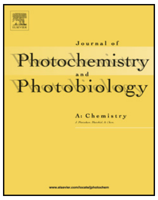
Journal of Photochemistry and Photobiology A: Chemistry xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Comprehensive spectroscopic studies of *cis* and *trans* isomers of red-phosphorescent heteroleptic iridium(III) complexes

Yang-Jin Cho[a], So-Yoen Kim[a], Ho-Jin Son[a], Won-Sik Han[b], Dae Won Cho[a,c,*], Sang Ook Kang[a,**]

[a] *Department of Advanced Materials Chemistry, Korea University (Sejong), Sejong 30019, South Korea*
[b] *Department of Chemistry, Seoul Women's University, Seoul 01797, South Korea*
[c] *Center for Photovoltaic Materials, Korea University (Sejong), Sejong 30019, South Korea*

ARTICLE INFO

Article history:
Received 25 January 2016
Received in revised form 31 March 2016
Accepted 7 May 2016
Available online xxx

Keywords:
Stereoisomer
Heteroleptic iridium complex
Time-resolved transient absorption spectroscopy
Metal-to-ligand charge transfer
Red-phosphorescent emission
Density function theory

ABSTRACT

We have synthesized heteroleptic Ir(III) complexes showing red phosphorescence, which can be separated as two geometrical isomers. Each isomer showed different absorption and emission spectral behaviours. The phosphorescence of the *cis* isomer is observed at shorter wavelengths than the *trans* one. Based on the results of electrochemical experiments and theoretical calculations, the LUMOs of both isomers are at the same energy level, but the HOMO of the *cis* isomer is shifted to a significantly lower energy than that of the *trans* isomer. The red emissions originate from the triplet metal-to-ligand charge transfer (MLCT) state, which is assigned by femtosecond time-resolved transient absorption spectroscopic analysis. The MLCT emission spectra of both isomers show highly structured bands with a vibronic spacing of *ca.* 1470 cm^{-1}. Observation of vibrational fine structure in the emission spectra is attributed to the limited excited state structural change imposed by the rigidity of metal coordination.

1. Introduction

Iridium(III) complexes are foremost candidates for highly efficient emissive dopants in organic light-emitting diodes (OLEDs), because of their outstanding thermal stability, moderate triplet lifetimes, and strong spin-orbital coupling effects [1–4]. Ir(III) complexes can be subdivided into two classes: homoleptic complexes containing three identical cyclometalating ligands and heteroleptic complexes with two identical cyclometalating ligands and an ancillary ligand [5,6]. Homoleptic Ir(III) complexes are difficult to synthesize because of harsh reaction conditions, low yields, and a large number of reaction byproducts [7]. For example, homoleptic Ir(III) complexes can exist as facial (*fac*) or meridional (*mer*) isomers.

Heteroleptic Ir(III) complexes are more readily synthesized under mild reaction conditions and exhibit good thermal stability, high emission quantum yield, and microsecond excited state lifetimes [8]. These complexes have therefore attracted a great deal of attention in the field of OLEDs. Many reports have described the heteroleptic isomers formed by thermal isomerization during OLED fabrication [9–13]. Although many geometric isomers may form during synthesis, only a single isomer is typically isolated [14]. The presence of other forms has not been of great concern, because heteroleptic Ir(III) complexes synthesized with an ancillary ligand were thought to exist only as a single isomer [9,15–17]. Therefore, motivation of this work is to obtain a comprehensive understanding of the photophysical properties of isomerically distinct heteroleptic Ir(III) complexes.

Facial isomers of homoleptic Ir(III) complexes show emission at shorter wavelengths with a higher quantum yield and longer lifetime than meridional isomers [18–20]. Presence of a *mer* isomer may be the cause of reduced emission intensities in OLEDs containing both isomers [20,21]. To date, many investigations of homoleptic Ir complexes have been reported, whereas the photophysical properties of isomeric heteroleptic complexes are not well known.

