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Phosphorescent cyanide sensor based on a 2-phenylpyridine(ppy)-type cyclometalated Ir(III) complex bearing dimesitylboron group with concentration distinguishing ability

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ABSTRACT

With a 2-phenylpyridine(ppy)-type cyclometalated Ir(III) complex with −B(Mes)$_2$ group **Ir−B**, the CN ions can bind effectively with the boron atom in the −B(Mes)$_2$ group to furnish CN sensing ability through inducing phosphorescence changing of the concerned Ir(III) complex. Uniquely, with increasing the added amount of CN ions, loose and tight binding between CN and boron atom in the −B(Mes)$_2$ group of **Ir−B** can occur in sequence to destabilize metal-to-ligand charge transfer (MLCT) excited states and then form new MLCT excited states in **Ir−B**. Accompanying this process, the red phosphorescence of **Ir−B** can be effectively quenched by adding CN ions, while new yellow and green emission bands can appear in sequent with increasing the amount of added CN ions, showing CN sensing behavior with unique concentration distinguishing ability. In addition, the new phosphorescent CN sensor can possess detection limit (DL) as low as 4.3×10^{-6} M and good selectivity to the CN ions. Clearly, these results can provide important information for developing new CN sensors with high performances.

1. Introduction

Recently, 2-phenylpyridine(ppy)-type cyclometalated Ir(III) complexes have drawn substantial research interests from both academic and industrial communities due to their strong phosphorescent ability and tunable emission color [1–3]. Owing to the strong spin-orbital coupling (SOC) effect induced by the heavy Ir(III) center, these complexes possess ability of emitting phosphorescent signal even at room temperature [4–6]. Hence, their phosphorescent ability have been applied to various fields, such as electroluminescence (EL) [7–9], bioimaging [10–12], optical power limiting [13–15], organic solar cells [16] and sensing [17] *etc.* Among all these applications, ppy-type cyclometalated Ir(III) complexes as sensors can show two major inherent advantages: 1) Generally, phosphorescent emission possesses large Stokes shift which can effectively avoid interference from the background emission; 2) With longer lifetime typically in the order of microsecond, phosphorescent emission can afford other detecting information except wavelength. Hence, various ppy-type cyclometalated Ir(III) complexes have been served as sensors with high performances [18–20]. Among all the ppy-type cyclometalated Ir(III) complex ion sensors, dimesitylboron (B(Mes)$_2$) unit is typically introduced into their ppy-type ligands. Owing to the strong bonding between F ions and the boron atom in the B(Mes)$_2$ units, ppy-type cyclometalated Ir(III) complexes with B(Mes)$_2$ group can act as F ion sensors [19,20]. Critically, these novel sensors can show unique concentration discrimination behavior in detecting F ions, indicating their great potential [19].

As another kind of important anions, CN ions are well-known for high toxic due to their inhibiting many heme-containing enzymes [21]. Hence, the United States Environmental Protection Agency (EPA) has set the maximum safe concentration for CN in drinking water at *ca.* 7.6 μM [22] and even lower safe CN concentration of *ca.* 2.5 μM is set by WHO International Standards [23]. As a result,

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sensing CN ions has become a very important research line. Recently, various CN sensors have been developed with diverse structures, such as organic molecules [24,25], metal complexes [26,27], nanoparticles [28] etc. Among them, CN sensors based on metal complexes can show advantages of easy preparation and environmental compatibility. Importantly, metal complexes can possess ability of phosphorescent emission which can guarantee high sensitivity and avoiding interference from background. For the time being, handful Zn(II) [29], Cu(II) [30], Co(II) [31], Os(II) [32] and Ni(II) [33] complexes have been prepared to detect CN ions with fluorescence or absorbance as reporting signal, which cannot afford the merits associated with phosphorescent reporting signal. Recently, phosphorescent Ir(III) [18–20] and Ru(II) [34,35] complexes have been employed to sense CN ions based on either addition reaction of the organic ligands with CN ions or bonding functional groups, such as -B(Mes)$_2$ [19,20,35]. Clearly, sensing CN ions by addition reaction may have chance to induce slow responding speed and high detection limit (DL). Generally, Ru(II) phosphorescent complexes possess low phosphorescent quantum yield (Φ_P), which might disfavor ion sensing with emission as reporting signal.

