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Nonlinear optical and all-optical switching studies of novel ruthenium complex

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ABSTRACT

We report the experimental investigation on third-order nonlinear optical parameters of a novel (2-thioxo-1,3-dithiole-4,5-dithiolato) triphenylphosphine Ru (III) [RuL] both in solution and solid form, by using Z-scan technique at the measurement wavelength of 532 nm. The films were prepared by spin-coating technique on glass substrate. The magnitude and sign of the third-order nonlinear absorption and refractive index n_2 of ruthenium complex were determined. The results reveal that ruthenium complex exhibits large negative nonlinear refractive index (n_2) of the order of 10^{-9} esu. The third-order nonlinear optical susceptibility ($\chi^{(3)}$) values were of the order 10^{-10} esu. The nonlinear optical properties were found to vary with concentration. The $\chi^{(3)}$ value is confirmed through degenerate four wave mixing (DFWM) experiment at the same wavelength. The effective excited-state absorption cross section was found to be larger than the ground state absorption cross section indicating that the operating nonlinear mechanism is reverse saturable absorption (RSA). It was found that the ruthenium complex exhibits good optical power limiting and also all-optical switching of nanosecond laser pulses. This new compound has potential application as photonic and optoelectronic devices.

1. Introduction

Nonlinear optical materials with large nonlinearity have received great attention because of their essentiality in new optical devices including all-optical switches, signal processors and optical power limiters [1–4]. Organometallic compounds have become interesting candidates for nonlinear optics because of the metal-to-ligand or ligand-to-metal charge transfer which is commonly related to enhanced optical nonlinearities [5]. Recently organometallic complexes with special π-electron conjugated systems like 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) have attracted much attention as promising third-order nonlinear optical (NLO) and optical power limiting materials [6,7]. These sulfur-containing chelating ligands such as dmit are attractive due to their high degree of electron delocalization, strong mixing of orbitals of the ligand and metal, and the possibility for stabilization of metal complexes in different oxidation states which induces larger NLO effects [8].

All-optical switching related devices have gained interest in optical communication and form building blocks of future information processing systems. All-optical devices have been proposed for a large variety of materials based on nonlinear absorption using pump-probe technique [9–11] and their theoretical and experimental investigations based on resonant nonlinearity using Fiber Bragg Grating technique [12–15].

The investigated ruthenium complex is the first and novel type among the synthesized dmit complex family which shows all-optical switching property. With the above facts in mind, we have investigated a new ruthenium complex $[RuCl(C_3S_5)(H_2O)(PPh_3)_2]$ (RuL) focusing on its third-order nonlinear optical properties using Z-scan and DFWM techniques. Also, the optical power limiting and all-optical switching behavior of the complex was observed by energy dependent transmission and pump-probe experiments respectively to check its suitability for photonic devices.

2. Experimental

The synthesis and characterization of the investigated ruthenium complex is reported in literature [16]. The molecular structure of the ruthenium complex is shown in Fig. 1. 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

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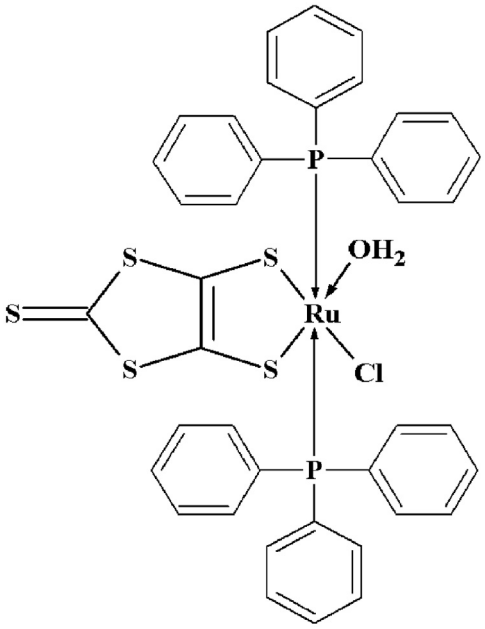

Fig. 1. Molecular structure of RuL.

