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Blue-Light-Emitting Complexes: Cationic (2-Phenylpyridinato)iridium(III) Complexes with Strong-Field Ancillary Ligands

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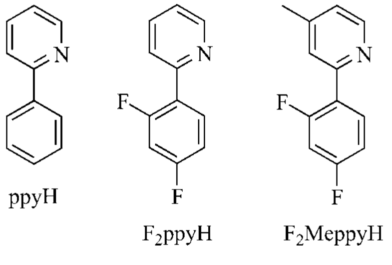
The emission λ_{max} are strikingly shorter (451, 482 nm) for the cationic dicarbonyl complex $[Ir(ppy)_2(CO)_2]^+$ (**2a**) than those (473, 495 nm) of the anionic dicyano complex $[Ir(ppy)_2(CN)_2]^-$, where CO and CN^- are both sp carbon coordinating ligands and known to be strong-field ligands showing a high *trans* effect. Sky-blue-light emission (λ_{max} = 441–443 and 470–471 nm) could be obtained by modifying the ppy ligand to F_2Meppy (2,4-difluoro-2-phenyl-*m*-methylpyridinato anion) to prepare $[Ir(F_2Meppy)_2LL']^+$ [LL′ = $(CO)_2$ (**2a**F_2Me), $(PPh_2Me)_2$ (**2b**F_2Me)].

Introduction

Research of blue-light-emitting materials is currently under thorough investigation because efficient blue-light emitters are in need in the display industry.[1] Iridium complexes of ppy (2-phenylpyridinato) have drawn much attention as they emit phosphorescence in the visible region with high quantum yields and the emission λ_{max} can be tuned by modification of the ligands.[1–4] Theoretical calculations for $[Ir(ppy)_3]$,[2c] $[Ir(ppy)_2L_2]$,[4b] and [Pt(ppy)(acac)][5] suggest that the HOMO of these metal complexes include dπ-orbitals of the metal and orbitals of L_2[4b] or acac.[5] Spectroscopic data analysis for $Ir(C^\wedge N)_2LL'$ ($C^\wedge N$ = ppy and its derivatives)[4b] revealed that ancillary ligands (L, L′) alter the ^{1}MLCT energy mainly by changing the HOMO energy level. The HOMO energy level may then be lowered by strong-field ancillary ligands, which causes a large d-orbital energy splitting. It is also likely that strong-field ancillary ligands L and L′ lengthen the bond lengths of Ir–C (ppy) *trans* to L and L′ to lower the energy levels of the dπ-orbitals of the metal as strong-field ligands are known to show a high *trans* effect.

Cationic complexes $[Ir(C^\wedge N)_2L_2]^+$ (L = neutral ligands such as CO) would be harder to oxidize than anionic complexes $[Ir(C^\wedge N)_2A_2]^-$ (A = anionic ligands such as CN^-) when L and A are the ligands having comparable ligand-field strength. One could expect, therefore, a larger energy gap between the HOMO and LUMO of the cationic complexes than that of the anionic complexes. A cationic complex such as $[Ir(C^\wedge N)_2(CO)_2]^+$ (not reported previously) would show a blueshifted emission λ_{max} from that of the anionic complex $[Ir(C^\wedge N)_2(CN)_2]^-$ because both CO and CN^- are well-known strong-field ligands that give large d-orbital energy splitting between dπ-orbitals (e_g) and dσ-orbitals (t_{2g}). One advantageous application of cationic complexes is their use for single-layer electroluminescent devices.[6]

We now wish to report new cationic complexes $[Ir(C^\wedge N)_2L_2]^+$ and $[Ir(C^\wedge N)_2LL']^+$ [$C^\wedge N$ = ppy, F_2ppy, F_2Meppy; L, L′ = strong-field ligands: CO, PPh_2Me, $P(OPh)_3$] and their photoluminescent characteristics in the blue color region.



ppyH F_2ppyH F_2MeppyH

Results and Discussion

Cationic complexes $[Ir(ppy)_2L_2]^+$ (**2**) and $[Ir(ppy)_2LL']^+$ (**3**, **4**) have been newly prepared (Scheme 1) and unambiguously characterized in detail by ^{1}H-, ^{13}C-, ^{31}P NMR, IR spectral and elemental analysis data and also X-ray diffraction data analysis for single crystals of $[Ir(ppy)_2(PPh_3)(NCMe)]^+$ (**4a**). Assignment of the spectral signals is straightforward by comparison with those of related compounds previously reported (see Supporting Information).

