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Iridium(III) phosphorescent complexes with dual stereogenic centers: single crystal, electronic circular dichroism evidence and circularly polarized luminescence properties†

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Iridium complexes with a chiral metal center and chiral carbons, Λ/Δ -(dfppy)₂Ir(chty-*R*) and Λ/Δ -(dfppy)₂Ir(chty-*S*), were synthesized and characterized. These isomers have the same steady-state photophysical properties, and obvious offsets in ECD spectra highlight both the chiral sources. Each enantiomeric couple shows mirror-image CPL bands with a dissymmetry factor in the order of 10^{−3}.

As promising phosphorescent emitters, Ir(III) octahedral complexes with 2-phenylpyridine analogue ligands and various ancillary ligands have been investigated extensively.¹ With tunable photophysical properties, many of these complexes have been applied in organic light-emitting diodes (OLEDs),² chemical sensing³ and biological probing.⁴ Due to the nature of six-coordinated complexes, these Ir(III) complexes have isomers with two configurations, which are marked as Λ and Δ .⁵ According to the well-established synthetic route *via* a chloro-bridge dimer, a mixture of an equal molar ratio of Λ and Δ isomers is obtained. However, these two isomers present exactly the same steady-state photophysical properties, and the racemoids do not influence their applications in the fields mentioned above.

Recently, a growing number of publications have focused on the separation, characterization and application of Ir(III) phosphor isomers.⁶ In a previous study, we demonstrated that almost all conventional Ir(III) phosphors with the structure of

fac/mer-Ir(L_m)₃ and (L_m)₂Ir(L_a) (where L_m is the main ligand and L_a is the ancillary ligand) can be separated into configurational isomers.⁷ Obvious circularly polarized luminescence (CPL) signals were observed for each pair of enantiomers. It is well known that CPL has potential application in various fields, and control of the polarisation of light is essential for optical data processing and display devices such as optical data storage,⁸ highly efficient three-dimensional displays and liquid crystal display backlights,⁹ effective spin sources in optical spintronics,¹⁰ optical quantum information processing and communication,¹¹ and information carriers in quantum computation¹² as well as the induction of exotic quantum phenomena such as the Floquet topological state.¹³ However, research studies for the complexes with dual stereogenic centers are still rare. Recently, Abbate *et al.* reported a series of Ir(III) ionic complexes with a chiral metal center and chiral ancillary ligands, which show obvious vibrational circular dichroism (VCD).¹⁴

In this contribution, we synthesized two Schiff base ancillary ligands, chty-*R* and chty-*S* containing a chiral carbon atom (Scheme S1† and Scheme 1). Then, Ir(III) complexes (dfppy)₂Ir(chty-*R*) and (dfppy)₂Ir(chty-*S*) with 2-(2,4-difluorophenyl)pyridine (dfppy) as the main ligand were synthesized. The chloro-

Scheme 1 Synthetic strategy for the isomers with chiral configurations and chiral carbon atoms.

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bridged dimer medium product was prepared by heating 2.2 equiv. of dfppy and 1 equiv. of iridium chloride in 2-ethoxyethanol at 120 °C. The Schiff base ancillary ligands were synthesized according to the reported method starting from optically pure *R* or *S* isomers.¹⁵ For the final splitting reaction, 2.2 equiv. of Schiff base ancillary ligands, 1 equiv. of the dimer complex and 10 equiv. of potassium carbonate were heated at 120 °C in 2-ethoxyethanol overnight.¹⁶ The raw products were purified by chromatography and recrystallization to afford the final racemic complexes (dfppy)₂Ir(chty-*R*) and (dfppy)₂Ir(chty-*S*) as yellow block crystals. Chiral synthetic HPLC was used to separate four isomers, termed Λ/Δ -(dfppy)₂Ir(chty-*R*) and Λ/Δ -(dfppy)₂Ir(chty-*S*) hereafter, with ee values higher than 95% (Fig. S1 and S2†).

