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Heteroleptic [Bis(oxazoline)](dipyrrinato)zinc(II) Complexes: Bright and Circularly Polarized Luminescence from an Originally Achiral Dipyrrinato Ligand

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Abstract: *Heteroleptic zinc(II) complexes synthesized using achiral dipyrrinato and chiral bis(oxazoline) ligands show bright fluorescence with quantum efficiencies of up to 0.70. The fluorescence originates from the $^1\pi$–π^* photoexcited state localized exclusively on the dipyrrinato ligand. Furthermore, the luminescence is circularly polarized despite the achirality of the dipyrrinato ligand. Single-crystal X-ray structure analysis discloses that the chiral bis(oxazoline) ligand undergoes intramolecular π–π stacking with the dipyrrinato ligand, inducing axial chirality in the dipyrrinato moiety.*

The 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene fluorophores (BODIPYs) are the best characterized dipyrrin complexes because of their photostability, intense light absorption, and high fluorescence quantum yields.[1] Although the light-emitting properties of BODIPYs are well known, it has long been believed that metal complexes of this ligand structure are non-emissive. Efforts over the last decade to develop fluorescent dipyrrin metal complexes (for example, Zn^{II},[2] In^{III},[3] Ga^{III},[3] Sn^{II},[4] Sn^{IV},[5] and Al^{III}[6] complexes) have met with limited success.[7] Thus, dipyrrin metal complexes have been regarded as useful components for self-assembled supramolecular and coordination polymer architectures[8] rather than luminophores. Although heteroleptic bis and tris(dipyrrinato)metal complexes were synthesized previously,[9] we have recently found that heteroleptic bis(dipyrrinato)zinc(II) complex **1** (Figure 1a) exhibits a high fluorescence quantum yield.[10] Note that heteroleptic-

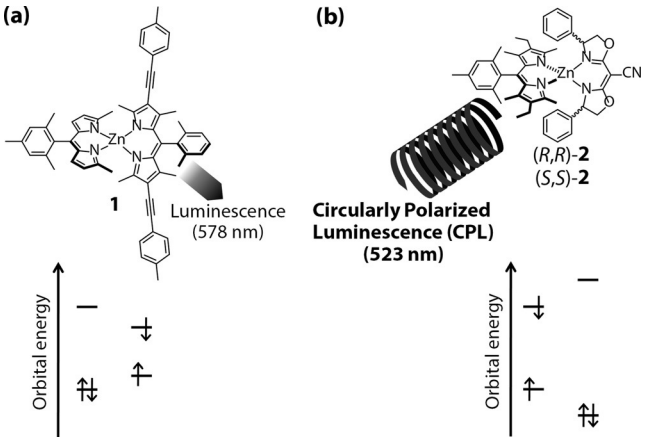

Figure 1. a) Luminescent heteroleptic bis(dipyrrinato)zinc(II) complex **1** and its frontier-orbital ordering.[10a] b) Heteroleptic complexes (*R*,*R*)-**2** and (*S*,*S*)-**2** and their frontier-orbital ordering. The short horizontal black lines denote the π and π^* orbitals of the ligand molecules, the arrows indicate electrons, and the electron configurations represent emissive photoexcited states.

ity has been reported to improve the optical properties of several metal complexes.[11] The bright luminescence of **1** arises from appropriate engineering of the frontier orbitals of the dipyrrinato ligands. The HOMO and LUMO of **1** are located exclusively on the right-hand dipyrrinato ligand (containing the arylacetylene functional groups) because of the narrowing of the HOMO–LUMO gap upon π expansion (Figure 1a). This electronic structure leads to the suppression of non-emissive symmetry-breaking charge separation.[10,12] The validity of our strategy has been further verified by heteroleptic tris(dipyrrinato)indium(III)[13a] and (azadipyrrinato)(dipyrrinato)zinc(II)[13b] complexes that also show brighter luminescence than the corresponding homoleptic complexes. The limitation of this strategy is clear when attempting to gain bright fluorescence from a simple, non-π-

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expanded dipyrrinato ligand (for example, the left-hand dipyrrinato ligand of **1** in Figure 1a). Therefore, another ancillary ligand suitable for non-π-expanded dipyrrinato ligands is needed.

