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Phosphorescent Dimesitylboryl-Appended Iridium(III) Complex for Fluoride Anion Sensing

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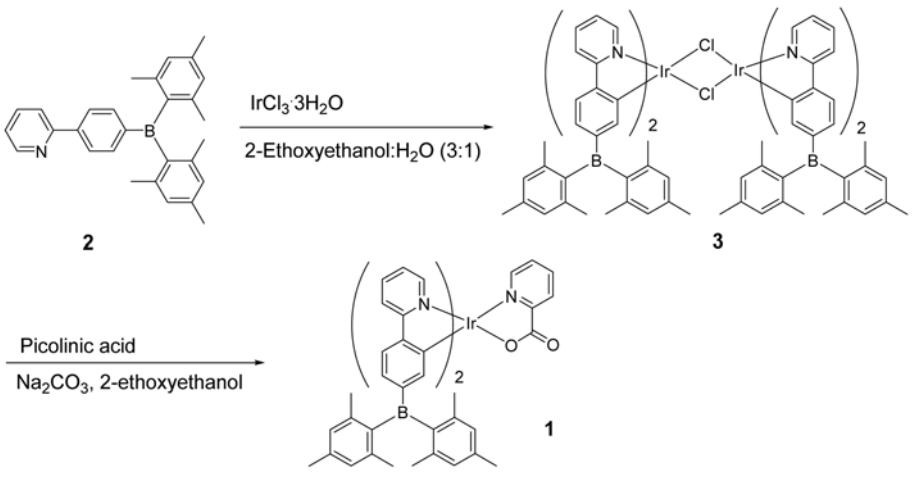
Key Words : Iridium(III) complex, Dimesitylboryl group, Phosphorescence quenching, Fluoride anion detection, Phosphorescent chemosensor

Owing to the importance of fluoride anion (F^-) in the treatment of osteoporosis[1] and dental care,[2] the recognition and sensing of fluoride anion is attracting attention. Many fluoride chemosensors containing (thio) ureas,[3] amides,[3c,4] pyrrole,[3d,5] and imidazolium ring[6] have been prepared to date. Those chemosensors usually form strong hydrogen bonds between their N-H hydrogens and fluoride anion. Recently, tri-coordinate organoboron compounds such as dimesitylboryl [$B(Mes)_2$] compounds have been found to achieve highly efficient fluoride anion detection using specific Lewis acid-base interaction.[7] Fluoride chemosensors based on tri-coordinate boron moiety such as $B(Mes)_2$ bind with fluoride anion to afford strong B-F interaction, which can change the lowest excited state or block the intramolecular charge transfer.[8] Thereby, the photophysical properties can be changed. However, the output signals of fluoride anion selective chemosensors have usually been absorption and/or fluorescence.[3c,9,10] Nowadays, phosphorescent chemosensors have also been developed for the detection of fluoride anions[11-13] since the first phosphorescent fluoride sensor reported by Gabbai *et al*.[14] Phosphorescent chemosensors are quite attractive because the relatively long life time of phosphorescence can eliminate the interference of the shorter-lived background fluorescence and/or scatterring light usually present in biological samples.[12] Among the various types of phosphors, cyclometalated iridium(III) complexes that have been used, for example, as an efficient phosphorescent dopant in organic light emitting diodes (OLEDs)[15] or as a phosphorescent chemosensor for the selective detection of mercuric ion[16] have excellent photophysical and electrochemical properties. However, only a few fluoride anion chemosensors based on iridium(III) complex have been reported.[12,17]

In this paper, we report the synthesis of a novel phosphorescent iridium(III) complex, Ir(*p*-B-ppy)$_2$picolinate (**1**), where *p*-B-ppy is 2-(4-(dimesitylboryl)phenyl)pyridine, and its application to the selective phosphorescent detection of fluoride anion.

A multi-step synthetic pathway leading to Ir(*p*-B-ppy)$_2$picolinate (**1**) is shown in Scheme 1. The main ligand (**2**), which was prepared by Suzuki coupling of 4-bromophenylboronic acid with 2-bromopyridine and then substitution of the bromo group with $B(Mes)_2$ group *via* the procedure reported,[18] was treated with iridium(III) chloride trihydrate in the mixed solvent of 2-ethoxyethanol and water to afford iridium chloride-bridged dimer **3**, [(*p*-B-ppy)$_2$IrCl]$_2$. The iridium chloride-bridged dimer **3** was then treated with picolinic acid in 2-ethoxyethanol in the presence of sodium carbonate to afford Ir(*p*-B-ppy)$_2$picolinate (**1**).

