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Sign control of circularly polarized luminescence of chiral Schiff-base Zn(II) complexes through coordination geometry changes

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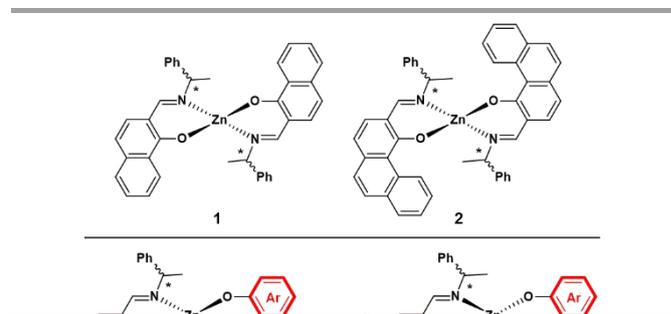
The handedness of circularly polarized luminescence (CPL) of Zn(II) complexes with chiral Schiff-base ligand can be controlled by coordination geometry changes in solution and in the solid state. The relationships between molecular structure and chiroptical properties were discussed with the results of X-ray diffraction analysis and DFT calculations.

Controlling circularly polarized luminescence (CPL)¹ which is the differential emission of right- and left-circularly polarized light, has been attracting particular interest for the purpose of creating novel functional luminescent materials due to their wide potential applications for next-generation optical devices.² Recently, research on small organic and organometallic molecules with CPL activity has attracted much attention because they can be easily derivatized to provide wavelength tunability and external stimuli responsiveness.³ The intensity and the handedness of CPL of small molecules are sensitive to the environment of the luminophore, and much efforts have been devoted to control their CPL properties by inducing conformational changes in both the ground and excited states, either by changing the solvent⁴ or by altering the molecular structure and arrangement in the aggregate state.⁵

Among various luminescent materials, zinc(II) complexes have been known to exhibit efficient photoluminescence properties and they are expected to be applied to fluorescent probes,⁶ organic light emitting diodes (OLEDs)⁷ as well as CPL materials.⁸ Schiff-base zinc(II) complexes are one of the important families of emissive zinc(II) complexes because of their luminescence tunability and easy molecular modification.^{8g,9} Recently, Cheng, Tang and co-workers reported Schiff-base zinc(II) complexes exhibiting strong circularly polarized electroluminescence and applied them as an emissive layer in CP-OLEDs.¹⁰

Our research group has been interested in the stereochemistry of Schiff-base transition metal complexes¹¹ and recently reported that Schiff-base platinum(II) complexes having chiral distorted square planar coordination geometry with Δ or Λ absolute configuration exhibit tunable CPL properties in the poly(methyl methacrylate) (PMMA) film-dispersed state.^{11d} Motivated by the discovery of CPL control of such transition metal complexes associated with coordination geometry changes, we focused on chiral $N^{\wedge}O$ -chelate tetrahedral Schiff-base zinc(II) complexes as CPL emitter. These types of complexes exhibit diastereomeric equilibria based on Δ or Λ chirality around metal center in solution¹² and Janiak's research group has reported that each diastereomers exhibit opposite handedness of the circular dichroism (CD) signal.^{12e,f} In the present study, we designed novel chiral $N^{\wedge}O$ -chelate Schiff-base zinc(II) complexes **1** and **2** and found that complex **1** exhibits sign-controllable CPL which depends on the external environment (Scheme 1). Theoretical studies using density functional theory (DFT) and time dependent (TD)-DFT calculations revealed the relationship between molecular structure and their chiroptical properties.