So, in this research, a highly phosphorescent ppy-type Ir(III) complex has been employed to detecting CN ions. It has been shown that both absorption and phosphorescent signals can show fast response to the external CN ions in THF solution with low DL. Critically, the phosphorescent signal of the this phosphorescent Ir(III) complex sensor can show multi emission-color response, indicating concentration distinguishing ability. The concerned results can provide useful information for design new phosphorescent CN ion sensors with high performance.

2. Experimental

2.1. General information

All commercially available chemicals used were not subjected to further purification. All solvents for the reactions were dried and distilled in the proper way. The reactions were checked with thin-layer chromatography (TLC) materials purchased from Merck & Co., Inc. Flash column chromatography and preparative TLC plates were made from silica gel from Shenghai Qingdao (300–400 mesh).

2.2. Synthesis

Synthesis for **Ir–B** was according to the well-established two-step strategy (Scheme S1 in Supporting Information, SI) [19,36]. The synthetic detail and spectral data for **Ir–B** was provided in SI.

2.3. Physical measurements

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 400 MHz spectrometer. Chemical shifts were referenced to the solvent residual peak at δ 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C NMR spectra, respectively. UV–vis absorption spectra were measured on a PerkinElmer Lambda 950 spectrophotometer. Emission spectra and lifetimes for the obtained complex were recorded on an Edinburgh Instruments, Ltd., (FLSP 920) fluorescence spectrophotometer. Phosphorescent quantum yields (Φ_p) was measured in CH_2Cl_2 solution against *fac*-[Ir(ppy)$_3$] ($\Phi_p = 0.97$) standard at 293 K [37]. The data of elemental analyses were obtained on a Flash EA 1112 elemental analyzer. Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT SSQ710 system.

2.4. Emission and absorption titration

A THF solution of [nBu$_4$N]CN (ca. 1×10^{-3} M) was added to a THF solution of the iridium complex (ca. 1×10^{-5} M) in a screw-capped UV or PL cell according to the target [B]: CN ratio *via* a micro-syringe. After gentle mixing, the solution in the UV or PL cell was allowed to stand in the dark for 5 min before measurement. The detection limit (DL) was determined from the absorption titration data based on the reported method [38]. The absorption intensity data at ca. 341 nm were taken to calculate the DL.

3. Results and discussion

3.1. Chemical structure and electronic spectra

Chemical structure of the employed phosphorescent ppy-type Ir(III) complex **Ir–B** is shown in Fig. 1a. It had been synthesized by our previous method [36]. In **Ir–B**, -B(Mes)$_2$ has been introduced to the pyridyl unit in each of the two ppy-type ligands (Fig. 1a). With sensing purpose, CN ions are supposed to bind with boron atom in the -B(Mes)$_2$ unit.

Fig. 1b shows the UV–vis absorption and photoluminescence (PL) spectra of **Ir–B** in THF. In the absorption spectrum of **Ir–B**, two kinds of absorption bands can be seen clearly with the strong π-π* absorption band from the organic ppy-type ligands and the low-energy weak absorption bands from metal-to-ligand charge transfer (MLCT) absorption bands (Fig. 1b). The strong red phosphorescent at ca. 600 nm in the PL spectrum of **Ir–B** has been confirmed to be induced by the radiative decay of the triplet MLCT excited states (^{3}MLCT). Importantly, **Ir–B** can possess very high phosphorescent quantum yield (Φ_P) of ca. 0.95, favoring its application in ion sensing by enhancing sensitivity.