The UV-vis and photoluminescence spectra of Ir(*p*-B-



Scheme 1. Synthesis of iridium(III) complex **1**, Ir(*p*-B-ppy)$_2$picolinate.

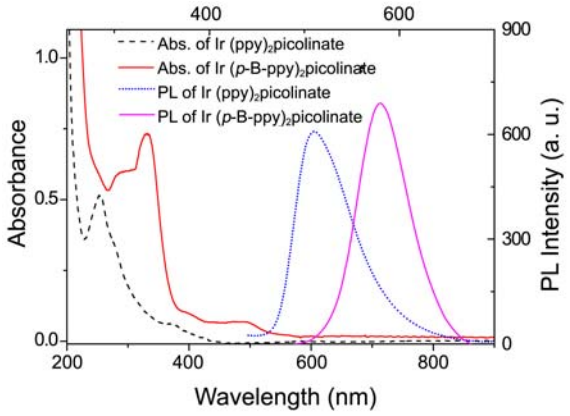


Figure 1. UV-vis and phosphorescence spectra of Ir(*p*-B-ppy)$_2$picolinate (**1**) (10 μM) and Ir(ppy)$_2$picolinate (10 μM) in acetonitrile (excitation: 392 nm for Ir(*p*-B-ppy)$_2$picolinate and 365 nm for Ir(ppy)$_2$picolinate).

ppy)$_2$picolinate (**1**) in acetonitrile were compared with those of Ir(ppy)$_2$picolinate, which does not contain B(Mes)$_2$ groups and was prepared according to the reported procedure,[19] in acetonitrile as shown in Figure 1. The weak absorption bands in the range of 400-600 nm of the UV-vis spectrum obtained with Ir(*p*-B-ppy)$_2$picolinate (**1**) (10 μM) can be assigned to spin-allowed metal-to-ligand charge transfer (^{1}MLCT) transition and spin-forbidden ^{3}MLCT transition. Due to the ligand-centered (LC) π-π* transition, there is an intense absorption band at around 280-350 nm. The photoluminescence spectrum of iridium(III) complex **1** (10 μM) in acetonitrile shows a maximum wavelength at 580 nm upon its excitation at 392 nm. The UV-vis and photoluminescence spectra of Ir(*p*-B-ppy)$_2$picolinate (**1**) shown in Figure 1 are quite red-shifted compared to those of Ir(ppy)$_2$-picolinate. The π conjugation in the phenylpyridine (ppy) ligand is expected to be extended through the boron atom of the B(Mes)$_2$ moiety and the extended π conjugation might be responsible for the red-shifted UV-vis and photoluminescence spectra of Ir(*p*-B-ppy)$_2$picolinate (**1**).

The binding affinities of the iridium(III) complex **1** (10 μM) for various anions (100 μM, tetrabutylammonium salts of F^-, Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, CN^-, $H_2PO_4^-$, AcO^-) were studied by the phosphorescence spectra in acetonitrile as shown in Figure 2. The phosphorescence was almost completely quenched upon the addition of fluoride anion while almost no-quenching was absorbed upon the addition of the other anions. The selectivity of iridium(III) complex **1** for various anions was graphically evaluated by the percent decrease ratio of the phosphorescence intensity, $(I_o–I)/I_o$ %, where I_o and I are the maximum emission intensities of iridium(III) complex **1** in the absence and presence of anion, as depicted in Figure 3. The iridium(III) complex **1** shows a pronounced selectivity for fluoride anion over the other anions. The high steric hindrance exerted by the B(Mes)$_2$ group of iridium(III) complex **1** might be responsible for the size-selective anion-boron binding interaction.[17]

To further investigate the binding properties of the iridium (III) complex **1** (10 μM) for fluoride anion, the absorption

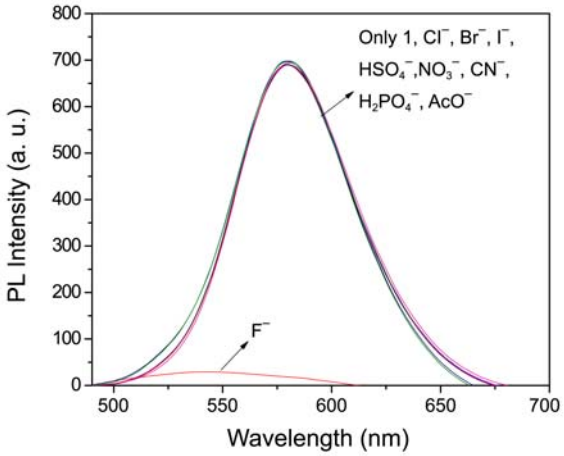


Figure 2. Phosphorescence spectra of iridium(III) complex **1** (10 μM) upon the addition of various anions (10 equiv) in acetonitrile (excitation: 392 nm).

