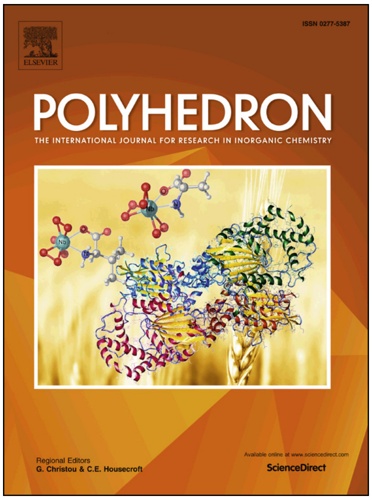

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# Development of iridium porphyrin arrays by axial coordination trough *N*-bidentate ligand: Synthesis and evaluation of the optical, electrochemical and thermal properties

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**Abstract:** Several organic compounds have been used in optoelectronics devices; porphyrins, due to their interesting optical and electronic properties, have shown an attractive potential to be used on molecular electronics. Among other advantages, porphyrins easily coordinate with several metal ions, which allows the assembly with peripheral or axial ligands introducing new properties to the supramolecular porphyrin. In this work, a new metalloporphyrin system with 5,10,15,20-(tetra-*p*-tolyl)porphyrin (ttp) and iridium(III) where 4,4'-bipyridine (bpy) coordinate in the axial positions was successfully synthetized, through the formation of "shish kebab" structures. This new compound was characterized through ultraviolet-visible, proton nuclear magnetic resonance, Fourier-transform infrared and Raman spectroscopies, thermogravimetry, differential scanning calorimeter and cyclic voltammetry. The introduction of the bpy on the metalloporphyrin moiety exhibited important influence on the optical, thermal and electrochemical properties.

## 1. Introduction

For several years, porphyrins and metalloporphyrins have attracted high interest from researchers due to their applications in molecular electronics, nonlinear optics, optical data storage, chemical sensors, photovoltaic materials, electrochromic and photocatalytic systems.[1-7] The great interest on porphyrins is related to their properties, in particular their large π-electron conjugation, which allows an effective pathway for electron transport, and small HOMO/LUMO energy gaps, allowing absorption in the visible region that results in exceptional electronic and optical properties.[3, 8] Another important characteristic of porphyrins, 18 π-electron aromatic macrocycles, is their ability to accommodate metal ions to form 1:1 metal complexes. The tetradentate anionic porphyrinato system, formed by losing two inner NH protons, is very versatile and can easily coordinate with almost all metal elements of the periodic table. However, the capacity of a porphyrin to coordinate the metal ion is restricted by the space available in the porphyrins' ring core and the ionic radius of the metal ion.[9-10] The porphyrin ring is flexible and is able to assume several conformations. Thus, in the case of 3*d* elements, the ionic radius fits into the porphyrins' ring core forming a planar geometry with the porphyrin, whereas in the case of large ions as some of 4*d* and 5*d* elements, the metal ion is coordinated outside the porphyrin plane forming an octahedral geometry. In both cases the