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Near-Infrared Photochromic Diarylethene Iridium (III) Complex

Wenjuan Tan, Qiong Zhang, Junji Zhang, and He Tian*

Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 20023, P. R. China

tianhe@ecust.edu.cn

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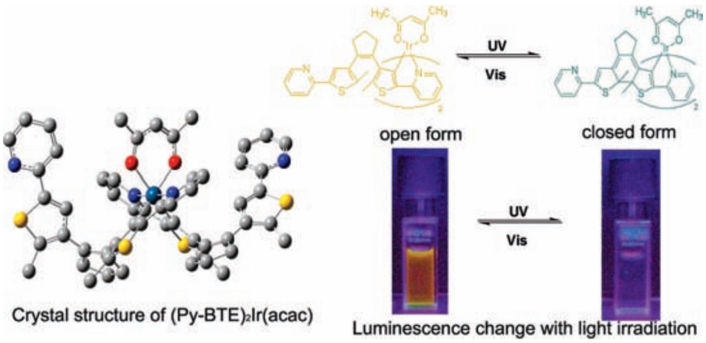
ABSTRACT



A novel iridium complex, $(Py\text{-}BTE)_2Ir(acac)$, coordinating to the photochromic diarylethene derivative is prepared. This complex showed excellent near-infrared photochromic behaviors accompanied by efficient quenching of phosphorescence emission.

Due to the potential applications in optical data storage and optoelectronic devices, the exploration of photochromic materials has aroused a surge of interest in materials science.[1] Photochromic diarylethene derivatives are one of the most attractive families among photochromic compounds because of their promising fatigue resistance and thermally irreversible properties.[2,3] Nowadays, to improve photochromic properties and photoswitching functionality, exploitation of involving the diarylethene moiety as ligand to form metal complexes has drawn much more attention, especially efforts on the phosphorescent investigation involving triplet-excitation of the metal complexes.[4−6] These metal complex systems have shown novel properties that can be potentially applied as photosensitizers for the photochromic activity, since the perturbation of the photochromic properties of the diarylethene moiety upon coordination to the metal center has been observed.[7] Although there are some reports about this kind of metal complex, studies on the exploitation of these diarylethenes frameworks as ligands to form an iridium (III) complex are extremely rare. It has been reported that highly emissive iridium complexes can be formed with two cyclometalated ligands and a single monoanionic, bidentate ancillary ligand.[8,9] Because of the strong spin−orbit coupling of the 5d ion, the related d^6 iridium complexes show intense phosphorescence at room temperature. The electronic transitions responsible for luminescence in these iridium complexes have been ascribed to a mixture of metal-to-ligand

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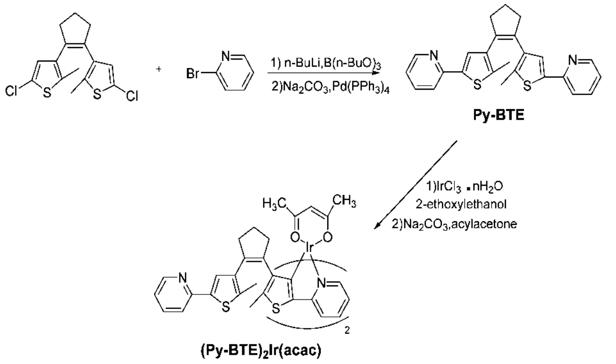
charge-transfer (MLCT)^3 and ($\pi \rightarrow \pi^*$)^3 ligand state.[10] With long-lived excited states and high luminescence efficiencies, the complexes containing iridium can serve as dopants for organic light emitting diodes (OLEDs).[11] This work reports on the first photochromic iridium (III) complex (Py-BTE)$_2$Ir(acac) (Scheme 1) coordinated directly to the thiophene ring of the photochromic unit, which is different from most other complexes in which the diarylethene ligands are coordinated by the ethene-bridge or the pendants to the bis(thienyl)cyclopentene core.[12] The molecular structure of (Py-BTE)$_2$Ir(acac) has been characterized by NMR, EI-MS, and X-ray crystallography. The photochromic properties, such as the absorption, luminescence of (Py-BTE)$_2$Ir(acac), were investigated in detail.

