 K) $\sim (4-5)$ (760 nm, 200 K)	13

The numbers in parentheses represent the excitation wavelength.



Fig. 4 (a) CD spectra and (b)  $g_{\text{abs}}$  spectra of **IrAu<sub>12</sub>-R** (red) and **IrAu<sub>12</sub>-S** (blue) in MeTHF. (c)  $g_{\text{abs}}$  spectra of **Au<sub>13</sub>-R** (red) and **Au<sub>13</sub>-S** (blue) in a MeOH–EtOH mixture (1 : 1 v/v). Solid and dotted lines denote the spectra recorded at 200 and 300 K, respectively.

and 530 nm corresponded to the absorption peaks and shoulder at  $\sim 305$ , 350, 420, 470 and 520 nm, respectively. The CD response for **IrAu<sub>12</sub>-R/S** in the visible region is associated with the optical transition within the chiral Ir@Au<sub>12</sub> core since the frontier orbitals are assigned to superatomic orbitals according to density functional theory calculations.<sup>26</sup> The  $|g_{\text{abs}}|$  spectra of **IrAu<sub>12</sub>-R/S** and **Au<sub>13</sub>-R/S** are presented in Fig. 4b and c, respectively. The  $|g_{\text{abs}}|$  values of **IrAu<sub>12</sub>-R/S** are  $\sim 3 \times 10^{-3}$  at 365 nm and  $\sim 4 \times 10^{-3}$  at 475 nm, respectively, at 300 K (Table 1). By contrast, the maximum  $|g_{\text{abs}}|$  value for **Au<sub>13</sub>-R/S** was  $\sim 2 \times 10^{-3}$  at 400 nm at 300 K (Table 1), which is consistent with the reported value.<sup>13</sup> According to the theoretical study in ref. 13, the higher  $|g_{\text{abs}}|$  value for **IrAu<sub>12</sub>-R/S** compared with that for **Au<sub>13</sub>-R/S** is ascribed to the larger torsion of the Ir@Au<sub>12</sub> core. The CD intensity of **IrAu<sub>12</sub>-R/S** was enhanced by lowering the temperature from 300 to 200 K (Fig. 4a). The  $|g_{\text{abs}}|$  value increased at 200 K to  $\sim 4 \times 10^{-3}$  at 365 nm and  $\sim 5 \times 10^{-3}$  at 474 nm, respectively (Fig. 4b, Table 1). The enhancement at the lower temperature is probably associated with the suppression of the thermal fluctuation of the Ir@Au<sub>12</sub> core structure. A similar temperature dependence was observed for the  $|g_{\text{abs}}|$  values of **Au<sub>13</sub>-R/S** (Fig. 4c). The  $|g_{\text{abs}}|$  value at 400 nm was enhanced to  $\sim 3 \times 10^{-3}$  by lowering the temperature to 200 K (Table 1).

## PL and CPL properties

The PL spectra of **IrAu<sub>12</sub>-S** were recorded in de-aerated MeTHF (Fig. 5a). The PL peak of **IrAu<sub>12</sub>-S** appeared at 609 nm at ambient temperature, which was shorter than that of **Au<sub>13</sub>-R/S** (792 nm).<sup>14</sup> This blueshift reflects the expansion of the HL gap by the doping with Ir. The  $\Phi_{\text{PL}}$  values of **IrAu<sub>12</sub>-R/S** in MeTHF at 300 K were 69.9% and 65.9%, respectively (Fig. S6, ESI† and Table 1), and were much higher than the reported value of **Au<sub>13</sub>-R/S** (15%).<sup>14</sup> The time-resolved PL decay of **IrAu<sub>12</sub>-S** and **Au<sub>13</sub>-S** was also measured (Fig. 5b and Fig. S7, ESI†). The PL lifetime ( $\tau_{\text{PL}}$ ), obtained through fitting with a single exponential function, of **IrAu<sub>12</sub>-S** (5.87  $\mu\text{s}$ ) was longer than that of **Au<sub>13</sub>-S** (3.19  $\mu\text{s}$ ) (Table 1). The increase in  $\Phi_{\text{PL}}$  and  $\tau_{\text{PL}}$  associated with the expansion of the HL gap was consistent with the case of **IrAu<sub>12</sub>-dppe** and **Au<sub>13</sub>-dppe**. According to the energy gap law, an increase in the PL energy suppresses the nonradiative relaxation process.<sup>36</sup>