Herein, a pair of enantiomers of bis(oxazoline) (abbreviated as box) has been chosen as ligands to complement a simple, non-π-expanded dipyrrinato ligand, resulting in the formation of heteroleptic complexes (*R*,*R*)-**2** and (*S*,*S*)-**2** (Figure 1b). Box is a mono-anionic ligand that chelates various metal ions with two nitrogen donor atoms.[14] The lesser degree of π-conjugation in the box ligand affords a wider HOMO–LUMO gap than the dipyrrinato ligand. This situation leads to the frontier-orbital ordering shown in Figure 1b, thereby realizing bright luminescence from the non-π-expanded dipyrrinato ligand. Another important feature of the box ligand is that it possesses chiral centers at the methine carbon atoms next to the nitrogen donor atoms. This feature is often useful in enantioselective catalysis.[14] However, here it is exploited to express circularly polarized luminescence (CPL) from the achiral dipyrrinato ligand.[15] CPL holds promise in applications such as enantioselective sensing,[16] CPL lasers,[17] and bioanalytical applications.[15c]

Complexes (*R*,*R*)-**2** and (*S*,*S*)-**2** were synthesized by mixing dipyrrin ligand **3**, the commercially available box ligand ((*R*,*R*)-**4** or (*S*,*S*)-**4**), and zinc(II) acetate in a mixture of methanol and chloroform at room temperature (Figure 2; see

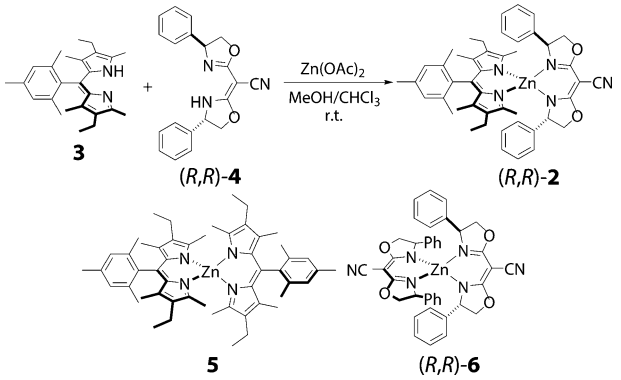

Figure 2. Synthesis of the heteroleptic complex (*R*,*R*)-**2** and structures of the reference homoleptic complexes **5** and (*R*,*R*)-**6**. (*S*,*S*)-**2** was synthesized employing the same method but employing (*S*,*S*)-**4** as the ligand.

the Supporting Information for details). The heteroleptic complexes were isolated and purified by silica gel column chromatography. The fact that the complex could be isolated and purified by column chromatography suggests that they have high stability; note that (dipyrrinato)zinc(II) complexes are sometimes unstable on silica gel. The NMR spectra of (*R*,*R*)-**2** and (*S*,*S*)-**2** appear identical, but are very different from those of corresponding homoleptic bis(dipyrrinato)zinc(II) complex **5** and bis[bis(oxazoline)]zinc(II) complexes (*R*,*R*)-**6** and (*S*,*S*)-**6** (Figure 2; Figures S1–S5 in the Supporting Information).

