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Design and synthesis of non-symmetric phenylpyridine type ligands. Experimental and theoretical studies of their corresponding iridium complexes

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ABSTRACT

In this work three non-symmetric phenylpyridine type ligands, **L1**, **L2** and **L3**, were designed, and their corresponding Iridium complexes, **C1**, **C2** and **C3**, synthetized, in order to understand the effect of ligand asymmetry on the properties of the complexes, and to explore their potentiality in devices. The complexes were structurally characterized by NMR experiments and by X-ray Diffraction, and physicochemically by technics as UV/Vis and cyclic voltammetry. Theoretical DFT calculations of the energy and electronic density of the frontier orbitals of the complexes under study were also performed. The energy of the HOMO and LUMO correlated well with the experimental electrochemical data, and supported the understanding of the processes observed.

1. Introduction

Transition Metal Chromophores have attracted great attention for their capacity to respond in different applications. In this ambit, polypiridyl compounds of transition metals, as $Ru(bpy)_3^{2+}$, or cyclometallated complexes, as $Ir(ppy)_2(acac)$, are good triplet emitters and have suitable spectral properties for different applications, *e.g.*, in OLEDs devices, or as dyes fixed to TiO_2 in solar cells, among others [1,2]. For this kind of complexes, the ligand plays an important role to induce different photophysical properties or electrochemical behaviors [3]. Accordingly, in the literature there are many spectral studies with ligands based on 2-phenylpyridine (ppy) or 2,2′-bipyridine (bpy), coordinated to different transition metals [4]. Complexes with red-orange to deep red phosphorescence and high emission quantum yields have been obtained. This kind of properties are related to the gap between the lowest unoccupied molecular orbital (LUMO) to the highest occupied molecular orbital (HOMO). In special, it is possible to adjust the HOMO–LUMO gap simply by changing the ligand framework; this change affects directly the emission color [5–7]. For example, given its donor properties, in complexes with ligands of 2-phenylpyridine (ppy) type, the HOMO energy level is destabilized compared to the equivalent complexes with bpy type ligands. This reduces the HOMO–LUMO energy gap, and shifts the absorption and emission maxima to the red. Additionally, in complexes with ppy type ligands the HOMO electronic density is localized both over the phenyl ring and the metal center, while the LUMO level is centered in the pyridine ring [8]. In literature, the reported synthetic procedures on substituted bpy or ppy type ligands has been mainly been focused on symmetrically substituted ligands.

The present study is oriented to the understanding of the effect of the symmetry of the ligand, and its substituents, on some of the properties of the corresponding complexes. The ligands used are non-symmetric derivatives of ppy, and are tested on Iridium complexes of type $Ir(R\text{-}ppy)_2(acac)$. The ligands and complexes were spectroscopically and crystallographically characterized. A theoretical study was also performed, in order to understand the tendencies observed in the experimental results for the series of Iridium complexes with non-symmetric ppy ligands studied.

2. Experimental

2.1. General methods

All starting materials were commercially available and used as received without further purification. Thin Layer Chromatography (TLC) was performed on silica gel 60 F_{254}, using aluminum plates and visualized with vanillin stain and UV lamp. Flash chromatography was carried out on hand packed columns of silica gel 60 (230–400 mesh). All NMR experiments were recorded on a Bruker

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Avance of 400 MHz, ^{1}H NMR spectra were recorded at 400 MHz using $CDCl_3$ as the solvent and TMS as internal standard (0.00 ppm). ^{13}C NMR spectra were recorded in $CDCl_3$ at 101 MHz. The electrochemical characterization of the Iridium complex was performed by means of cyclic voltammetry (CV) in ACN as a solvent, using a three-electrode cell consisting of a platinum working electrode, a platinum wire auxiliary electrode and standard Ag/AgCl electrode as the reference electrode with a scan rate of 100 mV * s^{-1}. The solutions were 1×10^{-1} mol/L^{-1} in the corresponding complex, and contained tetrabutylamonium hexafluorophosphate 1×10^{-1} mol/L^{-1} as supporting electrolyte. The emission spectra were recorder on a PerkinElmer LS 55 Fluorescence spectrometer with slit of 2.5 cm. The absorption spectra were recorder on a Shimadzu UV-3101PC UV–VIS-NIR Spectrophotometer. The X-rays diffraction were obtained on a STOE IPDS II two-circle. The structure was solved by direct methods using SHELXS; and Figures were created using the PLATON software. Finally, for the quantum yields for all complexes, using [Ru $(bpy)_3](PF_6)_2$ as reference compound was calculated using standard reported methods [9].