Chiral zinc(II) complexes **1** and **2** were prepared by the reaction of $ZnCl_2$ with the corresponding optically pure Schiff-



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Scheme. 1 Molecular structure and diastereomeric equilibrium of chiral Schiff-base Zn(II) complexes studied in this work.

base ligands in the presence of t BuOK in MeOH (Scheme S1, ESI †). The complexes were successfully characterized by ^1H and ^{13}C NMR (Fig. S1–6, ESI †), nuclear gradient correlation spectroscopy (gCOSY) and Overhauser effect spectroscopy (NOESY). Crystals of (*S,S*)-**1** and (*S,S*)-**2** employed for X-ray diffraction (XRD) studies were obtained by recrystallization from toluene/MeOH for (*S,S*)-**1** and $\text{CH}_2\text{Cl}_2/\text{EtOH}$ for (*S,S*)-**2**, respectively. ORTEP drawings of complexes (*S,S*)-**1** and (*S,S*)-**2** are shown in Fig. 1, where the chirality angles of O(1)–N(1)–O(2)–N(2) (φ) are provided to express the degree of distortion of the tetrahedral coordination geometries.¹³ The chirality angle φ of (*S,S*)-**1** has the negative value -67.48° . Hence, (*S,S*)-**1** has Δ configuration in the crystal. On the other hand, (*S,S*)-**2** has opposite Λ absolute configuration with a positive φ value of 64.82° , although the complex has the same chirality as (*S,S*)-**1** in the ligand.

^1H NMR spectra (500 MHz, CDCl_3) of (*S,S*)-**1** and (*S,S*)-**2** at 298 K show Δ/Λ equilibrium based on different signals associated with the Δ - or Λ -diastereomers (Fig. S1 and S4, ESI †). The proton signal of the Δ -form was successfully assigned by NOESY spectrum with strong correlations between the aromatic proton (H^4 for (*S,S*)-**1** and H^5 for (*S,S*)-**2**) and the methyl proton of the phenylethyl moiety (Fig. 2 and S7, ESI †). The diastereomeric ratio of each isomer was estimated to be Λ :

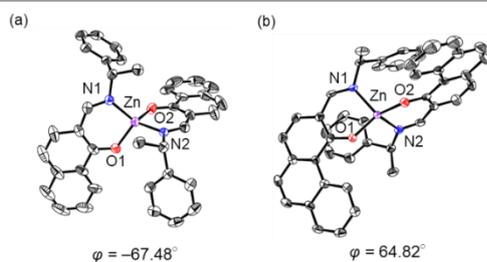
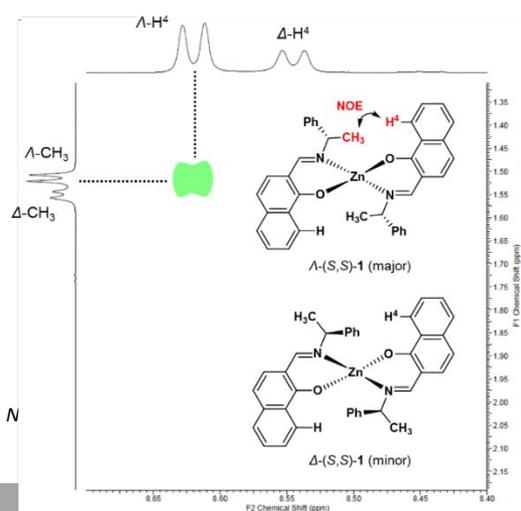


Fig. 1 ORTEP drawings of (a) Δ -(*S,S*)-**1** and (b) Λ -(*S,S*)-**2**. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. The dihedral angles of tetrahedral geometry O(1)–N(1)–O(2)–N(2) (φ) are given under each structure.



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Fig. 2 NOESY spectrum of (*S,S*)-**1** in CDCl_3 (500 MHz, 298 K).