According to the refinement results of X-ray single crystal diffraction measurements, all the samples have a Flack index near zero which indicates that the absolute structures of the chiral sources are reliable. As illustrated in Fig. 1 and Table S2,† the single crystal structures of four isomers leave no doubt with respect to the chirality assignment. As conventional Ir(III) phosphorescent complexes, all these four isomers adopt a twisted octahedral structure. The iridium center coordinates with two dfppy ligands *via* two *trans* nitrogen atoms and two *cis* carbon atoms and with the chiral Schiff base ancillary ligand chty-*R/S* *via* an oxygen atom and a nitrogen atom. The Ir–C, Ir–N bonds between iridium and dfppy are around 2.0 Å and Ir–O, Ir–N bonds with ancillary ligands are a bit longer around 2.1 Å (Table S3†). The chirality on the carbon atom in the ancillary ligands is easy to distinguish by single crystal structures, and it is noteworthy that [Λ -(dfppy)₂Ir(chty-*R*), Δ -(dfppy)₂Ir(chty-*S*)] and [Δ -(dfppy)₂Ir(chty-*R*), Λ -(dfppy)₂Ir(chty-*S*)] are two couples of antimeres with perfect mirror symmetry structures. Due to a favourable steric position, the free phenyl rings connecting to the chiral carbon atom in Λ -(dfppy)₂Ir(chty-*R*) and Δ -(dfppy)₂Ir(chty-*S*) present an obvious

π - π stacking effect with a pyridine ring in the dfppy ligand (Fig. S3†). The distance between two centers is around 3.9 Å. However, such stacking does not exist in Δ -(dfppy)₂Ir(chty-*R*) and Λ -(dfppy)₂Ir(chty-*S*). Consequently, Λ -(dfppy)₂Ir(chty-*R*) and Δ -(dfppy)₂Ir(chty-*S*) crystallized in an orthorhombic crystal system with the *P*₂₁₂₁₂₁ space group with higher symmetry than the *P*₂₁ space group in a monoclinic system which is adopted by Δ -(dfppy)₂Ir(chty-*R*) and Λ -(dfppy)₂Ir(chty-*S*).

The steady state photophysical properties were measured in diluted CH₂Cl₂ solutions (1×10^{-5} M for absorption and 5×10^{-5} M for emission, respectively, Fig. 2). All the isomers present almost the same spectral profile which corresponds to similar research conducted earlier.¹⁷ This demonstrates that neither the chiral configuration nor the chiral atoms in the ligands influences the steady state absorption and emission properties. As conventional Ir(III) complex phosphors, each of these four compounds has an intensive absorption band peaking at 250 nm, which is assigned to spin-allowed π - π transitions. Another weak absorption band is observed covering a

Fig. 2 The UV-vis absorption and photoluminescence spectra of all the isomers (absorption: empty, emission at 298 K: filled, emission at 77 K: half filled; lambda: square, delta: triangle).

Fig. 1 The molecular structures (top) and single crystal diagrams (bottom) of Λ/Δ -(dfppy)₂Ir(chty-*R*) and Λ/Δ -(dfppy)₂Ir(chty-*S*); (carbon: gray; nitrogen: blue; fluorine: green; oxygen: red; iridium: teal).

wide range from 350 to 500 nm and it is generated by MLCT transitions including $^1\text{MLCT}$ and $^3\text{MLCT}$ due to the strong spin-orbital coupling effect introduced by iridium atoms. The emission spectra of all the isomers at room temperature show a broad band covering a wide range from 500 to 700 nm, peaking at 580 nm, which makes them orange emitters. When measured at 77 K, the emission bands have a hypsochromic shift and the main peaks are around 520 nm. The broad emission spectra at low temperature indicate that the emitting state has more $^3\text{MLCT}$ character than $^3\text{LLCT}$ character.¹⁸

