



Synthesis and structural characterization of ruthenium(II) and iron(II) complexes containing 1,2-di-(2-thienyl)-ethene derived ligands as chromophores

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ARTICLE INFO

Article history:

Received 23 July 2008

Received in revised form 6 November 2008

Accepted 7 November 2008

Available online 14 November 2008

Keywords:

Ruthenium(II)

Iron(II)

Monocyclopentadienyl

1,2-Di-(2-thienyl)-ethene nitrile ligands

Cyclic voltammetry

Nonlinear optics

ABSTRACT

A new family of three-legged piano stool structured organometallic compounds containing the η^5 -cyclopentadienylruthenium(II)/iron(II) fragments $\{M(\eta^5\text{-C}_5\text{H}_5)(\text{DPPE})\}^+$, $\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\}^+$ and $\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{TMEDA})\}^+$ with coordinated thiophene based chromophores, namely 5-(2-thiophen-2-yl-vinyl)-thiophene-2-carbonitrile (L1) and 5-[2-(5-Nitro-thiophen-2-yl)-vinyl]-thiophene-2-carbonitrile (L2) has been synthesized and fully characterized by ^1H , ^{13}C , ^{31}P NMR, IR and UV–Vis spectroscopies. Also, electrochemical studies were carried out by cyclic voltammetry and all experimental data are interpreted and compared with related compounds under the scope of NLO properties. Compounds $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{DPPE})(\text{NC}(\text{C}_4\text{H}_2\text{S})\text{C}(\text{H})\text{C}(\text{H})(\text{C}_4\text{H}_2\text{S}))][\text{CF}_3\text{SO}_3]$ (1^{Ru}) $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{DPPE})(\text{NC}(\text{C}_4\text{H}_2\text{S})\text{C}(\text{H})\text{C}(\text{H})(\text{C}_4\text{H}_2\text{S}))][\text{PF}_6]$ (1^{Fe}) and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{DPPE})(\text{NC}(\text{C}_4\text{H}_2\text{S})\text{C}(\text{H})\text{C}(\text{H})(\text{C}_4\text{H}_2\text{S})\text{NO}_2)][\text{CF}_3\text{SO}_3]$ (4^{Ru}) were also crystallographically characterized.

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1. Introduction

Since the report by Green et al. [1], revealing good second harmonic generation efficiencies for ferrocenyl derivatives, the interest in organometallic chemistry for the development of new NLO materials has increased considerably, motivated by the potential relevance of these materials in optical device technology [2–9]. In order to obtain a nonzero second-order response (molecular hyperpolarizability β), strongly asymmetric systems are needed. These systems can be obtained by combining a π -conjugated chain with electron donor and/or acceptor groups (D- π -A or push–pull systems) in which metal centers can behave either as acceptor or donor group by simply varying the metal and/or its oxidation state. Although interesting results have been achieved with ferrocene systems [10], half-sandwich complexes, in which the metal center is coplanar with the π -conjugated backbone, have boosted the NLO response of organometallic complexes. Concerning this feature, systematic studies were made on η^5 -monocyclopentadienylmetal complexes with benzene-based conjugated ligands bound to the metal center through nitrile or acetylide linkages [11–15]. Iron and ruthenium organometallic moieties have proven to be very efficient donor groups for second-order NLO purposes,

leading to higher β values than the usual organic groups (NR_2 , NH_2 , etc.).

Thiophene moiety has been studied as chromophore both in organic [16–18] and organometallic [19–25] materials for NLO and it is nowadays recognized to exhibit enhanced second-order polarizabilities compared to π -systems with phenylene bridges, mainly due to its lower delocalization energy, leading to a more effective conjugation. We recently reported the synthesis and NLO properties of η^5 -monocyclopentadienyliron(II) complexes with substituted oligo-thiophene nitrile derived ligands [26]. The observed constancy of β_0 upon chain-lengthening was attributed to a lowering of the charge transfer efficiency with increasing conjugation length, considering torsion angles in oligo-thiophenes to be small and thus not a significant factor to be considered in the observed trend [27,28]. In order to complement this study and also to confirm these conclusions, a set of new compounds was synthesized, where the extension of the π system was featured by the introduction of one vinylene unit between two thiophene rings, also assuring the planarity of the chromophore.

