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Communication

Photophysical and Electrochemical Properties of Heteroleptic Tris-Cyclometalated Iridium(III) Complexes

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Mixed (difluoro)phenylpyridine/(difluoro)phenylpyrazole tris-cyclo-metalated iridium complexes were prepared in order to study the effect of fluorination and the pyridine/pyrazole ratio on the emission and electrochemical properties. Increasing fluorination and replacement of pyridine by pyrazole both leads to a widening of the HOMO–LUMO gap and generally leads to a blue shift in emission.

Recently, there has been growing interest in the use of cyclometalated iridium(III) complexes in a variety of applications such as oxygen sensing[1] and biological labeling and, in particular, as phosphors in organic light-emitting diodes (OLEDs).[2] Large improvements in OLED efficiencies have been realized by incorporating triplet-state emitters such as *fac*-Ir(ppy)$_3$ (ppy = 2-phenylpyridine) as dopants in the emissive layer.[3,4] Iridium cyclometalates often exhibit favorable photoproperties for OLEDs including short phosphorescent lifetimes, high quantum efficiencies, and good stability. The emission color can be readily tuned from blue/green to red by judicious modification of the coordinated ligands; however, there are fewer reports of blue emission from these species.[5–8]

To design efficient blue phosphors, it is critical to understand the structure−photophysical property relationship. To this end, we have prepared several heteroleptic tris-cyclometalated iridium compounds with systematic changes in their ligand systems. The mixed cyclometalates comprise the ligands 2-phenylpyridine, 1-phenylpyrazole (ppz), and two difluorophenyl derivatives (Chart 1). The new complexes **3**−**8**, along with the previously reported homoleptic compounds **1**, **2**, **9**, and **10**,[9] form three homologous series, two of which feature pyridine replacement by pyrazole: **1** → **3** → **5** → **9** (aryl = phenyl) and **2** → **4** → **8** → **10** (aryl = difluorophenyl). A third series, of the (pyridyl)(pyrazolyl)$_2$ group, **5** → **6** → **7** → **8**, is characterized by increasing fluorination, where difluorophenyl is attached first to the pyridyl ligand, then to the pyrazolyl ligands, and finally to all three.
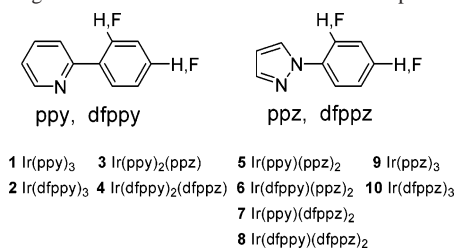
We have focused our study on the facial isomers of these octahedral complexes, as they are much more photostable and emissive than their meridional isomers. Room-temperature emission is observed only for complexes **1**−**8**, and each replacement of pyridine by pyrazole results in a blue shift of the emission maxima by several nanometers. The highest-energy emission in this group occurs at 460 nm for *fac*-Ir-(dfppy)(dfppz)$_2$. The quantum yields of **1**−**8** are moderate to high, ranging from 0.27 to 0.77.

The heteroleptic tris complexes were first prepared as meridional isomers from the corresponding dichloro-bridged dimers, [Ir(N∧C)$_2$Cl]$_2$, using a modified literature procedure[1] (see Supporting Information). Subsequently, complexes **4**−**8** were photochemically converted to their facial isomers by irradiating oxygen-purged MeCN solutions in a photochemical reactor.[9,10] Under conditions that are known to produce the facial isomer directly from the dimer,[1] that is, hot alcoholic solvent, we observed, in the mass spectrum, scrambling of the ligands and the formation of multiple products, which are difficult to separate. The slow photoconversion of **3**, however, required this route.