The ECD spectra of all the four isomers after chiral HPLC together with the non-separated racemic complexes after the chromatography were recorded in CH_2Cl_2 solutions (Fig. 3a and S5†). Since the electron circular dichroism (ECD) peaks of the two types of chiral sources were separated from each other, signals generated by both chiral configuration and the chiral carbon atoms can be distinguished clearly. For the racemic complexes, the configuration chirality is counteracted because of the 1 : 1 mixing ratio of Λ and Δ isomers out of the synthesis from the chloro-bridged intermediate into racemic products. Thus, the ECD signals for these samples are exclusively from the chiral carbon atoms in the ancillary ligands. In the range from 350 to 480 nm, (Λ/Δ) -(dfppy)₂Ir(chty-R) show a broad peak in the positive direction and (Λ/Δ) -(dfppy)₂Ir(chty-S) show a perfect mirror-image peak in the negative direction. The peak values for the differences of the extinction coefficients between right and left circularly polarized light are 6.5 and $-4.6 \text{ M}^{-1} \text{ cm}^{-1}$. In the range lower than 350 nm, no response caused by chiral carbon atoms is observed. In the case of the isomers, the joint effects of both the chiral metal center and the chiral carbon atoms make the spectra more complicated. For Λ -(dfppy)₂Ir(chty-R) and Δ -(dfppy)₂Ir(chty-R), in the range lower than 350 nm, only signals from chiral configurations are observed, and the spectra in this part present a mirror-image relationship due to the chiral metal center. The peaks at 310 nm have $\Delta\epsilon$ values around 20 and $-21 \text{ M}^{-1} \text{ cm}^{-1}$ respectively. However, from 350 nm onward, influence from chiral carbon atoms starts to appear and the spectra are no longer symmetric, being disturbed by a positive shift from chiral carbon atoms. Due to the same concentration, the cross of the two curves is exactly on the line of the racemic mixture instead of on the horizontal axis. The same situation can be also observed in the Λ -(dfppy)₂Ir(chty-S), Δ -(dfppy)₂Ir(chty-S) and (Λ/Δ) -(dfppy)₂Ir(chty-S). The peak values for Λ -(dfppy)₂Ir

(chty-S) and Δ -(dfppy)₂Ir(chty-S) at 310 nm are around $\pm 14 \text{ M}^{-1} \text{ cm}^{-1}$. As a result, the spectra of Λ -(dfppy)₂Ir(chty-R) and Δ -(dfppy)₂Ir(chty-S), and Δ -(dfppy)₂Ir(chty-R) and Λ -(dfppy)₂Ir(chty-S) present crosses on the horizontal axis at 416 and 436 nm with $\Delta\epsilon$ values of 6.3 and $4.3 \text{ M}^{-1} \text{ cm}^{-1}$ respectively. It is noteworthy that the ECD signals from chiral carbon atoms in the Schiff base ancillary ligands are strong enough to generate positive or negative shifts on the ECD signals from chiral metal centers, making the ECD an available and efficacious method to characterize these isomers.

The CPL properties of the isomers were studied in CH_2Cl_2 solutions (Fig. 3b) as further chiroptical characterization. Λ -(dfppy)₂Ir(chty-R) and Δ -(dfppy)₂Ir(chty-R) have mirror-image profiles with a single band in the range from 500 to 750 nm peaking around 620 nm. A similar relationship is observed for Λ -(dfppy)₂Ir(chty-S) and Δ -(dfppy)₂Ir(chty-S). It is noteworthy that isomers with Δ configuration show positive CPL signals and the isomers with Λ configuration give negative signals. Since no significant differences are observed in isomers with the same chiral configuration but different chiral carbon atoms, the CPL properties are mainly determined by the configurations, and the effects applied by the chiral carbon atoms in the ancillary ligands are negligible. The calculated dissymmetry factor g_{Lum} is in the scope of 10^{-3} and those at the peaks are around 0.005 (Fig. S6†). This observation is comparable to the reported values for CPL complexes.¹⁹

Conclusions

In conclusion, two Schiff base ancillary ligands with *R/S* chiral carbon atoms were synthesized and two iridium complexes with racemic configuration (Λ/Δ) -(dfppy)₂Ir(chty-R) and (Λ/Δ) -(dfppy)₂Ir(chty-S) were obtained. Furthermore, four isomers Λ -(dfppy)₂Ir(chty-R), Δ -(dfppy)₂Ir(chty-R), Λ -(dfppy)₂Ir(chty-S) and Δ -(dfppy)₂Ir(chty-S) were separated by chiral synthetic HPLC with high ee values. All the isomers were characterized by X-ray single crystal diffraction. In Λ -(dfppy)₂Ir(chty-R) and Δ -(dfppy)₂Ir(chty-S), the π - π stacking is found between the main ligand and the ancillary ligand, but this is not observed in Δ -(dfppy)₂Ir(chty-R) and Λ -(dfppy)₂Ir(chty-S) due to disadvantageous steric arrangements of the phenyl ring for packing on chiral carbon atoms. All the isomers have exactly the same steady state photophysical properties, but the ECD spectra are significantly disturbed by the chiral carbon atoms, which give strong evidence for the dual stereogenic centers. The isomers with Λ and Δ configurations show negative and positive CPL signals, respectively, and the g_{Lum} values are constantly in the scope of 10^{-3} .

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Fig. 3 The ECD spectra (a) and CPL spectra (b) of the four isomers in CH_2Cl_2 solutions.

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