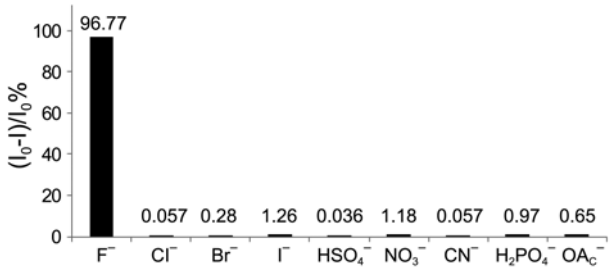


Figure 3. Comparison of the percent decrease ratio of the phosphorescence intensity of iridium(III) complex **1** (10 μM) in acetonitrile in the presence of 10 equiv of anions.

and phosphorescence titration experiments were carried out. The absorption titration spectra of iridium (III) complex **1** upon the addition of fluoride anion are shown in Figure 4. Upon the addition of fluoride anion, the absorption intensity of iridium(III) complex **1** at 330 nm was found to decrease constantly and, consequently, the color was changed from

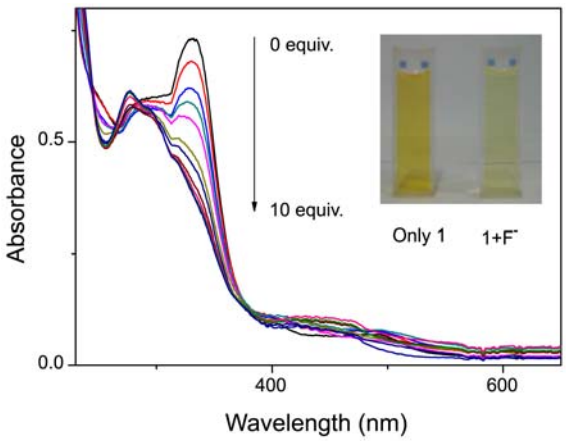


Figure 4. UV-vis titration spectra of iridium(III) complex **1**(10 μM) upon the addition of fluoride anion (10 μM, 20 μM, 30 μM, 40 μM, 50 μM, 60 μM, 70 μM, 80 μM, 90 μM, 100 μM) in acetonitrile.

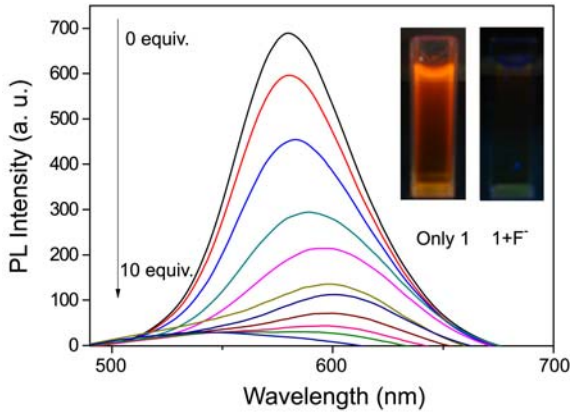


Figure 5. Phosphorescence titration spectra of iridium(III) complex **1** (10 μM) upon the addition of fluoride anion (10 μM, 20 μM, 30 μM, 40 μM, 50 μM, 60 μM, 70 μM, 80 μM, 90 μM, 100 μM) in acetonitrile (excitation: 392 nm).

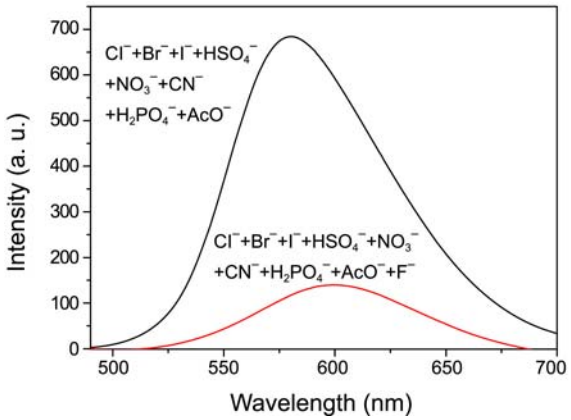


Figure 6. Phosphorescence spectra of iridium(III) complex **1** (10 μM) upon the addition of various anions together (Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, CN^-, $H_2PO_4^-$, AcO^-, 5.0 equiv for each) without fluoride anion and with fluoride anion (5.0 equiv for F^-). (excitation: 392 nm).

orange to pale yellow in the ambient light, which can be observed by the naked eye (Figure 4 inset). The strong B-F interaction between the $B(Mes)_2$ moieties of the complex and fluoride anion is expected to interrupt the π conjugation extended through the boron atom and, consequently, the absorption maximum should be blue-shifted upon the addition of fluoride anion.

