Investigation of Nonlinear Optical and All-Optical Switching Properties of Novel Ruthenium Complex

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Abstract: The nonlinear optical, optical limiting and all-optical switching properties of novel ruthenium complex doped PMMA film were investigated at 532 nm. The investigations show that the complex is a potential molecule for photonic applications.
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1. Introduction

Novel materials with large nonlinearity and fast response-time play an important role in optical information processing, optical switching, optical power limiting, etc. [1]. Large varieties of materials including organics, organometallics, semiconductors, etc. [2] have been investigated for these applications. Organic molecules are attractive because, their optical properties can be tuned by structural modification, and they have large nonlinearity and fast response-time [3]. Further, these properties can be suitably tuned to the required value by the addition of transition metal ion into the π-conjugated organic molecules because, addition metal ions inserts more energy sublevels which tend to enhance electronic transition and charge-transfer from metal to ligand or from ligand to metal. It leads to intramolecular electron delocalization, giving rise to larger NLO properties [2]. In this work, we report third-order NLO properties of [Ru (salen) (H_2O) (Cl)], salen = *N*, *N*′- disalicylidene - 1,2-ethylenediimine dianion complex doped PMMA film [RuL] using Z-scan technique, and optical power limiting (OPL) performance using energy dependent transmission studies. The all-optical switching property was also demonstrated by using standard pump-probe technique.

2. Experimental

The synthesis and characterization of the titled ruthenium complex is done based on the literature. Molecular structure of the ruthenium complex is shown in inset of Fig.1(a). The different wt. % of the ruthenium complex was doped in PMMA matrix and 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 linear absorption spectrum of the ruthenium complex was obtained using the UV-Visible fiber optic spectrometer (Model SD2000, Ocean Optics Inc.). The Z-scan experiment [4] was performed using a Q-switched, frequency doubled Nd: YAG laser with a pulse width of 7 ns and 10 Hz repetition rate at 532 nm wavelength. In the Z-scan experiment, the Gaussian laser beam of input intensity 1.20 GW/cm^2. Optical power limiting property of the films was studied by keeping the sample at the focus of the laser beam and measuring the transmitted energy at various input laser energies. In all these measurements, two Pyroelectric detectors (RjP-735) were used with a dual channel energy meter (Laser Probe Inc. Rj-7620). All-optical switching property of the sample was also investigated using standard pump-probe technique. Q-Switched Nd: YAG laser pulses of wavelength 532 nm and 7 ns pulse width was used as the pump beam. The probe beam was a low-power (2 mW) continuous wave He-Ne laser beam of wavelength 633 nm. The time-dependent transmitted probe beam was detected using a photomultiplier tube (PMT) (R928P, Hamamatsu). The signal was analyzed using a digital storage oscilloscope (500 MHz, HP 54616B), which was triggered by the Nd: YAG laser.

3. Results and Discussion

The absorption-spectra of is shown in Fig. 1(a). The bands appearing in the region 230-350 nm are assigned to intraligand charge transfer transitions and less intense bands in the range 390–500 nm correspond to the d-d forbidden transitions.

Fig. 1(b) shows open aperture Z-scan curves along with the corresponding theoretical fits [5] of RuL and the signature of the scans implies the intensity dependent absorption. By fitting the open aperture Z-scan data, the nonlinear absorption coefficient (β_{eff}) of RuL was determined. By using β_{eff}, the imaginary part of third-order nonlinear optical susceptibility ($Im\chi^{(3)}$) of RuL is estimated for different concentrations in PMMA film and tabulated in Table 1. Since β_{eff} value is positive, the observed NLA is due Reverse Saturation Absorption (RSA) [6].