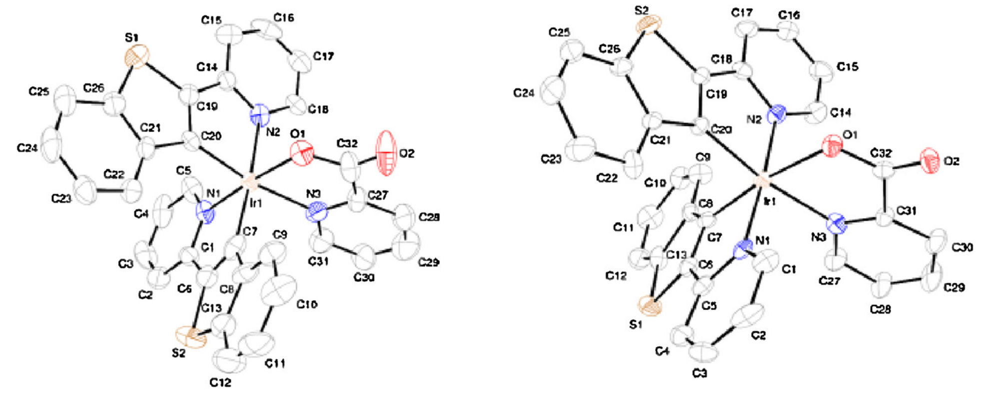
In this work, we have synthesized red-phosphorescent Ir$(\text{btp})_2(\text{pic})$ complexes (btp^- is benzothienylpyridinate, and pic^- is hydroxypicolinate) and have successfully separated the two isomers, Ir(*cis*-N/btp)$_2$(pic) and Ir(*trans*-N/btp)$_2$(pic), shown in the Oak Ridge Thermal Ellipsoid Plot (ORTEP) diagrams in Scheme 1. The isomers exhibit *cis* and *trans* orientations of the

---

* Corresponding author at: Department of Advanced Materials Chemistry, Korea University (Sejong), Sejong 30019, South Korea.
** Corresponding author.
E-mail addresses: dwcho@korea.ac.kr (D.W. Cho), sangok@korea.ac.kr (S.O. Kang).

http://dx.doi.org/10.1016/j.jphotochem.2016.05.007

Please cite this article in press as: Y.-J. Cho, et al., Comprehensive spectroscopic studies of *cis* and *trans* isomers of red-phosphorescent heteroleptic iridium(III) complexes, J. Photochem. Photobiol. A: Chem. (2016), http://dx.doi.org/10.1016/j.jphotochem.2016.05.007



Ir(*cis*-N/btp)$_2$(pic) **Ir(*trans*-N/btp)$_2$(pic)**

Scheme 1. ORTEP diagrams showing 30% probability thermal ellipsoids and atom labels for Ir(*cis*-N/btp)$_2$(pic) (left) and Ir(*trans*-N/btp)$_2$(pic) (right). Hydrogen atoms were omitted for clarity.

N-atoms in the two btp$^-$ ligands [22] which were synthesized concurrently and separated by flash column chromatography. Both isomeric Ir(III) complexes were fully characterized by ^{1}H NMR, ^{13}C NMR, and HRMS (ESI–MS), and their conformations were confirmed by single crystal structures. Herein, we report the dramatically different photophysical and electrochemical properties of the *cis* and *trans* isomers.

2. Results and discussion

2.1. Absorption and emission properties

The absorption spectra of both isomers show intense bands in the ultraviolet (UV) region at 250–350 nm, as shown in Fig. 1. These absorption bands are assigned to spin-allowed, ligand-centred (LC) $^1(\pi\pi^*)$ transitions of the btp$^-$ ligand in the complexes [23,24], because free btp$^-$ also shows a strong π–π^* transition at about 310 nm (Fig. S1 in the Supplementary Data, SD). The absorption bands at longer wavelengths are assigned to metal-to-ligand charge transfer (MLCT) in the Ir(III) complexes. The absorption bands of the two isomers at 350–525 nm are assigned to spin-allowed ^{1}MLCTs [23,24]. The absorption maximum of the ^{1}MLCT band for the *trans* isomer is observed near 475 nm. For the *cis* isomer, the intense band at 400 nm may result from effective mixing of the ^{1}MLCT with the higher lying spin-allowed $^1(\pi$–$\pi^*)$ transitions of the btp$^-$ ligand.

