

# Mono( $\eta^5$ -cyclopentadienyl)metal(II) Complexes with Thienyl Acetylide Chromophores: Synthesis, Electrochemical Studies, and First Hyperpolarizabilities

Tiago J. L. Silva,<sup>†</sup> Paulo J. Mendes,<sup>\*,‡</sup> Ana M. Santos,<sup>†</sup> M. Helena Garcia,<sup>†</sup> M. Paula Robalo,<sup>§,||</sup> J. P. Prates Ramalho,<sup>‡</sup> A. J. Palace Carvalho,<sup>‡</sup> Marina Büchert,<sup>⊥</sup> Christian Wittenburg,<sup>⊥</sup> and Jürgen Heck<sup>⊥</sup>

<sup>†</sup>Centro de Ciências Moleculares e Materiais, Faculdade de Ciências, Universidade de Lisboa, Ed. C8, Campo Grande, 1749-016 Lisboa, Portugal

<sup>‡</sup>Centro de Química de Évora, Departamento de Química, Escola de Ciências e Tecnologia, Universidade de Évora, Rua Romão Ramalho 59, 7002-554 Évora, Portugal

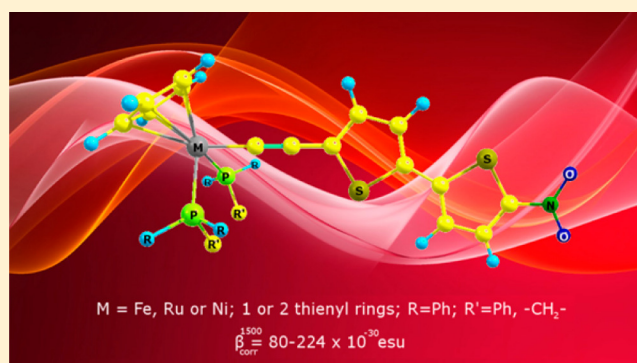
<sup>§</sup>Centro de Química Estrutural, Instituto Superior Técnico, Universidade Técnica de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

<sup>||</sup>Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emídio Navarro, 1, 1959-007 Lisboa, Portugal

<sup>⊥</sup>Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg

## Supporting Information

**ABSTRACT:** A series of mono( $\eta^5$ -cyclopentadienyl)metal(II) complexes with nitro-substituted thienyl acetylide ligands of general formula  $[M(\eta^5-C_5H_5)(L)(C\equiv C\{C_4H_2S\}_nNO_2)]$  ( $M = Fe, Ru, Ni$ ;  $L = \kappa^2$ -DPPE,  $n = 1, 2$ ;  $M = Ru, Ni$ ;  $L = \kappa^2$ -DPPE, 2 PPh<sub>3</sub>,  $n = 1, 2$ ;  $M = Ni$ ;  $L = PPh_3$ ,  $n = 1, 2$ ) has been synthesized and fully characterized by NMR, FT-IR, and UV-Vis spectroscopy. The electrochemical behavior of the complexes was explored by cyclic voltammetry. Quadratic hyperpolarizabilities ( $\beta$ ) of the complexes have been determined by hyper-Rayleigh scattering (HRS) measurements at 1500 nm. The effect of donor abilities of different organometallic fragments on the quadratic hyperpolarizabilities was studied and correlated with spectroscopic and electrochemical data. Density functional theory (DFT) and time-dependent DFT (TDDFT) calculations were employed to get a better understanding of the second-order nonlinear optical properties in these complexes. In this series, the complexity of the push-pull systems is revealed; even so, several trends in the second-order hyperpolarizability can still be recognized. In particular, the overall data seem to indicate that the existence of other electronic transitions in addition to the main MLCT clearly controls the effectiveness of the organometallic donor ability on the second-order NLO properties of these push-pull systems.



## INTRODUCTION

Organometallic compounds have given rise to a great deal of interest owing to their application in the field of nonlinear optics (NLO).<sup>1–11</sup> Organometallic complexes (and organic molecules) have been shown as potential alternatives to the traditional inorganics due to fast and large NLO response, high optical damage thresholds, and structural diversity. In comparison to organic chromophores, organometallics can offer additional flexibility due to the presence of metal–ligand charge transfer excitations, usually at low energy and of high intensity, which are tunable due to the diversity of metal centers, oxidation states, ligand environments, and coordination geometries.

In order to obtain high second-order responses (molecular quadratic hyperpolarizability,  $\beta$ ), strongly asymmetric systems

are needed. These systems can be obtained by combining a  $\pi$ -conjugated chain with electron donor and/or acceptor groups (D- $\pi$ -A) in which metal centers can behave either as acceptor or donor groups by simply varying the metal and/or its oxidation state. During the last two decades, it has been found that high  $\beta$  values could be found for molecules in which the metal center is coplanar with the  $\pi$ -conjugated chain. Concerning this feature, systematic studies were made by our group and others on mono( $\eta^5$ -cyclopentadienyl)metal and pseudo-octahedral complexes with benzene- or thiophene-

**Special Issue:** Organometallic Electrochemistry

**Received:** February 11, 2013

**Published:** February 21, 2014

