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Research Note

Nonlinear optical study of palladium Schiff base complex using femtosecond differential optical Kerr gate and Z-scan techniques

Bada Jayappa Rudresha^a, Badekai Ramachandra Bhat^{a,*}, Dileep Ramakrishna^a, John Kiran Anthony^{b,c}, H.W. Lee^b, F. Rotermund^b^a Catalysis and Materials Laboratory, Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Srinivasanagar 575025, India^b Division of Energy Systems Research, Ajou University, Suwon 443749, South Korea^c Department of Applied Physics and Chemistry, University of Electro-Communications, 1-5-1 Chofugaoka, Chofu 182 8585, Tokyo, Japan

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ABSTRACT

A femtosecond differential optical Kerr gate (DOKG) and Z-scan techniques, have been applied to investigate the third-order optical nonlinearity of composite film of the coordination complex [PdLPPh₃] (L=N-(2-pyridyl)-N'-(salicylidene)hydrazine, PPh₃=triphenylphosphine). Film exhibits superior nonlinear optical properties in the near-infrared spectral region. The nonlinear response time and third-order nonlinear optical susceptibility of complex were found to be ≤ 90 fs and 3.9×10^{-10} esu, respectively. The Z-scan result shows that saturable absorption property of the film and its nonlinear absorption coefficient of the sample was found to be -23 cm/GW.

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1. Introduction

With the rapid development of optical communication, the novel materials with large and ultrafast nonlinear optical responses are needed for fabricating the ultrafast optical switching and processing devices [1–5]. For these purposes, many materials, including semiconductors, polymers, nanomaterials, and inorganic materials have been investigated. Among metal–organic compounds, the first report is on the NLO properties of a ferrocene derivative [6]. The results show that these compounds possess good NLO properties, it is thought that ferrocenyl conjugated system offers the possibility of electronic communication between terminal subunits, this being of particular interest in nonlinear optics [7]. The incorporation of transition metal ions introduces more sublevels into the energy hierarchy, thus permitting more allowed electronic transitions and giving larger NLO effects [8]. Metal ions being excellent templates, can gather organic one dimensional dipolar chromophores around to form predetermined two or three dimensional NLO-phores with various symmetries and charge-transfer dimensions; by virtue of which the coordinated metal center as well as the presence of polarizable *d* orbital electrons would contribute to the larger nonlinear activity [9,10].

From the last few decades, scientists have searched for materials with high nonlinear susceptibilities and ultrafast response times. For practical applications, nonlinear materials will also require adequate transparency, stability, speed, and processability [11]. Furthermore,

transition-metal based nonlinear optical organometallic fullerene derivatives C₆₀M₂ (M=Pd, Pt) have shown to exhibit large value $\chi^{(3)}$ compared to that of C₆₀. Considering the existence of partial charge transfer from metal atom to C₆₀ molecule, would result in a larger nonlinear optical response [12]. It is shown that the metal–ligand bonding in coordination complexes displays very large molecular hyperpolarizability because of transfer of electron density between the metal atom and the conjugated ligands. These materials possess additional advantages in that they can be grown as crystals as well as being incorporated into polymers such as poly(methyl methacrylate) (PMMA) to fabricate films. Despite a number of previous reports on the NLO properties of various metal complexes in solutions, the interest in ultrafast NLO properties of high quality thin film and crystalline forms of novel metal complexes has been sustained over the recent years since they are crucial for any photonic devices.

Based on the above consideration, in this communication, ultrafast and nonresonant nonlinear optical characteristics of metal complex, N-(2-pyridyl)-N'-(salicylidene)hydrazine triphenylphosphine palladium(I) (PdLPPh₃), incorporated into PMMA film was studied using time-resolved differential optical Kerr gate (DOKG) and open aperture Z-scan experiments.

2. Experimental

2.1. Synthesis of [PdLPPh₃] complex

The complex (Fig. 1) was prepared and characterized according to the following reported procedure [13]. The complex [PdLPPh₃]

* Corresponding author. Tel.: +91 824 2474000x3204; fax: +91 824 2474033.
E-mail address: chandpoorna@yahoo.com (B.R. Bhat).

