



Novel iridium-pentafluorophenyl porphyrin complex



Ana Delgado-Lima^{a,*}, António M. Fonseca^b, Ana V. Machado^a

^a Institute for Polymers and Composites/13N, University of Minho, Azurém, 4800-0581 Guimarães, Portugal

^b Department of Chemistry, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

ARTICLE INFO

Article history:

Received 31 July 2016

Received in revised form 24 March 2017

Accepted 30 March 2017

Available online 4 April 2017

Keywords:

Coordination chemistry

Synthesis

Porphyrins

Iridium

Spectroscopy

ABSTRACT

The novel iridium-pentafluorophenyl porphyrin complex (TPFPPIrCl(CO)) was successfully synthesized by chemical reaction with the iridium (I) metal precursor $[\text{Ir}(\text{COD})\text{Cl}]_2$. The final complex was identified linked to the axial Cl and CO ligands by UV–Visible, ^1H , ^{13}C NMR spectroscopy as well the $^1\text{H}/^{13}\text{C}$ correlated techniques and by mass spectrometry.

© 2017 Published by Elsevier B.V.

1. Introduction

Porphyrins are an important class of compounds directly involved in biological phenomena, but also in other very appealing applications, such as, as reaction catalyst and photosensitizers in photodynamic therapy, molecular electronic devices and solar energy conversion [1–11]. These macromolecules derive from porphyrin and consists of aromatic macrocycles of four pyrrole rings, which are substituted at β and/or meso positions linked by a methine bridge [1,2,5,11]. Porphyrins are also very attractive molecules due to their capability of forming complexes with most of the elements in the periodic system, by the loss of the two inner NH protons and further metal coordination, showing distinctive properties from the porphyrin initial precursor [6,12,13]. In the case of a favored octahedral geometry by the metal ion, the porphyrin coordination sphere is normally completed with ligands [11]. It is also of great importance to mention that the facility of coordination of a metal ion with a porphyrin depends mainly on the available space between the porphyrin core (approximately radius = 75–90 pm), and the ionic radius of the metal ion. Therefore, there does not exist a single metal insertion procedure that can be applied to all metals and porphyrins [5,6,11,12]. And while for 3d metals, the ionic radius matches the available space of the porphyrin core, resulting in a planar geometry with the porphyrin [12]. For larger ions coordination, 4d and 5d, the metal ion is usually positioned outside the porphyrin plane [5]. Iridium, a 5d⁹ transition metal,

has attractive properties, such as, high melting point, chemical stability, superior oxidation resistance and high electrical resistivity. Which makes iridium complexes promising materials for a wide range of applications from heavy-metal-ion sensors, catalysis and switching layers in electrochromic devices [13–21]. Although iridium has been successfully employed in the preparation of cyclometalated compounds [22–26] with remarkable photophysical and photochemical properties with applications in important fields, such as organic emitting diodes (OLEDs), dyes sensitizing solar cells, sensors, biology and photocatalysis, only a few examples can be found in the literature about its incorporation in porphyrins [27–31]. Therefore, the synthesis of iridium porphyrins complexes would be of great scientific and technological importance. The pentafluorophenyl substituted porphyrin (TPFP), which is oxidatively more robust and has better solubility in common organic solvents than its phenyl analogue, is a promising candidate [14]. The substitution of hydrogen terminated species by fluorine atoms are known to turn possible the electronic transport properties to switch from a p- to a n- type, making this porphyrin of particular relevance and a capable candidate for thin film based electronic devices [32]. Gas sensor is also a suitable application, since TPFP coordinated with Zn atoms have demonstrated a significant enhancement in gas-response of ammonia-sensing [15]. Moreover, the TPFP is an appropriate platform to several substitutions, once the pentafluorophenyl group of the porphyrin is not a chemically inert group, suffering aromatic nucleophilic substitutions with a range of nucleophiles (RO⁻, RNH₂, RS) [14,16–23]. For example, Samaroo et al. [16] showed the efficacy of using TPFP as a core platform to obtain porphyrins bearing

* Corresponding author.

E-mail address: ana.lima@dep.uminho.pt (A. Delgado-Lima).

functionalities that are important to photodynamic therapeutics (PDT) and that can be used for noble purposes as treatment for cancer or as a potential antibacterial or antiviral compound [16].

