Sign inversion of magnetic circularly polarized luminescence in Iridium(III) complexes bearing achiral ligands

Journal:	*Physical Chemistry Chemical Physics*
Manuscript ID	CP-ART-11-2020-005775.R3
Article Type:	Paper
Date Submitted by the Author:	29-Jan-2021
Complete List of Authors:	Matsudaira, Kana; Kindai University, Department of Applied Chemistry Izumoto, Atsushi; Kindai University, Department of Applied Chemistry Mimura, Yuki; Kinki Daigaku Kondo, Yoshiro; JASCO Corporation Suzuki, Satoko; JASCO Corporation Yagi, Shigeyuki; Osaka Prefecture University, Department of Applied Chemistry, Graduate School of Engineering FUJIKI, Michiya; Nara Institute of Science and Technology, Division of Materials Science; Imai, Yoshitane; Kinki University, Department of Applied Chemistry

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Sign inversion of magnetic circularly polarized luminescence in Iridium(III) complexes bearing achiral ligands

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Kana Matsudaira,[a] Atsushi Izumoto,[a] Yuki Mimura,[a] Yoshiro Kondo,[b] Satoko Suzuki,[b] Shigeyuki Yagi,[c] Michiya Fujiki[d] and Yoshitane Imai*[a]

Optically inactive, paramagnetic Ir(III)(ppy)$_3$ and Ir(III)(ppy)$_2$(acac) (ppy: 2-phenylpyridinate and acac: acetylacetonate) showed nearly mirror-symmetric magnetic circularly polarised luminescence (MCPL) spectra in dilute dichloromethane and dimethyl sulfoxide under N-up and S-up geometries in a 1.6-T magnetic field. However, the MCPL signs of Ir(III)(ppy)$_3$ and Ir(III)(ppy)$_2$(acac) under the same N-up (or S-up) Faraday geometry were opposite to each other when one ppy was replaced with an acac. This ligand exchange approach provides facile control of the MCPL sign, irrespective of the Faraday geometry.

Introduction

Chiral luminophores exhibiting circularly polarised luminescence (CPL) with high quantum yield (Φ_{PL}) and high anisotropy (g_{CPL}) have been studied recently for potential applications in organic light-emitting diodes (OLEDs), which display circularly polarised electroluminescence.[1] In particular, several optically active organometallic complexes composed of chiral organic ligands have provided sharper CPL bands with high g_{CPL} values in the visible-to-near-infrared region.

Recently, optically inactive Eu(III)(hfa)$_3$ and Tb(III)(hfa)$_3$ (hfa: 1,1,1,5,5,5-hexafluoropentane-1,4-dione) were found to exhibit CPL upon coordination with the C_2-symmetric axially chiral 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) and C_2-symmetric planar-chiral 4,12-bis(diphenylphosphino)-[2.2]-paracyclophane (Phanephos) in the solution state.[2] In such CPL-exhibiting systems, a chiral organic ligand is indispensable. Moreover, the selective emission of light via left-handed or right-handed CPL requires organometallic luminophores with opposite chirality. Consequently, access to chiral organic ligands with opposite chirality is crucial; however, such ligands are not always readily available. Therefore, it is desirable to develop a novel system for controlling the CPL signs of chiral organometallic luminophores, which do not depend on ligand chirality.

In this context, it had been demonstrated magnetic circularly polarised luminescence (MCPL) in optically inactive luminophores such as racemic Eu(III)(hfa)$_3$ and Tb(III)(hfa)$_3$, which exhibited strong CPL from Eu(III) and Tb(III) under an external magnetic field, in both solution and solid states.[3] In general, the control of chiroptical properties, such as CPL, in chiral organometallic luminophores composed of chiral organic ligands by using other organic ligands with the same chirality is challenging because of (i) the availability of several coordination modes of the metal and (ii) the potential differences in the coordination structures of the ground and photoexcited states. The signs of these MCPL spectra were successfully inverted by solely choosing the Faraday-type N→S (N-up) or S→N (S-up) geometry. Faraday N-up/S-up geometry means that the longitudinal magnetic field is colinear/anti-colinear to unpolarized incident light.

