



## Circular dichroism enhancement by the coordination of different metal ions with a pair of chiral tripodal ligands



Hai-Ping Wang<sup>a</sup>, Shao-Yun Yin<sup>a</sup>, Mei Pan<sup>a,b,\*</sup>, Kai Wu<sup>a</sup>, Ling Chen<sup>a</sup>, Yi-Xuan Zhu<sup>a</sup>, Ya-Jun Hou<sup>a</sup>

<sup>a</sup> MOE Laboratory of Bioinorganic and Synthetic Chemistry, State Key Laboratory of Optoelectronic Materials and Technologies, Lehn Institute of Functional Materials, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China

<sup>b</sup> State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China

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### ABSTRACT

The coordination of metal ions with a pair of chiral tripodal ligands (*R* or *S*)-2-(2-((bis(pyridin-2-ylmethyl)amino)methyl)phenoxy)-*N*-(1-phenylethyl)acetamide (*R*- or *S*-**L**) results in the circular dichroism (CD) enhancement distinctly, giving fingerprint information among different metals. Specifically, the CD signals show more obvious magnification upon coordination with Ln<sup>3+</sup> compared with Zn<sup>2+</sup> and other metals. Structural analyses show that in Eu-complex (**1**), the Eu<sup>3+</sup> metal center is surrounded in a 10-coordinating geometry and the ligand takes fan-like configuration, while in Zn-complex (**2**), Zn<sup>2+</sup> is surrounded in a 7-coordinating geometry and the ligand takes pincer-like configuration. These differences in the coordination structure as well as intramolecular packing effects are responsible for the variation in CD signal responses of different metal-coordinated systems.

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Circular dichroism (CD) spectroscopy is a widely used technique to detect and determine the optical signal and absolute configuration of a chiral substrate [1]. Because CD spectroscopy uses a circularly polarized light source, enantiomers with absorptions in the UV–vis or even near infrared region can be differentiated clearly and this allows for a non-destructive and rapid analysis. Among which, the detection of CD signals in coordination system containing both metal ions and organic ligands is of particular interest [2–5]. There are mainly two different mechanisms about the origin of CD signals in these metal–organic systems: a) exciton-coupled circular dichroism (ECCD) induced by the coupling of the excited states of at least two proximal and asymmetrically oriented  $\pi$ – $\pi^*$  chromophores, which can either come from the intrinsic chiral ligands or the chiral arrangement of the chromophores in a metal–organic complex with achiral ligands; and b) relational transition based on  $d$ – $d$  or  $f$ – $f$  electronic transitions in the metal centers, but this kind of CD signals is usually weak compared with the first kind ones [6–8]. In applicable view, when the metal ions are coordinated with chromophoric organic ligands, the CD signals can be induced or amplified by combinations of intense chromophoric ligands with suitable metal centers. Since the metal complexes have versatile coordination characteristics, there are many possibilities for their application in recognition and sensing of chiral substrates [9].

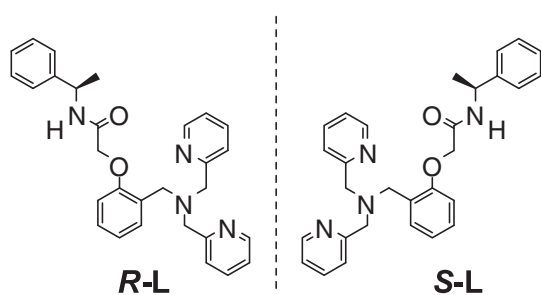
Herein, we report the CD enhancement induced by the coordination of different metal ions with a pair of chiral tripodal ligands *R*- and *S*-**L**

(Scheme 1). Some “fingerprint” information can be detected in the CD responses by the addition of different types of metal ions into the ligand. CD signals with the largest magnification were observed in Ln<sup>3+</sup> coordinated system, almost double of Zn<sup>2+</sup> or other transition metal and alkaline-earth metal (M<sup>2+</sup>) coordinated systems. Solid/solution structural study of Eu<sup>3+</sup> and Zn<sup>2+</sup> complexes clearly shows that the metal-induced magnification of the ligand CD signals is related to the coordination configuration and crystal packing of the metal complexes.