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 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 a UV–visible fiber optic spectrometer (Model SD2000, Ocean Optics Inc.).

The Z-scan and DFWM experiments [17,18] 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 input intensity 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 BOXCARS 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 on to the sample a fourth beam (signal beam) is generated due to nonlinear interaction and is well separated spatially from other beams. This signal beam is detected using a detector [19]. Optical power limiting was examined by keeping the sample at the focus of the laser beam and measuring the transmitted laser energy at various input laser energies using the detector. 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 [9]. Q-switched Nd:YAG laser of wavelength 532 nm and 7 ns pulse width was used as a strong pump beam and the 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 17 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.

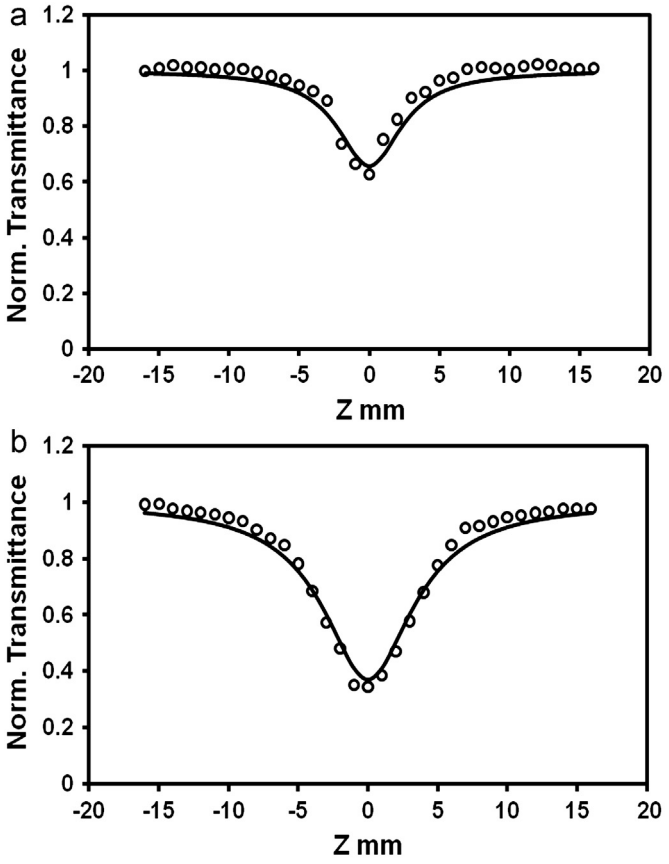

Fig. 2. Open aperture Z-scan of (a) RuL:DMF and (b) RuL:PMMA, solid line depicts theoretical fit.

3. Results and discussions

It is evident from the UV–vis spectrum of RuL that it shows the two intraligand π–π^* transitions and one forbidden metal d–d transition [16].

3.1. Z-scan studies

The normalized open aperture Z-scan traces of the RuL in solution (RuL:DMF) and film form (RuL:PMMA) 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 [17,20],

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

where $q_0 = \beta_{eff} I_0(1-\exp^{-\alpha L})/(1+z^2/z_0^2)\alpha$, α is the linear absorption coefficient, L is the sample length, β_{eff} is the nonlinear absorption coefficient of the sample, I_0 is the intensity of the laser beam at the focus and z_0 is the Rayleigh range for the lens. Nonlinear absorption coefficient (β_{eff}) of the ruthenium complex is obtained by fitting the experimental data using Eq. (1). The imaginary part of $\chi^{(3)}$ (Im $\chi^{(3)}$) for the ruthenium complex is determined using the relations available in literature [21]. The calculated β_{eff} and Im $\chi^{(3)}$ values of RuL:DMF and RuL:PMMA are tabulated in Tables 1 and 2 respectively.

The nonlinear absorption of nanosecond pulses is generally explained by a five-level model [22,23]. It consists of S_0 as the ground state, S_1 and S_2 as the first and second excited singlet states and T_1 and T_2 as the first and second excited triplet states, respectively, as shown in Fig. 3. Each electronic state has many vibrational levels. Exposure of the molecule to 532 nm, 7 ns laser