



# Synthesis of organometallic Ru(II) and Fe(II) complexes containing fused rings hemi-helical ligands as chromophores. Evaluation of non-linear optical properties by HRS

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## ABSTRACT

A new family of three-legged piano stool structured organometallic compounds containing the fragment  $\eta^5$ -cyclopentadienyl-ruthenium(II)/iron(II) has been synthesized to evaluate the existence of electronic metal to ligand charge transfer upon coordination of the novel benzodithiophene ligands (**BDT**), benzo[1,2-*b*;4,3-*b'*]dithiophen-2-carbonitrile (**L1**) and benzo[1,2-*b*;4,3-*b'*]dithiophen-2-nitro-2-carbonitrile (**L2**). All the compounds were characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR, IR and UV–Vis. spectroscopies and their electrochemistry studied by cyclic voltammetry. The X-ray structures of [Ru( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>-(NCC<sub>10</sub>H<sub>5</sub>S<sub>2</sub>)] [PF<sub>6</sub>] (**1Ru**), [Ru( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>(NCC<sub>10</sub>H<sub>5</sub>S<sub>2</sub>)] [CF<sub>3</sub>SO<sub>3</sub>] (**1' Ru**), [Ru( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(DPPE)(NCC<sub>10</sub>-H<sub>5</sub>S<sub>2</sub>)] [PF<sub>6</sub>] (**2Ru**) and [Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(DPPE)(NCC<sub>10</sub>H<sub>5</sub>S<sub>2</sub>)] [PF<sub>6</sub>] (**2Fe**) were determined by X-ray diffraction showing centric crystallization on groups P1 and P2<sub>1</sub>/n, respectively.

Quadratic hyperpolarizabilities ( $\beta$ ) of some of the complexes (**2Fe**, **2Ru** and **3Fe**) have been determined by hyper-Rayleigh scattering (HRS) measurements at a fundamental wavelength of 1500 nm, to minimize the probability of fluorescence due to two-photon absorption and to reduce the effect of resonance enhancement, in order to estimate static  $\beta$  values.

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## 1. Introduction

The search for new organometallic materials with nonlinear optical (NLO) properties has been an area of considerable interest due to its relevance to optical device technology [1–6].

The high values of first molecular hyperpolarizability ( $\beta$ ) found in organometallic compounds has been related to low energy electronic metal-to-ligand or ligand-to-metal charge transfer excitations. In addition, this charge transfer energy can be tuned by variation of the metal itself and its oxidation state, ligand environment and coordination geometries in order to optimize the second order NLO response. Significant results have been achieved in push–pull systems in which the metal centre, bonded to a polarizable organic conjugated backbone (chromophore), acts as an electron releasing or withdrawing group [1–6]. In particular, structures presenting the metal centre and the chromophore in the same

plane, have been found of potential interest for second-order optical nonlinearities, due to the charge delocalization through a  $d_{\text{metal}}-\pi_{\text{ligand}}^*$  interaction. This is widely illustrated in the literature by the families of  $\eta^5$ -monocyclopentadienyl iron and ruthenium molecular materials presenting *p*-nitrobenzonitriles [7–10], *p*-nitrobenzoacetylides [11–13], nitrothienylacetylides [14] and thiophene derivatives [15].

Although the first molecular hyperpolarizability of purely organic push–pull molecules increases strongly with the length of the conjugated chain [16,17], this is not the case for the benzoderivatives, due to the torsion angle between the rings. Nevertheless, the extension of conjugation turns out effective by insertion of a vinylene unit between two phenyl rings. Yet, extended conjugated chain in systems based on thiophene rings, is expected to present an improved planarity since the torsion angle between rings can become quite small. In accordance, *ab initio* calculations [18] suggests that for terthiophene, although the gas-phase structure is not planar, the conformational inter-conversion energy is very low and sensitive to the chemical environment. Also a

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semi-empirical calculation, indicating that the structure of bithiophene becomes planar in water solution [19], supports the assumption of easier planarity on oligothiophene compounds.