The chiral tripodal ligands (*R* or *S*)-2-(2-((bis(pyridin-2-ylmethyl)amino)methyl)phenoxy)-*N*-(1-phenylethyl)acetamide (*R*- or *S*-**L**), as shown in Scheme 1, contain four  $\pi$  conjugate rings, of which three surround the apical N, and one lies on the end of the substituted chiral side chain. DFT calculation shows that the optimized structure of the ligand (Fig. S1) has a fan-like configuration. The four  $\pi$  rings are arranged as far apart in the space, without obvious intramolecular  $\pi$ – $\pi$  interactions among each other. As shown in Fig. 1a, the CD spectra of *R*-**L** and *S*-**L** clearly show the contour of a pair of optical enantiomers. Among which, the *R*-**L** presents a negative peak at about 225 nm and a positive one at about 210 nm. It is well-known that a pair of first negative and second positive Cotton effect CD signals from longer to shorter wavelength usually indicates a clockwise screw sense. This is in accordance with the *R*-configuration of the ligand, and vice versa for the *S*-**L**. Compared with the UV absorption spectra (Fig. 1b), the CD signal observed for the *R*- and *S*-ligands from 200 to 235 nm should correspond to absorptions enveloped in the broad band with the peak maximum cutting by the instrument limit. However, the absorption peak centered at 265 nm shows no corresponding CD signal for both *R*- and *S*-ligands.

\* Corresponding author at: School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China.

E-mail address: [panm@mail.sysu.edu.cn](mailto:panm@mail.sysu.edu.cn) (M. Pan).



Scheme 1. Molecular structure of the ligands.

The single-crystal structures of  $[R\text{-L}\cdot\text{Eu}(\text{NO}_3)_3]$  (**1**) and  $[R\text{-L}\cdot\text{Zn}(\text{NO}_3)_2]\cdot\text{NO}_3$  (**2**) are shown in Fig. 2 and detailed crystallographic data are provided in Tables S1 and S2. From Fig. 2, we can see that in complex **1**,  $\text{Eu}^{3+}$  is surrounded in a 10-coordinating environment. One apical N, two pyridine N, one amide O, and six nitrate O atoms participate in coordination with  $\text{Eu}^{3+}$  center. The two pyridine and one benzene rings linked by the apical N take a fan-like configuration. One pyridine ring bends downward to form C-H $\cdots$  $\pi$  interaction with the benzene ring on the side chain ( $d = 3.671 \text{ \AA}$ ). In complex **2**,  $\text{Zn}^{2+}$  is surrounded in a 7-coordinating atmosphere. One apical N, two pyridine N, one amide O, one ether O, and two nitrate O atoms participate in coordination with  $\text{Zn}^{2+}$  center. The two pyridine and one benzene rings around the apical N are compressed in complex

**2** to form a pincer-like configuration. With such configuration, one pyridine ring forms offset face-to-face  $\pi$ - $\pi$  interaction ( $d = 3.513 \text{ \AA}$ ) with the benzene ring near the apical N (not the one on the side chain as in **1**). Based on the above structural analysis, we can deduce that upon coordination with metals, the robustness of chromophoric groups around the chiral  $\text{C}^*$  centers in the ligand is strengthened due to structural rigidity. And furthermore, intramolecular  $\pi$ - $\pi$  interactions are formed in the coordination systems to enhance the conjugation among the multi-chromophoric groups inside the ligand. These structural informations could be reflected in the CD signals of the ligand upon metal coordination. Moreover, since different coordination motifs are formed in complexes **1** and **2**, the CD signal responses in  $\text{Eu}^{3+}$  and  $\text{Zn}^{2+}$ -coordinated systems will be different, as will be discussed below.