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The values of effective excited-state absorption cross-section σ_{exc} of the ruthenium complex were obtained by fitting the open aperture data using the equation given in literature [5] and the ground-state absorption cross-section σ_g was calculated

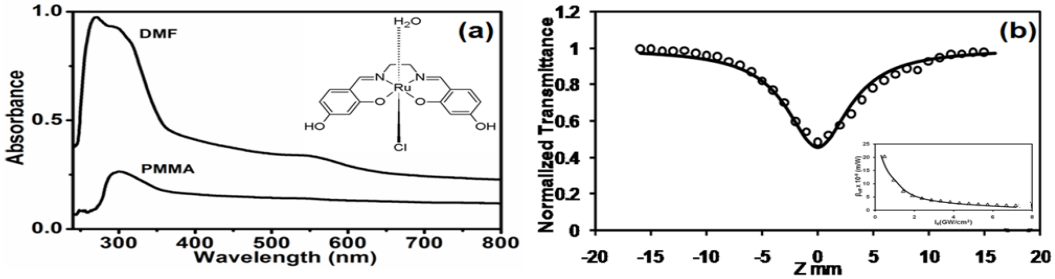

Fig. 1. (a)The UV-Vis spectra of RuL (inset molecular structure of RuL) and (b) Open aperture Z-scan traces of PdL. The solid lines are the fitting results using the model described in the text (inset β_{eff} Vs on-axis intensity I_0).

using the relation $\sigma_g = \alpha / N_a C$, where N_a is the Avogadro's number and C is the concentration in mol/L. The values of σ_g and σ_{exc} for RuL are given in Table 1. Since the values of $\sigma_{exc} > \sigma_g$, it is confirmed that, the observed nonlinear optical process is due to RSA. Further, if the NLA mechanism belongs to simple two-photon absorption, β_{eff} should be a constant independent of the on-axis input intensity I_0 [7]. But the Fig. 1(b) inset shows the value of β_{eff} decrease with increasing on-axis intensity I_0, which is a consequence of the RSA [7].

Fig. 2(a) shows the pure nonlinear refraction Z-scan curve along with the corresponding theoretical fit of the RuL. The peak-valley characteristic suggests that the nonlinear refractive index (n_2) is negative (self-defocusing effect). The nonlinear refractive index (n_2) is obtained by fitting the experimental data and the real part of third-order nonlinear optical susceptibility (Re $\chi^{(3)}$) is determined using the relation given in the literature [5]. The concentration dependent n_2 and Re$\chi^{(3)}$ values of the RuL are given in Table 1.

3.3. Optical power limiting studies

The complex shows good optical power limiting performance because of its large NLA is shown in Fig. 2(b). In RuL the output energy is clamped at ~60, ~46, ~39 and 30 μJ at the concentrations of 0.5, 1.0, 1.5 and 2.0 wt% respectively.

Salen is a quadridentate ligand which will coordinate with the metal using two oxygen and two nitrogen atoms, which will form a chelate around the metal. Central diimine part is electron acceptor, which will accept the electron from metal center (redox center). This donor-accept nature of ligand and metal increases NLO activity.

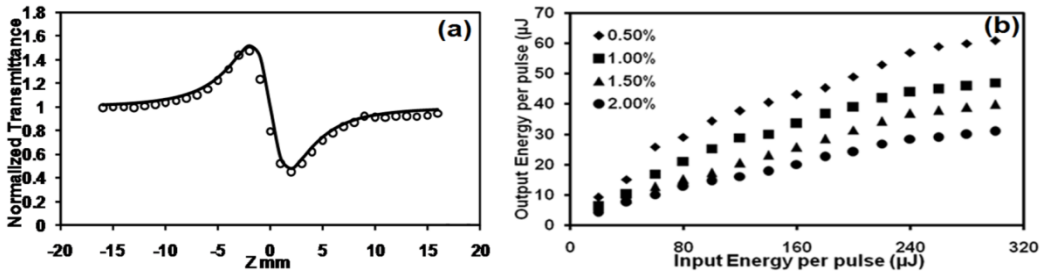

Fig. 2. (a) Pure nonlinear Z-scan traces of RuL. The solid lines are the fitting results using the model described in the text and (b) Optical power limiting of RuL at different concentrations.