Our recent studies in complexes containing the organometallic donor fragment  $[\text{FeCp}(\text{P-P})]^+$  ( $\text{P-P} = \text{DPPE}, (+)\text{-DIOP}$ ) and conjugated thiophene derived ligands, showed an improved electronic  $\pi$ -coupling between the  $\eta^5$ -cyclopentadienyl iron fragment and the  $\pi$ -system of the conjugated thiophene ligands, when compared to the previously reported *p*-benzonitrile analogues [15]. As a result, the first hyperpolarizabilities at 1.064  $\mu\text{m}$  are indeed higher than for the related benzonitrile compounds, and they could be scaled up by increasing the conjugation length, leading to the high  $\beta$   $910 \times 10^{-30}$  esu for the complex with three thiophene units. Nevertheless, the increased conjugation originated by that chain-lengthening can also be on the basis of a lowering of the charge-transfer (CT) efficiency, as was suggested by our published electrochemical and spectroscopic experimental data and also by the solvatochromic studies. The constancy of  $\beta_0 \sim 100 \times 10^{-30}$  esu upon chain-lengthening is a consequence of the compensation of two favourable effects, namely the increasing of conjugation length and the lowering of the charge transfer efficiency [15].

Therefore, it seems that the exploitation of promising thiophene based ligands for NLO purposes, should not be limited to the chain lengthening alternative, within this family of organometallic compounds, but instead, other alternatives seem to be quite pertinent.

In this work we explore the potentialities of new benzo[1,2-*b*;4,3-*b'*]dithiophene based chromophores where the fused rings structure guarantees the rigidity of the ligand to be coordinated on the same plan of the metal centre, in a family of cyclopentadienyl iron/ruthenium derivatives.

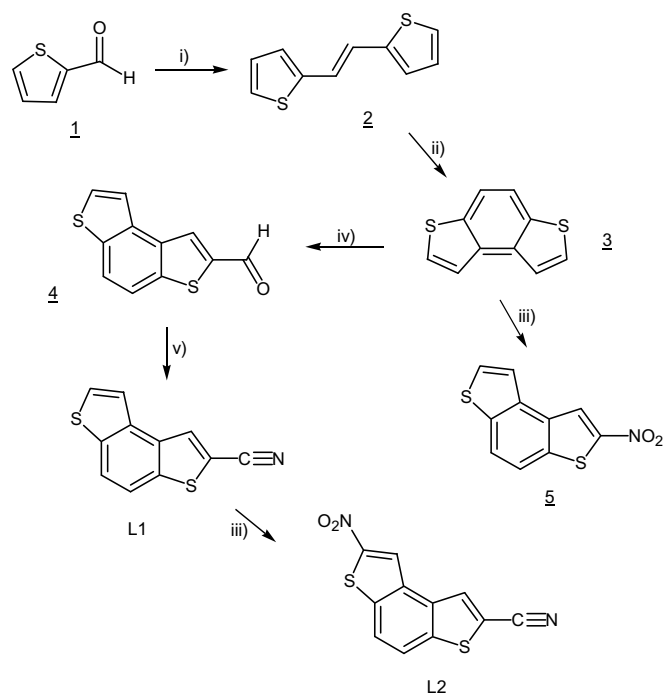
Although some reports concerning the NLO properties of thiophene-based organometallic complexes have been published, they are mainly about ferrocenyl and tricarbonyl chromium arene derivatives [20–26] in which the metal is unfavourably placed outside of the conjugation plane [27], in contrast with the present complexes and our previously reported oligothiophene containing complexes [15].

A new class of compounds for second-order NLO materials was developed, combining the organometallic donor fragment  $[\text{MCp}(\text{L}_L)]^+$ , ( $\text{M} = \text{Ru}(\text{II}), \text{L}_L = \text{DPPE}, 2\text{PPh}_3$  and  $\text{TMEDA}$ ;  $\text{M} = \text{Fe}(\text{II}), \text{L}_L = \text{DPPE}$ ) with the benzodithiophene functionalized molecules (**BDT**), namely benzo[1,2-*b*;4,3-*b'*]dithiophen-2-carbonitrile (**L1**) and benzo[1,2-*b*;4,3-*b'*]dithiophen-2'-nitro-2-carbonitrile (**L2**). The coligand  $\text{TMEDA}$  (*N,N,N',N'*-tetramethyl-ethylenediamine) was introduced in these studies to evaluate the ability of  $[\text{RuCp}(\text{TMEDA})]^+$  fragment as donor group comparatively to the well studied  $[\text{RuCp}(\text{P}_2)]^+$ . Spectroscopic and cyclic voltammetry data were analyzed to get some understanding about the electronic  $\pi$ -coupling between the  $\eta^5$ -cyclopentadienyliron/ruthenium fragment and the  $\pi$ -system of the benzodithiophene derived ligands. Quadratic hyperpolarizabilities of three compounds of this family have been determined by hyper-Rayleigh scattering (HRS) measurements at the fundamental wavelength of 1500 nm. These measurements revealed that the first hyperpolarizabilities are lower than expected.