The phosphorescence titration spectra of iridium(III) complex **1** upon the addition of fluoride anion are shown in Figures 5. As the concentration of fluoride anion was increased from 0 equiv to 7 equiv, the emission maximum shifted from 580 nm to 599 nm and the emission intensity was found to decrease constantly. As the concentration of fluoride anion was increased from 7 equiv to 8 equiv, the emission maximum shifted slightly from 599 nm 597 nm and the emission intensity was found to decrease slightly. As the concentration of fluoride anion was increased further from 8 equiv to 9 equiv and then to 10 equiv, the emission maximum shifted from 597 nm to 585 nm and then to 543 nm, but the emission intensity was found to remain almost constant. From the phosphorescence titration data, association constant (K) of iridium(III) complex **1** with fluoride anion was calculated to be 2.50×10^4 M^{-1} according to the Benesi-Hindebrand expression.[20]

Addition of other anions (5.0 equiv, Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, CN^-, $H_2PO_4^-$, AcO^-) together with fluoride anion (5.0 equiv), the phosphorescence was quenched quite much as show in Figure 6. It means that iridium(III) complex **1** displays high sensitivity for fluoride anion even in the presence of other anions. Iridium(III) complex **1** was found to form 1:2 complex with fluoride anion as shown by the Job's plot experiment (Figure 7).

In summary, a novel fluoride anion selective phosphorescent chemosensor based on iridium(III) complex bearing $B(Mes)_2$ groups was prepared. The chemosensor was found to exhibit outstanding high selectivity for fluoride anion. Upon the addition of fluoride anion to the acetonitrile solution of the chemosensor, the color of the solution was changed from orange to pale yellow and the phosphorescence was almost completely quenched. Consequently, the new iridium(III) complex (**1**) prepared in this study could be used for the selective detection of fluoride anion in acetonitrile even in the presence of other anions.

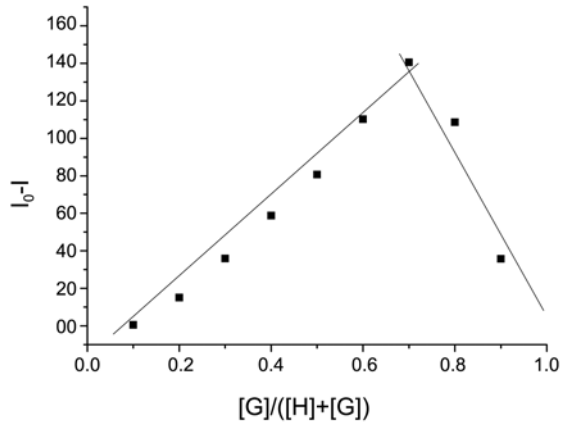


Figure 7. Job's plot for the complex formation between iridium(III) complex **1** and fluoride anion in acetonitrile.

Experimental Section

General. 4-Bromophenylboronic acid, *n*-BuLi (1.6 M in hexane), 2-bromopyridine, $Pd(PPh_3)_4$, dimesitylboron fluoride [$B(Mes)_2F$] were purchased from Aldrich. Iridium(III) chloride trihydrate was purchased from Acros organics.

All glass wares, syringes, magnetic stirring bars were completely dried. Reactions were monitored with thin layer chromatography (TLC). Commercial TLC plates (Silica gel 60 F_{254}, Merck Co.) were developed and the spots were seen under UV light at short wavelength of 254 nm and long wavelength of 365 nm. Silica column chromatography was done with silica gel 60 G (particle size 0.063-0.200 mm, 70-230 mesh ASTM, Merck. Co.)

The ^1H NMR and ^{13}CNMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer. High-resolu-

tion mass spectral data were obtained from the Korea Basic Science Institute Daegu Center (HR-FAB Mass) on a Jeol JMS 700 high resolution mass spectrometrer. Photoluminescentce (PL) spectra were measured in the range of 450-750 nm on a Jasco model FP-750 spectrofluorometer.