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(1) DeRosa, M. C.; Hodgson, D. J.; Enright, G. D.; Dawson, B.; Evans, C. E. B.; Crutchley, R. J. *J. Am. Chem. Soc.* **2004**, *126*, 7619−7626.
(2) See, for example: (a) Adachi, C.; Baldo, M. A.; Forrest, S. R. *Appl. Phys. Lett.* **2000**, *77*, 904−906. (b) D'Andrade, B. W.; Thompson, M. E.; Forrest, S. R. *Adv. Mater.* **2002**, *14*, 147−151. (c) Ostrowski, J. C.; Robinson, M. R.; Heeger, A. J.; Bazan, G. C. *Chem. Commun.* **2002**, 784−785. (d) Wang, Y.; Herron, N.; Grushin, V. V.; LeCloux, D. D.; Petrov, V. A. *Appl. Phys. Lett.* **2001**, *79*, 449−451. Markham, J. P. J.; Lo, S.-C.; Magennis, S. W.; Burn, P. L.; Samuel, I. D. W. *Appl. Phys. Lett.* **2002**, *80*, 2645−2647.
(3) Adachi, C.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *J. Appl. Phys.* **2001**, *90*, 5048−5051.
(4) He, G.; Schneider, O.; Qin, D.; Zhou, X.; Pfeiffer, M.; Leo, K. *J. Appl. Phys.* **2004**, *95*, 5773−5777.
(5) Laskar, I. R.; Hsu, S.-F.; Chen, T.-M. *Polyhedron* **2005**, *24*, 189−200.
(6) Holmes, R. J.; D'Andrade, B. W.; Forrest, S. R.; Ren, X.; Li, J.; Thompson, M. E. *Appl. Phys. Lett.* **2003**, *83*, 3818−3820.
(7) Li, J.; Djurovich, P. I.; Alleyne, B. D.; Tsyba, I.; Ho, N. N.; Bau, R.; Thompson, M. E. *Polyhedron* **2004**, *23*, 419−428.
(8) Coppo, P.; Plummer, E. A.; De Cola, L. *Chem. Commun.* **2004**, 1774−1775.
(9) Tamayo, A. B.; Alleyne, B. D.; Djurovich, P. I.; Lamansky, S.; Tsyba, I.; Ho, N. N.; Bau, R.; Thompson, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 7377−7387.
(10) Karatsu, T.; Nakamura, T.; Yagai, S.; Kitamura, A.; Yamaguchi, K.; Matsushima, Y.; Iwata, T.; Hori, Y.; Hagiwara, T. *Chem. Lett.* **2003**, *32*, 886−887.

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Chart 1. Ligand Structures and Formula of Tris Complexes

ppy, dfppy   ppz, dfppz

1 Ir(ppy)₃	**3** Ir(ppy)₂(ppz)	**5** Ir(ppy)(ppz)₂	**9** Ir(ppz)₃

1 Ir(ppy)₃ 3 Ir(ppy)₂(ppz) 5 Ir(ppy)(ppz)₂ 9 Ir(ppz)₃
2 Ir(dfppy)₃ 4 Ir(dfppy)₂(dfppz) 6 Ir(dfppy)(ppz)₂ 10 Ir(dfppz)₃
                                    7 Ir(ppy)(dfppz)₂
                                    8 Ir(dfppy)(dfppz)₂

Within each of the series $1 \rightarrow 3 \rightarrow 5$ and $2 \rightarrow 4 \rightarrow 8$, there is a progressive blue shift of ∼5 nm (∼210 cm⁻¹) in the emission maxima as pyridine is replaced by pyrazole (Table 1, Figure 1). A much larger blue shift of ∼39 nm (∼1670 cm⁻¹) occurs between each nonfluorinated complex and its corresponding version with three difluorophenyl groups. Complex **1** is known to emit from a metal-to-ligand charge-transfer (MLCT) state but with an admixture of ligand-centered (LC) character.[11−13] The vibronic structure is more pronounced in spectra at progressively higher energies, which indicates increasing contribution by the LC state. The lowest-energy absorption features listed correspond to ¹MLCT and mixed ¹MLCT/³LC transitions, respectively.[14,15] Similar bands for the phenylpyrazole-based complexes **9** and **10** occur at much higher energies[9] because of the poor electron-accepting nature of pyrazole as compared to pyridine. Therefore, the lowest-energy transitions of **1−8** are assigned as MLCT/LC involving arylpyridine. Consistently, the extinction coefficients decrease along the series $1 \rightarrow 3 \rightarrow 5$ and $2 \rightarrow 4 \rightarrow 8$ as the number of pyridine ligands decreases. Emissions from **9** and **10** have been previously observed only at 77 K with maxima at 414 and 390 nm, respectively, and were also assigned as mixed MLCT/LC, but to the arylpyrazole.[9]

Within the nonfluorinated complexes **1**, **3**, and **5**, the photoluminescence quantum yields of 68−73% are essentially equivalent to within the margin or error for this measurement. However, for the fully fluorinated complexes $2 \rightarrow 4 \rightarrow 8$, the yield drops significantly from 77% to 50% to 38%, respectively. Radiative rate constants calculated for these two series decrease somewhat as pyridine is replaced by pyrazole. However, whereas little change occurs in the nonradiative rate constants for the nonfluorinated series, there is a significant increase in k_{nr} across the fluorinated series $2 \rightarrow 4 \rightarrow 8$. We propose that the pyrazole moiety is associated with the increase in k_{nr} and the subsequent drop in quantum yield, possibly by Ir−N$_{pyrazole}$ bond breakage or pyrazole ring distortion, but that this becomes a factor only for the higher-energy excited states of **4** and **8**. A weaker Ir−pyrazole bond, in an excited complex, is consistent with mass spectra results

where fragments corresponding to the loss of arylpyrazole are several times more abundant than fragments produced by the loss of arylpyridine.