Several paramagnetic Ir(III) complexes coordinated with organic ligands have received considerable attention for their LED applications owing to their high photoluminescence (PL) quantum yields and the facile control of their luminescence colour by the introduction of electron-donating or electron-withdrawing substituents as the ligands.[4] A recent study reported the MCPL of Ir(III)(ppy)$_3$ (ppy: 2-phenylpyridinate) under an external magnetic field at cryogenic temperatures.[5]

Herein, we demonstrate nearly mirror-symmetric MCPL spectra by an unconventional control of the MCPL signs of optically inactive Ir(III)(acac)$_3$, Ir(III)(ppy)$_3$,[4c] and Ir(III)(ppy)$_2$(acac)[4a] (acac: acetylacetonate, Fig. 1) under N-up and S-up Faraday geometries. Notably, ppy and acac are achiral organic ligand, and Ir(III)(acac)$_3$ and Ir(III)(ppy)$_3$ have three identical acac and ppy ligands, respectively, whereas Ir(III)(ppy)$_2$(acac) has two ppy and one acac. The optically inactive Ir(III)(ppy)$_3$ and Ir(III)(ppy)$_2$(acac) complexes in the solution state revealed nearly mirror-symmetric MCPL spectra under the N-up and S-up fields. Further, their MCPL signs at all transitions were reversed with respect to not only the

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[a] Department of Applied Chemistry, Faculty of Science and Engineering, Kindai University, 3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502, Japan. E-mail: y-imai@apch.kindai.ac.jp
[b] JASCO Corporation, 2967-5 Ishikawa, Hachioji, Tokyo 192-8537, Japan
[c] Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan
[d] Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0192, Japan

direction of the N-up/S-up geometry, but also the fraction of ppy and acac ligands.

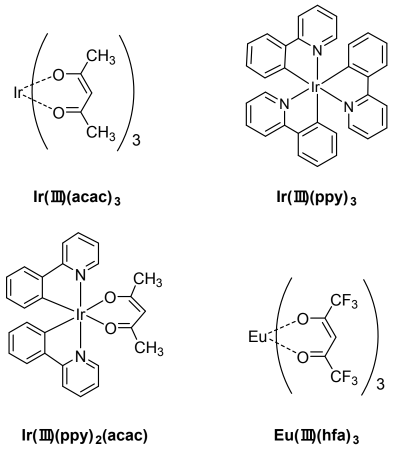

Fig. 1 Structures of Ir(III) and Eu(III) luminophores.

Experimental methods

Materials

Ir(III)(acac)$_3$, Ir(III)(ppy)$_3$, and Ir(III)(ppy)$_2$(acac) were purchased from Tokyo Chemical Industry Co., Ltd (Tokyo, Japan). Oxygen-free dichloromethane (CH_2Cl_2), dimethyl sulfoxide (DMSO), and spectral-grade acetone were purchased from FUJIFILM Wako Pure Chemical Corp (Osaka, Japan).

Measurement of PL, CPL, and MCPL spectra

The unpolarised PL, CPL, and MCPL spectra of the luminophores in dilute CH_2Cl_2, DMSO, and acetone were acquired using a JASCO CPL-300 spectrofluoropolarimeter and a JASCO PM-491 1.6-T permanent magnet at room temperature. The sample solutions, with a path length of 2 mm, were excited at 410 nm with a 10-nm bandwidth.

