Relation between Macroscopic and Microscopic Hyperpolarizability of Er(III) complexes with organic mixed ligands

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Photonics concerns the generation, transport, processing and detection of light. The field has received a powerful impetus recently with the introduction of nano-scale concepts. Moreover, organic materials now appear as key components in photonic devices such as light-emitting diodes, integrated lasers, or photovoltaic cells. Organic molecular systems offer unique opportunities in nano-photonics since both top-down and bottom-up strategies can be pursued towards the nano-scale.

The emerging fields of biophotonics, nonlinear microscopy, nanofabrication, optical sensing, optical memory and information storage require knowledge of nonlinear optical parameters of materials and design strategies to synthetise materials with NLO effects applicable in the technologies.

Aiming at developing new types of hybrid NLO materials with enhanced properties (for instance with stronger ionic bond) we have synthesize and investigated Er(III) cation coordinated with organic ligands with coordinative groups (OH, COOH) and Donor D and respective Acceptor A in 4,4` related to COOH donor group. L is a neutral ligand. The coordinative anion complexes were precipitated with a bulk cation of tetra-alkyl ammonium. The general formula is presented in Figure.1

Organic molecules coordinated to a cation represent a great potential for applications in electro-optic and all optical devices. This is due to different factors such as large molecular hyperpolarizability, fast electronic response time, versatility, easy thin films or single crystals processing and low cost. One of the simplest and most precise methods of second order nonlinear optical property characterization is the electric field induced second harmonic generation technique EFISH. This technique provides directly the sum of second hyperpolarizability and orientationally induced part of the first molecular hyperpolarizability.

In this paper we deal with the molecular dipole moment determination in solution by the effect of solvents on the absorption and fluorescence characteristics of organic compounds. Dipole moments of short-lived species are of considerable interest because they provide information on electronic and geometrical structure of these transient species. Knowledge of dipole moment of electronically excited species is often useful in the design of non-linear optical materials and elucidation of the nature of the excited state, as well as the course of any photochemical transformation. Experimental data on excited states are useful in the parameterizations of semi-empirical quantum chemical procedures for these states.

Among the techniques available for the determination of excited state dipole moments, the most popular is that based on the Lippert–Mataga equation [1]. In this technique, absorption and fluorescence shift followed using the solvent polarity, described by dielectric constant ε and refractive index n. The increase in the dipole moment value in the excited state, $\Delta\mu$, was estimated using the dependence of either the fluorescence wavenumber, ν_F, or the Stokes shift, $\Delta\nu$, on some solvent polarisation functions, the Lippert-Mataga [1,2] model and the E_T^N solvent parameter given by Reichardt. [3,4,5]

The dipole moment values in fundamental and excited states, calculated from absorption and emission fluorescence spectra of the above mentioned organic complexes in solvents with different dielectric constant ε and refractive indices are presented. The dipole moments in fundamental states were also determined by Guggenheim method. [6]

References:

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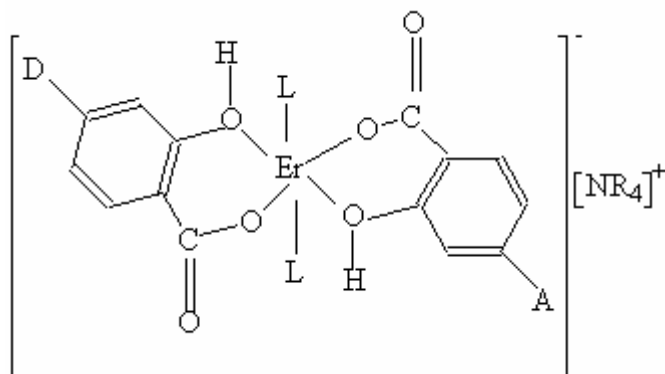[6]B. Thompson, J. Chem. Educ., 43, (1996),66.

Figures:

Figure 1. General formula of organic complexes : Er(III) cation coordinated with organic ligands with coordinative groups (OH, COOH) and Donor D and respective Acceptor A in 4,4` related to COOH donor group, L