The VT CPL spectra of **IrAu<sub>12</sub>-R/S** and **Au<sub>13</sub>-R/S** were recorded in de-aerated MeTHF and a MeOH–EtOH mixture (1 : 1 v/v), respectively (Fig. 6). The spectral profiles of the enantiomeric pairs of both samples are mirror images. The CPL bands peaked at  $\sim 600$  and  $\sim 760$  nm for **IrAu<sub>12</sub>-R/S** and **Au<sub>13</sub>-R/S**, respectively, which are comparable to the positions of the corresponding PL bands at 300 K. The  $|g_{\text{PL}}|$  values for **IrAu<sub>12</sub>-R/S** at 300 K were  $\sim 3 \times 10^{-3}$  and  $\sim 2 \times 10^{-3}$ , respectively (Table 1), whereas those for **Au<sub>13</sub>-R/S** were  $\sim 2 \times 10^{-3}$ , which are comparable to the reported values ( $2.5 \times 10^{-3}$  and  $-2.3 \times 10^{-3}$  for **Au<sub>13</sub>-R/S**, respectively).<sup>14</sup> Note that the different  $|g_{\text{PL}}|$  values between **IrAu<sub>12</sub>-R/S** are due to the limited sensitivity of the CPL measurement setup. The similarity of the  $|g_{\text{PL}}|$  values between **IrAu<sub>12</sub>-R/S** and **Au<sub>13</sub>-R/S** is probably associated with the similar structures in the photoexcited state responsible for PL. The  $|g_{\text{PL}}|$  values of **IrAu<sub>12</sub>-R/S** and **Au<sub>13</sub>-R/S** increased to  $\sim 4 \times 10^{-3}$  and  $\sim (4-5) \times 10^{-3}$ , respectively, upon lowering

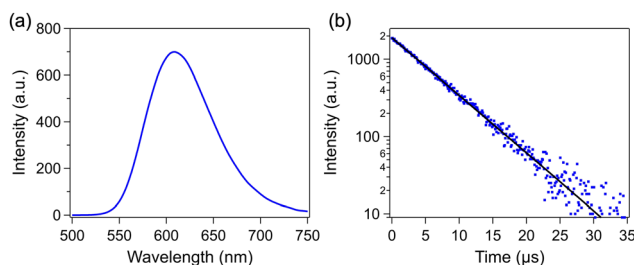
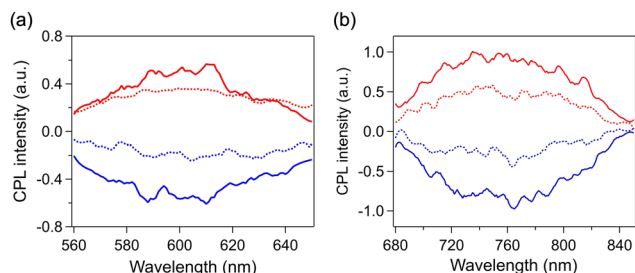


Fig. 5 (a) PL spectrum of **IrAu<sub>12</sub>-S** in MeTHF recorded at the excitation wavelength of 400 nm. (b) Time-resolved PL decay of **IrAu<sub>12</sub>-S** probed at 400 nm in MeTHF. The black line represents the fitting result.





**Fig. 6** CPL spectra of (a)  $\text{IrAu}_{12}\text{-R}$  (red) and  $\text{IrAu}_{12}\text{-S}$  (blue) in MeTHF and (b)  $\text{Au}_{13}\text{-R}$  (red) and  $\text{Au}_{13}\text{-S}$  (blue) in a MeOH–EtOH mixture (1:1 v/v) recorded at the excitation wavelength of 375 nm. Solid and dotted lines denote the spectra recorded at 200 and 300 K, respectively.

the temperature to 200 K (Fig. 6 and Table 1). The  $|g_{\text{PL}}|$  values of  $\text{IrAu}_{12}\text{-R/S}$  were of the same order ( $\sim 10^{-3}$ ) as those reported for other superatoms, whereas the  $\Phi_{\text{PL}}$  values of  $\text{IrAu}_{12}\text{-R/S}$  were much higher than those of other chiral superatoms in either the solid or self-assembled state.<sup>11,15,19,21</sup> Therefore,  $\text{IrAu}_{12}\text{-R/S}$  are superior in terms of the CPL brightness ( $B_{\text{CPL}}$ ) defined using eqn (1).<sup>25</sup> The  $B_{\text{CPL}}$  value of  $\text{IrAu}_{12}\text{-S}$  was  $26 \text{ M}^{-1} \text{ cm}^{-1}$  ( $\lambda = 418 \text{ nm}$ ) at 300 K. This value is approximately five times higher than that of  $\text{Au}_{13}\text{-S}$  ( $B_{\text{CPL}} = 5.3 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $\lambda = 495 \text{ nm}$ ) at 300 K, indicating that doping with Ir brightened the CPL, mainly by increasing the molar absorption coefficient at 495 nm and the HL gap of  $\text{Au}_{13}\text{-R/S}$ .