Fig. 1 also shows the spectral changes of the CD signals induced by  $\text{Ln}^{3+}$  ( $\text{Ln} = \text{Eu}, \text{Tb}$ ) and  $\text{Zn}^{2+}$  ions upon coordination with the ligand. Firstly, a magnified, wide and one-directional peak at  $\lambda_{\text{max}} = 217 \text{ nm}$  was observed for the  $\text{Ln}^{3+}$ - or  $\text{Zn}^{2+}$ -coordinated systems, instead of the pair of opposite signals at about 225 and 210 nm of the pure ligand mentioned above. For comparison, this CD signal was magnified more dramatically in  $\text{Ln}^{3+}$ -coordinated system than  $\text{Zn}^{2+}$ -system (18.7 against 8.26 mdeg). Secondly, another CD signal was observed for the metal-coordinated system at longer wavelength centered around 265 nm, which was basically silent in the spectra of the pure ligand. It is noticeable that although the CD signal in the shorter wavelength shows more than double magnitude in the  $\text{Ln}^{3+}$ -system against  $\text{Zn}^{2+}$ -system, their magnitude in this longer wavelength region was almost the same. This implies that the coordination of the ligand with metal

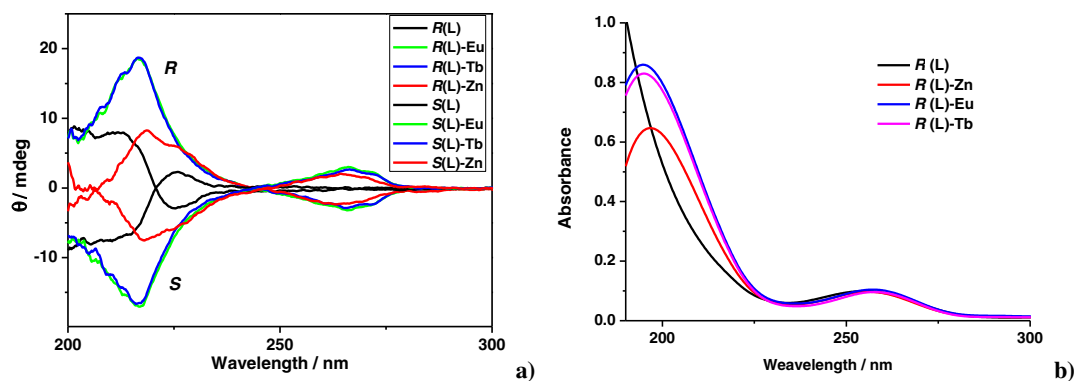


Fig. 1. CD spectra (a) and UV absorption spectra (b) of the pure ligand and its  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Zn}^{2+}$  complexes ( $1 \times 10^{-5} \text{ mol/L}$ ,  $\text{CH}_3\text{CN}$ ).

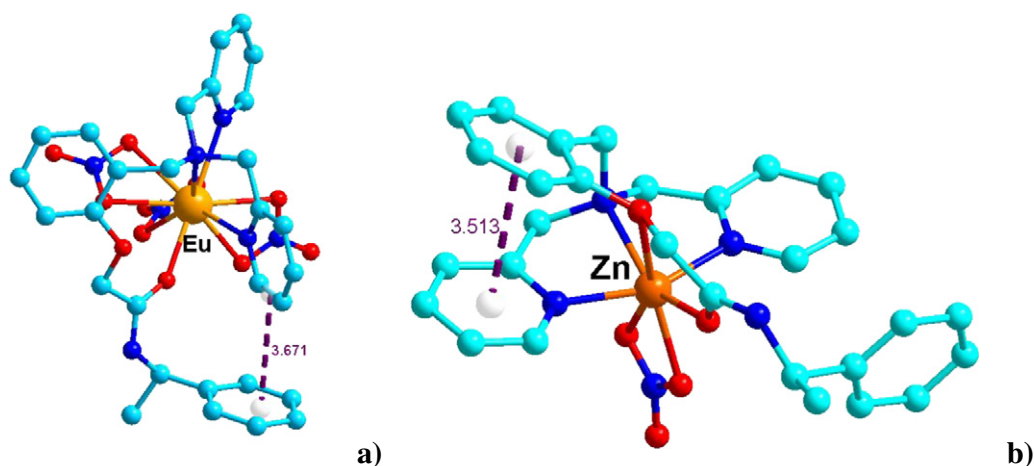


Fig. 2. Crystal structures of the complexes **1-Eu** (a) and **2-Zn** (b).

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