3. Computational details

All calculations were performed on ADF framework [10] and the geometries were optimized with the OPBE [11] exchange correlation functional, including the scalar relativistic correction [12] in conjunction with ZORA-TZP and DZP basis set for Iridium and atoms from the first row. Hirschfeld fragment analysis [13] was employed to study the composition of the molecular orbitals in sets of four fragments, including the metal core(M), the ancillary acac ligand(L), and the phenylpyridine ligand, which in turn is decomposed in the two fragments: phenyl(F) and piridyne(P). The TDDFT calculations were performed in presence of acetonitrile as solvent and employing a Klamt surface [14]. The first 40 allowed and not allowed excitations were calculated with ZORA-SZ basis set for C,H,N,O and the SOAP exchange correlation potential [15].

3.1. Procedure for ligand synthesis

3.1.1. Preparation of methyl 2-(m-tolyl)isonicotinate (**L1**) [16]

*3.1.1.1. 2-Bromoisonicotinic acid (**2**).* A mixture of 2-bromo-4-methylpiridine, 1, (9.27 g, 54 mmol) in 490 mL of water, and of $KMnO_4$ (16 g, 11 mmol) in 250 mL of water were stirred for 5 h at 110 °C. The resulting mixture was filtered and the filtrate was reduced to 1/3 and acidified with HCl until pH 3. The white precipitated obtained was filtered and dried, Yield: 36% of 2-bromoisonicotinic acid.

FT-IR (KBr) ν, 3100–2350 (stretching O–H), 1710 (str. C=O), 1597 (str. C=C), 1546 (str. C=N), 1285 (str. C–O), 667 (str. C-Br) cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ, 8.58 (dd, J = 5.0, 0.8 Hz), 7.95 (dd, J = 1.4, 0.8 Hz), 7.84 (dd, J = 5.0, 1.4 Hz).

*3.1.1.2. Methyl 2-bromoisonicotinate (**3**).* A mixture of 2-bromoisonicotinic acid, **2**, (0.200 g, 0.99 mmol) in acetone and K_3PO_4 (0.290 g, 1.09 mmol) was stirred for 30 min at room temperature. When the time was over CH_3I (0,155 g, 1.09 mmol) was added and the mixture refluxed for 2 h. Finally the mixture was cooled and left over ice, and the product extracted with $CHCl_3$. The organic phase was dried with Na_2SO_4, and purified by silica gel chromatography with $CHCl_3$ as mobile phase. The contents of the organic phase were removed *in vacuo* to obtain methyl 2-bromoisonicotinate with 82% yield.

FT-IR (KBr) ν = 3089 (str. C–H sp_3), 2955 (str. C–H sp2), 1722 (str. C=O), 1588 (str. C=C aromatic), 1546 (str. C=N), 670 (str. C-Br) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.36 (d, J = 5.1 Hz, 1H), 7.85 (s, 1H), 7.65 (d, J = 5.0 Hz, 1H), 3.82 (s, 3H).