## 2. Results and discussion

### 2.1. Synthesis of the benzodithiophene derived ligands (**BDT**)

The synthesis of the **BDT** ligands, benzo[1,2-*b*;4,3-*b'*]dithiophen-2-carbonitrile (**L1**) and benzo[1,2-*b*;4,3-*b'*]dithiophen-2'-nitro-2-carbonitrile (**L2**) is summarized in Scheme 1. The aldehyde starting material was prepared with good yield, by generation of the benzodithiophene  $\alpha$ -anion with *n*-BuLi and subsequent treatment with DMF, following Ref. [28].



- i) 1- dry THF,  $\text{TiCl}_4$ ,  $-20\text{ }^\circ\text{C}$ ; 2- Zn dust, reflux; ii)  $h\nu$ ,  $\text{I}_2$ , air, toluene, r.t.; iii)  $\text{HNO}_3/\text{Ac}_2\text{O}$ ; iv) 1- dry THF,  $\text{N}_2$ ,  $-78\text{ }^\circ\text{C}$ , *n*-BuLi; 2- DMF; v) 1- $\text{H}_2\text{NOH}\cdot\text{HCl}$ , py,  $-30\text{ }^\circ\text{C}$ ; 2- $\text{Ac}_2\text{O}$ , reflux

Scheme 1.

The new nitrile ligands, obtained with yields of 84% (**L1**) and 46% (**L2**), and the compounds **3** and **5**, were fully characterized by IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies and the elemental analysis were in accordance with the proposed formulations. The solid state FT-IR spectra (KBr pellets) showed the characteristic stretching vibration of the nitrile functional group at  $\sim 2215\text{ cm}^{-1}$  for both compounds. In addition, **L2** presented also the vibrations attributed to the  $\text{NO}_2$  group, at  $\sim 1515$  and  $1335\text{ cm}^{-1}$ .

### 2.2. Synthesis of the Ru(II)/Fe(II) complexes

Complexes of general formula  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{LL})(\text{BDT})][\text{Z}]$ , with  $\text{Z} = \text{PF}_6^-$  and/or  $\text{CF}_3\text{SO}_3^-$ ; ( $\text{LL} = \text{DPPE}, 2\text{PPh}_3$  and  $\text{TMEDA}$  when  $\text{M} = \text{Ru}(\text{II})$  and ( $\text{LL} = \text{DPPE}$  when  $\text{M} = \text{Fe}(\text{II})$ );  $\text{BDT} = \text{benzo}[1,2\text{-}b;4,3\text{-}b']\text{dithiophen-2-carbonitrile}$  ( $\text{Y} = \text{H}$ ) and  $\text{benzo}[1,2\text{-}b;4,3\text{-}b']\text{dithiophen-2'-nitro-2-carbonitrile}$  ( $\text{Y} = \text{NO}_2$ ), were prepared, as shown in Scheme 2, by halide abstraction with  $\text{TlPF}_6$  (or  $\text{AgCF}_3\text{SO}_3$ ) from the parent neutral complexes  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{LL})\text{X}]$  ( $\text{M} = \text{Fe}(\text{II}), \text{X} = \text{I}$ ;  $\text{M} = \text{Ru}(\text{II}), \text{X} = \text{Cl}$ ), in acetone, in the presence of an adequate excess of the corresponding nitrile.

The reactions were carried out at reflux, stirring overnight under inert atmosphere. The compounds were recrystallized by slow diffusion of *n*-heptane or *n*-hexane in acetone or dichloromethane solutions, giving crystalline yellow or orange products. With the exception of compound  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{TMEDA})(\text{NCC}_{10}\text{H}_5\text{S}_2)][\text{PF}_6]$  (**4Ru**), which was very air sensitive, all the compounds were fairly stable to air and moisture, either in the solid state or in solution and were obtained in good yields (70–90%). Attempts to characterize the iron analogue  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{TMEDA})(\text{NCC}_{10}\text{H}_5\text{S}_2)][\text{PF}_6]$  were unsuccessful, due to the instability of the compound. The formulation of all the new compounds is supported by analytical data, FT-IR and  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  NMR spectroscopic data. The solid state FT-IR spectra (KBr pellets) of the complexes presented a large number of bands which identify the presence of the various coligands.

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