Table 1. Third-order nonlinear optical parameters of the complex RuL

Dopant concentration (Wt.%)	β_{eff} (m/W)x10^{-9}	Im$\chi^{(3)}$ (esu)x10^{-11}	σ_g (cm^2)x10^{-17}	σ_{exc} (cm^2)x10^{-16}	n_2 (esu)x10^{-9}	Re$\chi^{(3)}$ (esu)x10^{-11}
0.50	15.888	3.497	8.827	3.626	-8.998	-12.237
1.00	22.375	4.925	5.698	4.683	-10.945	-14.885
1.50	25.519	5.617	5.442	5.824	-12.409	-16.876
2.00	34.113	7.509	4.687	7.785	-17.089	-23.241

3.4. All-Optical Switching Studies

The laser pulse shapes recorded in the pump-probe experiments on switching action of our sample films is shown in Fig. 3. When the pump pulse from the Nd: YAG laser passes through the sample, the output intensity of the probe beam from the He-Ne laser gets reduced drastically (*OFF*-state). When the pump pulse is turned off, the output probe beam regains its full intensity (*ON*-state). Thus, the CW He-Ne laser beam passing through the sample film can be switched *ON* and *OFF* by the 7 ns Q-switched Nd: YAG laser of 532 nm wavelength.

The physical mechanism responsible for all-optical switching is that, when the pump pulse passes through the sample, the population of the triplet state, T_1, increases, which results in strong absorption of the probe He-Ne beam, thereby reducing its transmission. After the pump pulse crosses the sample, the population of the triplet state drops drastically and the He-Ne laser output regains its original value. The modulation of the probe intensity was seen to be 12, 20 and 33%, for different pump-beam intensities of 5, 10 and 17 GW/cm^2, respectively. The modulation strength of the probe increases as the intensity of pump beam increases due to the increase in the population of triplet state. The switching times are seen to be in the range of few micro seconds. The relaxation of the triplet state to the ground state is forbidden, resulting in slow switching time of the molecules.

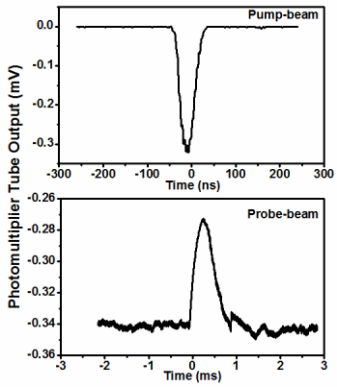

Fig.3. All-optical switching behavior of the RuL at pump intensity of 10 GW/cm^2.

4. Conclusions

In summary, the NLO properties and coefficients of the ruthenium complex were extracted from Z-scan studies at 532 nm with 7 ns pulses. Optical power limiting experiments indicate that the complex possesses good optical power limiting behavior. The operating NLA mechanism leading to optical power limiting was found to be RSA. The complex also exhibits all-optical switching behavior. Thus, the investigated complex has potential application in photonics and optoelectronics.

References

[1] G. de la Torre, P. Vazquez, F. Agullo-Lopez and T. Torres, "Role of Structural Factors in the Nonlinear Optical Properties of Phthalocyanines and Related Compounds," Chem Rev 104, 3723–3750 (2004).

[2] Hari S. Nalwa and Miyata S, *Nonlinear Optics of Organic Molecules and Polymers* (CRC Press, New York 1997).

[3] J. Clark and G. Lanzani, "Organic photonics for communications," Nat Photonics 4, 438-446 (2010).

[4] M. Sheik-Bahae M, A.A. Said, T.H. Wei, D.J. Hagan and E.W. Vanstyrland, "Sensitive measurement of optical nonlinearities using a single beam," IEEE J. Quantum Electron. **26**, 760–769 (1990).

[5] P. Poornesh, P.K. Hegde, G. Umesh, M.G. Manjunatha, K.B. Manjunatha, A.V. Adhikari, "Nonlinear optical and optical power limiting studies on a new thiophene-based conjugated polymer in solution and solid PMMA matrix, "Opt Laser Technol. 42, 230-236 (2010).

[6] F.J. Zhang, W.F. Guo, X.B. Sun, Q. Ren, Y. Gao, H.L. Yang, G.H. Zhang, Y.T. Chow, D. Xu, "Nonlinear optical absorption of [(C2H5)4N]2Cu(dmit)2 irradiated by picosecond and nanosecond laser pulses," Laser Phys. Lett., **4**, 230-233 (2007).

[7] S.L. Guo, L.I. Xu, H.T. Wang, X.Z. You and N.B. Ming, "Investigation of optical nonlinearities in Pd(po)$_2$ by Z-scan technique," Optik **114**, 58-62 (2003).