The new compounds of general formula $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{LL})(\text{NC}(\text{C}_4\text{H}_2\text{S})\text{C}(\text{H})\text{C}(\text{H})(\text{C}_4\text{H}_2\text{S})\text{Z})][\text{Y}]$, with $\text{Z} = \text{H}$, NO_2 ($\text{M} = \text{Ru}$, $\text{LL} = \text{DPPE}$ $\{\text{Y} = \text{PF}_6^-, \text{CF}_3\text{SO}_3^-\}$, 2PPh_3 $\{\text{Y} = \text{PF}_6^-\}$, TMEDA $\{\text{Y} = \text{PF}_6^-\}$; $\text{M} = \text{Fe}$, $\text{LL} = \text{DPPE}$ $\{\text{Y} = \text{PF}_6^-\}$) were characterized by the usual FT-IR, UV–Vis, ^1H , ^{13}C and ^{31}P NMR spectroscopic techniques. The organometallic fragment $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{TMEDA})]^+$ was introduced

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in these studies to evaluate the effect of the amine coligand on the donor ability of the organometallic moiety, relatively to the $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PP})]^+$ fragment (PP = DPPE and PPh_3) currently used in our published studies [8,11–13]. The electrochemical studies were performed by means of cyclic voltammetry in order to get an insight on the electronic properties of the complexes and the results, together with the spectroscopic data, are discussed under the scope of the structural features that can be related to the NLO properties. X-ray diffraction studies of compounds $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{DPPE})(\text{NC}(\text{C}_4\text{H}_2\text{S})\text{C}(\text{H})\text{C}(\text{H})(\text{C}_4\text{H}_3\text{S}))][\text{CF}_3\text{SO}_3]$ (**1Ru**) $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{DPPE})(\text{NC}(\text{C}_4\text{H}_2\text{S})\text{C}(\text{H})\text{C}(\text{H})(\text{C}_4\text{H}_3\text{S}))][\text{PF}_6]$ (**1Fe**) and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{DPPE})(\text{NC}(\text{C}_4\text{H}_2\text{S})\text{C}(\text{H})\text{C}(\text{H})(\text{C}_4\text{H}_2\text{S})\text{NO}_2)]-[\text{CF}_3\text{SO}_3]$ (**4Ru**) are also discussed.

2. Results and discussion

2.1. Synthesis of the ligands

The thiophene chromophores 5-(2-thiophen-2-yl-vinyl)-thiophene-2-carbonitrile (**L1**) and 5-[2-(5-nitro-thiophen-2-yl)-vinyl]-thiophene-2-carbonitrile (**L2**) were synthesized according to general procedures. The parent molecule 1,2-di-(2-thienyl)-ethene (**1**) was prepared with good yield from 2-thiophenecarboxaldehyde, by McMurry reaction [29]. Formylation of the thiophene unit was achieved by treatment of **1** with DMF and phosphorous oxychloride (Vilsmeier–Haack reaction). Reaction

