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3,5-Disubstituted-2-(2′-pyridylpyrroles) Ir(III) complexes: Structural and photophysical characterization

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ABSTRACT

The synthesis, crystal structure and luminescence properties of three neutral heteroleptic cyclometallated Ir(III) complexes of general formula **[(ppy)$_2$Ir(PyPr-R)]**, where **Hppy** = 2-phenylpyridine and **HPyPr-R** = 3,5-disubstituted-2-(2′-pyridyl)pyrrole with **R** = CH_3 (**1**), Ph (**2**) and CF_3, (**3**), are described. The cyclic voltammetry studies carried out on **1**–**3** showed oxidation potentials consistent with the nature of the -**R** substituent groups, indicating that the energy of the HOMO level is significantly affected by the overall electronegativity of the **PyPr-R** ancillary ligand. Single-crystal X-ray-structural determination was carried out in the case of **2** and **3**. While **3** crystallizes in a unique form, two pseudo-polymorphs, a solvated (**2a**) and non-solvated (**2b**) specie, have been obtained for compound **2**. The supramolecular assembly of the neutral complexes in their crystalline state is mainly directed by $\pi\cdots\pi$ stacking (**2a**, **2b**) and C–H$\cdots\pi$ interactions (**3**). The photophysical properties of the **HPyPr-R** ligands and complexes **1**–**3** have been investigated in solution and, for **2a**, **2b** and **3**, in their solid crystalline state. All complexes show phosphorescence emission in solution, significantly quenched in presence of dioxygen. In the solid crystalline state, the emission maxima of **2a**, **2b** and **3** show a significant spectral shift with respect to the solution. For complex **3** it was calculated a bathochromic shift of 1178 cm^{-1}, while the spectral maxima of complexes **2a** and **2b** are red-shifted of *ca.* 3150 cm^{-1}. Moreover, the average emission lifetime of **2a** and **2b** crystalline samples is one order of magnitude higher with respect to that of **3** (1.64 and 1.55 μs, respectively, versus 0.265 μs). This behaviour accounts for the presence of excimers in the solid sample of **2a** and **2b,** most likely due to the $\pi\cdots\pi$ stacking interactions involving the pyridine rings of either the cyclometallated and/or the ancyllary ligands. This type of interaction is absent in **3**, the presence of the C–H$\cdots\pi$ interactions being insufficient to produce photophysically observable effects.

Introduction

Luminescence from neutral cyclometallated Ir(III) complexes has recently received considerable attention due to their potential of tailoring the emission colour and efficiency of organic optoelectronic devices (OLED and LEEC) [1], and for their use in several applications, as diverse as detection and sensing systems, luminescent sensors, photovoltaic cells, non linear optics, photodynamic therapy and catalysts for artificial photosynthesis [2]. One of the critical issues related to the incorporation of these emitters in molecular based materials is the role played by the intermolecular interactions on the final emission efficiency.

Indeed, intermolecular interactions often lead to aggregate formation in both concentrated solution and condensed phase [3]. These aggregate states are usually characterized by changes in the fluorescence spectra and often result in luminescence quenching phenomena, a thorny obstacle to many applications. To mitigate the aggregation-caused quenching, various approaches have been developed, such as the chemical grafting of the ligands with branched bulky substituent group [4] or the confinement of the employed dyes in mesostructured materials [5].

In general, even if the metal centre and the cyclometallating ligands have an important role in designing the molecular

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structures and functionalities of the complexes, the choice of the ancillary ligand can be crucial as well for determining their ultimate properties [6]. Indeed, it is well established that the photophysical properties of Ir(III) complexes, such as the efficiency and colour of the emitted light, can be easily changed and tuned by opportunely drawing both the cyclometallating and ancillary ligand [7]. In particular, the appropriate variation of the substituent groups on the ancillary ligands can be a route for introducing suitable steric requirements on the metal-containing fragment, leading, at the same time, to tailored electronic changes. Particular attention has been recently given to 3,5-disubstituted-2-(2′-pyridyl)pyrrole ligands, because of their versatile coordination ability towards different metal ions [8]. Moreover, the chemical modification of these ancillary ligands can be straightforwardly accomplished by introducing in the 3,5-positions of the pyrrolic ring opportune substituent groups with different electronic and/or steric characteristics [9]. In this context, we have recently reported on the synthesis and properties of some Pd(II) complexes containing 3,5-disubstituted-2-(2′-pyridyl)pyrrole as ancillary ligands [10]. Our investigation proved that different behaviours, including unexpected mesomorphism and aggregated induced solid state emission, can be generated mainly as a function of the nature of the substituent groups and, hence, of the resulting supramolecular interaction. Concerning Ir(III) complexes, it has been also reported that the use of 3,5-di(trifluoromethyl)-2-(2′-pyridyl)pyrrole as ancillary ligand coupled with fluoro-substituted phenylpyridine as ciclometallating ligand allowed to obtain a deeper blue phosphoresce [11].