$\Lambda = 2 : 1$ (diastereomeric excess is 33%*de*) for both complexes from integration values of ^1H NMR spectra. ^1H NMR spectra of (*S,S*)-**1** and (*S,S*)-**2** also measured in CD_2Cl_2 and the results are almost identical with in CDCl_3 (Fig. S3 and S6, ESI †). The diastereomeric excess in CD_2Cl_2 were estimated to be 21%*de* for (*S,S*)-**1** and 33%*de* for (*S,S*)-**2**, respectively. These results indicate that the Λ -(*S,S*)-form is more stable in CDCl_3 and CD_2Cl_2 than the Δ -(*S,S*)-form, whereas (*S,S*)-**1** has Δ configuration in the crystalline state. Variable temperature (VT) NMR were measured in CD_2Cl_2 for further understanding of diastereomeric equilibrium (Fig. S11–14, ESI †). The equilibrium shifted to the minor diastereomeric isomer, Λ -(*S,S*)-form, at low temperatures, and the diastereomeric excess were reached to 8%*de* for (*S,S*)-**1** and 25%*de* for (*S,S*)-**2** at -60°C .

The UV–vis absorption spectra of complexes **1** and **2** measured in CH_2Cl_2 have a broad absorption band around 350–450 nm that is mainly attributable to the intra-ligand π – π^* transitions (Fig. 3a). The CD spectra of complexes **1** and **2** were recorded under the same conditions as the UV–vis absorption spectra (Fig. 3b). Both complexes, (*R,R*)-form and (*S,S*)-form, show exactly mirrored CD spectra indicating the existence of equimolar amounts of diastereomeric excess mixture for each enantiomer in solution. Complexes (*S,S*)-**1** and (*S,S*)-**2** exhibited positive Cotton effects in the range of 380–450 nm, which can be assigned to the intra-ligand π – π^* transitions from UV–vis spectra in the same region. Solid state CD spectra were also recorded in the KBr-dispersed pellet state obtained by grinding of single crystals with solid KBr (Fig. 4). Although complex (*S,S*)-**2** exhibited positive Cotton effect in the low energy region as same in solution (Fig. 4b), complex (*S,S*)-**1** showed an opposite negative Cotton effect in the visible region (Fig. 4a). This difference probably due to the fact that complexes (*S,S*)-**1** and (*S,S*)-**2** have opposite chirality of Δ and Λ in the crystal.

Complexes **1** and **2** exhibited blue to yellowish green photoluminescence under UV excitation at room temperature in solution and the solid state (Fig. S18, ESI †). Photophysical data

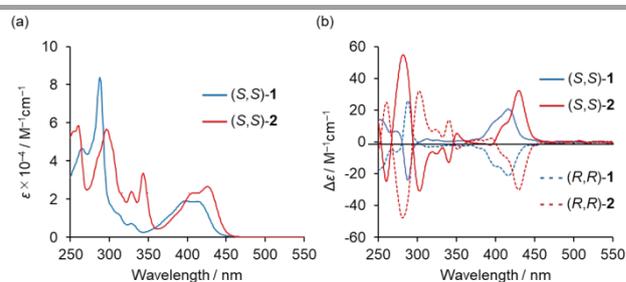


Fig. 3 (a) UV–vis and (b) CD spectra of 2.0×10^{-4} M solutions of **1** and **2** in CH_2Cl_2 at 298 K.