There are significant differences in the spectroscopic properties of the partially fluorinated complexes **6** and **7**, although they differ by a count of only one difluorophenyl moiety (Figure 2). The emission spectrum of **7** is quite structured, whereas for **6**, the spectrum is nearly featureless and broader (fwhm is 810 cm⁻¹ greater). The shape differences are also reflected in the lowest-energy absorption features. The Stokes shift for **7** at 360 cm⁻¹ is the smallest compared to the other complexes **1−5** and **8**, which range from 480 to 800 cm⁻¹, whereas **6** has the largest shift at 1900 cm⁻¹ (measured from the shoulder at 460 nm in toluene). Additionally, k_r is significantly larger than k_{nr} for **7**, whereas the opposite is true in the case of **6**.

To help understand why such large spectroscopic differences occur between **6** and **7**, density functional theory (DFT) calculations were performed for their ground-state geometries. The LUMOs of **6** and **7** are very similar, residing primarily on the dfppy and ppy ligands, respectively, and not at all on the pyrazole ligands (Figure 3). However, significant differences are seen for the HOMOs. The HOMO for **6** resides mostly on iridium, the phenyls of ppz, and somewhat on the pyrazole moieties, whereas for **7**, this orbital is primarily located on iridium and the phenyl ring of ppy. On the basis of the orbital diagrams, the HOMO-to-LUMO transition of **7** is MLCT with a relatively large LC component involving the ppy ligand. This is consistent with the small Stokes shift and pronounced vibronic structure. In the case of **6**, the HOMO-to-LUMO transition is associated with a large movement of electron density from ppz to dfppy. This suggests that the excited state of **6** could have, in addition to MLCT, some ligand-to-ligand charge-transfer (LLCT) character. This state might be distorted relative to the ground state, resulting in a large Stokes shift and broader spectra. Distortion might be a consequence of charge redistribution or might be due to involvement of the pyrazole orbitals in the HOMO.

To gain insight into the origin of the pyrazole- and fluorine-induced blue shifts, cyclic voltammetry measurements were performed (Table 1). All observable electrochemical processes were reversible or quasireversible. On average, the oxidation potential increases by 145 mV per difluorophenyl substitution and by 20 mV per pyrazole. Pyrazole is therefore slightly more electron withdrawing than is pyridine, and both fluorination and pyrazole substitution result in the lowering of the HOMO energy levels.

For complexes **3−8**, reduction occurs primarily on the relatively low-lying π* orbitals of ppy or dfppy and not at all on ppz or dfppz. This assignment is supported by DFT calculations and by the fact that the reductions of *fac*-Ir-(ppz)₃ and *fac*-Ir(dfppz)₃ are too difficult to observe electrochemically.[9] As pyrazole substitutes for pyridine, $1 \rightarrow 3 \rightarrow 5$ and $2 \rightarrow 4 \rightarrow 8$, the number of sites available for reduction decreases, and the reduced state increases by ∼25 mV per substitution. With increasing pyrazole substitution, the HOMO and LUMO move away from each other, and as

(11) Colombo, M. G.; Brunold, T. C.; Riedener, T.; Güdel, H. U.; Förtsch, M.; Bürgi, H.-B. *Inorg. Chem.* **1994**, *33*, 545−550.
(12) Hay, P. J. *J. Phys. Chem. A* **2002**, *106*, 1634−1641.
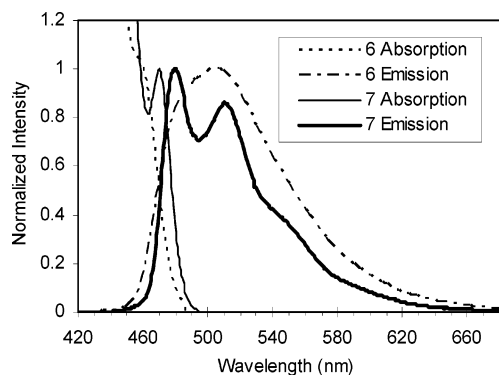(13) Finkenzeller, W. J.; Yersin, H. *Chem. Phys. Lett.* **2003**, *377*, 299−305.
(14) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 6647−6653.
(15) Li, J.; Djurovich, P. I.; Alleyne, B. D.; Yousufuddin, M.; Ho, N. N.; Thomas, J. C.; Peters, J. C.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2005**, *44*, 1713−1727.