Results and discussion

First, we attempted to obtain the MCPL and corresponding PL spectra of optically inactive Ir(III)(acac)$_3$ under a 1.6-T magnetic field in CH_2Cl_2, DMSO, and acetone; however, PL and MCPL were not observed. The inhibition of emission from Ir(III)(acac)$_3$ is attributed to the high energy of the acac ligand's π* orbital, and the consequent large contribution of the non-radiative 3d-3d transition.[6]

On the other hand, we obtained mirror-symmetrical structureless broad MCPL spectra associated with the corresponding PL spectra of optically inactive Ir(III)(ppy)$_3$ under 1.6 T N-up and S-up T magnetic fields in CH_2Cl_2, DMSO, and acetone, as shown in Fig. 2 (red lines for N-up, blue lines for S-up, and black lines at H_0 = 0.0 T) and Table 1. Although enantiomerically pure Ir(III)(ppy)$_3$ might exhibit CPL in solution, the racemic Ir(III)(ppy)$_3$ used herein did not reveal obvious CPL, as shown in Fig. 2a (upper panel, black line). The racemic Ir(III)(ppy)$_3$ exhibited MCPL in both CH_2Cl_2 and DMSO solutions (upper panels, Fig. 2a and 2b), whereas no obvious MCPL signals were detected in acetone (upper panel, Fig. 2c).

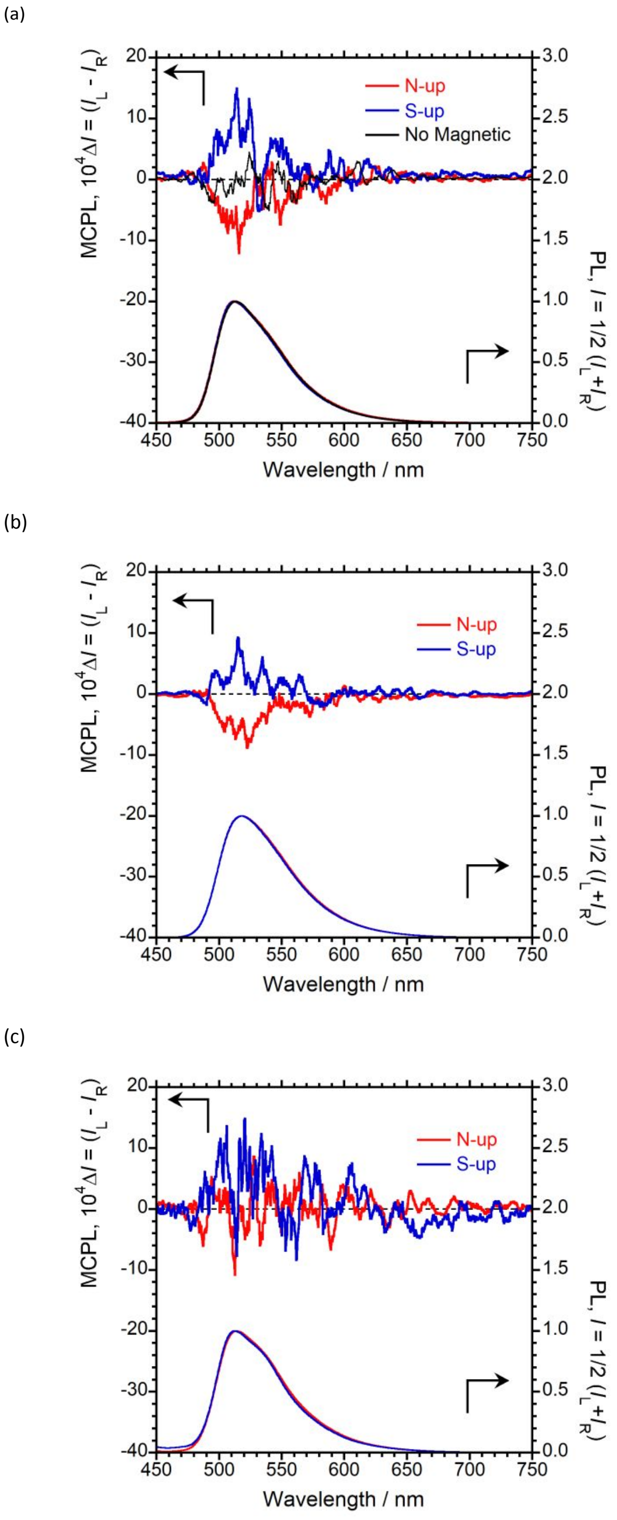

Fig. 2 MCPL (upper panel) and PL (lower panel) spectra of Ir(III)(ppy)$_3$ under N-up (red lines), S-up (blue lines), and zero (black lines) magnetic fields in (a) CH_2Cl_2 (1.0×10^{-3} M), (b) DMSO (1.0×10^{-3} M), and (c) acetone (1.0×10^{-3} M).