Scheme 1. Synthesis Route of the Complex (Py-BTE)$_2$Ir(acac)



The ligand Py-BTE was synthesized by a Suzuki coupling reaction of 1,2-bis(5-cholo-2-methyl-3-thienyl) cyclopentene with 2-bromine-pyridine (yield, 41%). The target complex was prepared according to a modified procedure for (C^N)$_2$Ir(LX)[13] from IrCl$_3$·nH$_2$O (see Supporting Information). The procedure involves two steps. In the first step, IrCl$_3$·nH$_2$O was reacted with excess of the Py-BTE ligand to give a dichloro-bridged dimer. Then the dimer can be readily converted to an emissive, monomeric complex by replacing the bridging chlorides with bidentate, acetylacetonate. Due to the steric hindrance, only one of the pyridine moieties in Py-BTE participated in the coordination and the single-crystal structure was confirmed by the X-ray crystallographic data.

The absorption spectra of (Py-BTE)$_2$Ir(acac) and Py-BTE are shown in Figure 1. The two compounds exhibit excellent photochromic performance in THF. After the irradiation at 313 nm, Py-BTE in THF turned from colorless to purple and its absorption maximum located at 560 nm. The absorption of open form Py-BTE in THF was at ca. 320 nm, which was ascribed to ($\pi \rightarrow \pi^*$)^1 and n $\rightarrow$ π^* transition of the pyridine moiety and thiophene rings. Upon ultraviolet (UV) irradiation at 313 nm, two additional absorption bands appeared at ca. 378 nm and 480−620 nm. These new absorption bands at longer wavelengths were tentatively assigned as absorptions of the closed form, resulting from the photocyclization of the open forms upon UV light irradiation. Similarly, (Py-BTE)$_2$Ir(acac) turned from light yellow to green and its absorption maximum located at 647 nm after $\lambda \leq 330$ nm light irradiation. In the UV region, the absorption band of (Py-BTE)$_2$Ir(acac) in its open form showed a slight red shift at ca. 330 nm compared with Py-BTE. Meanwhile, a new absorption band was observed at ca. 450 nm, similar to that found in other iridium complex like (thp)$_2$Ir(acac),[8] which could be ascribed to a MLCT [dπ(Ir) $\rightarrow$ π^*(Py-BTE)] transition and ($\pi \rightarrow \pi^*$),^{3} with some mixing of metal-perturbed intraligand (IL) ($\pi \rightarrow \pi^*$) transition. Upon irradiation into the bands ($\lambda > 550$ nm) of the closed form of (Py-BTE)$_2$Ir(acac), photocyclo-reversion could occur (Scheme 2). (Py-BTE)$_2$Ir(acac) also showed new absorption bands at ca. 378 nm, 492 and 649 nm after UV irradiation. Such a large shift of the absorption bands of the closed form of the complex (Py-BTE)$_2$Ir(acac) to the NIR region could be attributed to the delocalizaion of the π-conjugation leading to a reduced HOMO−LUMO energy gap for $\pi \rightarrow \pi^*$ and n $\rightarrow$ π^* transitions. The quantum yields corrected for the active conformer for the photocyclization were determined [Py-BTE, $\Phi_{330} = 0.30$, (Py-BTE)$_2$Ir(acac), $\Phi_{330} = 0.20$], which were found to be much higher than those for photocycloreversion [Py-BTE, $\Phi_{550} = 0.016$, (Py-BTE)$_2$Ir(acac), $\Phi_{550} = 0.01$]. The closed and open forms of

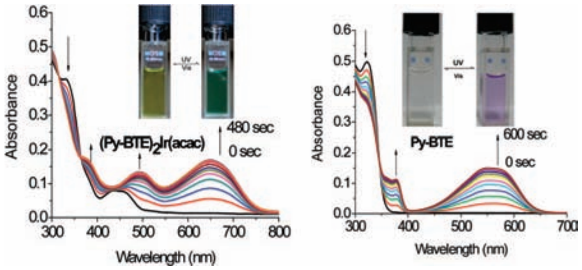
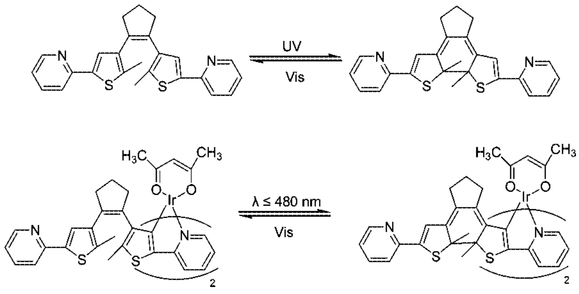


