Search for New Blue Phosphorescent Iridium(III) Complexes for OLED Applications

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1. Introduction

Recently, we initiated an investigation aimed at the development of new, blue phosphorescent iridium complexes. The approach employed a strategy involving the design of structures that contain a variety of ancillary ligands, incorporated into heteroleptic octahedral Ir(III) complexes along with substituted-2-phenylpyridines as main ligands. The goal was to uncover complexes that emit in the deep blue wavelength region with high quantum efficiencies. Below, we described the results of this effort, which demonstrate that iridium complexes containing 4-substituted picolines, 3-trifluoromethyl-5-(4-substituted-pyridyl)-1,2,4-triazoles, and *N*-methyl-imidazole carboxylates as ancillary ligands display these important emission properties for OLED applications.

2. Experiment

2.1 Synthesis of Iridium (III) Complexes

2-Phenylpyridine derivatives, serving as main ligands, were prepared by using slight modifications of the previously described method [1]. Pyridyltriazole ancillary ligands were synthesized by utilizing [2+3] cycloaddition reactions of cyano compounds with trifluoroacetic acid hydrazide under basic conditions. [2] 1-Methyl-2-imidazole carboxylic acid and 1-methyl-5-imidazole carboxylic acid, also used as ancillary ligands, were purchased from Aldrich Chemical Co. and used without purification. The new, blue-emitting heteroleptic iridium (III) complexes, **1–10** were prepared through conventional two-step reaction sequences [3]

involving the intermediacy of a μ -chloro-bridged iridium-main ligand dimeric complex. New iridium (III) complex **1** and **2** were synthesized by heating μ -chloro-bridged iridium dimer and 4-chloro-picolinic acid under basic condition in ethoxyethanol and di-*n*-butylamine as solvent and as nucleophile.

2.2 UV-Vis Absorption and Photoluminescence Spectra

Absorption and photoluminescence spectra were measured using dichloromethane solutions at room temperature and a Jasco V-570 UV-vis spectrometer and a Hitach F-4500 fluorescence spectrometer, respectively. Phosphorescence quantum yields (Φ_p) were estimated using a chloroform solution of Ir(tpy)₃ ($\Phi_p = 0.50$) [4] and Irpic ($\Phi_p = 0.42$) [5] as actinometers.

3. Results and Discussion

3.1 Phosphorescent Heteroleptic Iridium Complexes Containing 4-Substituted Picolines as Ancillary Ligands

The results of earlier molecular orbital calculations, focusing on the HOMO and LUMO orbitals of iridium (III) tris(2-phenylpyridinato-*N,C'*) complexes, showed that that *d*-orbitals of the metal contribute greatly to the HOMO (52.8%). In addition, the main ligand, phenyl group contributes to the HOMO to a larger extent (38.9%) than does the pyridine ring (8.2%) in this complex. In contrast, the 2-phenylpyridine π -main ligand was found to contribute exclusively to the LUMO with the pyridine moiety playing a

much greater role (73.5%) than does the phenyl group (52.9%).

These findings, which indicate that the LUMO is largely delocalized onto the pyridine ring of the main ligand while HOMO is delocalized largely on the phenyl ring, suggest that tuning the wavelengths and consequently colors of phosphorescence emission from iridium complexes by altering substitution patterns should be possible. Thus, raising the LUMO energy levels and lowering the HOMO levels through the introduction of electron donating substituents (4-CH₃-, 4-CH₃O-) on the pyridine ring and/or electron withdrawing substituents (4'- and 6'-F-, 5'-CF₃-) on the phenyl ring represents an ideal approach to inducing a hypsochromic (blue) shifted phosphorescence emission. In contrast, lowering the LUMO and raising the HOMO energies by utilizing the reverse substitution patterns can be used to promote bathochromic (red) shifted emission.

Scheme 1. Substitution patterns for blue phosphorescent iridium (III) complexes.

Based on the results of the molecular orbital calculations, it is possible to propose proper substitution patterns that should lead to hypsochromic shifted phosphorescence emission bands from iridium complexes. These substitution patterns are found in the complexes listed in Scheme 1, which include both homoleptic iridium (III) tris(2-phenylpyridinato-N,C^{2'}) (Scheme 1(a)) and heteroleptic iridium (III) bis(2-phenylpyridinato-N,C^{2'})(acetoacetate) (Scheme 1(b)) complexes. The heteroleptic iridium (III) bis(substituted 2-phenylpyridinato-N,C^{2'})-(acetoacetate) complexes contain nonchromophoric acetoacetate as an ancillary ligand, which should not influence phosphorescence emission properties. However, the well-known heteroleptic iridium complexes, FIrpic (Iridium (III) bis(2-(2',4'-difluorophenyl)-pyridinato-N,C^{2'})(picolinate)), contain picolinate as the ancillary ligand which can be altered to influence both the efficiency and wavelength of triplet state emission.