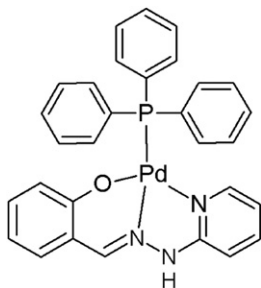


Fig. 1. Molecular structure of [PdLPPPh₃].

was prepared by stirring a mixture of [PdCl₂(PPh₃)₂] in 0.1 M sodium acetate and N-(2-pyridyl)-N'-(salicylidene) hydrazine in alcohol with 1:1 M ratio for 5 h. The red colored solid was filtered off, washed with ethanol and dried in vacuo.

2.2. Film preparation

In order to prepare a composite film of complex and PMMA, 250 mg of PMMA (M.W. 140,000) and 2 mg of complex were dissolved in 2.5 mL of dichlorobenzene (DCB). The concentration of the complex in the solution was 0.001 mol/L. The solution was mixed thoroughly by stirring and via ultrasonication to ensure homogenous mixing. The solution was subsequently spin coated at 1200 rpm on a glass substrate and the coated film was dried in a vacuum oven at 100°C for about 20 h. The film thickness (*L*) of composite film was measured to be 1.48 μm, by an Alpha-step surface profiler (Tencor P-10).

2.3. Differential optical Kerr gate and Z-scan measurements

The time-resolved DOKG [14] experiment with a Ti:sapphire laser delivering 90 fs pulses at a repetition rate of 92 MHz at 800 nm was used to investigate the nonlinear response time and third-order nonlinear optical susceptibility of the composite film. The laser beam was divided into pump and probe beams with 20:1 intensity ratio by a beam splitter. The polarization of the probe beam was set to 45° with respect to that of the pump beam by a half wave plate. Two beams were focused on the sample by a convex lens of focal length of 7 cm. The time delay of the probe with respect to the pump was controlled by a PC-driven linear translator (PI, M-014.D01). At the zero time delay, the two beams overlap spatially and temporally, and the probe beam polarization rotates due to the birefringence induced in the sample by the pump beam. The pump beam, after passing through the sample, was blocked and the probe beam was passed through a quarter wave plate. The circularly polarized probe beam was then split into two beams by a polarizing cube beam splitter and the two beams were detected by a photo detector pair connected to a lock-in amplifier. CS₂ was used to check the reliability of the setup as well as to estimate the $\chi^{(3)}$ of the sample. Additionally, single beam Z-scan technique [15] was used to investigate the nonlinear absorption property of the composite near 800 nm. An optical parametric oscillator synchronously pumped with a Ti:sapphire laser operating at 92 MHz (800 nm, 110 fs), was employed in the study. The laser beam was focused by a convex lens on the sample. The beam waist at 800 nm was estimated to be 16 μm, by the knife edge method.

3. Results and discussion

3.1. UV-visible spectra

The molecular structure and the linear absorption spectra of the complex are displayed in Figs. 1 and 2, respectively. The metal

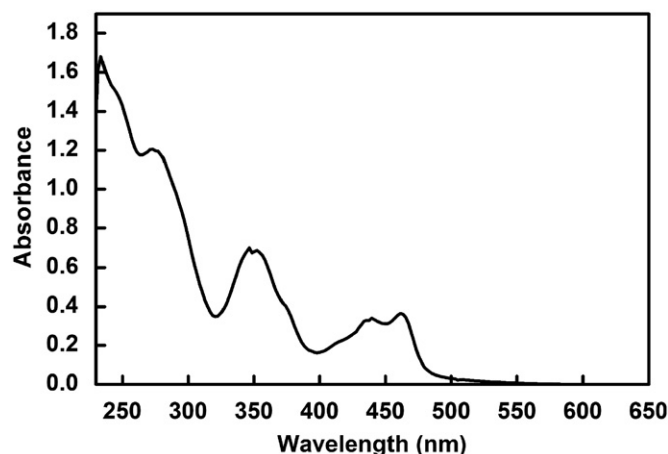


Fig. 2. Absorption spectra of the complex [PdLPPPh₃].

