All-optical switching and limiting properties of a Ru (II) Schiff-base complex for nonlinear optical applications

All-optical switching and limiting properties of a Ru (II) Schiff-base complex for nonlinear optical applications

K B Manjunatha[1,2], **Ravindra Rajarao**[3], **G Umesh**[4], **B Ramachandra Bhat**[5] and **P Poornesh**[6]

[1] Department of Physics, NMAM Institute of Technology, Nitte 574110, India
[2] Visvesvaraya Technological University, Belagavi 590018, India
[3] Centre for Sustainable Materials Research and Technology, School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia
[4] Optoelectronics Laboratory, Department of Physics, National Institute of Technology Karnataka, Mangalore 575025, India
[5] Catalysis and Materials Laboratory, Department of Chemistry, National Institute of Technology Karnataka, Mangalore 575025, India
[6] Nonlinear Optics Research Laboratory, Department of Physics, Manipal Institute of Technology, Manipal University, Manipal 576104, Karnataka, India

E-mail: poorneshp@gmail.com

CrossMark

Abstract

A salen-based ruthenium (Ru) (II) complex was synthesized for possible use in nonlinear optical device applications. The Ru complex was doped in a polymer matrix to fabricate films using a low-cost spin-coating technique. The third-order nonlinear optical parameters of the complex were investigated by Z-scan and degenerate four-wave mixing techniques. The study reveals two-order enhancement of third-order optical susceptibility $\chi^{(3)}$ and exhibits superior limiting capability due to a reverse saturable absorption process. All-optical switching action for the films indicates that the sample can function as an optical inverter or a NOT gate. Hence, the Ru (II) Schiff-base complex materializes as a possible candidate for use in nonlinear optical devices.

Keywords: Z-scan, DFWM, all-optical switching, Ru (II) complex, NLO, optical power limiting

(Some figures may appear in colour only in the online journal)

