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Bright Green-phosphorescence from Metal-to-boron Charge-transfer Excited State of a Novel Cyclometalated Iridium(III) Complex

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Tris[2-{3-(dimesitylboryl)phenyl}pyridinato]iridium(III) (**[Ir(Bppy)$_3$]**) showed bright green-phosphorescence with the emission lifetime and quantum yield of 1.0–1.4 μs and 1.0, respectively, in nonpolar–polar solvents at 298 K. Detailed spectroscopic experiments and DFT calculations demonstrated that the emissive state of the complex was the metal-to-boron charge-transfer (MBCT) excited state, in which the vacant p-orbital on the boron atom was occupied by the excited electron.

Cyclometalated iridium(III) complexes represented by **[Ir(ppy)$_3$]** (ppy: 2-phenylpyridine) are known to show bright phosphorescence at room temperature and have been applied to light-emitting materials in EL/OLED devices.[1] For such applications of the complexes, the study of synthetic tuning of emission-efficiency and -color is a very active research area, and work along the line mentioned above has been devoted to control the HOMO/LUMO energies of the complexes through introduction of electron-withdrawing substituent(s) on the ligand and/or that of heteroaromatic ring(s) other than pyridine ring.[2] As an another approach for modulation of the spectroscopic and photophysical properties of transition-metal complexes, we reported in 2006 that the intramolecular charge-transfer (CT) interaction between the π-orbital of the aryl group (π(aryl)) and the vacant p-orbital on the boron atom (p(B)) in the triarylborane group (π(aryl)–p(B) CT)[3] introduced to a ligand could modulate the MLCT state of the complex.[4] In practice, we demonstrated that introduction of a (dimesitylboryl)phenyl group on the 4′-position of the 2,2′:6′,2″-terpyridine ligand (**Btpy**) in a Pt(II) complex (**[Pt(Btpy)Cl]$^+$**) could increase the molar absorption coefficient of the MLCT band and emission quantum yield ($\Phi_{\rm em}$)/lifetime ($\tau_{\rm em}$) of the complex, compared to an analogous complex without the triarylborane group.[4] After our report on **[Pt(Btpy)Cl]$^+$**, several research groups reported transition-metal complexes with arylborane CT units,[5,6] and some of them have been reported to be highly luminescent in solution at room temperature.[6] Nonetheless, most of the work hitherto reported is application of the complexes to fluoride emission sensors, and detailed spectroscopic/photophysical study of transition-metal complexes bearing arylborane CT unit(s) is still limited. In this communication, we report a novel cyclometalated iridium(III) complex of the *facial*-isomer of tris[2-{3-(dimesitylboryl)phenyl}pyridinato]iridium(III) (**[Ir(Bppy)$_3$]**, see Chart 1 for the structure) shows bright green-phosphorescence with $\Phi_{\rm em}$ and $\tau_{\rm em}$ of 1.0 and 1.2 μs, respectively, in tetrahydrofuran (THF) at room temperature.

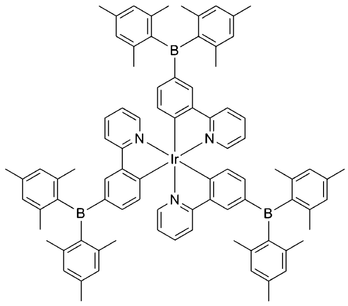

Chart 1. Structure of **[Ir(Bppy)$_3$]**.

