All optical nonlinear and switching characteristics of a novel ruthenium complex

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ABSTRACT

Third-order nonlinear optical properties of a novel ruthenium complex (2-thioxo-1,3-dithiole-4,5-dithiolato) triphenylarsenic Ru(III), have been investigated by employing Z-scan and DFWM techniques. The compound shows self-defocusing effect. Its nonlinear refractive index, third-order nonlinear optical susceptibility and the second-order hyperpolarizability are seen to be of the order of 10^{-9}, 10^{-10} and 10^{-30} esu respectively. The nonlinear absorption coefficient is of the order of 10^{-9} m/W. This material exhibits good optical power limiting capability which is seen to occur due to reverse saturable absorption. Experiments on all-optical switching action indicate that the sample can function as an optical inverter or a NOT gate.

1. Introduction

Recently exciting new developments have occurred in the domain of photonic devices due to the synthesis of several novel materials possessing large and ultrafast nonlinear optical responses which has led to the fabrication of ultrafast optical switching and processing devices [1–5]. For, such applications, a variety of materials including semiconductors, polymers, nanomaterials and inorganic materials have been researched. In recent years, π-conjugated organic materials have received considerable interest for their high nonlinear optical (NLO) properties and fast response time [6]. The exciting about such organic materials is the possibility of enhancing their third-order nonlinearity by incorporating metals into molecules. Organometallic and coordination chemistry offers a very large variety of NLO materials, differing in metal and configuration, oxidation state and spin state. Such materials are also seen to have good optical transmittance and thermal stability. The central metal atom of an organometallic and coordination complexes can readily coordinate with conjugated ligands and undergo metal–ligand orbital overlap facilitating effective electronic transport and electronic transitions between the metal ion and the ligand, leading to large changes in the dipole moment between the excited states [7].

Recently, ruthenium metal–organic complexes are widely studied metal–organic complexes for NLO [8–13]. Metal complexes with sulfur-containing chelating ligands have attracted attention of several researchers due to their unique physical and chemical properties. Among such ligands, dithiolate ligands have been studied most extensively [14]. Oxidation of dianionic complexes $[M(S_2C_2R^1R^2)_2]^{2-}$ leads to neutral compounds [15], in which sulfur-containing ligands may have dithiocarbonyl or dithiolate structure, depending on the different oxidation states of the metal atom. High degree of electron delocalization, strong mixing of orbitals of the ligand and metal ion, and the possibility for stabilization of metal complexes in different oxidation states are key factors responsible for unique properties of these compounds. Specially, π-electron conjugated systems like 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) and related ligands, have been used in the synthesis of good electrically conducting radical anion salts and charge-transfer complexes. Recently several investigation have been carried out on potential applications of dithiolene complexes to study their magnetic, electrical and nonlinear optical properties [14,16,17]. The nature of electronic structure of dithiolene metal complexes leads to a variety of important photonic devices.

With the above facts in mind, we have synthesized and investigated a new ruthenium complex ([RuCl(C₃S₅)(H₂O)(AsPh₃)₂]) (RuL)

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focusing on its third-order nonlinear optical, optical power limiting and all-optical switching properties. The origin of the nonlinearity mechanism has been experimentally studied.

2. Experimental

2.1. Materials and methods

[RuCl$_2$(AsPh$_3$)$_2$] was synthesized as per the reported procedure [18]. The C, H, O and S contents of the complex were determined by Thermoflash EA1112 series elemental analyzer. Magnetic susceptibility measurement was recorded on a Sherwood Scientific instrument (UK). Thermal analysis was carried out (EXSTAR-6000) from room temperature to 700 °C at a heating rate of 10 °C/min. The electronic spectrum of the complex was measured on a GBC Cintra 101 UV–Vis double beam spectrophotometer using DMF in the 200–800 nm range. FT-IR spectrum was recorded on a Thermo Nicolet Avatar FTIR spectrometer in the frequency range 400–4000 cm^{-1}. ^{1}H NMR and ^{31}P NMR spectra were recorded in Bruker AV 400 instrument using TMS and H$_3$PO$_4$ as internal standards respectively. Electrochemical study was performed using Versa STAT-3 in 0.005 M dichloromethane solutions of [(n-C$_4$H$_9$)$_4$N]ClO$_4$ (TBAP) as a supporting electrolyte. Coupling reactions were monitored by gas chromatography (Shimadzu 2014).

2.2. Synthesis of [RuCl$_2$(AsPh$_3$)$_2$]

The ruthenium complex (Fig. 1(a)) was prepared under strictly anhydrous conditions. To a methanol (20 ml) solution containing CS$_2$ (0.2 ml, 3 mmol) and sodium metal, was added ruthenium complex, [RuCl$_2$(AsPh$_3$)$_2$] (695 mg, 1 mmol) with constant stirring. The mixture was refluxed for 4 h. The dark brown precipitate obtained was filtered, washed with methanol, petroleum ether (60–80 °C) and dried in vacuo. Yield: 70%. M.P: 235 °C. Anal. Calc. for C$_{39}$H$_{32}$ClOAs$_2$RuS$_5$, Found (calculated) (%): C, 52.86 (53.50); H, 3.62 (3.68); O, 1.89 (1.83); S, 18.26 (18.31).