2. Material and methods

The porphyrin 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (TPFPF) (98% purity) was purchased from Sigma–Aldrich. Reagents and solvents, namely chloro(1,5-cyclooctadiene)iridium (I) dimer ($[\text{Ir}(\text{COD})\text{Cl}]_2$) (97% purity) was purchased from Sigma–Aldrich, xylene, dichloromethane and n-hexane were purchased from Acros Organics and used without further purification. Thin layer chromatography was performed in Merck pre-coated silica gel 60 F-254 plates and silica gel 60 M (0.04–0.063 mm) from Macherey–Nagel was used for column chromatography. All the compounds were characterized by ^1H and ^{13}C NMR spectroscopy, including $^1\text{H}/^{13}\text{C}$ correlation techniques, which were recorded on a Bruker Avance III, 400 MHz in deuterated CHCl_3 . The spectra were internally referenced to the residual proton tetramethylsilane (TMS, $\delta = 0.00$ ppm) and the chemical shifts (δ) are reported as part per million (ppm). Absorption spectra were measured at a Shimadzu UV-2401PC UV–Vis spectrophotometer in CH_2Cl_2 in a range between 300 and 700 nm, and mass spectrometry (ESI) was performed on an APEXQe FT-ICR MS (Bruker Daltonics, Billerica, MA), equipped with a 7T actively shielded magnet. Ions were generated using a Combi MALDI-electrospray ionization (ESI) source. Ionization was achieved by electrospray, using a voltage of 4500 V applied to the needle, and a counter voltage of 300 V applied to the capillary. Samples were prepared by adding a spray solution of 70:29.9:0.1 (v/v/v) $\text{CH}_3\text{OH}/\text{water}/\text{formic acid}$ or 70:29.9:0.1 (v/v/v) $\text{CH}_3\text{CN}/\text{water}/\text{formic acid}$ to a solution of the sample at a v/v ratio of 1 to 5 % to give the best signal-to-noise ratio. Data acquisition was performed using the ApexControl software version 3.0.0, and data processing was performed using the DataAnalysis software, version 4.0 both from Bruker Daltonics. [Supplementary data are given as electronic Supplementary material.](#)

2.1. Synthesis of the TPFPF metalloporphyrin

The TPFPF $\text{IrCl}(\text{CO})$ metalloporphyrin was synthesized by adding the dimer $[\text{Ir}(\text{COD})\text{Cl}]_2$ (261.9 mg, 0.39 mmol) to a solution of free-base porphyrin (246.9 mg, 0.26 mmol) in xylene ($[\text{C}] = 6.5\text{E}-3 \text{ M}$) (Fig. 1). The resulting mixture was refluxed for 4 days and allowed to cool to room temperature followed by solvent evaporation to dryness. The residue was purified by column chromatography on

silica gel with a mixture of n-hexane/dichloromethane and it was isolated in 5% yield. Found in ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ ppm: 9.02 (s, 8H, βH -pyrrole). And ^{13}C NMR (400 MHz, CDCl_3 , 25 °C) δ ppm: 105.98 ($\text{C}_{5,10,15,20}$), 128.98 ($\text{C}_{2,3,7,8,12,13,17,18}$), 141.52 ($\text{C}_{1,4,6,9,11,14,16,19}$), 119.84 (Cp) UV–Vis (CH_2Cl_2) λ abs nm: 413.5 ($1\text{E}10^5 \text{ M}^{-1}\text{cm}^{-1}$), 526.0 ($1.5\text{E}10^4 \text{ M}^{-1}\text{cm}^{-1}$), 557.5 ($5\text{E}10^3 \text{ M}^{-1}\text{cm}^{-1}$). ESI-MS: $\text{C}_{45}\text{H}_8\text{ClF}_{20}\text{IrN}_4\text{NaO}$ m/z = 1250.96.

