Reversible Photon-mode Phosphorescence Switching of Heteroleptic Cyclometalated Iridium(III) Complexes via Photochromic Bisthienylethene Switch Linked to Ancillary Ligand

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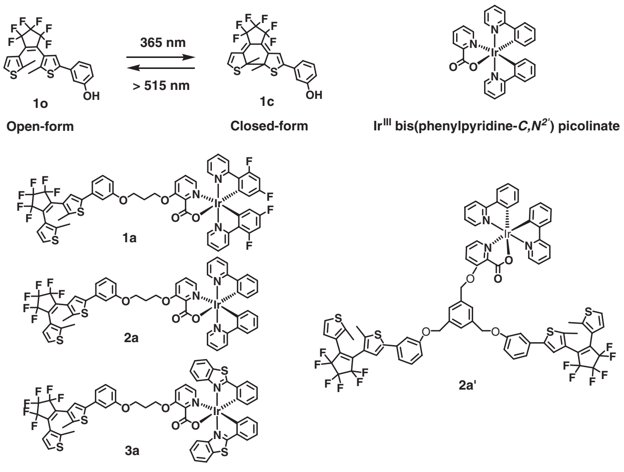
A novel class of heteroleptic Ir^{III} complexes covalently linked with photochromic bisthienylethene (BTE) switch showed optically addressed modulation in blue, green, and yellow phosphorescence. Additional enhancement of phosphorescence modulation was successfully achieved by the incorporation of multiple BTE switches or by the use of intermolecular energy transfer.

Photochromic compounds have attracted remarkable attention because of their potential capability as the optical memory media and optical switching devices.[1] Among the various photochromic compounds, 1,2-bisthienylethene (BTE) derivatives are the most promising candidate for the practical application owing to their high thermal stability, excellent photofatigue resistance, and fairly high photocyclization quantum yield.[2]

Cyclometalated Ir^{III} complexes are the most valuable emitting materials for the highly efficient organic light emitting diodes (OLEDs).[3] Strong spin–orbit coupling induced by the core Ir^{III} metal provides relatively short phosphorescent lifetime, which allows 100% of internal quantum efficiency, in principle. In this regard, many different classes of Ir^{III} complexes have been synthesized and are extending their application to the various interdisciplinary fields, such as oxygen sensing, biological imaging, and ion sensing.[4]

Considering the novel class of photoluminescence memories and switches, very recently, bistable emission switching of several metal complexes (metalloporphyrin,[5a] W complex,[5b] Os complex,[5c] Ru complex,[5c] and Eu complex[5d]) incorporating covalently linked BTE switches have been demonstrated. The photochromic switching of highly phosphorescent Ir^{III} complex emission, however, has not been attempted yet in spite of its technical significance. One of its potential applications, especially in polymer matrices, is related to the optically addressable electrophosphorescent memory device, in which signal write/erase processes are performed optically whereas the saved information is read electrically. In this letter, we report on the synthesis and phosphorescence switching behavior of a series of photochromic Ir^{III} complexes with ancillary ligands (*LX*) tethering BTE unit via covalent bonds ($Ir^{III}(C^\wedge N)_2(LX)$; **1a**, **2a**, **2a′**, and **3a** which show blue, green, and yellow phosphorescence, respectively: see Scheme 1).