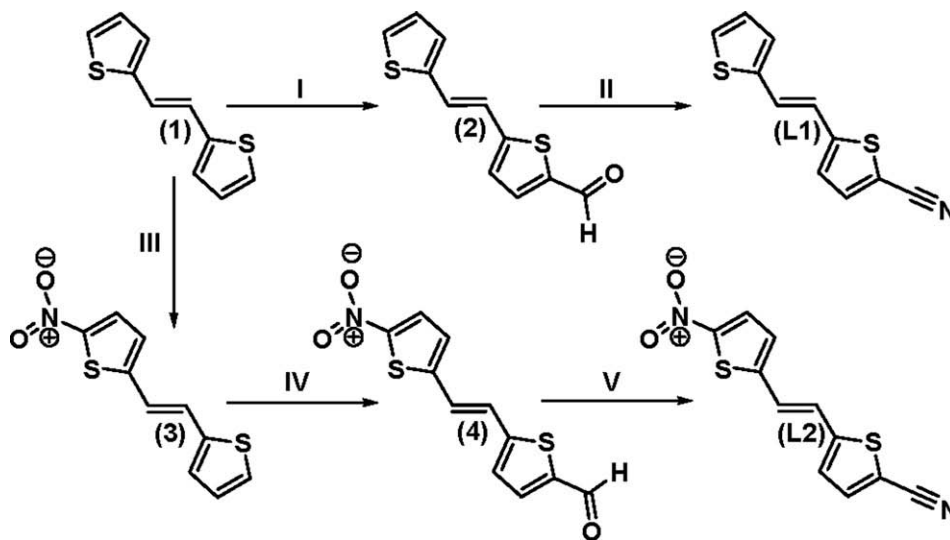
of the aldehyde **2** with hydroxylammonium chloride in pyridine and dehydration with acetic anhydride led to **L1**. Reaction of **1** with nitric acid in acetic acid afforded 2-nitro-5-(2-thiophen-2-yl-vinyl)-thiophene (**3**); **L2** was then obtained from **3**, by formylation and reduction to nitrile, applying the procedure described above for the synthesis of **L1**. All these reactions are summarized in Scheme 1.

The new nitrile ligands, obtained with yields of 74% (**L1**) and 33% (**L2**) from **1**, were fully characterized by IR, ^1H and ^{13}C NMR spectroscopies. Elemental analyses are in accordance with the proposed formulations.

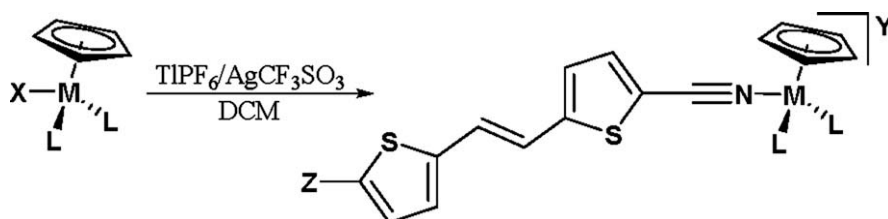
The solid state FT-IR spectra (KBr pellets) showed the characteristic stretching vibration of the nitrile functional group at $\approx 2215\text{ cm}^{-1}$ for both compounds. The FT-IR spectrum of **L2** also shows the NO_2 stretching bands at 1483 and 1337 cm^{-1} .

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

Complexes of general formula $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{LL})(\text{NC}(\text{C}_4\text{H}_2\text{S})\text{C}(\text{H})\text{C}(\text{H})(\text{C}_4\text{H}_2\text{S})\text{Z})][\text{Y}]$, with Z = H, NO_2 ; M = Ru, LL = DPPE {Y = PF_6^- , CF_3SO_3^- , 2PPh_3 {Y = PF_6^- }, TMEDA {Y = PF_6^- }; M = Fe, LL = DPPE {Y = PF_6^- }, were prepared by halide abstraction with a salt of the adequate counter-ion, in dichloromethane, from the corresponding neutral complex $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{LL})\text{X}]$ (M = Fe(II), X = I; M = Ru(II), X = Cl), in the presence of a slight excess of the corresponding nitrile (Scheme 2).



Scheme 1. Synthesis of nitrile ligands 5-(2-thiophen-2-yl-vinyl)-thiophene-2-carbonitrile (**L1**) and 5-[2-(5-nitro-thiophen-2-yl)-vinyl]-thiophene-2-carbonitrile (**L2**). (I) DMF, POCl_3 ; (II) (i) $\text{H}_2\text{NOH}\cdot\text{HCl}$, (ii) Ac_2O ; (III) HNO_3 , AcOH ; (IV) DMF, POCl_3 ; (V) (i) $\text{H}_2\text{NOH}\cdot\text{HCl}$, (ii) Ac_2O .



Scheme 2. Synthesis of the new complexes $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{LL})(\text{NC}(\text{C}_4\text{H}_2\text{S})\text{C}(\text{H})\text{C}(\text{H})(\text{C}_4\text{H}_2\text{S})\text{Z})][\text{Y}]$.

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