*3.1.1.3. Methyl 2-(m-tolyl)isonicotinate (**L1**).* In a micro reactor vessel, bromopyridne (**3**) (3.1 eq), 30 mL of DME, and $Pd(Ph_3)_4$ (0.015 eq) were added. The mixture was stirred for 10 min under inert atmosphere. When the time was over, boronic acid (**4,** 1.2 eq) and K_2CO_3 (2.4 eq) were added. The mixture was heated at its boiling point for 2 days. Finally the reaction was filtered under vacuum and the filtrate was extracted with $CHCl_3$. The crude product was purified by silica gel chromatography using petroleum benzine/ethyl acetate (1:1) as mobile phase. The contents of the organic phase were removed *in vacuo* to obtain an orange oil corresponding to methyl 2-(*m*-tolyl)isonicotinate, **L1**, with 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ, 8.81 (d, J = 5.0 Hz, 1H), 8.28 (s, 1H), 7.88 (s, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.75 (dd, J = 5.0, 1.3 Hz, 1H), 7.37 (t, J = 7.7 Hz, 1H), 7.27 – 7.23 (m, 1H), 3.97 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) 165.79, 158.62, 150.31, 138.57, 138.37, 138.14, 130.36, 128.79, 127.78, 127.64, 124.19, 121.05, 119.96, 119.77, 77.16, 52.75, 21.52.

*3.1.1.4. Methyl 2-phenylisonicotinate (**L2**).* This ligand was obtained with 86% yield using a similar procedure than the one described for **L1**.

^{1}H NMR (400 MHz, CDCl3, ppm) δ, 8.75 (d, J = 4.8 Hz, 1H), 8.21 (s, 1H), 7.97 (d, J = 7.2 Hz, 2H), 7.68 (d, J = 4.8 Hz, 1H), 7.39 (dt, J = 21.7, 7.0 Hz, 3H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm), 165.88, 158.57, 150.55, 138.61, 138.2, 129.58, 128.97, 127.10, 121.23, 119.81, 52.83.

*3.1.1.5. Methyl 2-(m-tolyl)pyridine (**L3**).* This ligand was obtained with 86% yield using a similar procedure than the one described for **L1**.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.53 (d, J = 4.9 Hz, 1H), 7.97 (d, J = 7.2 Hz, 2H), 7.52 (s, 1H), 7.45 (t, J = 7.3 Hz, 2H), 7.39 (d, J = 7.2 Hz, 1H), 7.02 (d, J = 4.4 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 157.45, 149.50, 147.79, 139.62, 128.81, 128.70, 127.01, 123.20, 121.60, 21.28.

3.2. General procedure to obtain [Ir(C^N)2(μ-Cl)]$_2$ dimers [17]

All dimers were synthetized by the following procedure:

To a 100 mL round bottom flask 1 eq of $IrCl_3$ in methylethylene glycol (5 mL for each 150 mg) were added. The flask was attached to a condenser and the system set under nitrogen atmosphere, and then the corresponding L(*i*) ligand (2.5 eq) was added. The reaction was carried out at reflux in a silicone bath for a period of 12 h. Then, the heating was stopped and the reaction allowed to cool. The contents of the flask were removed in *vacuo* to afford the crude compound was purified with a minimal amount of hexane/ethyl acetate (1:1) and stirred a few seconds. Finally, a few drops of hexane were added to precipitate the complex that was separated from the solution by filtering, yield 98%.

*3.2.1. Bis[μ-chloro di-(2-m-tolylisonicotinate)iridium III] (**5**),*

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.31 (d, J = 6.0 Hz, 3H), 8.42 (s, 3H), 7.44 (s, 3H), 7.39–7.08 (m, 5H), 6.45 (d, J = 7.5 Hz, 3H), 5.77 (d, J = 7.9 Hz, 3H), 4.12 (s, 9H), 2.15 (s, 10H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 169.30, 164.80, 151.54, 142.26, 140.85, 137.12, 130.87 (d), 129.99, 125.00, 120.80, 117.69, 52.89, 20.65.

*3.2.2. Bis[μ-chloro di(2-phenylisonicotinate)iridium III] (**6**)*

Yield 99%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.32 (s, 1H), 8.45 (s, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.20 (d, J = 5.5 Hz, 1H), 6.81 (t, J = 7.3 Hz, 1H), 6.61 (t, J = 7.4 Hz, 1H), 5.90 (d, J = 7.7 Hz, 1H), 4.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 169.64, 164.96,