The formation of the heteroleptic complexes was further confirmed by single-crystal X-ray diffraction analysis (Figure 3a,b and Table S1).[18] The crystal structures of (*R*,*R*)-**2** and (*S*,*S*)-**2** reveal tetrahedral coordination spheres around the zinc center, with dihedral angles close to 90° (88.84° and 88.39°, respectively). In addition, the results verify the

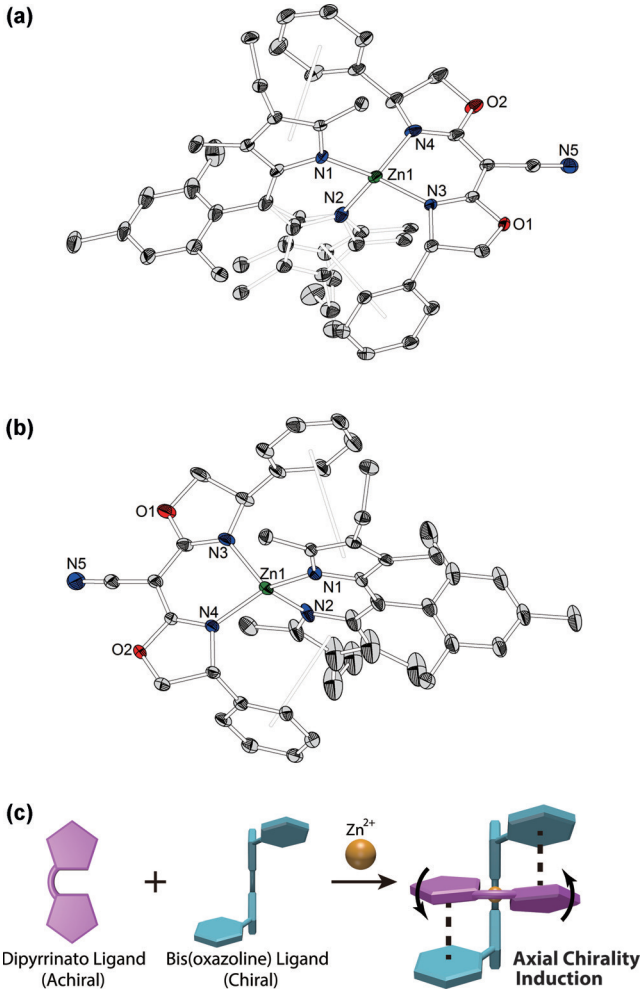

Figure 3. ORTEP drawings of a) (*R*,*R*)-**2** and b) (*S*,*S*)-**2** with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. One of the pyrrole rings in (*R*,*R*)-**2** is disordered. c) Schematic representation of the intramolecular interligand interaction in (*R*,*R*)-**2** that induces chirality in the achiral dipyrrinato ligand.

existence of the two enantiomers, with Flack parameters of −0.028(17) and 0.006(17). Of note is that the dipyrrinato ligand is distorted from planarity (Figure 3c; Figure S6). There are two sets of π–π interactions between the pyrrole ring of dipyrrinato ligand **3** and the phenyl ring of box ligand **4** (for example, distances between the ring centroids: 3.694(1) Å and 4.000(1) Å for (*R*,*R*)-**2**). As a result, dipyrrinato ligand **3** is bent in (*R*,*R*)-**2** and (*S*,*S*)-**2**, with each bent structure being the mirror image of the other (Figure S6). The structural characteristics of (*R*,*R*)-**2** and (*S*,*S*)-**2** indicate that axial chirality is induced in the originally achiral dipyrrinato ligand **3**.

Figure 4a (lower) shows the UV/Vis absorption spectra for (*R*,*R*)-**2**, **5**, and (*R*,*R*)-**6**, and circular dichroism (CD)