A careful comparison of the substitution profiles of homoleptic iridium (III) tris(2-

phenylpyridinato-N,C^{2'}) and blue phosphorescent heteroleptic iridium (III) bis(substituted 2-phenylpyridinato-N,C^{2'})(picolinate), led us to the recognition that the carboxyl group of a picolinate main ligand (Scheme 2) would serve as an electron withdrawing substituent in place of electron withdrawing phenyl substituents (Scheme 1(a)) present in 2-phenylpyridinato complexes. We believed that this feature, along with the presence of alkyl, alkoxy or dialkylamino electron-donating groups at C-4 of the picolinate (Scheme 2) ring, would lead to complexes that display hypsochromic (blue-shifted) phosphorescence in comparison to that of FIrpic complexes.

Scheme 2. Structures of blue phosphorescent iridium (III) complexes with picolinate as ancillary ligands.

Guided by the design principles presented above for generating new blue phosphorescent iridium complexes, we prepared and examined the photophysical properties of complexes **1** and **2**, containing respective electron-donating 4-ethoxyethoxy (4-CH₃CH₂O-CH₂CH₂-) and 4-di-*n*-butylamino (4-*n*-Bu₂N-) substituted picolinate as ancillary ligands. For comparison purposes, we also synthesized and investigated complex **3**, which contains a strongly electron-withdrawing trifluoromethyl (CF₃-) group substituted picolinate.

Fig.1. UV-vis absorption and photoluminescence spectra of iridium (III) complexes **1-3**.

The absorption and emission spectra of **1-3** along with those of FIrpic are displayed in Figure 1. As can be seen by viewing the data, the absorption spectrum of **1** has a weak but clear band at 412 nm corresponding to a MLCT^{*3} transition and its structured emission spectrum has maxima at 464 nm and 486 nm corresponding to a very high emission quantum efficiency of 0.69. Iridium

complex **2** is observed also to exhibit similar absorption and emission properties reflected in a weak absorption band at 418 nm and a structured emission with maxima at 466 nm and 491 and a very high emission quantum efficiency of 0.57. In contrast, the absorption spectrum of iridium complex **3**, possessing an electron-withdrawing group substituted picolinate, contains a broad emission band centered at the largely bathochromic shifted wavelength of 565 nm corresponding to a low quantum efficiency of 0.07.

These observations clearly demonstrate that the position and efficiencies of the emission bands of heteroleptic iridium (III) bis(2-phenylpyridine-*N,C*')(picolinate) complexes are dramatically impacted by the nature of substituents on the picolinate ancillary ligand. Specifically, the new phosphorescent iridium complexes **1** and **2**, designed through careful consideration of the nature and position of electron-donating and withdrawing substituent on the picolinate ancillary ligand, display blue-shifted phosphorescent emissions bands with 5-6 times higher quantum efficiencies in comparison to those of Flrpic (emission maxima at 468 nm and 495, and emission quantum efficiency of 0.11). [1(a)]

3.2 Phosphorescent Heteroleptic Iridium Complexes Containing 4'-Substituted Pyridyltriazoles as Ancillary Ligands

Since the time of the development of Flrpic as a reference cyan blue phosphor, many studies have been carried out to uncover deeper blue-emitting phosphors. In one of these efforts, the picolinate ancillary ligand Flrpic was replaced by a 5-(pyridine-2'-yl)-3-(trifluoromethyl)-1,2,4-triazole or 5-(pyridine-2'-yl)-1,2,3,4-tetrazole ligand [7], giving complexes that contain electron-deficient triazole and tetrazole ring in place of the pyridine carboxylate moiety. The results showed that this change results in a *ca.* 10 nm hypsochromic shift in the phosphorescent emission bands.

In a further investigation, Yamashita [1(a)] encountered success in designing deep blue phosphorescent iridium complexes through the utilization of 5-(pyridine-2'-yl)-3-trifluoromethyl-1,2,4-triazole as an ancillary ligand and 2-(4',6'-difluoro-phenyl)-4-methylpyridine or 2-(4',6'-difluoro-5'-(trifluoromethyl)phenyl)-4-methylpyridine as main ligands. Among the iridium complexes explored by this group, **6** comprised of 5-(pyridine-2'-yl)-3-trifluoromethyl-1,2,4-triazole as the ancillary ligand and 2-(4',6'-difluoro-5'-(trifluoromethyl)phenyl)-4-methylpyridine as the main ligand was observed