## Conclusions

We successfully synthesized the enantiomeric pair of  $\text{Ir@Au}_{12}$  superatoms protected by DIPAMP chiral diphosphine ligands and studied the single-atom doping effect on the chiroptical properties of the  $\text{Au@Au}_{12}$  superatoms. The icosahedral  $\text{Ir@Au}_{12}$  superatom was distorted more than the corresponding  $\text{Au@Au}_{12}$ , resulting in larger  $|g_{\text{abs}}|$  values for the former. Doping with the Ir atom expanded the HOMO–LUMO gap of the  $\text{Au}_{13}$  superatom, leading to the marked increase in  $\Phi_{\text{PL}}$  from 15% to  $\sim 70\%$ . By contrast, the  $|g_{\text{PL}}|$  values of the  $\text{IrAu}_{12}$  and  $\text{Au}_{13}$  superatoms were comparable. As a whole, the CPL brightness of the  $\text{Au}_{13}$  superatom was enhanced by nearly five times upon introducing Ir at the center. This work provides a new strategy to enhance the CPL brightness of Au superatoms *via* the doping-mediated control of geometric and electronic structures.

## Author contributions

Haru Hirai: data curation, investigation, writing – original draft. Takuya Nakashima: formal analysis, investigation. Shin-jiro Takano: conceptualization, investigation. Yukatsu Shichibu: data curation, methodology. Katsuaki Konishi: data curation, methodology. Tsuyoshi Kawai: resource. Tatsuya Tsukuda: funding acquisition, project administration, supervision, writing – review and editing. Each author contributed substantially to the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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## Notes and references

- S. Knoppe and T. Bürgi, *Acc. Chem. Res.*, 2014, **47**, 1318–1326.
- Y. Li, T. Higaki, X. Du and R. Jin, *Adv. Mater.*, 2020, **32**, 1905488.
- Y. Zhu, J. Guo, X. Qiu, S. Zhao and Z. Tang, *Acc. Mater. Res.*, 2021, **2**, 21–35.
- Y. Shichibu and K. Konishi, *ChemNanoMat*, 2022, **8**, e202200194.
- T. G. Schaaff, G. Knight, M. N. Shafiqullin, R. F. Borkman and R. L. Whetten, *J. Phys. Chem. B*, 1998, **102**, 10643–10646.
- S. Si, C. Gautier, J. Boudon, R. Taras, S. Gladiali and T. Bürgi, *J. Phys. Chem. C*, 2009, **113**, 12966–12969.
- S. Knoppe, A. C. Dharmaratne, E. Schreiner, A. Dass and T. Bürgi, *J. Am. Chem. Soc.*, 2010, **132**, 16783–16789.
- K. R. Krishnadas, L. Sementa, M. Medves, A. Fortunelli, M. Stener, A. Fürstenberg, G. Longhi and T. Bürgi, *ACS Nano*, 2020, **14**, 9687–9700.
- T. Nakashima, R. Tanibe, H. Yoshida, M. Ehara, M. Kuzuhara and T. Kawai, *Angew. Chem., Int. Ed.*, 2022, **61**, e202208273.
- S. Takano and T. Tsukuda, *J. Phys. Chem. Lett.*, 2016, **7**, 4509–4513.
- L. Shi, L. Zhu, J. Guo, L. Zhang, Y. Shi, Y. Zhang, K. Hou, Y. Zheng, Y. Zhu, J. Lv, S. Liu and Z. Tang, *Angew. Chem., Int. Ed.*, 2017, **56**, 15397–15401.
- J.-Q. Wang, Z.-J. Guan, W.-D. Liu, Y. Yang and Q.-M. Wang, *J. Am. Chem. Soc.*, 2019, **141**, 2384–2390.
- Y. Yang, Q. Zhang, Z.-J. Guan, Z.-A. Nan, J.-Q. Wang, T. Jia and W.-W. Zhan, *Inorg. Chem.*, 2019, **58**, 3670–3675.
- Y. Shichibu, Y. Ogawa, M. Sugiuchi and K. Konishi, *Nano-scale Adv.*, 2021, **3**, 1005–1011.
- M.-M. Zhang, X.-Y. Dong, Z.-Y. Wang, X.-M. Luo, J.-H. Huang, S.-Q. Zang and T. C. W. Mak, *J. Am. Chem. Soc.*, 2021, **143**, 6048–6053.
- R. W. Y. Man, H. Yi, S. Malola, S. Takano, T. Tsukuda, H. Häkkinen, M. Nambo and C. M. Crudden, *J. Am. Chem. Soc.*, 2022, **144**, 2056–2061.
- I. Dolamic, S. Knoppe, A. Dass and T. Bürgi, *Nat. Commun.*, 2012, **3**, 798.
- H. Yoshida, M. Ehara, U. D. Priyakumar, T. Kawai and T. Nakashima, *Chem. Sci.*, 2020, **11**, 2394–2400.
- S. Chen, W. Du, C. Qin, D. Liu, L. Tang, Y. Liu, S. Wang and M. Zhu, *Angew. Chem., Int. Ed.*, 2020, **59**, 7542–7547.
- H. Yi, K. M. Osten, T. I. Levchenko, A. J. Veinot, Y. Aramaki, T. Ooi, M. Nambo and C. M. Crudden, *Chem. Sci.*, 2021, **12**, 10436–10440.