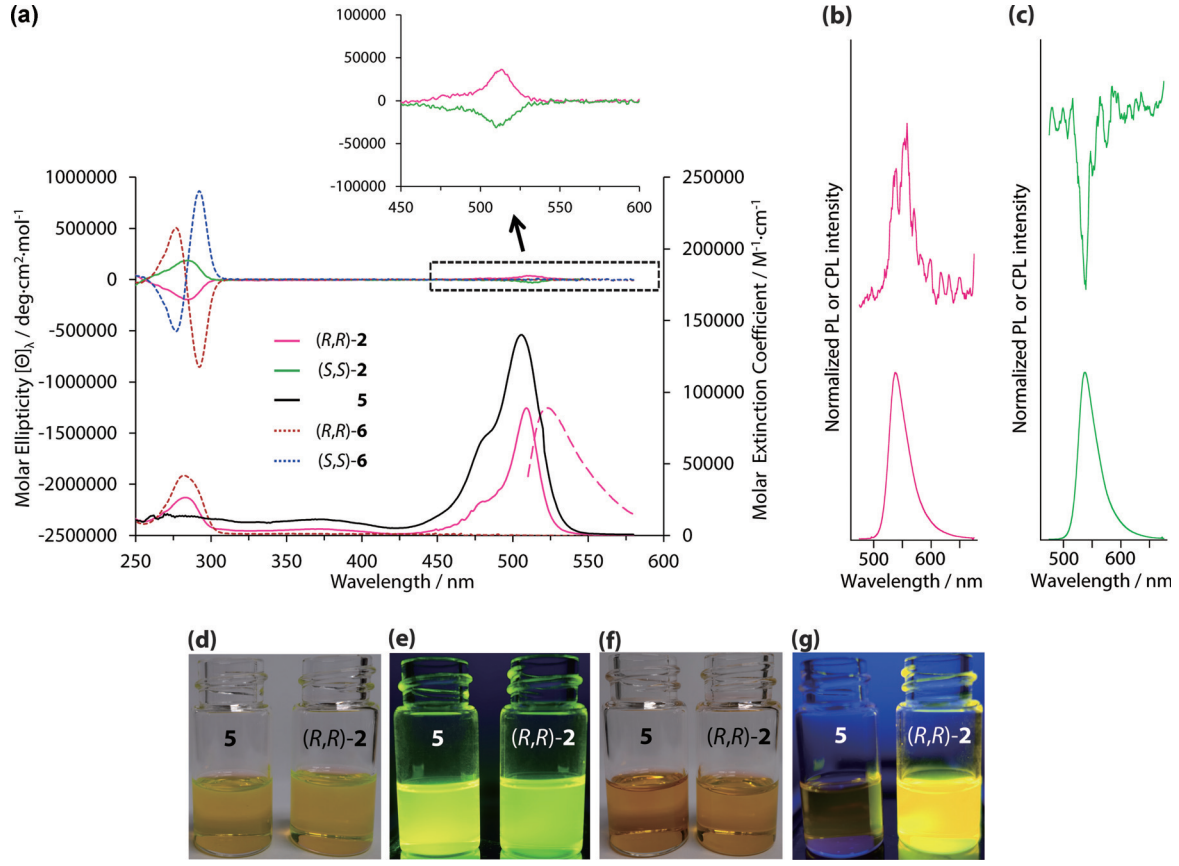

Figure 4. a) UV/Vis absorption spectra of (*R*,*R*)-**2**, **5**, and (*R*,*R*)-**6**, and CD spectra of (*R*,*R*)-**2**, (*S*,*S*)-**2**, (*R*,*R*)-**6**, and (*S*,*S*)-**6** in CH_2Cl_2. The PL spectrum of (*R*,*R*)-**2** is also shown (dashed magenta line). Inset: expanded portion of the CD spectra (spectra of (*R*,*R*)-**6** and (*S*,*S*)-**6** omitted as no signal found). b,c) Normalized PL (lower) and CPL (upper) spectra of (*R*,*R*)-**2** (b) and (*S*,*S*)-**2** (c) in CH_2Cl_2. d–g) Solutions of **5** and (*R*,*R*)-**2** d) in toluene under ambient lighting conditions, e) in toluene under UV irradiation ($\lambda = 365$ nm), f) in CH_2Cl_2 under ambient lighting conditions, and g) under UV irradiation ($\lambda = 365$ nm).

