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Turning On MLCT Phosphorescence of Iridium(III)—Borane Conjugates upon Fluoride Binding

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Supporting Information

ABSTRACT: The heteroleptic complexes $(C^{\wedge}N)_2 Ir^{III}$ ($C^{\wedge}N$: ppy, **2**; btp, **3**), bearing a 4-(dimesitylboryl)benzoate (Bbz) auxiliary ligand, and their fluoride adducts were prepared and characterized. While the PL spectra of **2** and **3** exhibit very weak emission in solution, the addition of fluoride turned on $(C^{\wedge}N)_2Ir$ -centered phosphorescence (λ_{em} 527 nm for **2** and 617 nm for **3**). Experimental and DFT calculations suggest that the weak emission is ascribable to a photoinduced electron transfer from the MLCT state of the $(C^{\wedge}N)_2Ir$ moiety to the Bbz ligand and is switched on by fluoride binding to the



to the Bbz ligand and is switched on by fluoride binding to the boron center of the Bbz ligand.

The detection of anions such as fluoride and cyanide has recently attracted great interest due to their detrimental effects on humans and the environment. Among various chemosensors that have been developed, triarylborane receptors which utilize a strong Lewis acid—base interaction between the boron atom of triarylborane and anions have been found to be very efficient for sensing small nucleophilic anions.¹ While most of the design principles for the sensing of anions using triarylboranes are based on absorption, color, and fluorescence changes upon anion binding, phosphorescent sensors based on heavy-metal complexes have also attracted great attention due to their advantageous photophysical properties, such as large Stokes shifts, long emission lifetimes, and high quantum efficiency, thereby providing high signal-to-noise ratios and easy separation of signal.²

In this regard, triarylboranes containing transition-metal moieties of Pt(II),^{3,4} Re(I),⁵ Ru(II),⁶ Cu(I),⁴ Hg(II),⁷ and $Ir(III)^{8,9}$ have been utilized successfully as phosphorescent sensors for anions over the past few years. Among these sensors, cyclometalated Ir(III) complexes are particularly intriguing, due to their easily tunable phosphorescence color depending on the type of cyclometalating ligand ($C^{N}N$), high quantum efficiency, and high stability under ambient conditions.¹⁰ In the reported examples to date, the borane moiety is linked directly to a $C^{N}N$ ligand to form a conjugate receptor ligand (Chart 1). Changes in the electronic structure of the $C^{N}N$ ligand before and after anion binding induce changes in the triplet (${}^{3}MLCT$, ${}^{3}LLCT$) signal of the complex, thereby realizing detection of the anion.

However, one drawback of such a sensing scheme may arise from the difficulty in predicting whether changes in the emission wavelength or intensity upon anion binding will be Chart 1



sufficiently perceivable. In addition, fluoride binding in the reported borane–Ir(III) conjugates was accompanied by a phosphorescence decrease, i.e., a turn-off response toward fluoride binding, although Huang and co-workers recently demonstrated that a triplet–singlet switch in the Ir(III) complex III bearing a borane– C^N conjugated ligand could provide an efficient ratiometric probe.⁸

Since turn-on responses would be beneficial from an analytical point of view,^{11,12} it is highly desirable to design and prepare "OFF–ON"-type phosphorescent sensors. To this end, we turned our attention to the design of nonemissive heteroleptic Ir(III) complexes. If the introduction of a triarylborane moiety into the LX ligand of the heteroleptic Ir(III) complex leads to a nonemissive lowest excited state, anion binding may induce $(C^{\Lambda}N)_2$ Ir-centered phosphorescence. To test this hypothesis, we prepared the heteroleptic $(C^{\Lambda}N)_2$ Ir^{III} complexes **2** and **3** $(C^{\Lambda}N = 2$ -phenylpyridinato- C^2 ,N (ppy), 2-(2-benzothienyl)pyridinato- C^2 ,N (btp)) bearing a (4-dimesitylboryl)benzoate (Bbz) auxiliary ligand and

Received: September 26, 2011 Published: December 14, 2011

investigated their photophysical response upon fluoride binding.