The two broad MCPL band at ~515 and at ~519 nm (shoulder) for CH_2Cl_2 and DMSO solutions respectively, correspond to the excited triplet state of Ir(III)(ppy)$_3$. These clear MCPL bands are ascribed to the triplet metal-to-ligand charge transfer (MLCT) transition, which is promoted by intersystem crossing due to the strong heavy-atom effect of Ir(III). The MCPL spectra obtained under the N-up and S-up Faraday geometries were nearly mirror-symmetrical but subtly different from each other, reflecting the N-up and S-up geometries. Thus, the external magnetic field induced the MCPL, even from racemic Ir(III)(ppy)$_3$ in CH_2Cl_2 and DMSO, and the N-up and S-up directions can control the MCPL sign of the racemic Ir(III)(ppy)$_3$.

To assess the MCPL intensities quantitatively, we used the g_{MCPL} value, defined as $g_{MCPL} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are the observed intensities of the left- and right-handed MCPL, respectively, upon excitation by unpolarised light. The $|g_{MCPL}|$ values of Ir(III)(ppy)$_3$ in the CH_2Cl_2 and DMSO solutions were 13.6 × 10^{-4} at 514 nm and 7.7 × 10^{-4} at 519 nm, respectively.

Table 1. MCPL characteristics of Ir(III)(ppy)$_3$ and Ir(III)(ppy)$_2$(acac) in CH_2Cl_2,DMSO, and Acetone.

Ir(III)(ppy)$_3$	*CH_2Cl_2*	*DMSO*	*Acetone*
λ_{MCPL}	515 nm	519 nm	n.d.
$|g_{MCPL}|$ /10^{-4}	13.6	7.7	n.d.
MCPL sign for S-up	(+)	(+)	n.d.
MCPL sign for N-up	(-)	(-)	n.d.
Ir(III)(ppy)$_2$(acac)			
λ_{MCPL}	539 nm	528 nm	n.d.
$|g_{MCPL}|$ /10^{-4}	16.8	14.9	n.d.
MCPL sign for S-up	(-)	(-)	n.d.
MCPL sign for N-up	(+)	(+)	n.d.

To evaluate the ability of the ligands to induce MCPL, we investigated the MCPL and PL spectra of optically inactive Ir(III)(ppy)$_2$(acac) in dilute CH_2Cl_2, DMSO, and acetone solutions, as shown in Fig. 3 (red lines for N-up, blue for S-up, and black at H_0 = 0.0 T) and Table 1. Similar to Ir(III)(ppy)$_3$, Ir(III)(ppy)$_2$(acac) did not exhibit obvious MCPL spectra in acetone (upper panel, Fig. 3c). However, optically inactive Ir(III)(ppy)$_2$(acac) in CH_2Cl_2 and DMSO showed clear MCPL maxima (λ_{MCPL}) at ~539 and 528 nm, respectively (upper panels, Fig. 3a and 3b). This emission corresponds to the excited triplet state of Ir(III)(ppy)$_2$(acac) owing to the MLCT transition, which is promoted by intersystem crossing due to the heavy-atom effect of Ir(III) (upper panel in Fig. 3a and 3b). Similar to the case of Ir(III)(ppy)$_3$, because Ir(III)(ppy)$_2$(acac) used herein is a racemic mixture, CPL was not observed at H_0 = 0.0 T, as shown in Fig. 3a (upper panel, black line). However, the racemic Ir(III)(ppy)$_2$(acac) showed nearly mirror-symmetrical MCPL spectra when the N-up and S-up directions were applied.