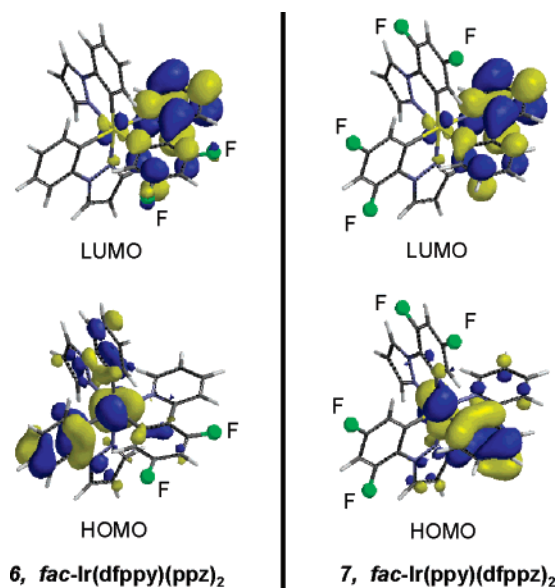**Table 1.** Spectroscopic and Electrochemical Data for Complexes **1−8**

	absorption[a,b]		room-temperature emission[b,c]					redox potentials[d]		
	λ, nm ($\epsilon \times 10^{-3}$, M^{-1} cm^{-1})		λ, nm	Φ	τ, μs	k_r, 10^5 s^{-1}	k_{nr}, 10^5 s^{-1}	E_{ox}, V	E_{red}, V	$\Delta E_{1/2}$, V
1	406 (8.0)	486 (1.2)	509	0.73	1.38	5.3	2.0	0.31	−2.70	3.01
2	383 (7.5)	453 (0.7)	469	0.77	1.64	4.7	1.4	0.76	−2.49	3.25
3	403 (5.2)	480 (0.7)	504	0.72	1.45	5.0	1.9	0.33	−2.73	3.06
4	380 (6.6)	450 (0.6)	465	0.50	1.13	4.4	4.4	0.78	−2.52	3.30
5	401 (3.2)	476 (0.3)	498	0.68	1.62	4.2	2.0	0.36	−2.74	3.10
6	390 (3.3)	457 (0.4)	504	0.27	0.76	3.6	9.6	0.51	−2.66	3.17
7	390 (3.1)	469 (0.15)	478	0.70	2.68	2.6	1.1	0.64	−2.62	3.26
8	378 (3.3)	448 (0.15)	460	0.38	1.05	3.6	5.9	0.80	−2.55	3.35

[a] Measured in dichloromethane solvent. [b] ϵ, Φ, and τ are ±10% or better. [c] Measured in nitrogen-saturated toluene solvent. [d] V vs Fc+/Fc. Measurements made in nitrogen-saturated anhydrous DMF solution containing 0.1 M [n-Bu$_4$N][PF$_6$] supporting electrolyte and ferrocene as an internal standard.
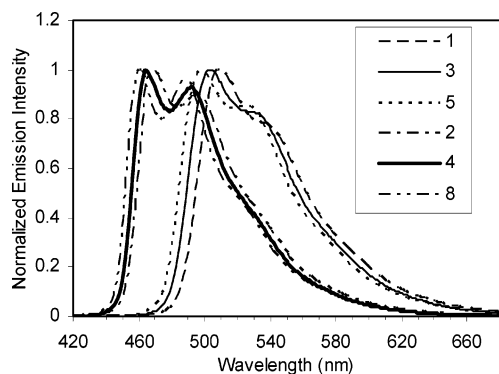
Figure 1. Room-temperature emission spectra in toluene solution.

Figure 2. Room-temperature absorption and emission spectra in toluene.

6, *fac*-Ir(dfppy)(ppz)$_2$ **7,** *fac*-Ir(ppy)(dfppz)$_2$

Figure 3. Contour plots of the HOMOs and LUMOs of **6** and **7**.

a result, the energy of emission increases across these metal complex series. In contrast, the magnitude of E_{red} *decreases* by 65 mV (±15 mV) for each difluorophenyl substitution. This lowering of the LUMO by fluorination is significantly less than that of the HOMO, resulting in a widening of the HOMO−LUMO gap and, with the noted exception of **6**, leading to an increase in the excited-state energy. This gap is reflected in $\Delta E_{1/2}$, which correlates closely with the energy of the ^{1}MLCT absorption peak.

In conclusion, it was found that the photoemission in phenylpyridine-based cyclometalated complexes can be blue shifted by sequential substitution with arylpyrazole. This occurs because of a simultaneous lowering and raising of the HOMO and LUMO energy levels, respectively. *fac*-Ir-(dfppy)(dfppz)$_2$ displays the bluest maximum at 460 nm, which is a 9 nm hypsochromic shift compared to the homoleptic species *fac*-Ir(dfppy)$_3$. It was also found that an uneven distribution of difluorophenyl moieties among the three bidentate ligands had a profound effect on the shape of the emission spectra. A drop in the photoluminescent quantum yield was seen for complexes **4**, **6**, and **8** that was associated with pyrazole. However, Φ_{pl} of the blue/green emitter **7**, with significant LC character, remained high. This suggests that it might be possible to design blue phosphors within this heteroleptic system with still higher Φ_{pl} efficiencies, provided they exhibit a similarly large degree of LC character.