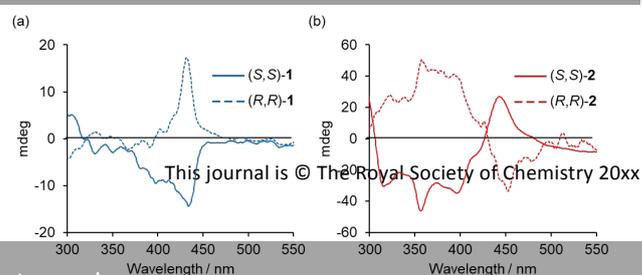


Fig. 4 CD spectra of **1** and **2** in the KBr-dispersed pellet state. are summarized in Table S2. The CPL and total luminescence spectra measured for complexes **1** and **2** in CH₂Cl₂ solution and in the KBr-dispersed pellet state at 298 K are shown in Fig. 5 and 6. The CPL spectra of **1** and **2** having opposite (*R,R*)- and (*S,S*)-configurations exhibit mirror-image signals around 480 nm in CH₂Cl₂ solution (Fig. 5 upper figures), which are corresponding to the emission peak maxima (λ_{max}) observed in their total emission spectra measured under the same conditions (Fig. 5 lower figures). The CPL sign was consistent between the two complexes, which was positive in the (*S,S*)-form and negative in the (*R,R*)-form. The luminescence dissymmetry factors $g_{\text{lum}} (= 2\Delta I/I = 2(I_L - I_R)/(I_L + I_R)$, in which I_L and I_R are the intensity of left- and right-circularly polarized luminescence) around the λ_{max} are 9.1×10^{-4} (485 nm) for (*S,S*)-**1** and 9.6×10^{-4} (490 nm) for (*S,S*)-**2**, respectively, which are a typical value for small organic and organometallic molecules.¹⁴ CPL spectra were also recorded in the KBr-dispersed pellet state. The sign of CPL of complex **1** was inverted compared with that measured in solution, whereas complex **2** exhibited identical CPL signs in both states. These results were consistent with the results of CD spectra and suggest that the

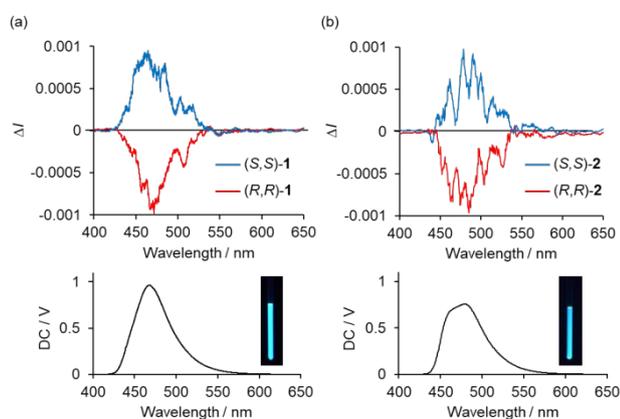
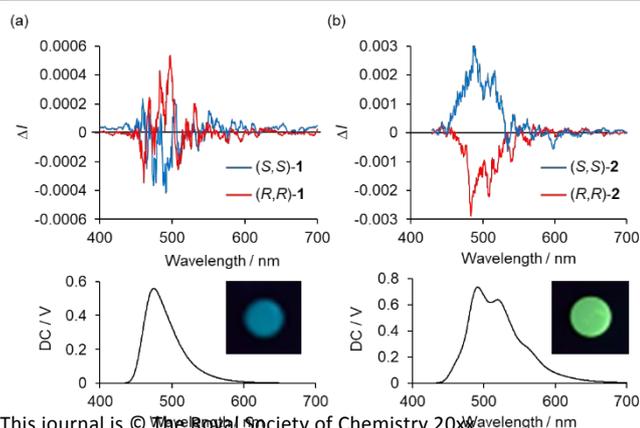


Fig. 5 CPL (upper plot) and emission (lower plot) spectra of 2.0×10^{-4} M solutions of (*R,R*)- and (*S,S*)- (a) **1** and (b) **2** in CH₂Cl₂ at 298 K ($\lambda_{\text{ex}} = 350$ nm). The insets in the lower figure show the photographs under UV irradiation (365 nm).



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Fig. 6 CPL (upper plot) and emission (lower plot) spectra of (*R,R*)- and (*S,S*)- (a) **1** and (b) **2** in the KBr-dispersed pellet state at 298 K ($\lambda_{\text{ex}} = 350$ nm (**1**), 400 nm (**2**)). The insets in the lower figure show the photographs under UV irradiation (365 nm). configurations of these complexes are maintained even in the excited state in the KBr-dispersed pellet state. The g_{lum} values around λ_{max} are 7.7×10^{-4} (483 nm) for (*S,S*)-**1** and 3.2×10^{-3} (487 nm) for (*S,S*)-**2**, respectively.