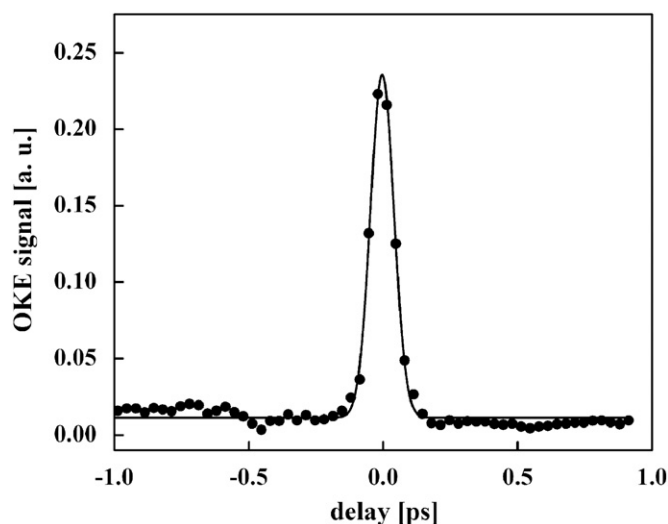


Fig. 3. Optical Kerr effect signal from [PdLPPPh₃]/PMMA composite film at 800 nm.

complex shows absorption peaks in the region 250–490 nm. The bands appearing in the region 250–350 nm were assigned to intraligand charge transfer transitions (ILCT) and less intense bands in the range 390–490 nm corresponds to the *d-d* forbidden transitions.

3.2. Nonlinear optical studies

3.2.1. Differential optical Kerr gate study

The result of the DOKG experiment performed at 800 nm is depicted in Fig. 3. The solid line shows a fit to the experimental data. The optical Kerr effect (OKE) signal is symmetric about the zero time delay, shows that the nonlinear response time of the composite film is faster than or comparable to the laser pulse width used (90 fs). CS₂ was used as the reference and its optical Kerr signal was recorded at the same experimental conditions. CS₂ exhibited a biexponential nonlinear response curve with response times of 0.2 and 1.8 ps, respectively. These values agree well with the previously reported values [16]. Maximum signal is observed at zero probe delay times, suggesting that the ultrafast electronic response is the dominant contributor to the observed nonlinearities. The magnitude of $\chi^{(3)}$ of the complex can be estimated by comparing its OKE signal amplitude with that of

CS₂ using the following Eq. (1) [14].

$$\chi_s^{(3)} = \chi_r^{(3)} \left(\frac{I_s}{I_r}\right)^{1/2} \left(\frac{n_s}{n_r}\right)^2 \left(\frac{L_r}{L_s}\right) \frac{\alpha_{L_s}}{\exp(-\alpha L_s/2)[1 - \exp(-\alpha L_s)]} \quad (1)$$

where the subscripts *s* and *r* represent the sample and the reference, *I* the absolute magnitude of OKE signal, *n* the refractive index, *L* the thickness and α the linear absorption coefficient. The $\chi_r^{(3)}$ of CS₂ was taken as 1×10^{-13} esu [17] and that of the composite film of complex was derived to be 3.9×10^{-10} esu. The $\chi^{(3)}$ value of the composite film is one order of magnitude larger than that of an organometallic polymer film measured near 1054 nm using picosecond pulses [18]. Also response time of our investigated complex is comparable with porous anodized aluminum oxide (AAO) nanostructures [17], and chloro(1,10-phenanthroline-*N,N'*) (triphenylphosphine)copper(I) complex [19]. Such an ultrafast response and third-order nonlinearity originates in this complex due to the π -conjugated triphenylphosphine ligand with its electron accepting character (*d*- σ^*) [20], which facilitates effective electronic communication and CT transitions between palladium (I) and ligands. This results in the large dipole moment changes between the excited states. The simplest way to achieve this is to have a donor (D)-acceptor (A) system with a bridge (D- π -A), which can help the electronic communication between the donor and the acceptor. Most metal complexes can be prepared within an above mentioned D- π -A system, in which donor and/or acceptor, or the bridge moieties are selectively replaced by an organometallic group. This is because metal complexes possess intense, low energy MLCT, LMCT or intraligand charge transfer (ILCT) excitations. Therefore they can effectively behave as donor and/or acceptor groups of the D- π -A system, or as constituents of the polarizable bridge [21]. Furthermore, the strength of the NLO properties can be altered by the π -back-donation capacity of the metal ions to the ligands and the increased π -back donation capacity of the metal ions to the ligands may enhance the extension of the electronic π system and improve the NLO properties. From these results it is clear that the resonance and structural effects are responsible for the observed response time and nonlinearity.