The dimesitylboryl (BMes₂)-substituted benzoic acid BbzH (1) was prepared in good yield (72%) by reaction between the lithium salts derived from (4-BrPh)BMes₂ and solid CO₂ after an acidic workup. Reaction of 1 with the dimeric iridium(III) compound $[(ppy)_2Ir(\mu-Cl)_2Ir(ppy)_2]$ (2a) afforded the heteroleptic $(ppy)_2Ir(Bbz)$ (2) in moderate yield (65%) (Scheme 1).

Scheme 1. a



^aLegend: (i) for 2, Na₂CO₃, 2-ethoxyethanol, 120 °C, 65%, for 3, NEt₃, toluene, 110 °C, 75%; (ii) Et₄NF, toluene, 25 °C, 95% ($[2F]^{-}$), 93% ($[3F]^{-}$).

While a similar reaction of **1** with the dimeric btp iridium(III) starting compound resulted in very low yield, the use of the monomeric btp starting compound **3a** afforded the corresponding $(btp)_2Ir(Bbz)$ complex **3** in good yield (75%). The identities of **2** and **3** have been characterized by NMR spectroscopy, elemental analysis, and X-ray diffraction.

While the ¹H and ¹³C NMR spectra showed the expected resonances corresponding to the $(C^{\Lambda}N)_2$ Ir and Bbz moieties, the crystal structure of **2** confirmed the formation of a borane—Ir(III) conjugate (Figure S1 in the Supporting Information). The boron atom of the triarylborane adopts a trigonal-planar geometry ($\sum_{C-B-C} = 359.9^{\circ}$), and the benzoate is bound to the Ir atom via bidentate $O^{\Lambda}O$ chelation. The Ir-centered moiety bears two ppy ligands having a trans disposition of the pyridine rings, similar to the case for other $(ppy)_2$ Ir(LX) complexes.¹³⁻¹⁵ Geometrical parameters such as bond lengths and angles around the Ir atom are in a range similar to that reported for $(ppy)_2$ Ir($O^{\Lambda}O$) complexes containing three-atom chelates.¹³

To gain insight into the fluoride binding, neutral compounds 2 and 3 were converted into their fluoride adducts (Scheme 1). Treatment of 2 and 3 with Et₄NF in toluene smoothly led to tetraethylammonium salts of fluoroborate: $[2F]^-$ and $[3F]^-$, respectively. Along with the ¹¹B NMR signal at δ +5 ppm, the ¹⁹F NMR signal at δ –177 ppm confirmed the formation of a four-coordinate triarylfluoroborate. Moreover, the crystal structure of $[2F]^-$ was determined by an X-ray diffraction study (Figure 1). The asymmetric unit contains two independent molecules, denoted as **A** and **B**. Interestingly, despite very similar geometrical parameters, they exhibit Λ (molecule **A**) and Δ (molecule **B**) configurations for the Ir moiety (Figure S2 in the Supporting Information for molecule **B**). The structure of molecule **A** shows a fluoride coordinated



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Figure 1. Crystal structure of $[2F]^-$ in $[NEt_4][2F]$ (molecule A only) (40% thermal ellipsoids). The H atoms, solvent molecules, and $[NEt_4]^+$ are omitted for clarity.

to the boron center of the Bbz moiety accompanied by substantial pyramidalization ($\sum_{C-B-C} = 338.6^{\circ}$). In contrast, there is no noticeable change in the bonding geometry around the Ir center in terms of bond lengths and angles after fluoride binding.

To examine the fluoride ion binding properties, UV-vis titrations were first carried out with 2 (Figure 2, left).



Figure 2. (left) Spectral changes in the UV–vis absorption of **2** in CH₂Cl₂ (2.80 × 10⁻⁵ M) upon addition of Bu₄NF ((0–4.24) × 10⁻⁵ M). The inset shows the absorbance at 333 nm as a function of [F⁻]. The line corresponds to the binding isotherm calculated with $K = 8.0 \times 10^{6}$ M⁻¹. (right) PL spectra of **2** in aerated CH₂Cl₂ (2.87 × 10⁻⁵ M; λ_{ex} 420 nm) upon addition of Bu₄NF ((0–4.30) × 10⁻⁵ M).