3.2. CN ion sensing behavior

Based on the reported photophysical property of **Ir–B**, its phosphorescent emission is induced by the ^{3}MLCT excited states from by transferring electron from *d*-orbital of Ir(III) center to the p_π* orbital of the boron atom in the –B(Mes)$_2$ group [36]. If CN ions interact with boron atom, it should have a great chance to change the character of the ^{3}MLCT excited states of **Ir–B** and hence alter emission behavior of **Ir–B**. Obviously, response of the phosphorescent emission from **Ir–B** to the CN ions can act as the reporting signal for sensing CN ions. In addition, different from its Pt(II) analogs, **Ir–B** can possess two –B(Mes)$_2$ groups, which can facilitate interaction between –B(Mes)$_2$ groups and cyanide ions at low CN concentration. Obviously, it can lower the detecting limit in sensing CN ions. Hence, **Ir–B** should possess great potential to serve as novel CN ion sensor.

In order to evaluate ion sensing ability of **Ir–B**, with the controlled molar ratio between boron atom and CN ion (B: CN), THF solution of **Ir–B** had been titrated with the THF solution of [nBu$_4$N] CN employed to record variation of the phosphorescent spectrum of **Ir–B** at different B: CN. It has been found that the red phosphorescent emission at ca. 600 nm is quenched quickly with adding CN ion, while a new yellow emission band at ca. 550 nm gradually appears and is enhanced (Fig. 2). When B: CN value at 1:1, nearly 85% phosphorescent intensity at ca. 600 nm is quenched (Fig. 2). Adding more CN ion to maintain B: CNat about 1:4, the newly appeared yellow emission band reaches the highest intensity (Fig. 2). It should be noted that another new green-emission band at 520 nm can be detected obviously with B: CNat about 1:6 (Fig. 2). It means that low CN concentration can induce yellow emission and green emission can appear at higher CN concentration. The intensity variation for the three emission bands can be clearly

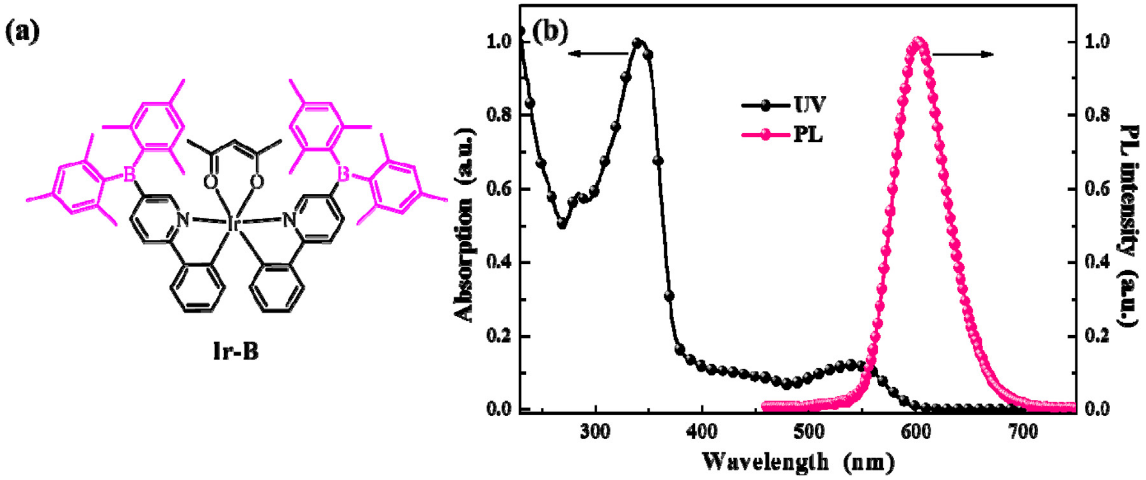

Fig. 1. (a) Chemical structure of **Ir**—**B**. (b) UV—vis absorption and PL spectra for **Ir**—**B** in THF at 298 K.