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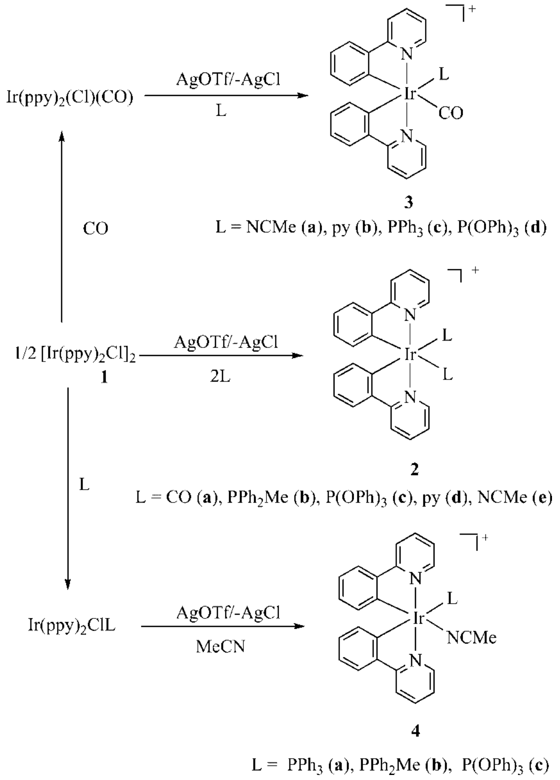
For example, the $Ir(ppy)_2$ moiety is unambiguously identified by detailed ^1H- and ^{13}C-NMR spectroscopic data while carbonyl (CO), cyano (CN), and MeCN complexes are characterized by IR absorptions due to ν(C≡O), ν(C≡N), and ν(N≡C).



Scheme 1. Synthetic routes for $[Ir(ppy)_2L_2]^+$ (**2**), $[Ir(ppy)_2(CO)L]^+$ (**3**), and $[Ir(ppy)_2(NCMe)L]^+$ (**4**).

Attempts to prepare bis(PPh_3) complex $[Ir(ppy)_2(PPh_3)_2]^+$ have been unsuccessful probably because PPh_3 is too large for the *cis*-$Ir(ppy)_2$ moiety to have two PPh_3 in the *cis* positions. Figure 1 shows that replacement of the MeCN ligand of **4a** with another PPh_3 would make the metal center too crowded to give the stable bis(PPh_3) complex. A smaller phosphane (PPh_2Me) and a less congested phosphite $[P(OPh)_3]$ fit into the *cis* positions of $[Ir(ppy)_2L_2]^+$ to give stable complexes, **2b** and **2c**.

Dicarbonyl complex $[Ir(ppy)_2(CO)_2]^+$ (**2a**) was the first complex synthesized in this study because the ligand-field strength of CO is as strong as that of CN^- and photophysical data for the anionic complex $[Ir(ppy)_2(CN)_2]^-$ (**5**)[4a] are available to compare with those of **2a**.

Cationic complex **2a** shows emission λ_{max} at 451 and 482 nm which are much shorter than those (473, 495 nm) of anionic complex **5** (see Table 1). Cationic complexes **2b** and **2c** with other strong-field ligands PPh_2Me and $P(OPh)_3$ also emit blue color, whereas a longer emission λ_{max} (480, 508 nm) is measured for complex **2d** containing the medium-strength-field ligand pyridine (Figure 2). Complex **2e** with the other N-based ligand MeCN shows the emission at λ_{max} at 469 and 500 nm in MeCN where the dissociation of the labile MeCN ligand from **2** is suppressed, although no measurable emission is found in CH_2Cl_2 for **2e** as reported previously by Watts.[7]