Figure 1. UV−vis absorption spectral changes of the complex (Py-BTE)$_2$Ir(acac) (1×10^{-5} M) and Py-BTE (1×10^{-5} M) in THF at 298 K upon irradiation with UV light.

Scheme 2. Photochromism of Py-BTE and (Py-BTE)$_2$Ir(acac)



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$(Py\text{-}BTE)_2Ir(acac)$ were stable after stored for seven days at 353 K in the dark.

Referring to a similar metal complex with a photochromic moiety just like $[Re(CO)_3(\mathbf{L})Cl]$,[5c] $Pt(\mathbf{L})(C{\equiv}CPh)_2$,[14] besides irradiation at 313 nm that triggered photocyclization originated from the IL transition, irradiation into the MLCT absorption bands of $(Py\text{-}BTE)_2Ir(acac)$ with $\lambda \leq 480$ nm also gave rise to photocyclization (see Scheme S1, Supporting Information).[6a]The spectra changes upon the irradiation at 480 nm was shown in Figure S1, Supporting Information. To verify the triplet photoreactivity of the ligands in $(Py\text{-}BTE)_2Ir(acac)$, a DFT computational study has been performed on Py-BTE. The properties of PES calculated for Py-BTE have much in common with those of the (1,2-bis(2-methylbenzothiophene-3-yl) maleimide) DAE unit in Ru-DAE (the photochromic DAE unit coupled to a ruthenium polypyridine chromophore) and $Ru\text{-}CH_2\text{-}DAE$ dyads,[15] which reinforces the triplet photoreactivity of Py-BTE in $(Py\text{-}BTE)_2Ir(acac)$.

However, $(Py\text{-}BTE)_2Ir(acac)$ shows phosphorescence at room temperature (298 K), while the other metal complexes like Ru and Re complexes[5,14,15] give measurable emission only at low temperature (77 K). The optical properties of the compounds are summarized in Table S2, Supporting Information. The photochromic properties of $(Py\text{-}BTE)_2\text{-}Ir(acac)$ in solid film are similar with that in THF solution. Upon excitation at 313 nm, the Py-BTE in THF solution produced luminescence at 420 nm with very weak intensity ($\tau_o < 0.1\ \mu s$). This emission was assigned as IL ($\pi \rightarrow \pi^*$) fluorescence referring to the similar investigation,[12] most probably derived from pyridinthiophene moiety. On the other hand, upon MLCT excitation at 440 nm the open form of $(Py\text{-}BTE)_2Ir(acac)$ in THF resulted in light emission with a maximum at 570 nm [$\tau_o = 0.16\ \mu s$, Φ_{em} (λ_{ex} 440 nm) = 0.06, see Supporting Information]. With reference to previous spectroscopic studies on related bis-cyclometalated iridium (III) complexes,[8] this emission could be assigned as ^{3}MLCT phosphorescence. Upon $\lambda \leq 330$ nm irradiation on the open form of the complex $(Py\text{-}BTE)_2Ir(acac)$, photocyclization took place, and the emission intensity at ca. 570 nm was found to be decreased and finally quenched. When the closed form of $(Py\text{-}BTE)_2Ir(acac)$ was exposed to visible light, the emission could be slowly recovered and the cycle could be repeated many times without any significant degradation in fluorescence intensity (Figure 2b). The emission spectral changes of the complex $(Py\text{-}BTE)_2Ir(acac)$ are shown in Figure 2a. Strong spin−orbit coupling of the iridium ion in the complex leads to efficient intersystem crossing of the singlet and triplet excited states, via spin−orbit coupling, removes the spin-forbidden nature of the radiative relaxation of the triplet state, leading to long lifetime phosphorescence. Viewing the absorption and emission spectra in Figure 1a and Figure 2a, there is efficient overlap between the absorbance for the closed form of $(Py\text{-}BTE)_2Ir(acac)$ and the emission from the triplet-state, while for the open form the overlap was absent. It is suggested that intramolecular quenching of the triplet-state through energy transfer should be efficient only in the closed form, resulting in a decrease in the emission intensity relative to its open form. Thus the luminescence quenching can be ascribed to intramolecular energy transfer due to an efficient overlap between the absorption and emission band.

