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Iridium^{III} complex with N-Oxide ligand: Photophysical Properties and Luminescent films

Gustavo M. Martines[1,2], **Lívia B. Perrud**[1], **Renan C. Silva**[1,2] **Ana M. Pires**[1,2], **Sergio A. M. Lima**[1,2]

[1]*São Paulo State University (UNESP), School of Technology and Sciences, Presidente Prudente, Brazil.*
[2]*São Paulo State University (UNESP), Institute of Biosciences, Humanities and Exact Sciences, São José do Rio Preto, Brazil.*
E-mail: ***g.martines@unesp.br***

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The Ir^{III} ion readily forms coordination compounds with various classes of cyclometalating ligands, exhibiting attractive luminescent characteristics such as high quantum yields (Φ), modulation of both absorption and emission, as well as modulation of excited state lifetime. These complexes have promising applications in optoelectronics such as OLEDs (Organic Light-Emitting Diode), and several other optoelectronic devices. Additionally, they find application in the biological field, including oxygen sensing, bioimaging and agents in photodynamic therapy. Thus, this work describes the synthesis and spectroscopic characterization of an Ir^{III} complex with an N-oxide ligand (N^O) and its respective luminescent films. The synthesis consisted on the preparation of the cyclometalated Ir^{III} dimer [Ir(Fppy)$_2$(μ-Cl)$_2$Ir(Fppy)$_2$], followed by the preparation of the heteroleptic complex [Ir(Fppy)$_2$pzdc]: Fppy = 2-(2,4-Difluorophenyl)pyridine and pzdc = 2,3-pyrazinedicarboxylic acid. With the synthesized complex, PMMA films were fabricated with different (w/w) concentrations of the complex (0.1%, 0.25%, 0.50%, 0.75%, and 1.0%). The complex was structurally characterized by ^{1}H-NMR, elemental analysis, and FTIR-ATR. FTIR-ATR (υ_{max}/cm^{-1}): 1632 (υC=O)$_{pzdc}$, 1600, 1570, 1557 (υC=N, C=C)$_{fppy}$, 1333 (υCOO)$_s$, 1108 (υC=N, C=C)$_{pzdc}$. CHN analysis indicate agreement between calculated (found) values for the structure $IrC_{28}H_{23}N_4O_8F_4$: C, 41.43% (41.50%); H, 2.86% (3.02%); N, 6.90% (6,20%). Absorption and photoluminescence spectra were obtained in several solvents: DMSO, DCM, ACN, and MeOH. The complexes exhibited high molar absorptivity, attributed to singlet and triplet metal-to-ligand charge transfer (MLCT) and ligand-centered (LC) transitions, which were observed in the UV-Vis spectra. Excitation spectra showed a broad band with a similar profile for all tested solvents. In the emission spectra for each solvent tested, broad emissions ranging from yellow-orange to red were observed. Notably, the spectra exhibited emission maxima at approximately 510 and 617 nm in DMSO, 612 nm in DCM, 622 nm in ACN, and 630 nm in MeOH. This difference in emission maxima is attributed to the solvatocromic effect that leads to structural deformations, which influence the energy levels of the excited states. The emission spectra of the films showed broad bands with a maximum around 550 nm, and a red shift was observed as the concentration of the complex increased. The Φ of the complex was determined in: DMSO (7.7%), DCM (9.2%), ACN (6.9%), and MeOH (1.2%). Their photophysical properties indicate potential for applications in photonics, notable for their high molar absorptivity and tunable emission in different solvents.

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References

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