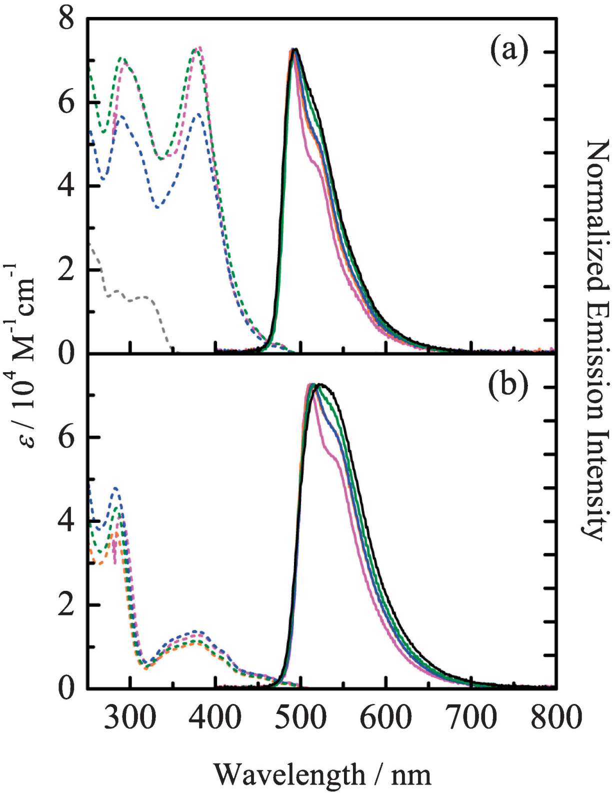

Figure 1. Absorption (broken curves) and emission spectra (solid curves) of **[Ir(Bppy)$_3$]** (a) and **[Ir(ppy)$_3$]** (b) in CH_3CN (black), CH_2Cl_2 (green), THF (blue), ethyl acetate (orange), and toluene (pink) at 298 K. The grey broken curve in (a) shows the absorption spectrum of **BppyH** in THF.

Figure 1 shows the absorption and emission spectra of **[Ir(Bppy)$_3$]** in several solvents together with those of **[Ir(ppy)$_3$]** as a reference, and Table 1 summarizes the spectroscopic and photophysical data of the complexes. **[Ir(Bppy)$_3$]** in THF exhibited absorption bands at around 290 and 380 nm similar to **[Ir(ppy)$_3$]**. Owing to the close similarities of the absorption

Table 1. Spectroscopic and photophysical properties of **[Ir(Bppy)$_3$]** and **[Ir(ppy)$_3$]** in several solvents at 77 and 298 K, and the dielectric constants of the solvents

Compound	Solvent	D_s[a]	λ_{abs}/nm (log ε)	λ_{em}/nm (λ_{em} at 77 K)	fwhm/cm^{-1}	Φ_{em}	τ_{em}/μs	k_r/10^5 s^{-1}	k_{nr}/10^5 s^{-1}
[Ir(Bppy)$_3$]	CH_3CN	37.5	283 (n.d.), 377 (n.d.)[b]	494	2550	1.0	1.4	7.1	>0.04
	CH_2Cl_2	8.93	290 (4.85), 377 (4.86), 472 (3.38)	493	2360	0.97	1.2	8.1	0.25
	THF	7.58	290 (4.76), 379 (4.76), 473 (3.24)	491	2280	1.0	1.2	8.3	>0.04
	Ethyl acetate	6.02	289 (n.d.), 378 (n.d.)[b]	490	2240	1.0	1.2	8.3	>0.04
	Toluene	2.379	294 (4.84), 380 (4.87), 474 (3.36)	490 (479)	2040	1.0	1.0	10	>0.05
[Ir(ppy)$_3$]	CH_3CN	37.5	280 (n.d.), 378 (n.d.), 489 (n.d.)[b]	521	2920	0.92	1.9	4.8	0.42
	CH_2Cl_2	8.93	283 (4.63), 378 (4.04), 483 (3.09)	516	2750	0.90	1.6	5.6	0.63
	THF	7.58	283 (4.67), 378 (4.15), 486 (3.13)	514	2630	0.91	1.6	5.7	0.56
	Ethyl acetate	6.02	283 (4.57), 378 (4.00), 484 (3.08)	513	2630	0.97	1.7	5.7	0.18
	Toluene	2.379	289 (4.61), 378 (4.11), 488 (3.16)	511 (498)	2430	0.90	1.4	6.4	0.71

[a]The data complied from ref. 7. [b]We could not determine the ε values owing to the low solubilities of the compounds.