spectra for all of the chiral complexes in dichloromethane. The UV/Vis spectra for (*S*,*S*)-**2** and (*S*,*S*)-**6** are shown in Figure S7, and the corresponding spectra in toluene are shown in Figures S8 and S9. Their numerical data are listed in Table 1. Complex **5** features an intense absorption band with a maximum at $\lambda = 508$ nm, assignable to the $^1\pi$–π^* transition of the dipyrrinato ligand **3**.[7,10a] On the other hand, the absorption maximum of (*R*,*R*)-**6** at $\lambda = 283$ nm is derived from box ligand (*R*,*R*)-**4**. The UV/Vis spectrum of (*R*,*R*)-**2** corresponds to the average of those of **5** and (*R*,*R*)-**6**, reflecting its composition. No signal for achiral complex **5** was observed by CD spectroscopy. In contrast, (*R*,*R*)-**6** showed an intense Cotton effect, with exciton coupling between the two chiral chromophores. Intriguingly, (*R*,*R*)-**2** shows a Cotton effect at not only the absorption band of the box ligand, but also the $^1\pi$–π^* band of the dipyrrinato ligand. Note that the same discussion is applicable to (*S*,*S*)-**2** and (*S*,*S*)-**6**, except that the sign of the CD spectra is reversed (Figure 4a). Therefore, the axial chirality of dipyrrinato ligand **3** propagated by box ligand (*R*,*R*)- or (*S*,*S*)-**4** (Figure S6) is also present even in the solution phase.

Figure 4b,c (lower traces) shows the photoluminescence (PL) spectra of (*R*,*R*)-**2** and (*S*,*S*)-**2** in dichloromethane, and their numerical data are listed in Table 1, along with those of **5**.[10a] Spectra recorded in toluene are shown in Figures S9 and S10. All three complexes show luminescence at around $\lambda = 530$ nm, typical of the $^1\pi$–π^* fluorescence of dipyrrin–zinc(II) complexes.[7,10a] Note that homoleptic bis[bis(oxazoline)]zinc(II) complexes (*R*,*R*)-**6** and (*S*,*S*)-**6** are nonfluorescent. Complexes (*R*,*R*)-**2** and (*S*,*S*)-**2** (both with Stokes shifts of 525 cm^{-1}) show smaller Stokes shifts than does **5** (888 cm^{-1}), presumably because structural relaxation in the photoexcited state is suppressed by the

Table 1: Photochemical properties of (*R*,*R*)-**2**, (*S*,*S*)-**2**, **5**, (*R*,*R*)-**6** and (*S*,*S*)-**6** in solution.

Compound	λ_{abs} (ε)[a] (CH_2Cl_2)	λ_{lum}[a] (CH_2Cl_2)	ϕ_F[b] (toluene)	ϕ_F[b] (CH_2Cl_2)	τ [ns][c] (toluene)	τ [ns][c] (CH_2Cl_2)
(*R*,*R*)-**2**	509 (90000)	523	0.67	0.59	3.70	3.27
(*S*,*S*)-**2**	509 (82000)	523	0.70	0.55	3.72	3.29
5[d]	508 (140000)	532	0.20	0.05	2.56	1.13
(*R*,*R*)-**6**	283 (42000)	–	0	0	–	–
(*S*,*S*)-**6**	282 (39000)	–	0	0	–	–

[a] λ_{abs} and λ_{lum} given in nm; molar extinction coefficient (ε) given in $M^{-1}\,cm^{-1}$. [b] PL quantum yield. [c] PL lifetime. [d] From Ref. [10a].

