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Benzo[*c*]thiophene Chromophores Linked to Cationic Fe and Ru Derivatives for NLO Materials: Synthesis Characterization and Quadratic Hyperpolarizabilities

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η^5-Monocyclopentadienyliron(II)/ruthenium(II) complexes of the general formula $[M(\eta^5\text{-}C_5H_5)(PP)(L\mathbf{1})][PF_6]$ {M = Fe, PP = dppe; M = Ru, PP = dppe or $2PPh_3$; **L1** = 5-[3-(thiophen-2-yl)-benzo[*c*]thiophenyl]thiophene-2-carbonitrile} have been synthesized and studied to evaluate their molecular quadratic hyperpolarizabilities. The compounds were fully characterized by NMR, FTIR and UV/Vis spectroscopy and their electrochemical behaviour studied by cyclic voltammetry. Quadratic hyperpolarizabilities (β) were determined by hyper-Rayleigh scattering measurements at a fundamental wavelength of 1500 nm. Density functional theory calculations were employed to rationalize the second-order non-linear optical properties of these complexes.

Introduction

The exploitation of organometallic chemistry for the synthesis of compounds with non-linear optical (NLO) properties has been mainly motivated by their use in optical devices.[1] During the last two decades, significant work has been published outlining the most important progress in the field.[2–11] According to the overall results, the general understanding is that second-order non-linearities are strongly related to asymmetric push–pull systems. In the case of organometallic compounds, the metal centre can be bound to a highly polarizable conjugated backbone, thereby acting as an electron-releasing or -withdrawing group. This type of structural feature leads to large quadratic hyperpolarizabilities arising from intense low-energy metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT) or intraligand charge transfer (ILCT) excitations. Among the organometallic compounds presenting this structural feature, our group and others have carried out systematic studies on η^5-monocyclopentadienylmetal complexes with benzene or oligothiophene conjugated chains coordinated to the metal centres through nitrile or acetylide linkages.[8,12–18] In particular, very efficient NLO responses were found when strong electron donors such as iron and ruthenium organometallic moieties were coupled with strong electron acceptors like NO_2.

Although fundamental research on NLO properties has mostly been devoted to the preparation of compounds with large optical non-linearities, the use of these properties in molecular switching has attracted considerable interest.[19–29] Organotransition-metal compounds revealed encouraging results because the presence of a redox-active metal centre within a conjugated system provides excellent opportunities for reversible modulation of the second-order non-linear optical (SONLO) properties. Our on-going work in this field was motivated by benzo[*c*]thiophene-based chromophores, the unique electronic behaviour of which, originating from their low HOMO–LUMO energy gaps,[30,31] can potentially yield interesting NLO effects. A soluble form of polyisothianaphthene was found to originate a large third-order non-linear optical response[32] and a ferrocenylethenyl-thienyl-2-thienylbenzo[*c*]thiophene organometallic complex exhibits moderate quadratic hyperpolarizabilities.[33] However, the structure of this metallocene derivative, in which the metal is placed orthogonally

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