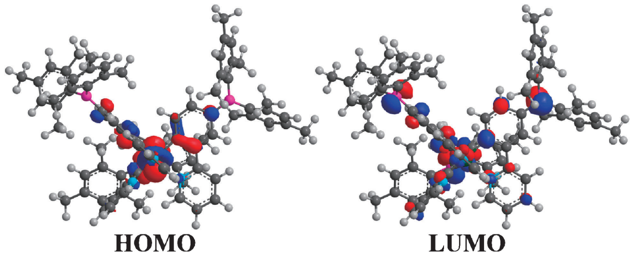

Figure 2. HOMO and LUMO representations of **[Ir(Bppy)$_3$]** obtained by the DFT calculations.

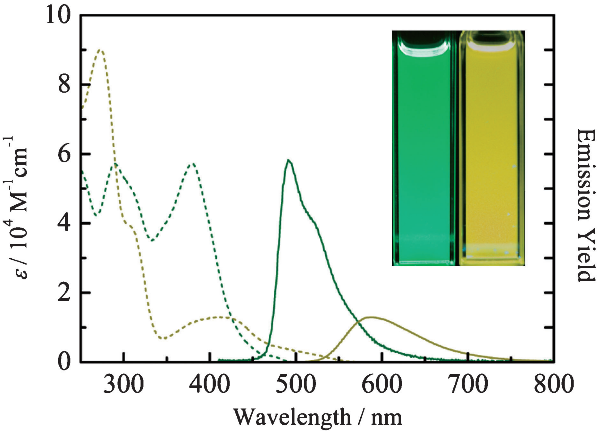

Figure 3. Absorption (broken curves) and emission spectra (solid curves) of **[Ir(Bppy)$_3$]** in the absence (green) and presence of an excess amount of TBAF (yellow) in THF. Inset: Emission colors of **[Ir(Bppy)$_3$]** in the absence (left) and presence of TBAF (right) in THF.

spectral band shapes between the two complexes, the shorter- and longer-wavelength bands observed for **[Ir(Bppy)$_3$]** could be assigned to the $\pi\pi^*$ and MLCT transitions, respectively. It is worth emphasizing that the molar absorption coefficient (ε) of the MLCT band of **[Ir(Bppy)$_3$]** in THF ($\log\varepsilon = 4.76$ at 379 nm) is almost four times larger than that of **[Ir(ppy)$_3$]** ($\log\varepsilon = 4.15$ at 378 nm). Since free ligand, **BppyH**, itself is transparent above 350 nm as the spectrum is included in Figure 1, it is evident that the large absorption intensity of the MLCT band in **[Ir(Bppy)$_3$]** is due essentially to the presence of the dimesitylboryl group and thus to the synergistic MLCT/π(aryl: dimesitylphenyl)–p(B) CT interactions. The participation of p(B) in the lowest-energy absorption transition in **[Ir(Bppy)$_3$]** is supported by DFT calculations as shown in Figure 2. The HOMO of **[Ir(Bppy)$_3$]** is localized on the iridium atom and the phenyl rings in the ppy groups similar to that of **[Ir(ppy)$_3$]**, while the LUMO of the complex is best characterized by the electron densities on the boron atoms. Thus, the lowest-energy absorption transition in **[Ir(Bppy)$_3$]** is assigned to metal-to-boron charge transfer (MBCT). MBCT through the phenyl rings in the ppy groups results in the increase in the transition dipole moment and thus the oscillator strength of the CT transition. This is also confirmed experimentally through the effects of fluoride ion on the absorption spectrum of **[Ir(Bppy)$_3$]** in Figure 3. It is known that an F$^-$ ion is likely to coordinate almost specifically with p(B) and this diminishes the effects of p(B) on the redox, spectroscopic, and photophysical properties of both arylboranes and transition-metal complexes bearing arylborane unit(s).[8] As seen in Figure 3, in practice, the absorption intensity in 350–400 nm decreases dramatically in the presence of an excess amount of F$^-$ (tetra-*n*-butylammonium fluoride: TBAF), proving the contribution of p(B) to the lowest-energy absorption transition in **[Ir(Bppy)$_3$]**: MBCT.