The MCPL efficiencies of Ir(III)(ppy)$_2$(acac) in CH_2Cl_2 and DMSO were 16.8 × 10^{-4} at 539 nm and 14.9 × 10^{-4} at 528 nm, respectively. The magnitudes of the $|g_{MCPL}|$ values (≈ 10^{-3}) were similar to Ir(III)(ppy)$_2$(acac) and Ir(III)(ppy)$_3$. These results show that the external magnetic field induces CPL in various Ir(III) organometallic luminophores containing organic cyclometalated ligands.

Notably, the MCPL spectral signs of Ir(III)(ppy)$_3$ and Ir(III)(ppy)$_2$(acac) in dilute CH_2Cl_2 and DMSO were opposite, with (−)-sign for Ir(III)(ppy)$_3$ and (+)-sign for Ir(III)(ppy)$_2$(acac) under the N-up and vice versa. In other words, the MCPL signs under the N-up and S-up were ideally inverted solely by replacing one ppy with one acac ligand at the time of complex formation.

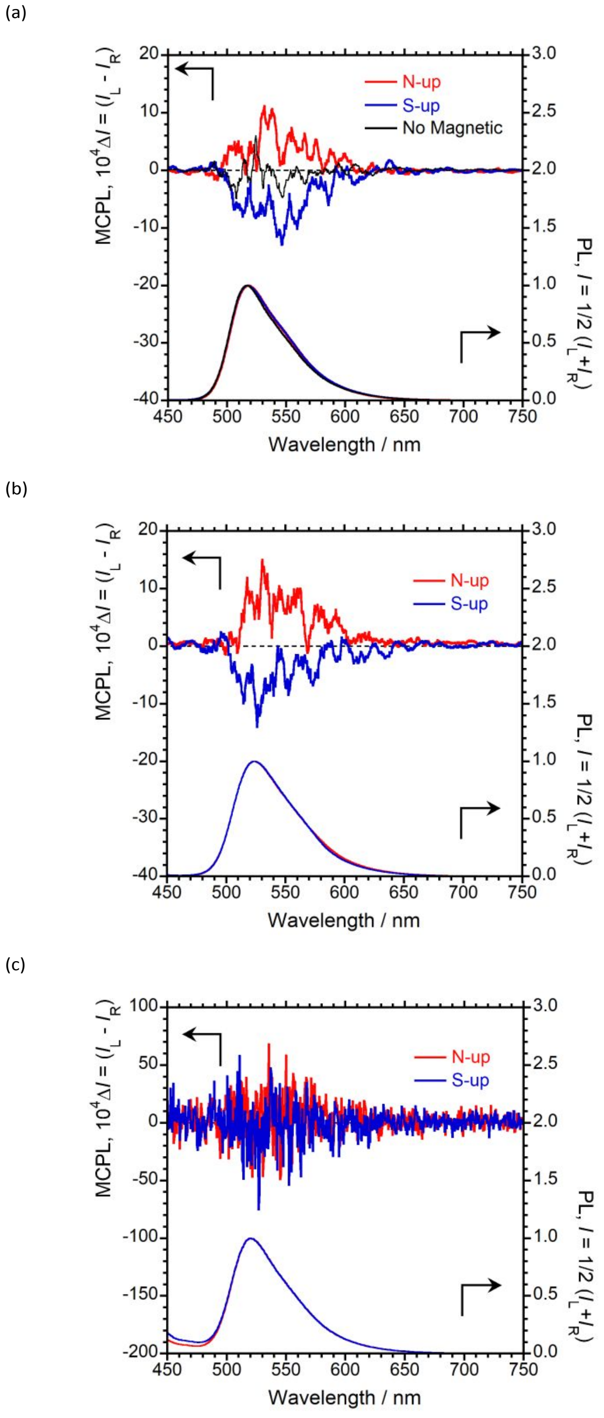

Fig. 3 MCPL (upper panel) and PL (lower panel) spectra of Ir(III)(ppy)$_2$(acac) under N-up (red lines), S-up (blue lines), and zero (black lines) magnetic fields in (a) CH_2Cl_2 (1.0 × 10^{-3} M), (b) DMSO (1.0 × 10^{-3} M), and (c) acetone (1.0 × 10^{-3} M).

