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Effect of the complexation on the NLO electronic contribution in film based conjugated quinoline ligand

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ABSTRACT

In this paper we present the complexation, single crystal structure and the third harmonic generation response of the quinoline ligand and its mercury complex. Crystals structure of Bis(quinoline) Mercury (II) dichloride, ($C_{18}H_{14}Cl_2HgN_2$) is obtained from aqueous solution and characterized by single crystal X-ray diffraction at room temperature. This complex crystallizes in centrosymmetric space group. The structure is formed by chains along c axis. These chains are constituted by the quinoline ligand. The electronic contribution $\chi^{(3)}_{THG}$ is measured using the third harmonic generation technique on thin films at 1064 nm for quinoline ligand and its mercury complex incorporated in PMMA matrices. The first hyperpolarizability (β), the polarizability (α) and the electric dipole moment (μ) were calculated using the density functional B3LYP method with the LANL2DZ basis set. The obtained results for the quinoline ligand and its Hg complex show non zero (β).

1. Introduction

Organometallic compounds of group II metal have been subject of many investigations due to their applications in the field of optoelectronics and photonics [1–4]. They are produced from the combination of organic ligands with a metal compound (complex) giving birth to crystals with high transparency and large nonlinear optical coefficients [5–7]. Therefore, the organometallic compounds are organic materials that incorporate nitrogen-metal bonds. These kinds of compounds have been known for a long time, and their unique properties have been widely used to affect synthetic transformations. Due to their importance, the preparation and structural characterization of this family of compounds have been widely studied [8–12].

Organometallic compounds are diverse and versatile molecules, containing bonds between carbon or nitrogen and metal. In these compounds, metal-element bonds give largely covalent character. The preparation and the functionalized of coordination complexes was the subject of many investigations motivated by their potential applications such as optical computers, imaging systems, memory storage and photodetectors [13]. Because of the presence of redox-active metal centers, metal organometallic transition and complexes coordination are an important class of nonlinear optical (NLO) molecules, providing extensive opportunities for modulation of NLO responses. Organic coordination compounds are considered as promising class of materials for many applications in photonics. Nonlinear optical metal-organic materials offer more advantages in comparison with other classes of NLO materials, due to their larger electro-optic coefficients, faster response time, larger bandwidth, lower dielectric constant and higher laser damage threshold. These advantages are explained by the structural motifs of these complex metals that are closely related to the environment and the redox activity of the metals as well as the number of coordination sites, which are provided by the donating groups of organic ligands.

As a continuation to our previous investigations on non linear optical properties of materials [14–17]. We are reporting in this work the synthesis, structural characterization and the electronic contribution NLO responses. Crystals structure of Bis (quinoline) Mercury (II) dichloride, ($C_{18}H_{14}C_{l2}HgN_2$) grown from aqueous solution containing quinoline ligand were characterized by a single crystal X-ray diffraction at 298 K. Their third-order NLO properties were measured using the

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third harmonic generation technique on thin films at 1064 nm. The quantum chemical parameters, such as EHOMO, ELUMO, ΔE (energy gap), first hyperpolarizability, average polarizability and dipole moment were calculated by using the Density Functional Theory (DFT). Therefore, this work was undertaken to explore the NLO properties of quinoline ligand and its mercury complex doped in PMMA matrices.

2. Experiment

2.1. Preparation

The crystals of the complex [Bis(quinoline) Mercury (II) dichloride] were prepared by the mixture of the Quinoline ligand and $HgCl_2$ with the ratio 2:1 in acetonitrile solution. The solution was stirred for 15 min at room temperature. The formed precipitate was separated by filtration and washed with H_2O then, was recrystallized by slow evaporation from a dichloromethane solution.

2.2. Preparation of thin films

Quinoline ligand and its Hg complex were dissolved in the chloromethane with PMMA (Sigma-Aldrich, Mw=15,000g/mol) at 20 wt% of the concentration of composition. The obtained solutions were deposited by spin coating technique on BK7 glass substrates with an angular speed of 800–1200 rpm. After the deposition, the thin films of the studied compounds were dried using an oven at 60 °C for 20 min, in order to eliminate any remaining solvent. The thicknesses of the layers around 100 nm were measured with a 6 M DEKTAK profilemeter.