3. Results and discussion

As mentioned, TPFPF is a porphyrin of huge interest and it is used on the research of new materials to be employed in a wide range of applications [24–26,32–43]. Therefore, combining the attractive properties of TPFPF with the iridium metal by the synthesis of a porphyrin complex became a great challenge. The experimental firsts attempts in our laboratory were performed in IrCl_4 without reaction success. Similarly, to the iridium coordination in other porphyrins procedure, the dimer $[\text{Ir}(\text{COD})\text{Cl}]_2$ (COD = cyclooctadiene) was used as the metal precursor [28–31,44]. Since iridium is a six-coordinated atom, CO and Cl axial ligands neutralize the molecule and complete the coordination sphere (Fig. 1). The first experiments were performed in smoother solvents, as acetone and pyridine, but no reaction evolution was detected. Clearly, the solvent selection was of major relevance and higher boiling temperatures were preferable [5]. Also, the coordination ability of the solvent by the presence of lone pairs or electron-rich donor atoms might affect the reaction, avoiding the coordination of the metal in the porphyrin. Thus, the iridium porphyrin (TPFPF $\text{IrCl}(\text{CO})$) was only successfully obtained after a 4-day reaction in reflux using a high boiling point and non-coordinating solvent, xylene. Despite the success of this reaction, the yield of 5% demonstrates that it is difficult to incorporate a large metal atom in sterically hindered porphyrins. The iridium porphyrin complex was isolated and its presence was confirmed by spectroscopy and spectrometry techniques. Fig. 2 presents the UV–Vis spectra of porphyrin TPFPF and metallated TPFPF $\text{IrCl}(\text{CO})$. The spectrum of porphyrin shows two π - π^* electronic transitions. An intense Soret band between 350–500 nm with molar absorptivities (ϵ) of $10^5 \text{ M}^{-1}\text{cm}^{-1}$, and four lower intense ($\epsilon \approx 10^4$ – $10^1 \text{ M}^{-1}\text{cm}^{-1}$) Q-bands between 500–750 nm as a result of the presence of protons on two diagonally situated pyrrole nitrogen [5,43,45]. The coordination of iridium with the porphyrin core induces significant changes in the UV–Vis spectrum. Specifically, the main difference consists in the 2 Q-bands of the metalloporphyrin with displaced wavelengths, which also reveals the existence of axial ligands by

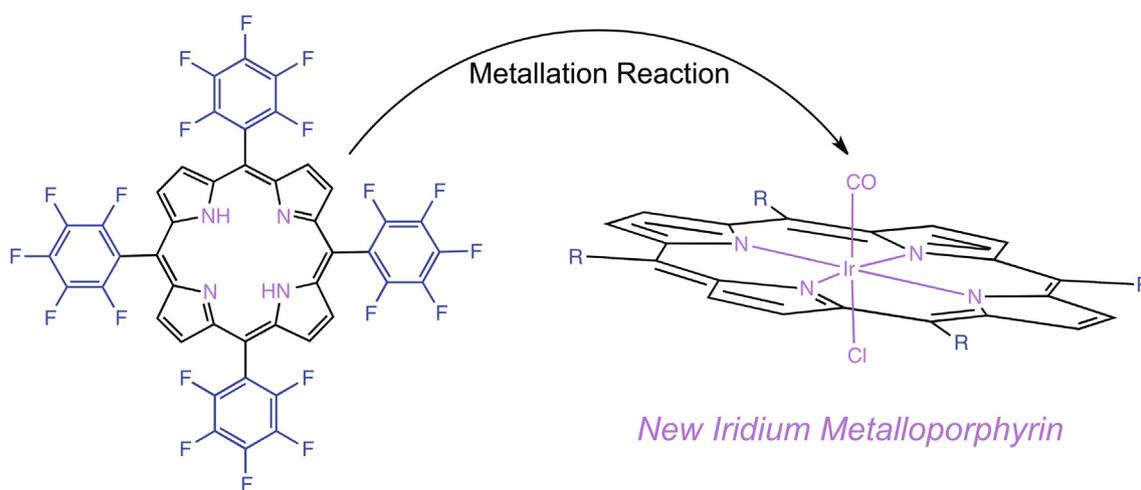


Fig. 1. Scheme reaction of TPFPF metallation with iridium.

Download English Version:

<https://daneshyari.com/en/article/5462821>

Download Persian Version:

<https://daneshyari.com/article/5462821>

[Daneshyari.com](https://daneshyari.com)