Enhancing the Photoluminescent Quantum Yields of Blue-Emitting Cationic Iridium(III) Complexes Bearing Bisphosphine Ligands


Introduction
During the last decade, cationic iridium(III) complexes have been drawing tremendous interest as emitters for lighting applications due to their relatively short-lived triplet excited states ($\tau_T$), high photoluminescence quantum yields ($\Phi_{PL}$), and the facile emission color tunability, which are crucial properties for emitters employed in organic light-emitting diodes (OLEDs) or light-emitting electrochemical cells (LEECs). Bisphosphine ligands have been extensively used in organometallic catalysis but their use as ligands for luminiferous Ir(III) complexes remains underexplored, despite their potentially high chemical stability and good tunability of the optoelectronic properties, particularly for achieving blue emission.[1,2]

Given the paucity of photoluminescent iridium complexes bearing P-P chelators and their promising properties, herein we report a structure-property relationship study of thirteen cationic iridium (III) complexes of the form of [Ir(CN)2(P2P)]PF6 in both solution and the solid state, through systematic evaluation of six bisphosphine (P2P) ligands (xanthphos, nixoxtphos, dpophos, depe, Dpe and isoxepxanthphos) and four C-N cyclometalating ligands (ppy, mepy, dpf and dfmepy) (figure 1).

By optimizing the bite angle of the P-P chelate and coupling it with bulky C-N ligands, bright blue emitters with high photoluminescence quantum yield and long-lived excited states have been obtained. Light-Emitting Electrochemical Cells (LEECs) and Organic Light-Emitting Diodes (OLEDs) have been fabricated using lead complexes from this study and their performances in device have been investigated.

Optoelectronics
Figure 3: UV-Vis spectra of complexes 1a, 2a, 4a, 1b, 1c, 1d, 1f (a) and 2b, 4b, 1c, 2c, 4c, 3c (b) recorded in MeCN at 298 K.

Figure 4: Normalized luminescence spectra of complexes 1a, 2a, 4a, 1f (a) and 1b, 2b, 4b, 1c, 2c, 4c, 3c, 1d (b) recorded in degassed MeCN at 298 K.

Figure 5: Oxidation processes of complexes 1 - 4 in MeCN with 0.1 M TBAPF6 as the supporting electrolyte. Scan rate: 0.1 V sec⁻¹

Figure 6: UV-Vis (in blue, in MeCN at 298 K), excitation (in red) and emission spectra (in green) of complexes 4a recorded in degassed MeCN at 298 K. In solution, complexes 4a emits at 360 nm with a slight shoulder at 410 nm. Upon excitation at 360 nm, the emission is at 510 nm.

In summary, thirteen blue to blue-green emitting (λem 477 - 510 nm) cationic heteroleptic iridium(III) complexes bearing bisphosphine ancillary ligands have been synthesized and their optoelectronic properties investigated. Through optimization of the bite angle of the P-P chelate and introduction of bulky and fluorinated C-N ligands, we have rationally designed the brightest reported blue-emitting (λem 477 nm) complex of this class in 4c ($\Phi_{PL}$: 52%). However, these complexes exhibit irreversible electrochemistry, which perhaps accounts for the poor LEEC performances observed using complexes 1b, 4a, 4b, and 4c. OLED devices have been fabricated using complexes 4c and 3c as emitters but unfortunately low External Quantum Efficiencies (EQE) of 0.23% and 0.17%, respectively, have been achieved.