



Synthesis of new Fe(II) and Ru(II) η^5 -monocyclopentadienyl compounds showing significant second order NLO properties

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ABSTRACT

A series of new ruthenium(II) complexes of the general formula $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PP})(\text{L})][\text{PF}_6]$ (PP = DPPE or 2PPh₃, L = 4-butoxybenzotrile or N-(3-cyanophenyl)formamide) and the binuclear iron(II) complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{PP})(\mu\text{-L})(\text{PP})(\eta^5\text{-C}_5\text{H}_5)\text{Fe}][\text{PF}_6]_2$ (L = (E)-2-(3-(4-nitrophenyl)allylidene)malononitrile, that has been also newly synthesized) have been prepared and studied to evaluate their potential in the second harmonic generation property. All the new compounds were fully characterized by NMR, IR and UV–Vis spectroscopies and their electrochemistry behaviour was studied by cyclic voltammetry. Quadratic hyperpolarizabilities (β) of three of the complexes have been determined by hyper-Rayleigh scattering (HRS) measurements at fundamental wavelength of 1500 nm and the calculated static β_0 values are found to fall in the range $65\text{--}212 \times 10^{-30}$ esu. Compound presenting $\beta_0 = 212 \times 10^{-30}$ esu has revealed to be 1.2 times more efficient than urea standard in the second harmonic generation (SHG) property, measured in the solid state by Kurtz powder technique, using a Nd:YAG laser (1064 nm).

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1. Introduction

There is current research interest in the development of second-order nonlinear optical (NLO) materials exhibiting large first hyperpolarizabilities β because of their applications in laser frequency conversion, optical parameter oscillators and signal communication and the inherent employ in electrooptic devices [1–9]. The most intensively studied NLO chromophores are based in highly polarizable conjugated backbones presenting an electron donor and an acceptor group attached to both ends of the backbone in order to create an asymmetric “push–pull” system. Coordination of such systems to organometallic moieties bring additional possibilities to enhance high hyperpolarizabilities due to the occurrence of low energy ligand to metal or metal to ligand charge transfer. In this frame, the organometallic moiety forms an alternative type of donor or acceptor group for the traditional push–pull system. Additional advantages of complexes are related with the

variation of coligands that can fine tune the energy of these charge transfer transitions besides the introduction of other variables related with size, nature and redox ability of the transition metal.

Our approach in the search of organometallic molecular materials with strong NLO properties has been based on “MCp” piano-stool structures where the chromophores are linked to the metal centre (Fe^{II}, Ru^{II}, Ni^{II} and Co^{III}) by functional groups such as nitrile (N≡C) or acetylide (C≡C) that allow interactions of the suitable metal *d* orbitals with the two π sets of orthogonal π and π^* orbitals of the functional group, leading consequently to an extension of the π -electron system between the metal and the terminal donor/acceptor substituting group of the ligand. Experimental values of the hyperpolarizabilities obtained by Hyper Rayleigh Scattering measurements were corroborated by our theoretical calculations, showing that “FeCp” and “RuCp” were the best partners for this kind of interaction, behaving more efficiently as electron donors than the traditional donor groups (such as alkyl substituted amine groups) [10]. Within this prospective to search for a large NLO response in molecular materials, we continue to explore the field and we report here our recent results concerning four new compounds. As new approaches for structural diversity and

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