2.3. X-ray diffraction measurements

A single crystal of the studied complex, *$HgCl_2(Quin)_2$*, with dimensions of 0.13×0.12×0.09 mm^3, was selected for single crystal X-ray diffraction analysis. Data collection was performed at 298 K, on a Bruker APEXII diffractometer, CCD area detector equipped with a graphite monochromatized MoKα radiation (λ=0.71073 Å). The crystallographic data and experimental details for structural analysis are summarized in Table 1. The reported structure was solved by direct methods with SIR2002 [18] to locate all the non-H atoms which were refined anisotropically with SHELXL97 [19], using full-matrix least-squares on F^2 procedure from the software WinGX suite [20]. All the H atoms were placed in the calculated positions and constrained to ride on their parent atoms.

2.4. THG Nonlinear optical properties measurements

Third-order NLO effects of the quinoline ligand and its mercury complex are evaluated by using the third harmonic generation (THG) measurement which is carried out by means of the rotational Maker fringe technique [21]. We used the output beam of a mode-locked Nd:YAG/YVO4 laser generating at λ=1064 nm as a fundamental beam, with 16 ps pulse duration and 10 Hz repetition rate. The input laser pulses energy was controlled by a laser power-energy meter to be 160 mJ pulse power. Details about the experimental setup are reported in our previous works [22,23].

2.5. Computational studies

Our theoretical calculations are done by using the Gaussian 09 package [24]. The geometry optimization of the studied compounds was carried out with Density Functional Theory (DFT) using the hybrid functional density B3LYP method (Becke's three-parameter nonlocal exchange functional) [25] and the functional correlation of Lee et al. [26], with the LANL2DZ basis set (Los Alamos National Laboratory 2 Double f). We have used the imaginary frequencies number (NIMAG=0) to identified the stationary points. The Gauss-View molecular visualization program [27] is used to realize the vibrational band assignments. All quantum chemical parameters, such as: E_{HOMO}, E_{LUMO}, energy gap, dipole moment (μ), average polarizability, anisotropy of the polarizability and first static hyperpolarizability are calculated and discussed in this study.

Table 1
Crystallographic data and refinement parameters for $HgCl_2(Quin)_2$.

	Complex
Formula	$C_{18}H_{14}C_{l2}HgN_2$
Formula weight	529.8
Crystal habit, color	Prism, Colorless
Crystal system	monoclinic
Space group	*C* 2/*c*
a (Å)	7.7849(7)
b (Å)	14.1080(14)
c (Å)	14.8582(14)
α (deg.)	90
β (deg.)	92.244(3)
γ (deg.)	90
Volume ($Å^3$)	1630.62(3)
Z	4
Density (calculated, g cm^{-3})	2.158
Absorption coefficient (mm^{-1})	9.766
F(000)	1000
Crystal size (mm)	0.15×0.1×0.1
θ range for data collection (deg.)	2.74–28.11
Reflections collected	7126
Independent reflections	1994
R_{int}	0.030
Reflections with I≥2σ(*I*)	1941
Number of parameters	105
Goodness-of-fit on F^2	1.10
Final R indices [I≥2σ(*I*)]	0.015
R indices [all data]	R_1=0.0156, wR_2=0.0342
Largest difference peak and hole ($Å^{-3}$)	0.76, −0.68

3. Results and discussion

3.1. Structure and crystal packing

The asymmetric unit of Bis(quinoline) Mercury (II) dichloride compound (see Fig. 1) consists of one Hg metal located at two fold axis, bonded at two quinoline ligands monodentate via N atoms and coordinated by two chloride atoms.

The projection of the structure on the plan (b,c) (see Fig. 2) shows that this one is formed by chains along the [001] crystallographic direction. These chains are constituted by the quinoline ligand. The packing is consolidated by slippest P-P stacking with centroid to centroid distance of 3.6872(14) Å to 3.9240(14) Å between quinoline rings; no classical hydrogen bonds are found.

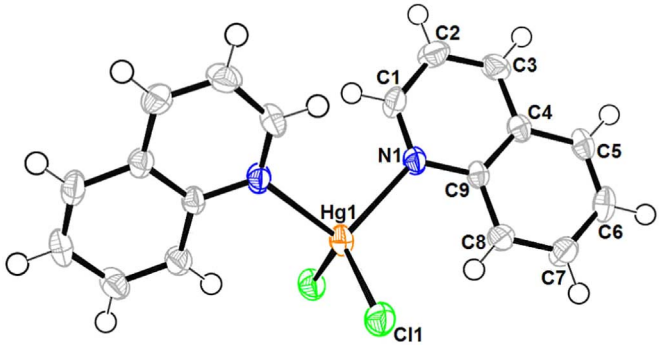

Fig. 1. The related complex molecular geometry of Mercury. Displacement ellipsoids are drawn at 50% level of probability. H atoms are represented as small spheres of arbitrary radius. Non-labelled atoms are generated by two fold axis.