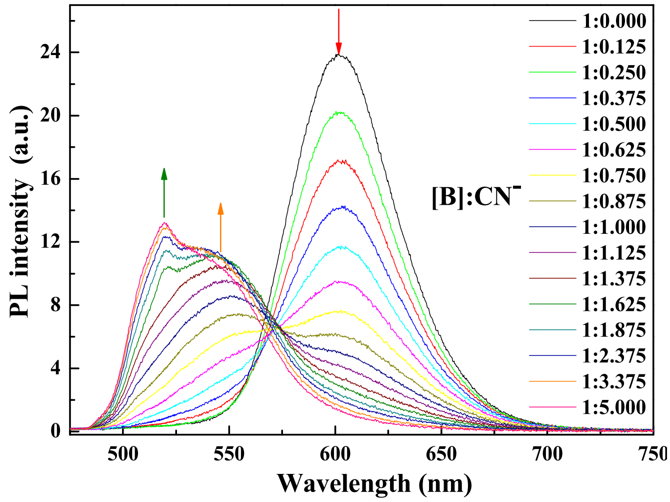

Fig. 2. Phosphorescence titration of **Ir**—**B** by [nBu$_4$N]CN in THF solution at 293 K.

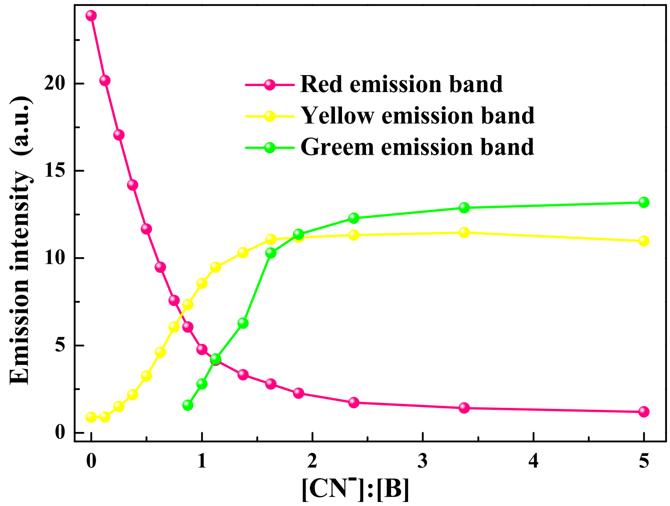

Fig. 3. Intensity variation for the three emission bands of **Ir**—**B** during the titration process with [nBu$_4$N]CN in THF solution at 293 K.

indicated by Fig. 3. Obviously, for ion sensor with emission as reporting signal, this is very unique sensing behavior with concentration distinguishing ability which typically cannot be observed in traditional sensors. Furthermore, the “off-on” phosphorescent response of **Ir**—**B** to the CN ions can benefit its practical application by avoiding using advanced instrument to detect emission signal with very low intensity in the “turn-on” ion sensors.

The unique sensing behavior of **Ir**—**B** can be explained as follows: When adding CN ions to the solution of **Ir**—**B**, the nucleophilic ability associated with CN ions make them inline to bind with empty p_π orbital of boron atom in the —B(Mes)$_2$ group of **Ir**—**B**. As aforementioned, the empty p_π orbital of boron atom in the —B(Mes)$_2$ group has host electron in the MLCT transition process to form MLCT excited states which induce the red phosphorescence of **Ir**—**B** (Fig. 4). Obviously, binding negative-charged CN ions will induce electrostatic repulsion between CN ions and the hosted electron from the MLCT procedure (Fig. 4). Obviously, the electrostatic repulsion will make the —B(Mes)$_2$ group reluctant to host electron and hence elevate energy-level of the MLCT excited states in **Ir**—**B**. As a result, new yellow-emission band with higher energy-level appears after adding CN ions (Fig. 2). At this stage, there is loose binding between CN ions and the boron atom in the —B(Mes)$_2$ group due to electrostatic repulsion (Fig. 4).