To get further insight into the photophysical properties of present zinc(II) complexes, we performed density functional theory (DFT) calculations on the CAM-B3LYP/6-31+G(d,p) level, using the Gaussian 16 program. The optimized structures and molecular orbitals of Δ -(*S,S*)-**1** and Λ -(*S,S*)-**2** in the S_0 (ground state) and S_1 (excited state) states are shown in Fig. S22 and S23. The HOMOs consist of π -orbitals of the ligand, whereas the LUMOs are in the ligand (π^*). The major electronic configurations of the S_1 states were HOMO-to-LUMO transitions, which implies that the present emission is principally attributable to π - π^* transition (Tables S3 and S4).

In order to consider the sign inversion of CD and CPL spectra of (*S,S*)-**1** observed in solution and in the KBr-dispersed pellet state, theoretical simulations of these spectra were performed using TD-DFT (CAM-B3LYP/6-31+G(d,p)) calculations on the basis of the optimized structures. To obtain optimized structures of Λ -(*S,S*)-**1** which have opposite Δ configuration observed in X-ray diffraction analysis, we inverted the configuration of Δ -(*S,S*)-**1** at the metal centre and repeated the optimization procedure (Fig S24 and S25). The results of simulated CD and CPL spectra are shown in Fig. 7, where the opposite handedness signal was observed in each diastereomer which might be caused by exciton coupling between the chromophores.^{12e,15} Since the two isomers are in equilibrium in solution, the simulation of CD spectrum of (*S,S*)-**1** with the diastereomeric ratio $\Delta : \Lambda = 2 : 1$ reproduced well experimental result (Fig. 3b and S27a). The CPL spectrum of (*S,S*)-**1** in solution is considered to be close to those of major isomer Λ -(*S,S*)-**1** which has positive CPL signal. In the KBr-dispersed pellet state, the configuration is maintained from the crystalline state, and the CPL spectrum of (*S,S*)-**1** is considered to be close to that of Δ -(*S,S*)-**1** which has a negative CPL signal. From these results, we conclude that the eventual reversal of the CD and CPL spectra observed in (*S,S*)-**1** is attributed to the geometry changes of Δ - or Λ -chirality around the metal centre.

In summary, we have developed novel CPL-active zinc(II) complexes with chiral Schiff base ligands. Complexes **1** and **2** exhibit intense CPL in solution and in the KBr-dispersed pellet state. Noteworthy, the sign of CD and CPL spectra of complex **1** was inverted in the KBr-dispersed pellet state compared to the solution state. Results of X-ray diffraction analysis and DFT

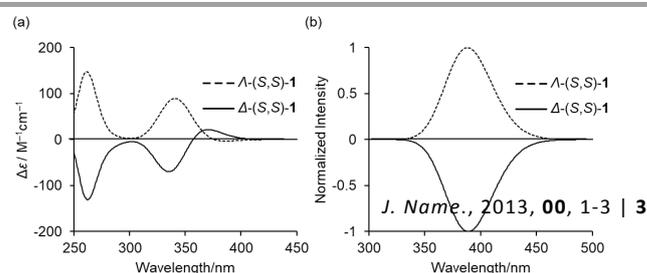


Fig. 7 Theoretical (a) CD and (b) CPL spectra of Δ - and Λ -(S,S)-1 estimated by TD-DFT calculation (CAM-B3LYP/6-31+G(d,p)).

calculations revealed that Δ and Λ chirality around the metal centre is the key to control the sign of CD and CPL. We believe that our results can contribute to the design for further sophisticated stimuli-responsive CPL materials through coordination geometry changes.

The project was conceived by M. I., who also directed all experiment work, theoretical calculation and wrote the manuscript. M. M. and T. I. performed experiment work except for CPL spectra. K. M. and M. K. measured CPL spectra. Y. I. and T. T. gave constructive guidance for this study. The manuscript has received the approval of all authors.

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Conflicts of interest

There are no conflicts to declare.

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