



Compromise between conjugation length and charge-transfer in nonlinear optical η^5 -monocyclopentadienyliron(II) complexes with substituted oligo-thiophene nitrile ligands: Synthesis, electrochemical studies and first hyperpolarizabilities

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Abstract

A systematic series of η^5 -monocyclopentadienyliron(II) complexes with substituted oligo-thiophene nitrile ligands of general formula $[\text{FeCp}(\text{P}_\text{P})(\text{NC}\{\text{SC}_4\text{H}_2\}_n\text{NO}_2)] [\text{PF}_6]$ (P_P = dppe, (+)-diop; n = 1–3) has been synthesized and characterized. The electrochemical behaviour of the new compounds was explored by cyclic voltammetry. Quadratic hyperpolarizabilities (β) of the complexes with dppe coligands have been determined by hyper-Rayleigh scattering (HRS) measurements at two fundamental wavelengths of 1.064 and 1.550 μm , to uncover the two-photon resonance effect and to estimate static β values. The obtained overall results are found to be better than for the related η^5 -monocyclopentadienyliron(II) complexes with *p*-benzonitrile derivatives. Although an increase of the resonant β at 1.064 μm with increasing number of thiophene units in the conjugated ligand was found (up to 910×10^{-30} esu), the static values β_0 remain practically unchanged, as shown by the 1.550 μm measurements. Combined with the electrochemical and spectroscopic data (IR, NMR, UV–vis), this remarkable evolution of β shows that the increase of conjugation length is balanced by a decrease in charge-transfer efficiency.

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1. Introduction

Organometallic compounds have given rise to a great deal of interest owing to their application in the field of

nonlinear optics (NLO) [1–6]. For second-order nonlinear optics, strongly asymmetric systems are needed, which led to the development of typical push–pull systems in which the metal centre, bound to a highly polarizable conjugated backbone, acts as an electron releasing or withdrawing group. The strong charge-transfer (CT) transitions occurring in organometallic compounds are expected to lead to high molecular first hyperpolarizabilities β . In addition, the position of the CT band, usually at visible wavelengths, can be tuned by variation of the ligands and/or the metal

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