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Blue light emission from cyclometallated iridium(III) cyano complexes: Syntheses, crystal structures, and photophysical properties

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ABSTRACT

We describe the synthesis and crystal structures of four iridium compounds containing the 2-(4,6-difluorophenyl)pyridyl ligand. Cleavage of dichloro-bridged iridium(III) dimers with phosphorus ligands leads to $(46dfppy)_2Ir(L)(Cl)$ where L = PPh_3 or $P(OPh)_3$. Treatment of the chloro compounds with cyanide forms the cyano complexes $(46dfppy)_2Ir(L)(CN)$. All complexes exhibit a *trans* effect in their molecular structures due to the phosphorus ligands, with the phosphite having a greater effect than the phosphine. With L = PPh_3, blue photoluminescence with CIE coordinates ($x = 0.16$, $y = 0.24$), quantum yield of 0.66 ± 0.15 and 4.5 ± 0.5 μs decay time is measured. For L = $P(OPh)_3$, blue photoluminescence with CIE coordinates ($x = 0.16$, $y = 0.21$), quantum yield of 0.65 ± 0.15 and 2.9 ± 0.3 μs decay time is measured.

1. Introduction

Cyclometalated iridium(III) complexes have been investigated in recent years as emitters for organic light-emitting diodes (OLEDs) [1]. A common cyclometalating ligand is the 2-phenylpyridyl moiety (ppy) which has shown its usefulness in a host of compounds with widely varying emission characteristics. Representative examples display emission across the visible spectrum including red [2], orange [3], green [4] and blue [5].

To obtain the highest light yields in OLEDs [6] or in plastic scintillators [7], at low doping levels, the lowest-lying triplet state of the iridium complex must lie at lower energy than the host. For example, *N,N′*-dicarbazolyl-3,5-benzene (mCP, $T_1 = 2.9$ eV) offers excellent efficiency with the best known blue–green iridium complex, bis[2-(4,6-difluorophenyl)pyridinato-C2,N](picolinato)iridium, $Ir(46dfppy)_2(pic)$, or FIrpic ($T_1 = 2.7$ eV), at doping levels of ~1% [8]. A variety of deeper blue-emitting iridium complexes have been reported, many with modest quantum yields, and some have limited stability under operating conditions in OLED devices [5,6,8–13]. For these reasons, alternative blue phosphorescent emitters, in particular, blue emitters with low-lying T_1 states for use in the full range of hosts, are of interest.

We have sought to prepare compounds with emission in the deep blue which can be realized by maximizing the HOMO–LUMO energy gap of the complex. Our approach is to focus on lowering the energy of the predominantly metal-centered t_{2g} HOMO while leaving the ligand-centered LUMO relatively unchanged. Thus, strong field electron-withdrawing ancillary ligands such as triphenylphosphine and cyanide merit investigation [14–18]. In addition to ancillary ligand effects, substitution of the phenyl hydrogens on the phenylpyridine group has been shown to influence the HOMO–LUMO gap. The use of electron-withdrawing fluorine atoms, particularly at the 4 and 6 positions, stabilizes the HOMO more than the LUMO and causes a blue shift in emission [19,20]. Prior workers have reported the use of the difluorophenylpyridyl ligand with an ancillary phosphine ligand as in $Ir(46dfppy)_2(PPh_3)(L)$, where 46dfppy = 2-(4,6-difluorophenyl)pyridyl and L = (NCS^-) or (NCO^-) [10]. Also, phosphine complexes using nonfluorinated phenylpyridine ligands are known, as in $Ir(ppy)_2(PPh_3)(L)$, where L = (NCS^-), (N_3^-), or (NCO^-) [21] and $Ir(ppy)_2(L)(CN)$, where L = PPh_3, $P(n\text{-}Bu)_3$, or $P(OPh)_3$ [22]. We report herein the synthesis, X-ray structural characterization, and electronic spectroscopy of four compounds: $(46dfppy)_2Ir(PPh_3)(X)$ and $(46dfppy)_2Ir[P(OPh)_3](X)$, where X = (Cl^-) or (CN^-). We examine the differences in the steric and electronic properties of the two phosphorus ligands [23] and their influence on the structures and emission spectra of the complexes.

2. Results and discussion

2.1. Synthesis and structure

The reaction sequence is depicted in Scheme 1. Thus, cyclometalated dichloro-bridged iridium dimer $[(46dfppy)_2Ir(Cl)]_2$ was smoothly cleaved by phosphine or phosphite ligands in methylene

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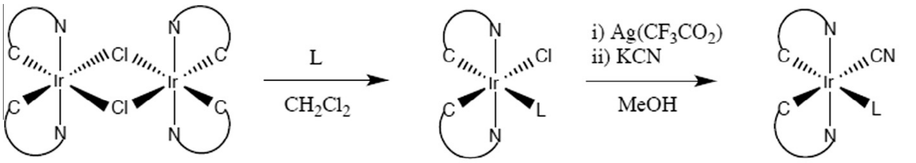


1 [L = PPh_3]
2 [L = $P(OPh)_3$]

3 [L = PPh_3]
4 [L = $P(OPh)_3$]

Scheme 1. Synthetic procedures.

