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Synthesis and electrochemical studies of η^5 -monocyclopentadienylruthenium(II) complexes with substituted thiophene nitrile ligands. Crystal structure of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})(\text{NC}\{\text{SC}_4\text{H}_2\}_2\text{NO}_2)][\text{PF}_6]$

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ABSTRACT

A systematic series of η^5 -monocyclopentadienylruthenium(II) complexes with substituted thiophene nitrile ligands of general formula $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{P}_2\text{P})(\text{NC}\{\text{SC}_4\text{H}_2\}_n\text{NO}_2)][\text{PF}_6]$ ($\text{P}_2\text{P} = \text{dppe}, (+)\text{-diop}$; $n = 1\text{--}3$) has been synthesized and characterized. Spectroscopic and electrochemical data were used in order to get an insight on the molecular nonlinear optical properties of these complexes when compared to those found for the reported thiophene iron(II) and *p*-benzonitrile or 1,2-di-(2-thienyl)-ethene derived iron(II)/ruthenium(II) related complexes. The compound $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})(\text{NC}\{\text{SC}_4\text{H}_2\}_2\text{NO}_2)][\text{PF}_6]$ was also characterized by X-ray diffraction. The solid state nonlinear optical properties of the chiral compounds were also evaluated by Kurtz powder technique with a Nd:YAG laser emitting at 1064 nm.

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1. Introduction

The exploitation of organometallic chemistry for the synthesis of new compounds with nonlinear optical (NLO) properties has been mainly motivated by the optical devices technology [1]. The significant work already published in this area during the last two decades [2–11] is in agreement with the general understanding that second-order nonlinearities are strongly related to asymmetric push–pull systems, both in organic and organometallic molecular materials. In the case of metallo-organic compounds, the metal centre can be bound to a highly polarizable conjugated backbone, acting hence as an electron releasing or withdrawing group. Consequently, strong charge-transfer (CT) transitions can occur, leading to high molecular first hyperpolarizabilities (β). Moreover, the position of these CT bands, usually appearing at the visible region, can be tuned by variation of the coligands and/or the metal itself, to optimize the hyperpolarizability through (near) resonant enhancement. This is the case of the general family of η^5 -monocyclopentadienyliron(II)/ruthenium(II) complexes presenting benzene- or thiophene-based conjugated ligands coordinated to the metal centre through nitrile or acetylide linkages

[12–16], which revealed to be much more efficient donor groups for second-order NLO purposes than the traditional organic donor groups (NMe₂, NH₂, etc.), leading therefore to higher β values.

Recently we found significant values of quadratic hyperpolarizabilities in complexes combining the organometallic donor fragment {FeCp(P₂P)} (P₂P = dppe, (+)-diop) with conjugated thiophene derived ligands. Measurements by hyper-Rayleigh scattering (HRS), in $[\text{FeCp}(\text{dppe})(\text{NC}\{\text{SC}_4\text{H}_2\}_n\text{NO}_2)][\text{PF}_6]$ compounds with 1, 2 or 3 thiophene units presented values of β of 455, 710 and 910×10^{-30} esu, respectively, measured at 1064 nm [16]. Nevertheless, high values of β do not lead necessarily to good NLO efficiencies at the macroscopic level since the second-order NLO effects are strongly influenced by the crystal packing. Thus, crystallization in a non-centrosymmetric space group is a necessary criterion (not absolute) when solid state properties are evaluated, this being guaranteed in the present compounds by the chiral coligand, (+)-diop.

In order to get some hint about the solid state second harmonic generation efficiencies of the general family of compounds $[\text{FeCp}(\text{P}_2\text{P})(\text{NC}\{\text{SC}_4\text{H}_2\}_n\text{NO}_2)][\text{PF}_6]$ we had extended our studies to the analogous family of ruthenium derivatives, which have the advantage of a higher transparency than the iron ones, at the second harmonic wavelength (532 nm) of the used Nd:YAG laser. These studies on bulk materials become very important when solid

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