In addition, the electrostatic repulsion between CN ions and the hosted electron from the MLCT procedure should make the binding between CN ions and boron atom as equilibrium process. So, adding more CN ions should enhance the binding procedure to form “tight” binding between CN ions and boron atom. Perceptibly, the tight interaction will make the boron atom lost its ability of hosting electron in the MLCT excitation process. Alternatively, pyridyl ring in the ligand of **Ir**—**B** should host the electron in the MLCT process to form high-energy MLCT excited states due to the much weaker electron-accepting ability associated with the pyridyl ring. As a result, green-emission from these high-energy MLCT states can be observed at high CN concentration (Fig. 4). In addition, from the absorption titration results in Fig. 5, high-energy absorption bands at 400 and 470 nm do appear at high CN concentration with B: CN of 1:5. According to the published results, the complexes (ppy)$_2$Ir(acac) without —B(Mes)$_2$ can show green-emission (ca. 520 nm) induced by the ^{3}MLCT excited states formed by electron transferred from d-orbital of Ir(III) center to π* orbitals of the

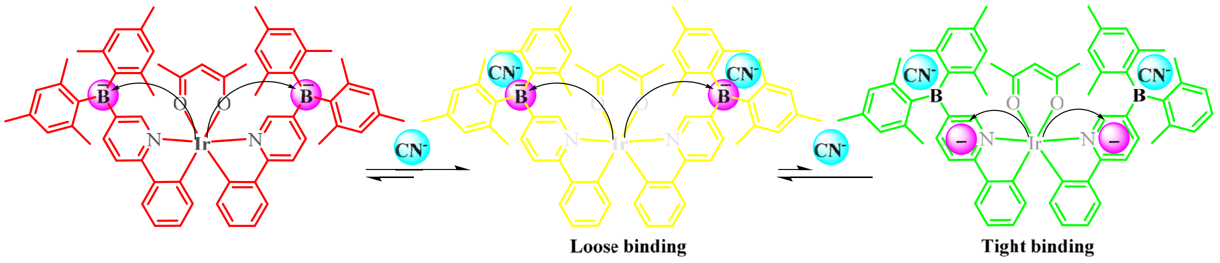

Fig. 4. Proposed CNsensing mechanism of **Ir**—**B**.

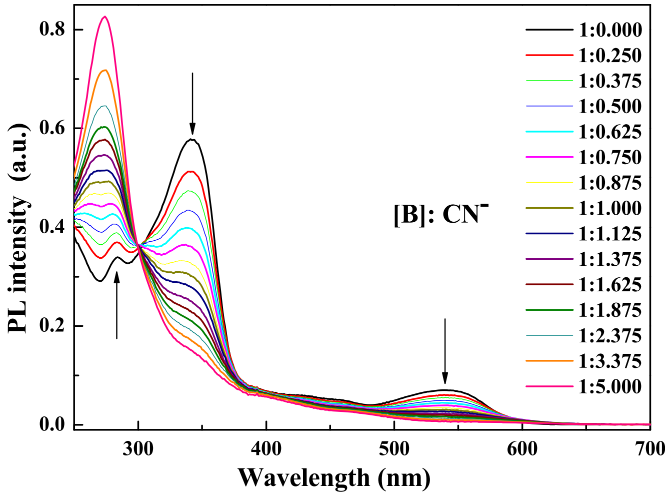

Fig. 5. Absorption titration of **Ir**—**B** by [*n*Bu$_4$N]CN in THF solution at 293 K.

pyridyl ring in the ligand. All these results can provide a solid based for explanation of the sensing mechanism presented in Fig. 4. From the PL titration result in Fig. 2, the green-emission cannot reach high intensity even at B: CN of 1:5 (Fig. 2). So, the “tight” binding between CN ions and boron atom in the —B(Mes)$_2$ group of **Ir**—**B** should be difficult to occur.