Synthesis of [(*p*-B-ppy)$_2$IrCl]$_2$ (3): 2-(4-(Dimesitylboryl)phenyl)pyridine (*p*-B-ppy, **2**, 0.5 g, 1.24 mmol), which was prepared by Suzuki coupling between 4-bromophenylboronic acid and 2-bromopyridine in the presence of $Pd(PPh_3)_4$ and then substitution of the bromo group with $B(Mes)_2$ group *via* the procedure reported,[18] $IrCl_3 \cdot 3H_2O$ (0.15 g, 0.41 mmol), 2-ethoxyethanol (21 mL), and H_2O (7 mL) were placed in a 100 mL one neck round bottom flask equipped with a condenser. The flask was evacuated and filled with nitrogen three times. The reaction mixture was refluxed for 24 hr and cooled to room temperature. The colored precipitate was filtered off and was washed with water and, then, ethanol to afford [(*p*-B-ppy)$_2$IrCl]$_2$ (**3**) as an orange-red solid. Yield: 0.4 g (80%). mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.16 (d, *J* = 7.69, 2H), 7.56 (d, *J* = 7.69, 2H), 7.29-7.36 (m, 4H), 6.85 (d, *J* = 7.69, 2H), 6.60 (s, 8H), 6.38 (m, 2H), 5.71 (s, 2H), 2.28 (s, 12H), 1.62 (s, 24H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 167.5, 151.9, 147.3, 146.4, 144.0, 142.2, 140.7, 138.9, 137.7, 135.7, 129.2, 127.9, 122.6, 122.0, 119.2, 23.2, 21.5. HR FAB-MS *m/z* [M$^+$] calcd for $C_{116}H_{116}B_4Cl_2Ir_2N_4$ 2064.8208, found 2064.8246; IR (KBr pellet) cm^{-1} 3445, 2916, 1606, 1238, 845.

Synthesis of Ir(*p*-B-ppy)$_2$picolinate (1): In a 50 mL one-necked round bottom flask equipped with a condenser were placed [(*p*-B-ppy)$_2$IrCl]$_2$ (**3**, 0.40 g, 0.19 mmol), picolinic acid (0.048 g, 0.39 mmol), sodium carbonate (0.21 g, 1.94 mmol) and 2-ethoxyethanol (20 mL). The reaction mixture was refluxed for 24 hr under N_2 and then cooled to room temperature. 2-Ethoxyethanol was removed by rotary evaporator. The residue was dissolved in dichloromethane. The organic solution was washed with brine and then dried over Na_2SO_4. The solvent was removed by rotary evaporator. The light yellow residue was purified by chromatography over silica gel (ethyl acetate/*n*-hexane/methanol, 1/1/0.1, v/v/v). Additional purification of the product by recrystallization (dichloromethane and *n*-hexane) afforded Ir(*p*-B-ppy)$_2$picolinate (**1**) as a red solid. Yield: 0.2 g (40%). mp 267-268 °C; ^{1}HNMR (300 MHz, $CDCl_3$) δ 8.58 (d, *J* = 7.67, 1H), 8.32 (d, *J* = 7.69, 1H), 7.83-7.89 (m, 2H), 7.63 (d, *J* = 7.69, 1H), 7.44-7.53 (m, 2H), 7.37-7.42 (m, 4H), 7.27-7.34 (m, 1H), 7.23-7.25 (m, 2H), 7.04 (d, *J* = 7.69, 1H), 6.97 (d, *J* = 7.69, 1H), 6.83 (t, *J* = 7.14, 1H), 6.65 (s, 9H), 6.16 (s, 1H), 5.98 (s, 1H), 2.30 (s, 12H), 1.75 (s, 24H); ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 173.2, 168.5, 166.9, 152.4, 149.0, 148.1, 147.8, 147.7, 146.1, 142.4, 142.3, 140.8, 140.7, 138.1, 137.7, 136.4, 128.0, 127.8, 122.4, 119.7, 23.4, 21.5; HR FAB-MS *m/z* [M$^+$] calcd for $C_{64}H_{62}B_2IrN_3O_2$ 1119.4657, found 1119.4653; IR (KBr pellet) cm^{-1} 3446, 2916, 1658, 1238, 897.

Phosphorescent Spectra Measurements. The phosphorescence measurements were carried out by exciting at 392 nm with excitation and emission band width of 20 nm. The sample solutions were prepared by mixing a measured amount of the stock solution of Ir(*p*-B-ppy)$_2$picolinate (**1**) with a measured amount of the stock solution containing anions and then diluting with acetonitrile to achieve the desired concentrations of Ir(*p*-B-ppy)$_2$picolinate (**1**) and anions.

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