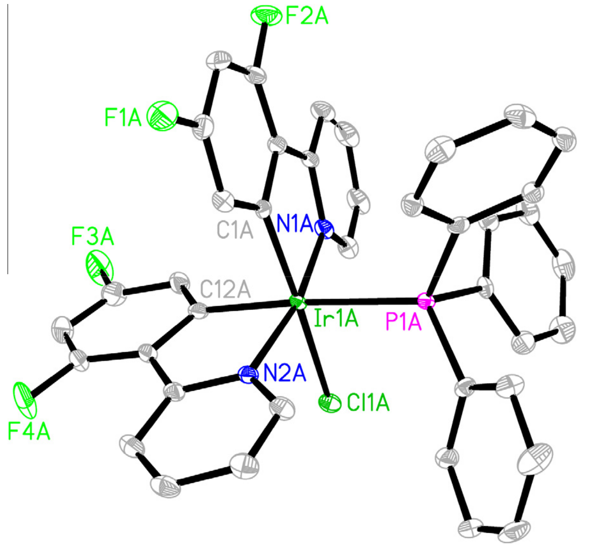
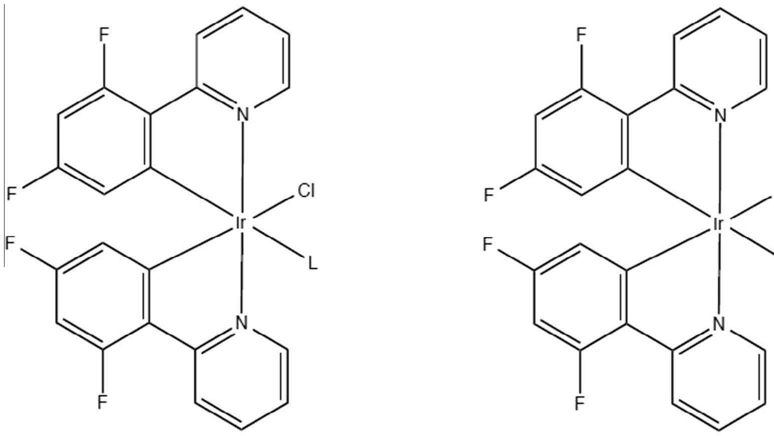


Fig. 2. Thermal ellipsoid drawing of **1a** is presented at the 50% probability level with the hydrogen atoms omitted for clarity. Two molecules are found in the asymmetric unit; only molecule A is shown in the figure. Selected bond distances (Å) and bond angles (°) for **1a**: Ir1A–C1A 2.008(3), Ir1A–N1A 2.043(2), Ir1A–C12A 2.044(3), Ir1A–N2A 2.067(2), Ir1A–P1A 2.4415(6), Ir1A–Cl1A 2.4726(7), N1A–Ir1A–N2A 169.03(9), C12A–Ir1A–P1A 174.79(8), and C1A–Ir1A–Cl1A 172.31(8); for **1b**: Ir1B–C1B 2.009(3), Ir1B–C12B 2.039(3), Ir1B–N1B 2.043(2), Ir1B–N2B 2.065(2), Ir1B–P1B 2.4293(6), Ir1B–Cl1B 2.4642(7), N1B–Ir1B–N2B 168.25(9), C12B–Ir1B–P1B 174.48(8), and C1B–Ir1B–Cl1B 171.48(8).

chloride to yield the chloro monomers $Ir(46dfppy)_2(L)(Cl)$, where L = PPh_3 (**1**) [10] or $P(OPh)_3$ (**2**). The *trans*-N,N and *cis*-C,C bonding of the difluorophenylpyridine ligands about the iridium center is maintained upon addition of the monodentate phosphorus ligand (vide infra). Treatment of these chloro monomers with silver trifluoroacetate in methanol followed by potassium cyanide leads to replacement of the chloride ligand to form the cyano complexes $Ir(46dfppy)_2(L)(CN)$, where L = PPh_3 (**3**) or $P(OPh)_3$ (**4**), again with retention of geometry about the iridium. The chemical structures for the compounds under discussion are shown in Fig. 1.

The molecular structures of compounds **1**–**4** have been confirmed by X-ray crystallography and ORTEP diagrams of these complexes are shown in Figs. 2–5; crystal and structure refinement data are provided in Table 1. All of the complexes exhibit the same distorted octahedral geometry: the pyridyl nitrogen atoms of the 46dfppy ligands are *trans* to each other while the phenyl carbon atoms bound to the iridium are *cis*. The phosphorus ligand and anionic ligand (Cl^- or CN^-) are both mutually *cis* to the pyridyl nitrogens as well as *cis* to each other. The octahedral symmetry around the iridium atom is distorted in that the non-phosphorus ligands are pushed away from the phosphorus ligands presumably due to steric factors. Thus the N–Ir–N bond angles (ideally 180°) are collapsed in all complexes, ranging from 167° to 168°. In the chloride complexes the Cl–Ir–C bond angles are collapsed somewhat (172° and 174°) while in the cyanide complexes the C–Ir–C(N) angles are 171° and 174°. The phenyl and pyridine rings in each 46dfppy ligand are slightly twisted with respect to each other across the C–C bond linking the two rings. The dihedral angle between best planes for the two rings averages 5° in **1**, **2**, and **4** and 7.5° in **3**. There is a pronounced *trans* effect due to the phosphorus ligand. Thus, in **1**, the Ir–C bond length *trans* to the phosphine is 0.036 Å longer than the Ir–C bond *trans* to the chloride. The difference in **2** is even more pronounced with an elongation of 0.054 Å for the bond *trans* to the phosphite. This is in accord with Tolman's substituent effect parameter [23], which is larger



1 [L = PPh_3]
2 [L = $P(OPh)_3$]

3 [L = PPh_3]
4 [L = $P(OPh)_3$]

Fig. 1. Chemical structures of compounds **1**, **2**, **3** and **4**.