



# Synthesis and electrochemical studies of organometallic cobalt(III) complexes with substituted benzonitrile chromophores: NMR spectroscopic data as a probe on the second-order non-linear optical properties

M. Helena Garcia<sup>a,b,\*</sup>, Paulo J. Mendes<sup>b,c</sup>, A. Romão Dias<sup>b</sup>

<sup>a</sup> Faculdade de Ciências da Universidade de Lisboa, Ed. C8, Campo Grande, 1749-016 Lisboa, Portugal

<sup>b</sup> Centro de Química Estrutural, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

<sup>c</sup> Centro de Química de Évora, Universidade de Évora, Rua Romão Ramalho 59, 7002-554 Évora, Portugal

Received 25 February 2005; received in revised form 3 June 2005; accepted 3 June 2005

Available online 11 July 2005

## Abstract

The family of organometallic Co(III) benzonitrile derivatives of general formula  $[\text{CoCp}(\text{dppe})(p\text{-NCR})][\text{PF}_6]_2$  ( $\text{R} = \text{C}_6\text{H}_4\text{NMe}_2$ ,  $\text{C}_6\text{H}_4\text{NH}_2$ ,  $\text{C}_6\text{H}_4\text{OMe}$ ,  $\text{C}_6\text{H}_4\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{NO}_2$ , and  $\text{C}_6\text{H}_4\text{NO}_2$ ) have been synthesized. Spectroscopic and electrochemical data were analyzed in order to evaluate the extent of electronic coupling between the organometallic fragment and the nitrile ligands. An attempt of correlation between NMR spectroscopic data and the second-order non-linear optical properties is presented, based on this work and available published data for related  $\eta^5$ -monocyclopentadienyliron, ruthenium and nickel complexes.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Cobalt complexes; Benzonitrile derivatives; Cyclic voltammetry; Electronic coupling; Non-linear optics

## 1. Introduction

The search for new organometallic materials with non-linear optical (NLO) properties is currently the subject of considerable interest due to their potential technological applications in the area of integrated optics [1–6]. It is well known that organometallic complexes can possess low energy, sometimes intense, electronic metal-to-ligand or ligand-to-metal charge transfer excitations which can be responsible for high values of molecular first hyperpolarizability  $\beta$ . The value of these systems is that the energy of the charge transfer excitation can be tuned by variation of the metal itself and its oxidation state, ligand environment and coordination geometries to optimize the second-order NLO response.

The main studies have been made in push-pull systems in which the metal center, bonded to a polarizable organic conjugated backbone (chromophore), acts as an electron releasing or withdrawing group.

Among the organometallic compounds presenting this donor– $\pi$ -system–acceptor interaction, the family of  $\eta^5$ -monocyclopentadienylmetal derivatives revealed significant second-order optical non-linearities, especially those of iron and ruthenium complexes coordinated to *p*-nitrobenzonitriles, *p*-nitrobenzoacetylides and *p*-nitrothienylnitriles [7–15]. Compared with the metallocene systems, which were the first organometallic compounds to be studied for their NLO properties, the main structural feature of this family of compounds is the existence of the metal center in the same plane of the chromophore, thus allowing a better coupling between the organometallic fragment and the conjugated chromophores. In fact, the existence of metal–ligand

\* Corresponding author. Tel.: +351 217500972; fax: +351 217500088.  
E-mail address: [lena.garcia@fc.ul.pt](mailto:lena.garcia@fc.ul.pt) (M.H. Garcia).