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Design and Synthesis of NLO Efficient Organometallic Molecules

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Abstract. Second-order nonlinear optical (SO-NLO) properties of group 8 half-sandwich organometallic complexes have been intensively studied throughout the last 15 years, making this class of compounds relevant for the continuous search of NLO materials. This contribution surveys the ongoing efforts to design, characterize and optimize the NLO properties of this class of compounds. Computational studies, namely DFT calculations, were performed for several model molecules in order to predict the first hyperpolarizabilities and to support experimental evidences.

Keywords: Non-linear optics; first hyperpolarizability β.organometallics; half-sandwich complexes; ruthenium (II); iron(II);
PACS: 85.60.Bt

INTRODUCTION

Nonlinear optical (NLO) properties arise from the interaction of strong electromagnetic fields, such as the ones of laser beams, with matter. Due to the need for materials with exceptional NLO properties and fast response times in conjunction with mechanical and thermal stability and easy processing as well, intense research activity has been carried out in second-order nonlinear optical molecular materials. From the physics background it is known that the electronic structural requirement for SHG is a large value of polarizability which can be originated by a large variation of dipole moment between the ground and low lying excited states. This feature can be found either in organic or organometallic molecules providing they possess a donor and an acceptor group connected by a delocalized π system. However, metallo-complexes offer the possibility, relatively to organic compounds, of variation of the metal, coordination geometry, type of ligands, oxidation state, electron donating and/or withdrawing capabilities. Thus new structures can be designed considering several items such as: (i) possibility of incorporating several types of organic chromophores with various substitution patterns; (ii) possibility of intense low-lying metal to ligand charge-transfer (MLCT) excitations; (iii) control of metal centre donor ability that can give rise to tunable NLO properties by variation of the ligand sphere of coordination. Accordingly, various classes of metal complexes have systematically been explored in terms of new and optimized NLO materials, with the large amount of review articles published on NLO metal complexes in the last years indicating the breadth of the active research in this field [1-6].

RESULTS

The contribution of our research group for the development of this area has been mainly devoted - to the family of half-sandwich cyclopentadienyl Fe(II) and Ru(II) complexes possessing aromatic chromophores coordinated by nitrile or acetylide functional groups and extended in some cases to Ni(II) and Co(III) analogues as well. NLO properties of the several families of compounds were experimentally determined at molecular level, by evaluation of the first hyperpolarizability β using the Hyper-Rayleigh Scattering (HRS) technique.

The best values of the first hyperpolarizability β up to 2315 x 10^{-30} esu were found for some iron and ruthenium compounds [7]. Additional studies by Kurtz powder technique were carried out for some of our materials in the solid state, having in mind the variety of applications in the photonic and optoelectronic technologies. Some of the compounds revealed efficiencies up to 38 times better than the urea reference in doubling the frequency of a Nd:YAG laser emitting at 1907 nm [8].

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