intramolecular interligand π–π interaction. Note that the fluorescence quantum yields (ϕ_F) of (*R*,*R*)-**2** and (*S*,*S*)-**2** (ϕ_F = 0.67 and 0.70, respectively) in toluene are much higher than that detected for homoleptic complex **5** (ϕ_F = 0.20). In addition, (*R*,*R*)-**2** and (*S*,*S*)-**2** maintain high ϕ_F values in more polar dichloromethane (0.55 and 0.59, respectively), whereas the quantum yield for complex **5** in CH_2Cl_2 is very low (ϕ_F = 0.05). This series of facts is visualized in photos of **5** and (*R*,*R*)-**2** solutions under various lighting conditions (Figure 4d–g). These findings suggest that (*R*,*R*)-**2** and (*S*,*S*)-**2** meet the requirements for bright luminescence, as shown in Figure 1b.[10a] In fact, DFT calculations reveals that the HOMO and LUMO of (*R*,*R*)-**2** and (*S*,*S*)-**2** are localized on dipyrrinato ligand **3**, whereas the HOMO−1 and LUMO + 1 are dominated by box ligand **4** (Figure 5 and S10).

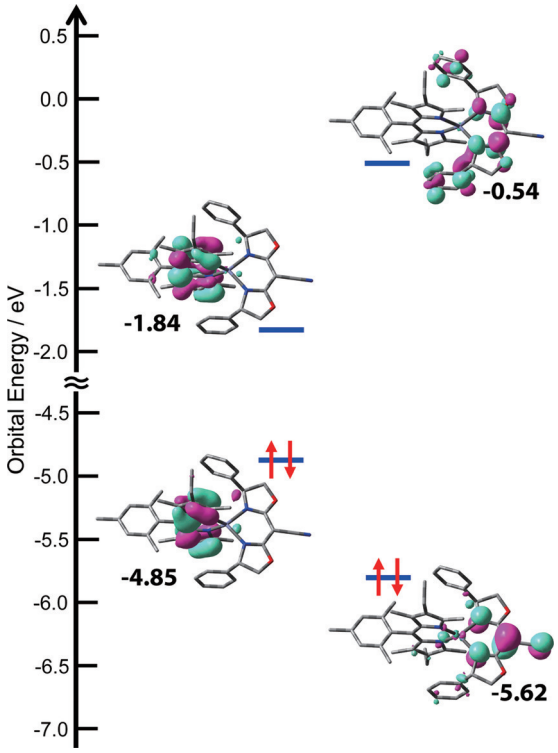

Figure 5. Frontier orbitals and their energy levels of (*R*,*R*)-**2**.

The CPL properties of the complexes in dichloromethane are also shown in Figure 4b,c. Complex **5** did not exhibit CPL (data not shown). In sharp contrast, (*R*,*R*)-**2** and (*S*,*S*)-**2** showed luminescence dissymmetry factors (g_{lum}) with opposite signs (circa $\pm 1.0 \times 10^{-3}$), in agreement with the CD spectroscopy result (Figure 4a). Thus, the axial chirality induction in originally achiral dipyrrinato ligand **3** by chiral box ligand (*R*,*R*)-**4** or (*S*,*S*)-**4** leads to CPL from **3**. Our strategy (that is, realization of bright fluorescence from a simple, non-π-expanded dipyrrinato ligand and subsequent acquisition of CPL from the achiral dipyrrinato ligand using commercially available chiral box ligands) differentiates the present work from previous research on CPL focusing on non-lanthanide-based, non-aggregated small molecules.[19]

In conclusion, a new type of heteroleptic (dipyrrinato)zinc(II) complexes (*R*,*R*)-**2** and (*S*,*S*)-**2** was designed and synthesized. They consist of an achiral dipyrrinato ligand (**3**) and a chiral box ligand ((*R*,*R*)-**4** or (*S*,*S*)-**4**). The box ligands stabilized the complexes, allowing their isolation and an investigation of their structural and optical features. Complexation effectively enabled bright fluorescence from non-π-expanded dipyrrinato ligand **3**, which was realized through appropriate engineering of the frontier orbitals. Box ligands (*R*,*R*)-**4** and (*S*,*S*)-**4** transmitted their chirality to achiral dipyrrinato ligand **3**, rendering ligand **3** CPL-active. Box ligands (*R*,*R*)-**4** and (*S*,*S*)-**4** are promising complementary moieties to dipyrrinato ligands in terms of their photochemical properties.

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