to display deep blue phosphorescence with maxima at 447 nm and 476 nm [8] and an emission quantum efficiency of 0.11 (Figure 2). This observation combined with those made in our studies with **1** and **2** guided the design of the new, more deeply blue phosphorescent iridium complexes **4-5**. These substances contain an additional, electron-donating methyl group at C-4' of the 5-(pyridine-2'-yl)-3-trifluoromethyl-1,2,4-triazole ancillary ligand. In Figure 2 are shown the absorption and emission spectra of **4-5** along with those of Yamashita's [1(a)] iridium complex **6**. The new iridium complexes were observed to display structured phosphorescence with emission maxima in the deep blue region (**4**; 456 nm and 483 nm, **5**; 448 nm and 475 nm, **6**; 456 nm and 482 nm) and very high emission quantum efficiencies (**4**; $\Phi=0.39$, **5**; $\Phi=0.42$, **6**; $\Phi=0.20$) [8].

Fig.2. UV-vis absorption and photoluminescence spectra of iridium (III) complexes **4-6**.

The results show that electron-donating methyl substitution at C-4' of the 5-(pyridine-2'-yl)-3-trifluoromethyl-1,2,4-triazole ancillary ligand has a significant impact on the spectral properties of the heteroleptic iridium complexes, leading to a large hypsochromic shift (8 nm) of the phosphorescence emission maximum. Specifically, the new iridium complex **5** displays more deeply blue phosphorescence (8 nm) than that of the previously reported complex **6**. In addition, iridium complex **4**, missing an electron-withdrawing trifluoromethyl substituent on the main ligand, also displays phosphorescence emission at a wavelength (456 nm) that is similar to that of complex **6**.

3.3 Phosphorescent Heteroleptic Iridium Complexes Containing Imidazole Carboxylates as Ancillary Ligands

As demonstrated by the results of the effort described above, raising the LUMO energy of picolinate ancillary ligand in phosphorescent iridium complexes (*eg.*, **1** and **2**) by introduction of an electron-donating substituent at C-4 leads to a hypsochromic shift of the emission band into the blue region. The results of earlier HOMO and LUMO energy calculations with several

heteroaromatic substances, carried out by Tamao [9], indicate that imidazole has a higher energy LUMO (5.35 eV) than does pyridine (3.45 eV). Based on these calculations and observations made in the current effort, we reasoned that blue phosphorescent iridium complexes would be generated when imidazole carboxylates of instead of picolinates are employed as ancillary ligands. To explore this proposal, iridium complexes **7-10**, which contain 2-(4',6'-difluorophenyl)-4-methylpyridine and 2-(4',6'-difluoro-5'-(trifluoro-methyl)phenyl)-4-methylpyridine as main ligands and *N*-methyl-2-imidazole carboxylate and *N*-methyl-5-imidazole carboxylate as ancillary ligands, were prepared and subjected to photophysical studies.

Inspection of the absorption and emission spectra of these new iridium complexes, given in Figure 3, shows that they display weak absorption bands in the 444- 453 nm region (**7**; 452 nm, **8**; 453 nm, **9**; 444 nm, **10**; 444 nm) and strong structured emission bands with maxima in the region of 458-467 nm (**7**; 467 and 491 nm, **8**; 467 and 491 nm, **9**; 458 and 483 nm, **10**; 458 and 483 nm) and emission quantum efficiencies range of 0.2-0.8 (**7**; $\Phi=0.2$, **8**; $\Phi=0.2$, **9**; $\Phi=0.5$, **10**; $\Phi=0.8$). Importantly, all of the iridium complexes exhibit phosphorescence emission in the blue region with excellent to good quantum efficiencies. Moreover, iridium complexes **9** and **10**, which contain 2-(4',6'-difluoro-5'-(trifluoro-methyl)phenyl)-4-methylpyridine as the main ligand, have 8-9 nm hypsochromic shifted emissions and 2.5-4 times higher quantum efficiencies than those of the iridium complex containing 2-(4',6'-difluorophenyl)-4-methylpyridine as the main ligand.

Fig.3. UV-vis absorption and photoluminescence spectra of iridium (III) complexes **7-10**.

4. Conclusion

The investigations described above, aimed at the development of new and more deeply blue phosphorescent iridium(III) complexes has resulted in the finding that calculation guided structural modifications of picolinates and 3-trifluoromethyl-5-(pyridine-2'-yl)-1,2,4-triazole ancillary ligands can be used to bring about the desired emission

properties. Specifically, the introduction of electron-donating substituents at C-4 of the pyridyl moiety of main ligands and the use of high LUMO energy *N*-methylimidazole carboxylates leads to iridium complexes that phosphoresce in the deep blue region with high efficiencies. These observations should serve as the foundation for design principles that can be utilized to tune the emission wavelengths and efficiencies of iridium complexes, which play an essential role in the OLED technology.

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