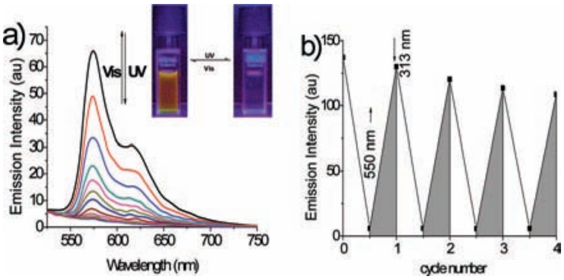

Figure 2. (a) Emission spectral changes of $(Py\text{-}BTE)_2Ir(acac)$ (1×10^{-5} M) in THF upon MLCT excitation at 440 nm at 298 K. (b) The figure shows modulated emission of the complex at 570 nm when the sample is alternately irradiated with 313 nm and 550 nm light.

X-ray crystallographic studies have been carried out for the complex $(Py\text{-}BTE)_2Ir(acac)$ (CCDC 690447). The single crystal was obtained by controlling a very slow evaporation of its solution in chloroform and hexane at room temperature. Only the crystallographic data of the open form is available. The Ir atom in this complex is octahedrally coordinated by three chelating ligands, with the pyridyl groups in a trans disposition, as shown schematically in Figure 3. Since the photocyclization reactivity of diarylethene crystals with antiparallel conformational molecules is determined by the

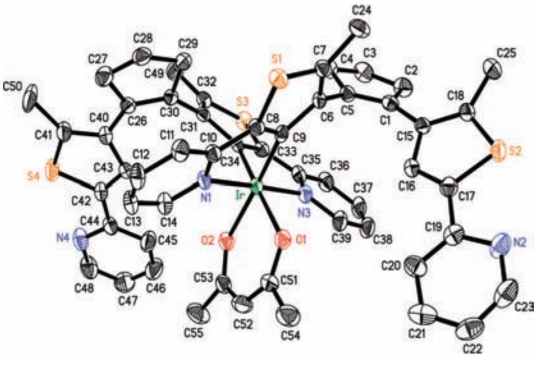

Figure 3. Crystal structure of $(Py\text{-}BTE)_2Ir(acac)$.

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distance between the reactive carbon atoms in the single-crystalline phase orientation,[16] the photocyclization of (Py-BTE)$_2$Ir(acac) single crystal is suppressed. The crystal structure can not carry out photochromic reaction since the intramolecular distance between the reactive carbon atoms $C_7 \cdots C_{18}$ and $C_{32} \cdots C_{41}$ are 4.575(1) and 4.713(1) Å, respectively. Furthermore, the Py-BTE ligand in the complex adopts a parallel conformation in the crystalline phase with the dihedral angles of 66.55(2) and 75.81(2)°.

In summary, a novel iridium complex coordinating to the photochromic diarylethene derivative Py-BTE was prepared and near-infrared photochromic behaviors of (Py-BTE)$_2$-Ir(acac) complex were investigated. (Py-BTE)$_2$Ir(acac) showed excellent photochromic properties such as thermal stability and fatigue resistance accompanied by efficient quenching of phosphorescence emission by the closed form of the diarylethene moiety. Currently, there still are two active pyridine moieties of complex (Py-BTE)$_2$Ir(acac), we are developing utilization of the active spot for further investigation.

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Supporting Information Available: Synthetic procedures of (Py-BTE)$_2$Ir(acac), the DFT computional study of Py-BTE, full characterization for the new compounds described in this paper, and the crystal data (CCDC 690447) of the complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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