1. Introduction

Nonlinear optical (NLO) materials are widely investigated for applications in optical storage, optical computing, harmonic generation, power limiting, rectifying devices and optical switching [1–3] for which a large nonlinear response is a prerequisite. Various organic and inorganic materials have been extensively used [4–9]. Organic NLO materials used for optical devices should satisfy optimal dipole moments of active chromophore and matrices [10, 11]. A ferrocene derivative belonging to the class of metal–organic compounds was reported for the first time depicting NLO properties [12]. It was observed that these compounds possess good NLO properties due to the presence of a ferrocenyl conjugated system which efficiently acts as electronic transport between terminal subunits [13, 14]. The integration of transition metal ions results in more sublevels in the energy hierarchy, thus a large number of allowed electronic transitions resulting in higher nonlinear effects [14]. Metal ions can gather organic 1D dipolar chromophores to form predetermined 2D or 3D NLO-chromophores 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 large nonlinear activity [15, 16]. N_2O_2 Schiff-base ligands
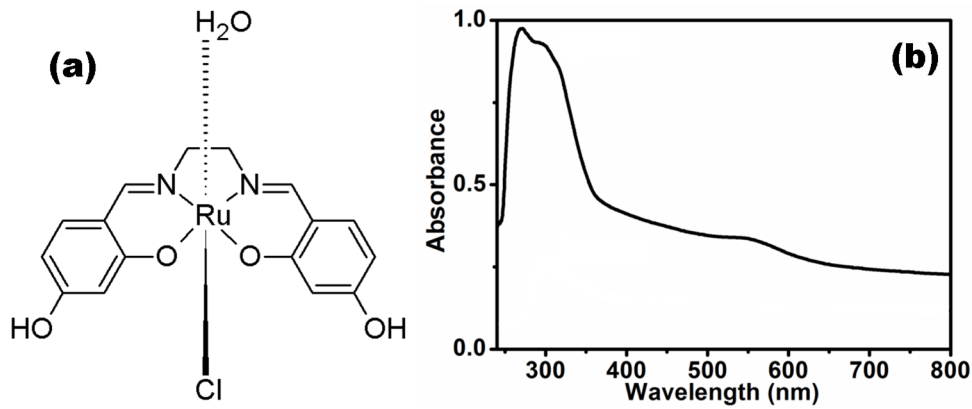
Figure 1. (a) Molecular structure of RuL and (b) the UV–visible absorption spectrum of RuL.
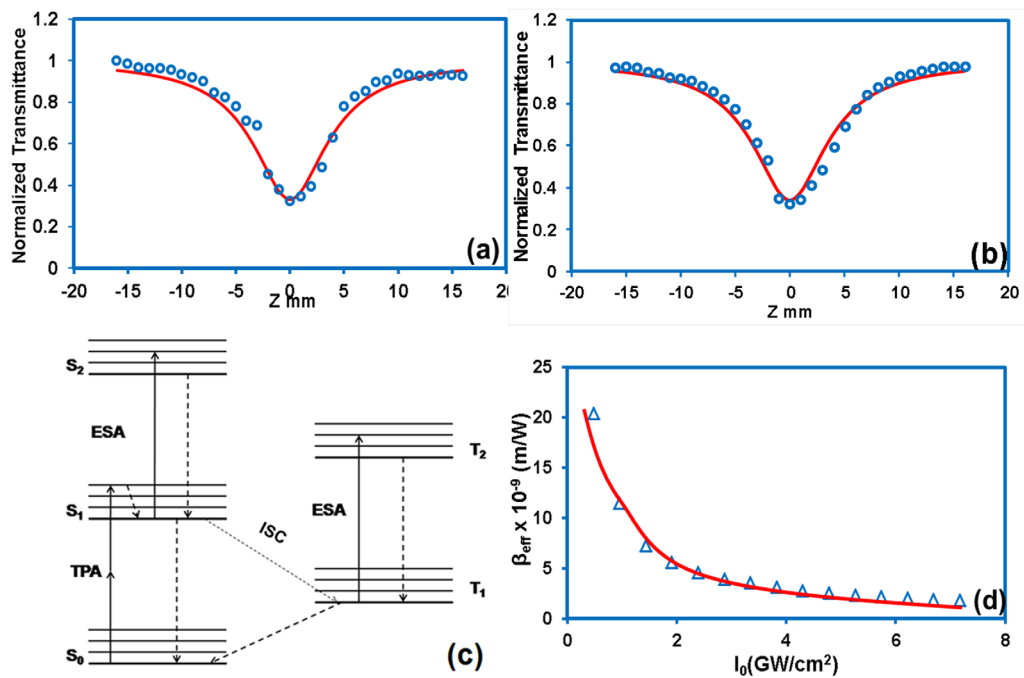
Figure 2. Open aperture Z-scan of (a) RuL:solution at a concentration of 1×10^{-3} mol l^{-1} and (b) RuL:film at a concentration of 1 wt.%. In (a) and (b), the solid line depicts the theoretical fit. (c) Five-level model for NLO absorption. Solid and dashed lines represent the optical excitation and radiative relaxation, respectively. (d) The nonlinear absorption coefficient (β_{eff}) versus on-axis input intensity I_0 of RuL:film (1 wt.%) at a film thickness of 11 μm.

are derived from salicyladehyde and diamines can be used as alternative building blocks in designing novel NLO materials. The transition metal cations in different oxidation states results in exhibiting NLO responses. Insertion of metal centres in Schiff-base ligands enhances the NLO response compared to free ligands. The metal center acts as a donor as well as π-bridging moiety [17–19] therefore the optical response can be tailored for specific applications by modifying the ligands [20].

In this paper, we report synthesis and experimental studies on NLO properties of the ruthenium (Ru) metal–organic complex with salen ligands in solution and thin film form. In addition, all-optical power limiting and switching actions of the Ru complex were also deliberated for possible use in optoelectronics device applications.