3.2.2. Open aperture Z-scan study

Fig. 4 shows the open-aperture Z-scan data obtained for composite film at 800 nm. The negative nonlinear absorption coefficient of the complex is found to be -23 cm/GW. The open aperture traces could be reproduced in the input intensity range

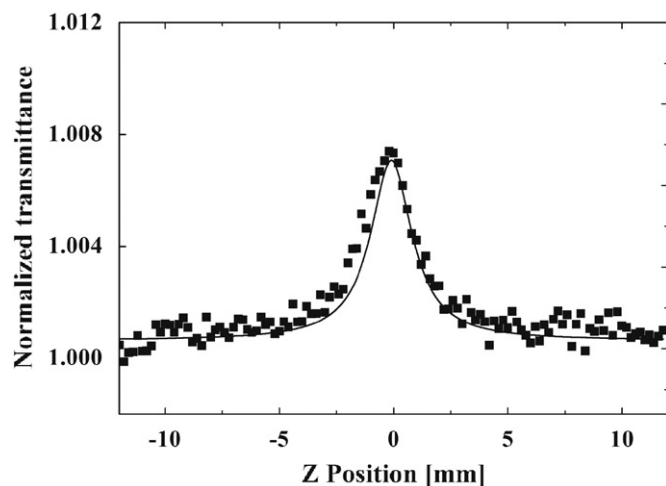


Fig. 4. Open aperture Z-scan traces for the complex in PMMA at 800 nm. The data corresponds to the input intensity 8 GW/cm². The solid line is a theoretical fit of the experimental data.

involved in the experiments and also shows the presence of strong saturable absorption. The combined saturable absorption and the two-photon absorption (TPA) coefficient, yielding the total absorption coefficient, can be obtained from a best fitting performed on the experimental data of the OA measurement by the equation with a negative $\beta \approx (-\alpha_0/I_s)$,

$$\alpha(I) = \alpha_0 \frac{1}{1 + (I/I_s)} + \beta I \quad (2)$$

where the first term describes negative nonlinear absorption such as saturable absorption, and the second term describes positive nonlinear absorption such as reverse saturable absorption and/or two-photon absorption. α_0 is the linear absorption coefficient. *I* and *I_s* are laser radiation intensity and saturation intensity, respectively. β is the two-photon absorption coefficient. As for open aperture Z-scan, the normalized transmittance may be expressed as [15]

$$T(z) = \sum_{m=0}^{\infty} \frac{[(-\alpha I_0 L_{eff}/1 + (z^2/z_0^2))]^m}{(m+1)} \quad (3)$$

where $L_{eff} = ((1 - e^{-\alpha_0 L})/\alpha_0)$, *z* is the longitudinal displacement of the sample from the focus (*z*=0), α is the nonlinear absorption coefficient, *I₀* is the on-axis peak intensity at the focus, *L_{eff}* is the effective interaction length, *L* is the sample length, *z₀* is the Rayleigh diffraction length. Theoretical fit of the experimental data could be conducted by the substitution of Eq. (2) into Eq. (3). A direct comparison of this study with those of other organometallic or coordination compounds is rather hard because of different experimental conditions and reports on solutions. As for the observed negative nonlinear absorption (saturable absorption) in the present case, more work is required to identify the exact phenomena causing such behavior in these materials. Recent literatures show that some metal complexes have been reported in solution state for saturable absorption phenomenon [22–24]. The compound is thermally stable up to 300 °C and exhibits no remarkable laser damage in the intensity range (~ 9 GWcm⁻²) involved in the experiment.

4. Conclusions

In summary, the ultrafast third-order nonlinearity of composite film of coordination complex and PMMA was estimated to be as large as 3.9×10^{-10} esu by femtosecond optical Kerr gate method. Open aperture Z-scan measurement, shows that the complex exhibits saturable absorption. The nonlinear absorption coefficient of complex is found to be -23 cm/GW. The NLO studies on a series of metal complexes derived from this reported complex will help us to understand metal–ligand charge transfer and identify ways to enhance the nonlinear absorption cross sections in these complexes. Having large value of $\chi^{(3)}$ and ultrafast response time makes [PdLPPH₃] a potential optical material in ultrafast photonic devices.

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