[Ir(Bppy)$_3$] in THF exhibited the emission spectrum at around 490 nm and the maximum wavelenghth (λ_{em}) was shifted to shorter wavelength ($\lambda_{em} = 491$ nm and $\nu_{em} = 20.4 \times 10^3$ cm^{-1}) compared to that of **[Ir(ppy)$_3$]** ($\lambda_{em} = 514$ nm, $\nu_{em} = 19.5 \times 10^3$ cm^{-1}). A similar trend to that in THF was also observed in other solvents, while the λ_{em} values of the complexes shifted to longer wavelength with an increase in solvent polarity: see Table 1. Nonetheless, the solvent-polarity-induced shift of λ_{em} (ν_{em}) on going from toluene (dielectric constant (D_s) = 2.379) to CH_3CN ($D_s = 37.5$) was much smaller for **[Ir(Bppy)$_3$]** ($\Delta\nu_{em} = 170$ cm^{-1}) compared to that for **[Ir(ppy)$_3$]** ($\Delta\nu_{em} = 380$ cm^{-1}). Since the excited electron localizes on p(B) surrounded by the bulky dimesityl groups in **[Ir(Bppy)$_3$]**, solvent-induced stabilization of the CT excited state plays a minor role in determining λ_{em} compared with the excited state of **[Ir(ppy)$_3$]**. The smaller full-width at half maximum (fwhm) value of the emission band of **[Ir(Bppy)$_3$]** relative to that of **[Ir(ppy)$_3$]** in a given solvent (Table 1) may also indicate the weak interaction of the MBCT excited state of the complex with solvent molecules. As can be seen in Figure 3, furthermore, the emission from **[Ir(Bppy)$_3$]** is quenched by F$^-$. The effects of added F$^-$on the absorption and emission spectra of the complex demonstrate explicitly that the emissive state of **[Ir(Bppy)$_3$]** is the MBCT excited state.

The MBCT excited state of **[Ir(Bppy)$_3$]** exhibited very bright emission with the absolute Φ_{em} value determined by an integration sphere[9] being almost unity except for the value in CH_2Cl_2. In a given solvent, Φ_{em} of **[Ir(ppy)$_3$]** determined under analogous conditions was always smaller than that of **[Ir(Bppy)$_3$]**, and thus **[Ir(Bppy)$_3$]** is a brighter emitter than **[Ir(ppy)$_3$]**. The large Φ_{em} value of **[Ir(Bppy)$_3$]** accompanies the short emission lifetime ($\tau_{\mathrm{em}} = 1.2\,\mu\mathrm{s}$ in THF) compared with that of **[Ir(ppy)$_3$]** ($\tau_{\mathrm{em}} = 1.6\,\mu\mathrm{s}$), leading to the larger radiative rate constant (k_{r}) of **[Ir(Bppy)$_3$]** ($8.3 \times 10^5\,\mathrm{s}^{-1}$) relative to that of **[Ir(ppy)$_3$]** ($5.7 \times 10^5\,\mathrm{s}^{-1}$). This could be explained by intensity borrowing through mixing the emitting MBCT state with the spin-allowed excited singlet state(s) showing the large oscillator strength (i.e., ε value). Similar enhancement of the k_{r} value through that of the absorption strength has been also confirmed for **[Pt(Btpy)Cl]$^+$** as mentioned before.[4] Therefore, a peripheral arylborane group on the ligand can enhance the transition dipole moment of a transition-metal complex through synergistic MLCT and π(aryl)–p(B) CT interactions and this gives rise to the increase in the emission probability of the complex.

In conclusion, introduction of arylborane CT unit(s) to a ligand in a transition-metal complex can enhance both the absorption and emission efficiencies of the complex through metal-to-boron charge-transfer (MBCT) interactions. In addition to **[Ir(Bppy)$_3$]** and **[Pt(Btpy)Cl]$^+$**,[4] we recently found that a **Ru(phen)$_3^{2+}$** (phen: 1,10-phenanthroline) complex bearing an arylborane CT unit on one of the three phen ligands also showed intense emission in solution at 298 K with Φ_{em} and τ_{em} of 0.11 and 12 µs, respectively.[10] Therefore, we expect that an arylborane CT unit introduced to the periphery of the ligand can tune the spectroscopic and photophysical properties of various transition-metal complexes. In particular, bright emission from a transition-metal complex will be realized by employing an arylborane CT-type ligand(s).

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