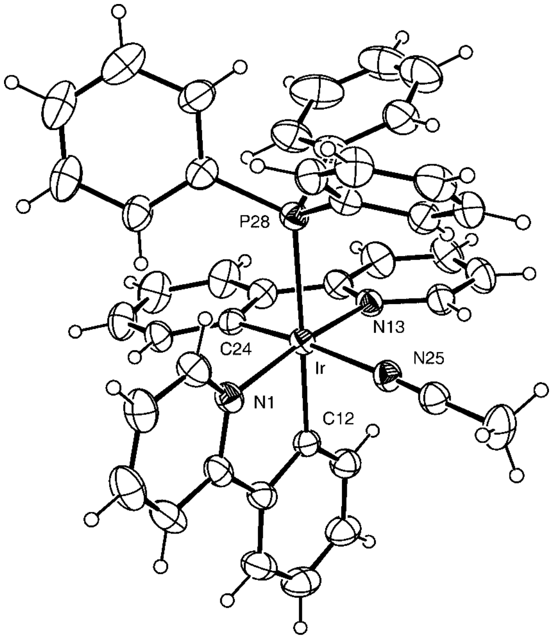


Figure 1. ORTEP drawing of $[Ir(ppy)_2(NCMe)(PPh_3)]^+$ (**4a**) with 50% thermal ellipsoids probability. Selected bond lengths [Å]: $Ir–N^1 = 2.081(6)$; $Ir–N^{13} = 2.046(6)$; $Ir–N^{25} = 2.111(7)$; $Ir–C^{12} = 2.052(7)$; $Ir–C^{24} = 2.026(8)$, $Ir–P^{28} = 2.4342(19)$. Selected bond angles [°]: $N^1–Ir–N^{13} = 171.3(2)$; $C^{12}–Ir–P^{28} = 178.44(19)$; $C^{24}–Ir–N^{25} = 171.3(3)$.

Table 1. Photophysical data[a,b,c] for cationic complexes $[Ir(ppy)_2L_2]^+$ (**2**), $[Ir(ppy)_2(CO)(L)]^+$ (**3**), and $[Ir(ppy)_2(NCMe)(L)]^+$ (**4**).[a]

	(L)(L′)	λ_{max} [nm]	Φ_{PL}	τ [c] [μsec]
2a	(CO)(CO)	451, 482	0.073	0.015
2b	(PPh_2Me)(PPh_2Me)	460, 491	0.32	0.29
2c	$[P(OPh)_3][P(OPh)_3]$	458, 486	0.092	0.10
2d	(py)(py)	480, 508	0.73	0.15
2e	(NCMe)(NCMe)	469, 500	0.021	0.019
3a	(CO)(NCMe)	454, 485	0.054	0.10
3b	(CO)(py)	466, 487	0.41	0.80
3c	(CO)(PPh_3)	455, 485	0.089	0.25
3d	(CO)$[P(OPh)_3]$	451, 482	0.19	1.1
4a	(PPh_3)(NCMe)	464, 495	0.034	0.027
4b	(PPh_2Me)(NCMe)	463, 493	0.040	0.029
4c	$[P(OPh)_3]$(NCMe)	457, 488	0.13	0.34
5	(CN)(CN)	473, 495	0.79[b]	2.6

[a] Compounds **2a–d** and **3b–d** in CH_2Cl_2 and **2e**, **3a**, **4a–4c**, and **5** in CH_3CN at 298 K under an atmosphere of Ar. [b] Measured in this study and in agreement with the reported value,[4a] within experimental errors. [c] Calculated employing *fac*-$Ir(ppy)_3$ (Φ_{PL} = 0.40[8]) as the standard.

The quantum yields of complexes **2a–d** decrease significantly with a shift of the emission λ_{max} to shorter wavelengths (see Table 1 and Figure 2). These results agree with the suggestion that the luminescence quantum yields decline with increasing emission energies.[4b] Among complexes prepared in this study, complex **2d** shows the longest emission λ_{max} and the highest quantum yield. Both emis-

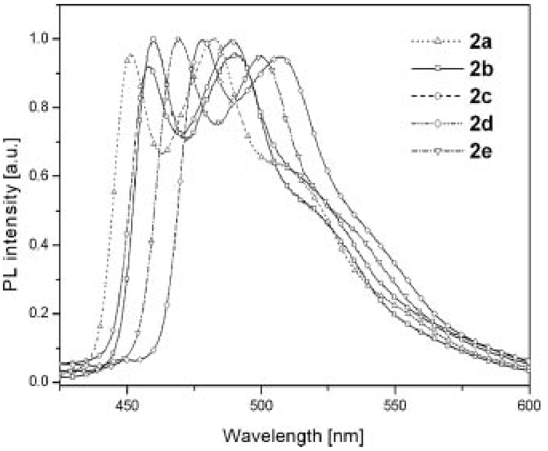


Figure 2. Normalized emission spectra of [Ir(ppy)$_2$L$_2$](OTf) (**2**, 1×10^{-4} M) in CH$_2$Cl$_2$ (**2a**–**d**), and MeCN (**2e**) at room temperature; L = CO (**2a**), PPh$_2$Me (**2b**), P(OPh)$_3$ (**2c**), py (**2d**), MeCN (**2e**).