Detecting limit and selectivity are two key parameters to characterize the performance of ion sensors. According to the phosphorescence titration result, the detecting limit (DL) of **Ir**—**B** to the CN ions has been obtained as low as 4.3×10^{-6} M according to the reported method, showing potential for application. When five folds excess different anions were added to the THF solution of **Ir**—**B**, most of them, such as Cl, Br, I, BF$_4$, Ac, PF$_6$ and ClO4, cannot quench the red phosphoresce at 600 nm (Fig. 6). However, CN ions can effectively quench the red phosphorescence of **Ir**—**B** (Fig. 6). However, as indicated by our previous result, F ions can also quench the phosphorescence signal at 600 nm [19]. Fortunately, it has been shown that F ions can show much stronger binding with boron atom in the —B(Mes)$_2$ group of **Ir**—**B**. Hence, at high concentration, F ions can induce much stronger and greener emission band than CN ions (Fig. S1). In addition, wavelength of the green phosphorescence induced by CN ions is different from that induced by F ions as well (Fig. S1). These can be employed to differentiate CN from F ions in the sensing process. Hence, the sensor of **Ir**—**B** can exhibit good selectivity to the CN ions. The good selectivity of **Ir**—**B** to the CN ions can be assigned to the strong nucleophilic interaction between the CN ions and the empty p_π orbital of the boron atom in the —B(Mes)$_2$ group.

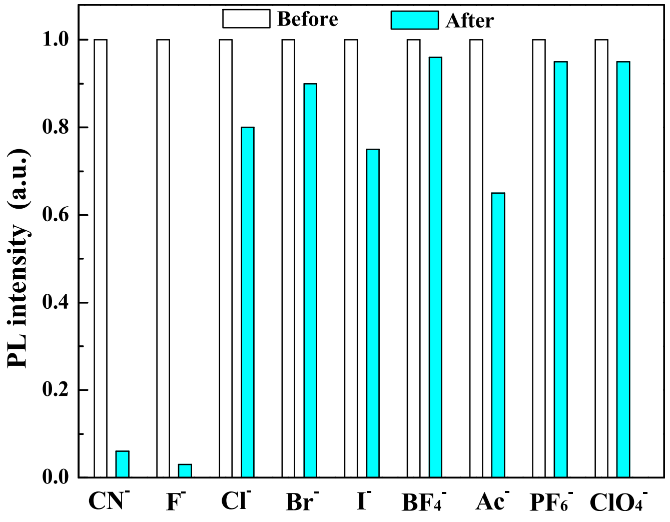

Fig. 6. Relative phosphorescence intensity at 600 nm for **Ir**—**B** THF solution before and after adding different anions at the [anion]: [B] value of 5.000 : 1.

4. Conclusions

Through loose and tight binding with boron atom in the —B(Mes)$_2$ group of **Ir**—**B**, CN ions can affect the ^{3}MLCT excited states of **Ir**—**B** in two sequent ways of destabilization MLCT excited states and then formation new MLCT excited states. By this way, the red phosphorescence of **Ir**—**B** can be effectively quenched by adding CN ions, while new yellow and green emission bands can appear in sequent with increasing the amount of added CN ions, showing CN sensing behavior with unique concentration distinguishing ability. Together with the novel sensing behavior to CN ions, the phosphorescent sensor **Ir**—**B** can possess DL as low as 4.3×10^{-6} M and good selectivity to the CN ions. The results obtained can provide important information for developing new CN sensors with high performances.

Declaration of competing interest

Manuscript title: **Phosphorescent cyanide sensor based on a 2-phenylpyridine(ppy)-type cyclometalated Ir(III) complex bearing dimesitylboron group with concentration distinguishing ability.** The authors whose names are listed immediately below certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers’ bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2020.121274.

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