- 21 X. Q. Liang, Y. Z. Li, Z. Wang, S. S. Zhang, Y. C. Liu, Z. Z. Cao, L. Feng, Z. Y. Gao, Q. W. Xue, C. H. Tung and D. Sun, *Nat. Commun.*, 2021, **12**, 4966.
- 22 S. Knoppe, O. A. Wong, S. Malola, H. Häkkinen, T. Bürgi, T. Verbiest and C. J. Ackerson, *J. Am. Chem. Soc.*, 2014, **136**, 4129–4132.
- 23 H. Yao and M. Iwatsu, *Langmuir*, 2016, **32**, 3284–3293.
- 24 J. Yan, H. Su, H. Yang, C. Hu, S. Malola, S. Lin, B. K. Teo, H. Häkkinen and N. Zheng, *J. Am. Chem. Soc.*, 2016, **138**, 12751–12754.
- 25 L. Arrico, L. di Bari and F. Zinna, *Chem. – Eur. J.*, 2021, **27**, 2920–2934.
- 26 H. Hirai, S. Takano, T. Nakashima, T. Iwasa, T. Taketsugu and T. Tsukuda, *Angew. Chem., Int. Ed.*, 2022, **61**, e202207290.
- 27 N. Shinjo, S. Takano and T. Tsukuda, *Bull. Korean Chem. Soc.*, 2021, **42**, 1265–1268.
- 28 Y. Shichibu and K. Konishi, *Small*, 2010, **6**, 1216–1220.
- 29 H. Hirai, S. Takano, T. Nakamura and T. Tsukuda, *Inorg. Chem.*, 2020, **59**, 17889–17895.
- 30 H. Tsumatori, T. Nakashima and T. Kawai, *Org. Lett.*, 2010, **12**, 2362–2365.
- 31 Z.-H. Gao, J. Dong, Q.-F. Zhang and L.-S. Wang, *Nanoscale Adv.*, 2020, **2**, 4902–4907.
- 32 S. S. Batsanov, *Inorg. Mater.*, 2001, **37**, 871–885.
- 33 M. S. Devadas, S. Bairu, H. Qian, E. Sinn, R. Jin and G. Ramakrishna, *J. Phys. Chem. Lett.*, 2011, **2**, 2752–2758.
- 34 H. C. Weissker, H. B. Escobar, V. D. Thanthirige, K. Kwak, D. Lee, G. Ramakrishna, R. L. Whetten and X. López-Lozano, *Nat. Commun.*, 2014, **5**, 3785.
- 35 Y. Negishi, T. Nakazaki, S. Malola, S. Takano, Y. Niihori, W. Kurashige, S. Yamazoe, T. Tsukuda and H. Häkkinen, *J. Am. Chem. Soc.*, 2015, **137**, 1206–1212.
- 36 K. Kwak, V. D. Thanthirige, K. Pyo, D. Lee and G. Ramakrishna, *J. Phys. Chem. Lett.*, 2017, **8**, 4898–4905.