Compound 2 features a broad absorption band in the region of 300–370 nm which was quenched upon addition of incremental amounts of fluoride. Comparison with the absorption spectra of 1 and $[2F]^-$ (Figures S3 and S4 in the Supporting Information) indicates that the band mainly arises from the dominant $\pi(\text{Mes})-p_{\pi}(\text{B})$ transition¹⁶ in the Bbz ligand and absorption quenching is associated with fluoride binding to the boron center of the Bbz ligand. The high fluoride binding constant (*K*) of $8.0 \times 10^6 \text{ M}^{-1}$ was estimated from the 1:1 binding isotherm.

While the lower energy band at 404 nm results from spinallowed metal-to-ligand charge transfer (¹MLCT), the band at 464 nm which tails to over 500 nm can be assigned to a mixture of spin-forbidden MLCT (³MLCT) and ³ π - π * transition of the ppy ligand (³LC). Both MLCT bands fall in a region similar to that reported for other (ppy)₂Ir(L) complexes (L = acetylacetonate,^{14,15} benzoate,¹³ bipyridine¹⁷). Interestingly, the MLCT bands remain almost unchanged after fluoride complexation, indicating that fluoride binding at the Bbz moiety has little effect on the electronic structure of the (ppy)₂Ir moiety. Next, changes in the PL spectrum of **2** upon fluoride addition were investigated. Compound 2 exhibits a very weak emission centered at 525 nm (λ_{ex} 420 nm, $\tau = 1.44$ μ s) (Figure 2, right). Comparison with PL spectra of other (ppy)₂Ir(L) complexes such as (ppy)₂Ir(benzoate)¹³ suggests that the weak emission corresponds to (ppy)₂Ir-centered phosphorescence originating from mixed ³MLCT and ³LC states. The structureless band shape also indicates the major involvement of ³MLCT in the emission. Remarkably, upon addition of fluoride, the intensity of the band gradually increases while retaining essentially the same emission wavelength (λ_{em} 527 nm, $\tau = 1.38 \ \mu s$ for $[2F]^-$). This result indicates that the formation of $[2F]^-$ activates efficient phosphorescence.

Similar absorption and emission features are also observed for 3 upon fluoride addition (Figure 3). While the absorption



Figure 3. (left) Spectral changes in the UV–vis absorption of **3** in CH₂Cl₂ (2.58 × 10⁻⁵ M) upon addition of Bu₄NF ((0–4.67) × 10⁻⁵ M). The inset shows the absorbance at 334 nm as a function of [F⁻]. The line corresponds to the binding isotherm calculated with $K = 9.0 \times 10^6$ M⁻¹. (right) PL spectra of **3** in aerated CH₂Cl₂ (2.68 × 10⁻⁵ M; λ_{ex} 470 nm) upon addition of Bu₄NF ((0–4.00) × 10⁻⁵ M).

band at 334 nm gradually decreases as a result of fluoride binding to the boron center of the Bbz ligand ($K = 9.0 \times 10^6$ M^{-1}), the red phosphorescence of 3 (λ_{em} 615 nm, $\tau = 1.25 \,\mu$ s), which is very weak in intensity, increases upon fluoride addition (λ_{em} 617 nm, $\tau = 1.61 \,\mu$ s for [3F]⁻). Moreover, the phosphorescence spectra clearly show mixed ³MLCT and ³LC (a shoulder) excited states in character, as typically observed in the emissive (btp)₂Ir complexes.^{14,18} The turn-on response for 3 (10-fold) is shown to be more pronounced than that for 2 (5.5-fold).