sion λ_{max} and quantum yield of cationic complex **2d** (λ_{max} = 480, 508 nm; $_{\mathrm{PL}}$ = 0.73 in CH$_2$Cl$_2$) are close to those of anionic complex **5** (λ_{max} = 473, 495 nm; Φ_{PL} = 0.79 in MeCN) although pyridine is a much weaker-field ligand than CN$^-$. The lifetimes of cationic complexes prepared in this study are significantly shorter than that of anionic complex **5** and shorter lifetimes are measured for the complexes with relatively higher quantum yields (see Table 1).

The results observed for [Ir(ppy)$_2$(L)$_2$]$^+$ (**2**) agree with the anticipation that the emission λ_{max} would be blueshifted by the strong-field (high *trans* effect) ancillary ligands L such as C- and P-based ligands, whereas a longer emission λ_{max} would be seen for medium-field ligands L such as N-based ligands.

Complexes having two different strong-field ligands, [Ir(ppy)$_2$(CO)(PPh$_3$)]$^+$ (**3c**) and [Ir(ppy)$_2$(CO){P(OPh)$_3$}]$^+$ (**3d**) also show shorter emission λ_{max}, whereas those with one MeCN or py (**3b** and **4a**–**c**) show λ_{max} at relatively longer wavelengths (Table 1). It seems certain that among the N-based ligands, the sp N-based ligand MeCN gives shorter emission λ_{max} than does the sp^2 N-based ligand pyridine as observed for **2d**, **2e**, **3a**, and **3b** (see Table 1). The effect of the field strength of the ancillary ligand on the emission energy is unambiguously confirmed again by replacing medium-field ligand pyridine with stronger-field ligand CO, which causes the emission λ_{max} to be blueshifted from 480 and 508 nm for [Ir(ppy)$_2$(py)$_2$]$^+$ (**2d**) to 466 and 487 nm for [Ir(ppy)$_2$(py)(CO)]$^+$ (**3b**).

It is noticed that the quantum yield is relatively higher for P(OPh)$_3$ complex **3d** (0.19) than it is for both MeCN (**3a**) and PPh$_3$ (**3c**) complexes although the emission λ_{max} is shorter for **3d** than it is for **3a** and **3c**, which may be understood by the fact that P(OPh)$_3$ is more basic than PPh$_3$ and MeCN and less dissociation of the ligand from the metal is expected for **3d** than for **3a** and **3c**.

Unlike bis-MeCN complex **2e**, mono-MeCN complexes **3a** and **4a**–**c** exhibit measurable emission in CH$_2$Cl$_2$ even in the absence of excess MeCN. Dissociation of the labile MeCN ligand, however, seems significant for most MeCN containing complexes and much lower quantum yields and redshifted emission λ_{max} are observed in the absence of excess MeCN.

Cyclic voltammetric measurements for complexes prepared in this study show, in general, poorly resolved reversible waves for both oxidation and reduction. It is, however, confirmed that cationic complex **2a** clearly shows a more positive oxidation potential at 1.15 V than anionic complexes **5** (0.9 V)[4a] in CH$_2$Cl$_2$ (vs. Fc^{2+}/Fc$^+$) while **5** shows a more negative reduction potential (–1.70 V)[4a] than **2a** (–1.20 V) (see Supporting Information for voltammograms).

In order to see the effects of ppy ligand modification on the emission of [Ir(ppy)$_2$L$_2$]$^+$ (**2**), complexes of F$_2$ppy and F$_2$Meppy (**2a**F$_2$, **2a**F$_2$Me, **2b**F$_2$, **2b**F$_2$Me) have been prepared by the same method used for the preparation of **2** (Scheme 1). The blueshifts of the emission λ_{max} caused by the modification of the ppy ligand are somewhat larger for the bisphosphane complexes (**2b**) than for the dicarbonyl complexes (**2a**) (see Table 2 and Figure 3). It should be