Synthesis was straightforward to give the photochromic Ir^{III} complexes with BTE unit.[6] To a BTE unit, which was synthesized by the literature method,[7a,b] an ancillary ligand (*LX*) of a methyl picolinate was covalently attached via a propyloxyphenyl linkage in order to restrict the electronic delocalization in the excited states. This is because the direct electronic coupling generally brings about the unfavorable interference of photochromic reaction and phosphorescence emission, which often limits the reversible photochromism of the BTE switches.[5a] In addition, the BTE-linked ancillary ligand was not expected to alter the phosphorescence emission because it is known that the triplet energy of the picolinate is sufficiently higher than those of cyclometalating ligands (2-(2,4-difluorophenyl)pyridine, 2-phenylpyridine, and 2-phenylbenzothiazole).[7c,d] From the μ-chloride-bridged Ir^{III} dimers and BTE-linked picolinate ligand, photochromic Ir^{III} complexes **1a**, **2a**, **2a′**, and **3a** were successfully synthesized under mild chelating condition. Phosphorescence emission of Ir^{III} complexes originating from the metal to the cyclometalating ligand charge-transfer (MLCT) state of Ir^{III} complexes must overlap with the absorption band of the closed-form BTE for the efficient energy transfer resulting in the phosphorescence switching. When the solutions of open-form isomers **1a**, **2a**, **2a′**, and **3a** (2.0×10^{-5} M in Ar-saturated THF) were irradiated with 365-nm UV light for 5 min, the closed-form isomers were effectively generated to reach the photostationary state (PSS) (the maximum conversions were 90, 78, 90 (one closed-form 87 and two closed-forms 3), and 67%, respectively).[2] As shown in Figure 1b, representatively, a new broad absorption band in the visible region (450–700 nm) appeared upon the photocyclization of the BTE unit ($\Phi_{pc}{}^{o\rightarrow c} = 0.28$), which was reversibly restored to the initial open-form state by exposure to the visible light (>515 nm, $\Phi_{pc}{}^{c\rightarrow o} = 0.027$).



Scheme 1.

The open-form isomers of Ir^{III} complexes **1a**, **2a**, and **3a** were moderately phosphorescent ($\Phi_p = 0.04$, 0.08, and 0.03, respectively) with the maximum emission peaks at 483, 513, and 556 nm, respectively, when excited with 355 nm light.[6] On the other hand, the complexes showed significantly reduced

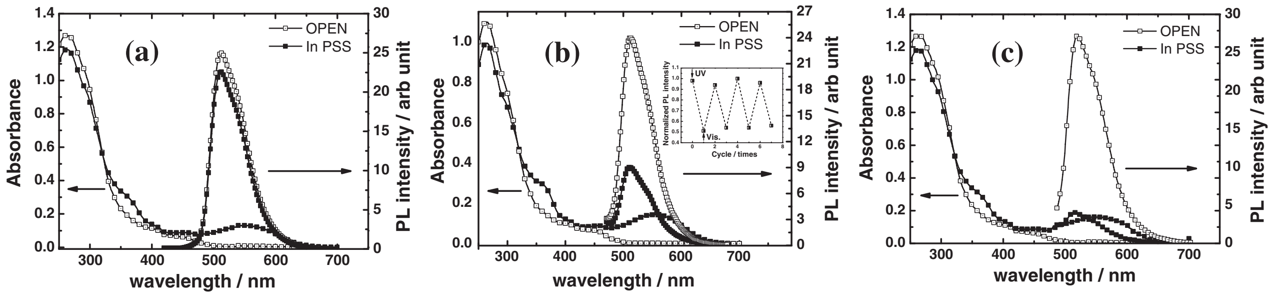


Figure 1. Absorption and phosphorescence spectra of (a) a simple mixture of **1o** and $\mathrm{Ir^{III}}$ bis(phenylpyridine-$C,N^{2'}$) picolinate (total 2×10^{-5} M in CH_2Cl_2, 1:1 by molar ratio), (b) **2a** (2.0×10^{-5} M in Ar-saturated THF, inset shows the bistable modulation of **2a** phosphorescence with alternate UV (365 nm, hand-held lamp, 4 W) and visible light (>515 nm, Xe arc lamp, 300 W) irradiation), and (c) **2a′** (2.0×10^{-5} M in Ar-saturated THF). For plots of **1a** and **3a**, see Supporting Information.