Thus, the MCPL signs of the Ir(III) complexes coordinated with achiral organic ligands can be controlled by the direction of the external magnetic field as well as the nature of the achiral ligands.

Generally, magnetic circular dichroism (MCD) characteristics, and possibly the MCPL ones, of diamagnetic substances dominantly arise from the temperature-independent Faraday A and B terms, rather than the temperature-dependent Faraday C term.[7] Although details are unknown, in this MCPL system, the steric and electric effects of the achiral acac ligands around the Ir core may affect the the sign of the Faraday A term (or the Faraday B term) depending on the orbital angular momenta and orbital degeneracies of the HOMOs and LUMOs of the Ir(III). From the view point of the steric effect, in a fluidic solution at ambient temperature, optically inactive Ir(III)$(ppy)_3$ exists as a mixture of main C_3-symmetric facial complex and minor C_1-symmetric meridional complex. In addition, C_3-symmetric facial complex exists as a mixture of 1:1 mixture of pseudo C_3-symmetric Δ-*fac*- and Λ-*fac*-isomers owing to the high energetic barrier between the two isomers. On the other hand, in optically inactive Ir(III)$(ppy)_2$(acac), the two ppy and one acac ligands no longer exist in a magnetically equivalent environment, because the pseudo C_1-symmetric molecular symmetry of Δ- and Λ-isomers was broken through the coordination of acac with Ir(III) although meridional isomers having C_2 symmetry might be existed. This structural difference may affect the orbital angular momenta and orbital degeneracies of the HOMOs and LUMOs of the Ir(III) luminophores.

In terms of electronic effects, both ppy and acac are considered electron acceptors for the Ir(III) ion. In Ir(III)$(ppy)_3$, the Ir–C bond of the ppy ligand is biased towards the carbon, and Ir–N coordination can form. In contrast, in Ir(III)$(ppy)_2$(acac), the acac ligand with an even number of conjugated electrons accepts electrons from the Ir core and became anion to form a complex.[8] The difference in the electron asymmetry and state of these ligands may affect the orbital angular momenta and orbital degeneracies of the HOMOs and LUMOs of the Ir(III) ions. These steric and electric differences are likely the key to generating the reversed MCPL signs of the photoexcited state in solution. In these Ir(III) luminophores, any MCPL signals in acetone, which comprises a carbonyl group, were not detected. This may be attributed to the asymmetric negative effect of the carbonyl group electrons on their orbital of the Ir(III) complexes.

Conclusion

In this study, we confirmed clear MCPL from two optically inactive Ir(III) complexes that were coordinated with three achiral organic ligands, including ppy and acac, in CH_2Cl_2 and DMSO solutions under a 1.6-T magnetic field. The signs of these MCPL spectra were controlled solely by changing between the N-up and S-up Faraday geometries and the achiral ligands. These unique MCPL characteristics should provide new insights into the MCPL characteristics of optically inactive Ir(III) complexes in the photoexcited state although the symmetry and degeneracy of the HOMOs and LUMOs of the Ir(III) ions are investigated in depth and are potentially useful for the development of novel organometallic MCPL systems derived from optically inactive luminophores.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

This study was supported by Grants-in-Aid for Scientific Research (18K05094, 19H02712, 19H04600, and 20H04678) from MEXT/Japan Society for the Promotion of Science; the Research Foundation for KDDI (2019-9); the Electrotechnology of Chubu (R-30506); Futaba (2019-6); Murata Science Foundation (H31-007); the Nippon Sheet Glass Foundation for Materials Science and Engineering (H30-4); the Yashima Environment Technology Foundation (2019-No9). This work was also supported by JST, CREST (JPMJCR2001), Japan.

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