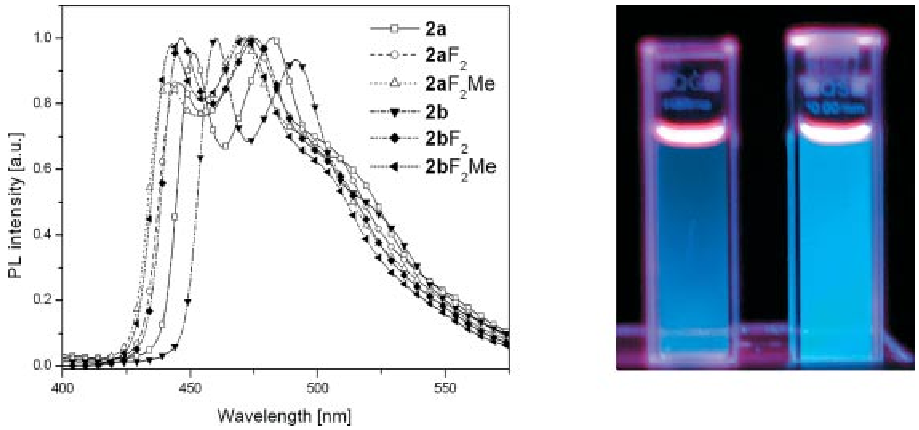


Figure 3. Normalized emission spectra of [Ir(ppy)$_2$(CO)$_2$]$^+$ (**2a**), [Ir(F$_2$ppy)$_2$(CO)$_2$]$^+$ (**2a**F$_2$), [Ir(F$_2$Meppy)$_2$(CO)$_2$]$^+$ (**2a**F$_2$Me), [Ir(ppy)$_2$(PPh$_2$Me)$_2$]$^+$ (**2b**), [Ir(F$_2$ppy)$_2$(PPh$_2$Me)$_2$]$^+$ (**2b**F$_2$) and [Ir(F$_2$Meppy)$_2$(PPh$_2$Me)$_2$]$^+$ (**2b**F$_2$Me) in CH$_2$Cl$_2$ at 25 °C. Complex **2a**F$_2$Me (left) displays somewhat of a more bluish emission than does **2b**F$_2$Me (right).

mentioned that blue-light emission is obtained by modification of the ppy ligand to produce **2a**F$_2$, **2a**F$_2$Me, **2b**F$_2$, and **2b**F$_2$Me while complexes **2a** and **2b** emit only greenish-blue light.

Increases in both the quantum yield and the lifetime of the emission are significant for phosphane complexes (**2b**, **2b**F$_2$, **2b**F$_2$Me), whereas no notable increase in the lifetime is observed for carbonyl complexes (**2a**, **2a**F$_2$, **2a**F$_2$Me) (see Table 2).

Table 2. Emission spectral data for $[\mathrm{Ir}(C^{\wedge}N)_2\mathrm{L}_2]^+$ (**2**) in CH_2Cl_2 at 25 °C.

Complex	$C^{\wedge}N$	L	$\lambda_{\max}$ [nm]	Φ_{PL}	τ [µsec]
2aF$_2$	F$_2$ppy	(CO)	445, 474	0.079	0.17
2aF$_2$Me	F$_2$Meppy	(CO)	441, 470	0.097	0.15
2bF$_2$	F$_2$ppy	(PPh$_2$Me)	446, 475	0.71	1.41
2bF$_2$Me	F$_2$Meppy	(PPh$_2$Me)	443, 471	0.80	1.16

In summary, the emission $\lambda_{\max}$ of $[\mathrm{Ir(ppy)_2(L)_2}]^+$ and $[\mathrm{Ir(ppy)_2(L)(L')}]^+$ significantly shifts to shorter wavelengths with strong-ligand-field ancillary ligands (L and L′) such as CO and phosphorus-based ligands [PPh$_3$, PPh$_2$Me, P(OPh)$_3$] compared with the emission $\lambda_{\max}$ of less-strong-field ligands such as nitrogen-based ligands (MeCN, py). For ancillary ligands of comparable ligand-field strengths such as CO and CN$^-$, the cationic complex $[\mathrm{Ir(ppy)_2(CO)_2}]^+$ emits shorter wavelength than does the anionic one $[\mathrm{Ir(ppy)_2(CN)_2}]^-$. Blue-light emission is obtained from cationic complexes **2a**F$_2$Me and **2b**F$_2$Me which contain strong-field ancillary ligands, CO and PPh$_2$Me, and a modified ppy ligand, F$_2$Meppy.

CCDC-619899 (for **4a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Experimental details and spectroscopic data for **2**–**4**. ^{1}H- and ^{13}C-NMR spectra of **2**–**4**. Photoluminescence decay diagrams and cyclic voltammograms of **2**.

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