2.3. Sample preparation

Samples for the experiments were prepared in both liquid state and solid state. For liquid sample RuL was dissolved in N,N-dimethylformamide (DMF) with a concentration of 1×10^{-3} mol/L and was taken in a quartz cuvette of path length 1 mm. The solid sample in the form of a film was prepared by incorporating 1 wt.% of the ruthenium complex in PMMA matrix. The film was obtained by spin coating technique. Its thickness measured by spectroscopic ellipsometry

Fig. 1. (a) Molecular structure of RuL and (b) UV–visible absorption spectrum of RuL.

method (Sentech, SE 800) was found to be ≈11 μm. The films having different wt.% of ruthenium complex dispersed into PMMA were prepared for investigating the concentration dependence of the NLO parameters. The linear absorption spectrum of the ruthenium complex was obtained using the UV–Visible fiber optic spectrometer (Model SD2000, Ocean Optics Inc.).

2.4. Z-scan and degenerate four wave mixing (DFWM) measurements

The Z-scan and DFWM experiments [10,19–21] were performed using a Q-switched, frequency doubled Nd: YAG laser with 10 Hz repetition rate. The laser pulses had a pulse width of 7 ns at 532 nm wavelength. In the Z-scan experiment, the Gaussian laser beam of intensity of 1.2 GW/cm^2 was focused using a lens of 25 cm focal length. The laser beam waist at the focal spot was estimated to be 18.9 μm and the corresponding Rayleigh length was 2.11 mm. In the DFWM experiment, we used the forward folded boxcar geometry, wherein a laser beam is split into three and the beams are aligned such that they form three corners of a square. The diametrically opposite beams are the pump beams, and the third beam is the probe. When the three beams are simultaneously focused onto the sample, a fourth beam (signal beam) is generated due to nonlinear interaction and is well separated spatially from the other beams. This signal beam is detected using a detector [22].

2.5. Optical power limiting and all-optical switching studies

Optical power limiting was studied by keeping the sample at the focus of the laser beam and measuring the transmitted laser energy at various input laser energies. For all measurements, two Pyroelectric detectors (RjP-735) were used with the Energy Meter (Laser Probe Inc. Rj-7620). All-optical switching function was also performed using standard pump–probe technique [23]. Q-Switched Nd: YAG laser pulses of wavelength 532 nm was used as a strong pump beam and a low-power 2 mW continuous wave (CW) He–Ne laser of wavelength 633 nm was used as a weak probe beam. The intensities of the pump beam were chosen to be 5, 10 and 15 GW/cm^2. The time-dependent probe beam signal was detected using a photomultiplier tube (R928P, Hamamatsu). The signal was analyzed using a Digital Storage Oscilloscope (500 MHz, HP 54616B), which was triggered by the Nd: YAG laser. The output signal was observed to have pulsed nature having the same repetition rate as the Nd: YAG laser pulses.

3. Results and discussion

3.1. Spectral analysis

UV–Vis spectrum of the ruthenium complex is shown in the Fig. 1(b). In spectrum of the RuL it is seen that many bands appearing in the range of 250–490 nm. The bands appeared in the range of 250–375 nm is assigned to be intraligand π–π* transitions and peaks appearing in the range of 400–450 nm which corresponds to forbidden metal d–d transition.

3.2. Z-scan studies

The normalized open aperture Z-scan traces of the RuL in solution (RuL:solution) and film form (RuL:film) are shown in Fig. 2(a) and (b), respectively. It is seen that the transmission is symmetric with respect to the focus ($z = 0$), where it has a minimum. The corresponding normalized transmission as a function of sample position in open aperture condition is given by [19,24],

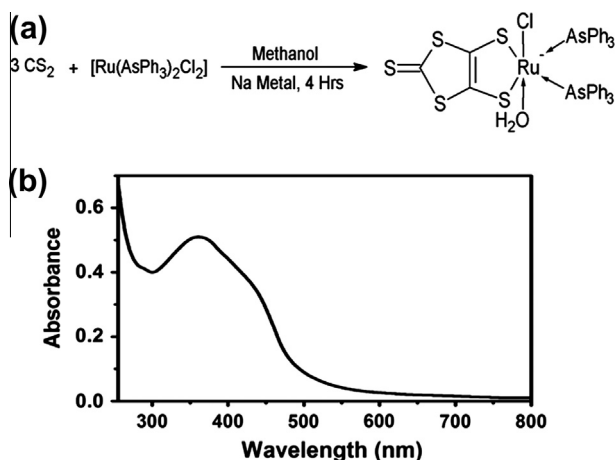$$T(z) = 1 - \left(q_0/2\sqrt{2} \right) \quad \text{for } |q_0| < 1 \tag{1}$$