As shown in inset of Fig. 1, both complexes show absorption bands with very low extinction coefficients at 500–620 nm. These bands are assigned to spin-forbidden ^{3}MLCT transitions based on their extinction coefficients of less than 100 M^{-1} cm^{-1}. These values are approximately two orders smaller than those of the ^{1}MLCT absorption bands. It is noteworthy that the ^{3}MLCT absorption bands exhibit vibronic structures with a spacing of ~1460 cm^{-1}.

The Ir(btp)$_2$(pic) complexes display intense red emissions at 550–750 nm in both fluid solution at 300 K and in a glassy matrix at 77 K, as shown in Fig. 2. The emission spectra at 77 K exhibit highly structured bands with a vibronic spacing of *ca.* 1470 cm^{-1}. The emission spectra of both isomers are effectively mirror images of the ^{3}MLCT absorption spectra in terms of vibronic structure and spacing. The vibronic bands at 300 K exhibit spectral broadening, but the spacing of *ca.* 1445–60 cm^{-1} obtained by curve fitting analysis is close to that at 77 K (Fig. S2 in SD). This result indicates that the spacing of vibrational energy levels in the ground state is independent of temperature. Emissions of the *cis* isomer are observed at shorter wavelengths than those of the *trans* isomer at 77 K and 300 K.

For homoleptic Ir(III) complexes, it is well known that the emissions of the *fac* isomer are observed at shorter wavelength

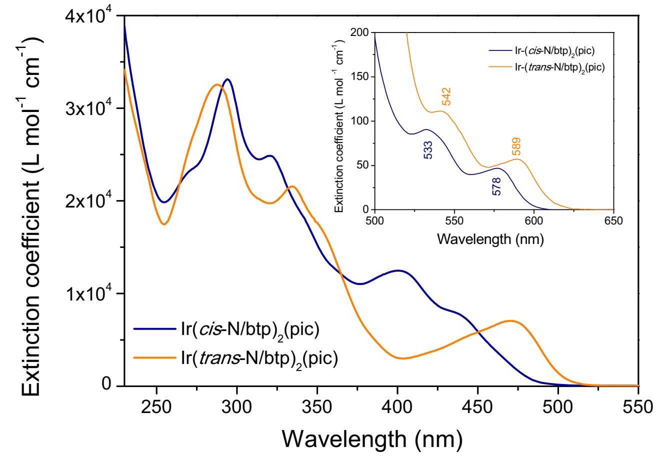


Fig. 1. Absorption spectra of Ir(*cis*-N/btp)$_2$(pic) and Ir(*trans*-N/btp)$_2$(pic) in CH$_2$Cl$_2$. Inset figure indicates absorption spectra of highly concentrated (0.5 mM) Ir(*cis*-N/btp)$_2$(pic) and Ir(*trans*-N/btp)$_2$(pic) in CH$_2$Cl$_2$.

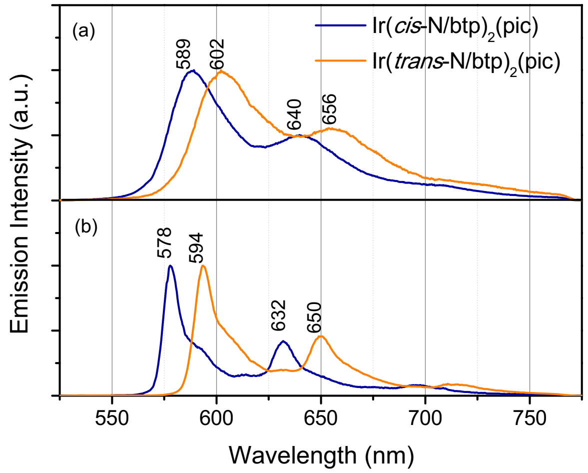


Fig. 2. The emission spectra of Ir(*cis*-N/btp)$_2$(pic) and Ir(*trans*-N/btp)$_2$(pic) measured in CH$_2$Cl$_2$ at 300 K (a), and in 2-MeTHF at 77 K (b). λ_{ex} = 355 nm.

Please cite this article in press as: Y.-J. Cho, et al., Comprehensive spectroscopic studies of *cis* and *trans* isomers of red-phosphorescent heteroleptic iridium(III) complexes, J. Photochem. Photobiol. A: Chem. (2016), http://dx.doi.org/10.1016/j.jphotochem.2016.05.007