In the frame of our research work, aimed at improving the molecular-based devices performances by controlling the supramolecular organization of the emitters into specific suprastructures [12], we synthesized and characterized three new cyclometallated Ir(III) complexes of general formula **[(ppy)$_2$Ir(PyPr-R)]**, where **Hppy** = 2-phenylpyridine and **HPyPr-R** = 3,5-disubstituted-2-(2′-pyridyl)pyrrole with **R** = CH_3 (**1**), Ph (**2**) or CF_3 (**3**). At a molecular level, the substituent groups on the ancillary ligands are expected to determine different degrees of ligand conjugation, and generate distinct electronic effects. Furthermore, different arrangements can be envisaged at a supramolecular level, due to a combination of steric effects and possible modes of intermolecular interactions.

The luminescence properties of **1**–**3** have been characterized in both solution and crystalline solid state, and the differences observed have been substantiate through a careful analysis and comparison of their crystal packing.

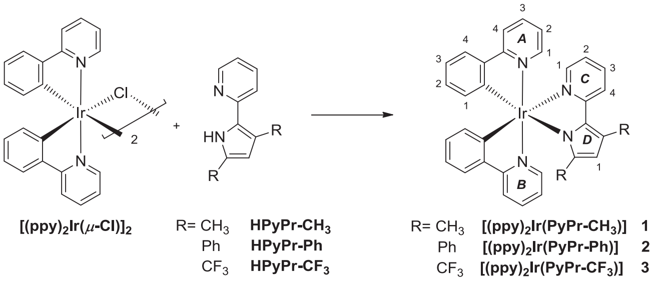
Results and discussion

Synthesis

The **HPyPr-R** ligands were prepared according to the literature procedures [9,10a]. The synthesis of complexes **1**–**3** was performed adapting the reported method [11] (Scheme 1).

In particular, the typical reaction of the dimeric bridged precursor **[(ppy)$_2$Ir(μ-Cl)]$_2$** with the relative disubstituted **HPyPr-R** ligand in the presence of Na_2CO_3 and in 2-ethoxyethanol, under inert atmosphere, yielded the desired products **1**–**3**, in relatively high yields. The complexes **1**–**3** were characterised by IR and ^{1}H NMR spectroscopies and elemental analysis (see the Experimental Section for more details).

In the ^{1}H NMR spectrum of complexes **1** and **3**, the protons of the ppy moieties are equivalent, whereas in the case of complex **2** a relatively small difference in the chemical shifts due to the ring current anisotropies of the phenyl groups belonging to the ancillary ligand **PyPr-Ph** induces a multiplicity of the signals. Furthermore, the chemical shifts of the pyridinic protons (C1–C4) belonging to the ancillary ligand **PyPr-R** follow the electron-donor ability of the substitution group (**R**). Indeed, the protons C1–C4 are more shielded in the case of complex **1** with respect to complex **3** (Experimental Section), but complex **2** suffer an additional deshielding, again due to the ring current anisotropies of the phenyl groups.



Scheme 1. Synthesis and proton numbering for complexes **[(ppy)$_2$Ir(PyPr-R)]**, **1**–**3**.

Electrochemical properties

The redox properties of complexes **1**–**3** were studied by cyclic voltammetry. The typical voltammetry cell was composed of a Pt disk as working electrode, a Pt wire as counter electrode, and an Ag wire as a pseudo reference electrode. Voltammograms were registered in *ca.* 3 mL degassed (Ar) dichloromethane solution containing $[N(C_4H_9)_4]PF_6$ (0.1 M) as supporting electrolyte. In these experimental conditions for which the potential window is limited to *ca.* − 1.3 V, no reduction process was observed for all complexes, neither in dry dimethylformamide solution for which this limit can be moved up to − 2.0 V. The oxidation potentials of all complexes together with the estimated energy values of the highest occupied molecular orbital (HOMO) are reported in Table 1. The HOMO was evaluated by comparison between the oxidation potentials of the complexes and of ferrocene used as internal reference and taking into account −4.8 eV for Fc/Fc^+ [13].

Considering the oxidation of complexes **1**–**3**, an irreversible oxidation process was observed for **1**, while complexes **2**–**3** are characterised by a quasi-reversible oxidation process; corresponding voltammograms are presented in Fig. 1.

As clearly observed on the voltammograms overlay, the presence of highly electronegative substituents on the **PyPr** ligand results in a significant positive shift of the oxidation wave, hence oxidation potentials vary with the order **1** < **2** < **3** with a difference of *ca.* 580 mV on moving from CH_3 to CF_3 groups. In cationic Ir(III) complexes the oxidation is influenced nearly completely by the decoration on the cyclometallated ligands, with little effect from the ancillary ligand [14]. In contrast' being unchanged the cyclometallated ppy ligand within the series **1**–**3**, it is clearly observed that the HOMO energy level is governed for these complexes by the nature of the PyPr ancillary ligand substituents. For Ir(III) neutral or ionic complexes of the **(ppy)$_2$IrL** series, with **L** ancillary ligand such as acetylacetone [15], 2,2′-bipyridine [16], $(CN)_2$ [17], $(CN{-}Me)_2$

Table 1
Oxidation potentials of complexes **1**–**3** (*vs.* Fc/Fc^+) and corresponding estimated HOMO energy values.

Compounds	E^{ox} (mV)[a]	HOMO (eV)
1	60[b]	4.86
2	190[c]	4.99
3	640[c]	5.44

[a] All potential are given *vs.* Fc/Fc^+.
[b] Irreversible wave with $E^{ox} = E_{pa}$.
[c] Quasi-reversible wave with $E^{ox} = (E_{pa} + E_{pc})/2$.