phosphorescence emission ($\Phi_p = 0.013$, 0.018, and 0.011, respectively) in the 365-nm PSS in spite of the inconsistency in spin states of the triplet MLCT and the singlet HOMO–LUMO absorption of the closed-form BTE.[5a] It should be noted that a simple molecular mixture (total 2.0×10^{-5} M in CH_2Cl_2, 1:1 by molar ratio) of **1o** and $\mathrm{Ir^{III}}$ bis(phenylpyridine-$C,N^{2'}$) picolinate, which was a reference system of **2a**, exhibited virtually no phosphorescence switching as shown in Figure 1a. This observation implies that the design of $\mathrm{Ir^{III}}$ complexes with a covalently tethered photochromic BTE unit is an essential element in this phosphorescence switching. It was also noted that the phosphorescence switching was most pronounced for **2a** giving the Φ_p on/off ratio of ≈4.4 in the 365-nm PSS, whereas **1a** and **3a** gave the Φ_p ratios of ≈3.1 and ≈2.7, respectively.[8] This is because the phosphorescence spectrum of **2a** overlaps with the absorption spectrum of the closed-form BTE to the larger extent than those of **1a** and **3a**, enabling more efficient intramolecular energy transfer from the $\mathrm{Ir^{III}}$ complex to the closed-form BTE unit. It is also worth mentioning that the irradiation of the closed-form isomers in the 365-nm PSS with a wavelength greater than 515 nm regenerated the initial open-form isomers and concomitantly restored the initial phosphorescence intensity as shown in Figures 1b and 2 for the complex **2a**.

Aiming at the further enhancement of Φ_p on/off ratio in the 365-nm PSS, we have devised a new structure of $\mathrm{Ir^{III}}$ complex **2a′** having two energy accepting BTE units. As expected, the complex **2a′** showed enhanced Φ_p on/off ratio (≈10, Φ_p of **2a′** $= 0.09$, Φ_p in the 365-nm PSS $= 0.009$) compared with that of **2a** (≈4.4) due to the increased energy-transfer capacity as shown in Figure 1c ($\Phi_{pc}{}^{o\to c} = 0.23$ and $\Phi_{pc}{}^{c\to o} = 0.025$). Compared to the phosphorescent lifetime (1.4 µs) of the $\mathrm{Ir^{III}}$ bis(phenylpyridine-$C,N^{2'}$) picolinate, the complexes **2a** and **2a′** in the 365-nm PSS showed much shorter phosphorescent lifetimes (117 ns, $k_{ET} = 1.32 \times 10^5\ s^{-1}$ and 57 ns, $k_{ET} = 1.28 \times 10^5\ s^{-1}$, respectively).[6] Such significant reductions in lifetimes in the 365-nm PSS are most likely caused by the efficient intramolecular energy transfer from the phosphorescent $\mathrm{Ir^{III}}$ complexes to the closed-form BTE units. Shorter lifetime of **2a′** than that of **2a** in the 365-nm PSS is in good accordance with the higher Φ_p on/off ratio.

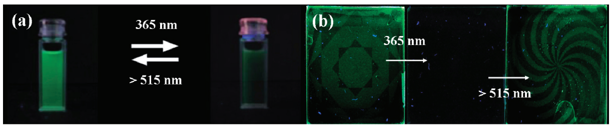


Figure 2. (a) Photographs showing bistable phosphorescence switching of **2a** (2.0×10^{-5} M in Ar-saturated THF) and (b) photopatterned images in a PMMA film doped with 2 wt % of **2a**.

Finally, even more enhanced Φ_p on/off ratio was successfully achieved when the $\mathrm{Ir^{III}}$ complexes were doped into the polymer matrix at high concentration owing to the effective intermolecular energy transfer in addition to the intramolecular energy transfer.[7a,b] Indeed, the Φ_p of **2a** in a poly(methyl methacrylate) (PMMA) matrix (2 wt %) was dramatically reduced in the 365-nm PSS (Φ_p on/off ratio > 50) as shown in Figure 2b, in which two different optical masks were used for the photoimaging process to fully demonstrate the bistability and erasability in a polymer matrix.

In conclusion, we have synthesized and demonstrated a novel class of photochromic $\mathrm{Ir^{III}}$ complexes showing reversible phosphorescence switching.

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6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett: Details of synthesis including spectroscopic identifications and plots of UV–vis absorption and photoluminescence spectra of **1a** and **3a** as well as the transient photoluminescence profiles of **2a**, **2a′**, and the reference material.

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8 The definition of Φ_p on/off ratio is (Φ_p in the open-form isomer)/(Φ_p in the 365-nm PSS).

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