To investigate the origin of the weak emission of 2 and 3, first the PL spectra with high-energy excitation were obtained. Irradiation of 2 and 3 at 330 nm resulted in an intense Bbz-centered fluorescence (λ_{em} 434 nm), indicating that the excited states of the Bbz ligand are not strongly coupled with those of the ($C^{\Lambda}N$)₂Ir moiety (Figure S5, Supporting Information). Next, the PL spectrum of 2 at 77 K showed an intense ³MLCT band centered at 510 nm (Figure S6, Supporting Information). We also prepared Gd(Bbz)₃·2H₂O and obtained its phosphorescence spectrum, which showed a phosphorescence band at 545 nm (Figure S8, Supporting Information). These findings suggest that the energy transfer from the ³MLCT to ³LX state

of the Bbz ligand is not likely to occur in 3 because of the lower ³MLCT energy and is also not responsible for the weak phosphorescence of 2. Otherwise, all higher energy emission bands in 2 should have been quenched except for the ³LX band, as usually found for nonemissive $(C^{\Lambda}N)_2 Ir(DBM)$ $(C^{\Lambda}N = ppy,^{14,19} dfppy;^{20} DBM = dibenzolylmethane)$ complexes. Instead, it can be suggested that the weak emission is a consequence of an intramolecular photoinduced electron transfer (PET) process between the MLCT state as a donor and the Bbz as an acceptor. A similar PET process from an organic fluorophore to borane has been recently observed in a turn-on fluorescence sensor.¹²

DFT calculation results also support the involvement of the PET process in the weak emission of **2**. Orbital analyses on the optimized ground-state structure of **2** show that while the HOMO of **2** predominantly resides on the Ir atom and phenyl ring of the ppy ligand, the LUMO is localized on the Bbz ligand with a large contribution from the empty $p_{\pi}(B)$ orbital and the LUMO+1 bears a major contribution from the pyridyl ring of the ppy ligand (Figure 4). These features indicate that the



Figure 4. HOMO, LUMO, and LUMO+1 of 2 (top) and $[2F]^-$ (bottom) (isovalue = 0.04).

MLCT excited state formed from the HOMO–LUMO+1 transition may be attenuated by electron transfer to the Bbz acceptor, leading to quenching of the MLCT emission. In the case of $[2F]^-$, on the other hand, the LUMO and LUMO+1 are mainly located on the pyridyl ring of the ppy ligand, as has usually been observed in emissive $(ppy)_2$ Ir complexes.

Finally, the weak phosphorescence band of **3** was not significantly affected in the presence of small amounts (1 equiv) of other anions such as Cl⁻, Br⁻, I⁻, OAc⁻, NO₃⁻, and ClO₄⁻, as usually observed in the triarylborane-based receptors, but the addition of excess amounts of Cl⁻ and Br⁻ (>2 equiv) led to a gradual increase in the emission intensity (Figure S10, Supporting Information). Since the absorption band of the Bbz moiety remained unaffected, this observation may be related to the slow dissociation of Ir(O^{AO}) chelation due to the high affinity of Ir(III) toward halides.

In conclusion, we have demonstrated that the addition of fluoride to the weakly emissive heteroleptic $(C^{\Lambda}N)_2$ Ir^{III} complexes (2 and 3) bearing a 4-(dimesitylboryl)benzoate auxiliary ligand (Bbz) turns on $(C^{\Lambda}N)_2$ Ir-centered phosphorescence. It was suggested that fluoride binding to the Bbz ligand inhibits the PET process responsible for weak emission of 2 and 3 while switching on $(C^{\Lambda}N)_2$ Ir-centered ³MLCT phosphorescence. Although 2 and 3 didn't work in water, the concept described in this report could be utilized in designing highly sensitive turn-on phosphorescent sensors including

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those compatible in aqueous media, and relevant studies are ongoing.

ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving experimental, UV–vis and PL data, computational details, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENTS

This work was supported by the Basic Science Research Program (2009-0093818), World Class University (WCU) program (R33-2008-000-10003), and Priority Research Centers program (2009-0093818) through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology. Computational resources for this work were provided by the KISTI (KSC-2011-C2-18).

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