2. Experiment

2.1. Synthesis of (Ru (salen) (H$_2$O) (Cl)) {salen = N, N'-disalicylidene—1,2-ethylenediimine dianion}(RuL)
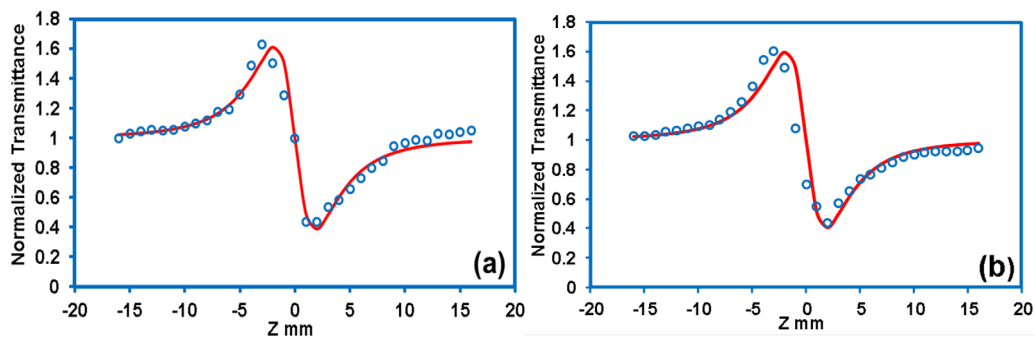
(Ru (salen) (H$_2$O) (Cl)) {salen = N, N'-disalicylidene—1,2-ethylenediimine dianion} was synthesized as per the reported procedure [21]. The Ru (II) Schiff-base complexes (RuL) shown in figure 1(a) were prepared in high yield via the interaction of the free Schiff-base, H$_2$L^1, with RuCl$_3$·3H$_2$O in a 1:1 mole ratio in refluxing absolute ethanol for 12 h. ^{1}H NMR (DMSO-d6): δ 8.40 (s, 2H, HC=N), 6.77–6.74 (m, 8H, ArH), 6.33 (t, 2H, ArH) and 3.71 (s, 4H, –NCH$_2$CH$_2$N–). IR (cm^{-1}, KBr): 3281 m, 1660 s, 1471 s, 1445 s, 1399 m, 1239 s, 1170 m,

Table 1. Third-order NLO parameters of the RuL:solution.

Concentrations $(\times 10^{-4}$ mol l$^{-1})$	β_{eff} (m W^{-1}) $\times$ 10^{-11}	Im $\chi^{(3)}$ (esu) $\times$ 10^{-13}	σ_g (cm^2) $\times$ 10^{-19}	σ_{exc} (cm^2) $\times$ 10^{-18}	n_2 (esu) $\times$ 10^{-11}	Re $\chi^{(3)}$ (esu) $\times$ 10^{-13}
2.5	9.119	1.372	15.577	3.410	-4.569	-4.822
5	11.596	1.745	13.853	4.336	-5.853	-6.177
10	21.717	3.267	11.252	7.120	-9.563	-10.092

Table 2. Third-order NLO parameters of the RuL:film.

Dopant concentration (wt.%)	β_{eff} (m W^{-1}) $\times 10^{-9}$	Im $\chi^{(3)}$ (esu) $\times 10^{-11}$	σ_g (cm^2) $\times 10^{-17}$	σ_{exc} (cm^2) $\times 10^{-16}$	n_2 (esu) $\times 10^{-9}$	Re $\chi^{(3)}$ (esu) $\times 10^{-11}$
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

Figure 3. Pure nonlinear refraction Z-scan of (a) RuL:solution at a concentration of 1×10^{-3} mol l^{-1} and (b) RuL:film at a concentration of 1 wt.%. The solid line depicts the theoretical fit.

978 m, 728 s cm^{-1}. Samples in solution form were prepared by dissolving in N,N-dimethylformamide. Thin films with complexes with different wt.% were prepared using the spin-coating technique by doping in to the *poly(methyl methacrylate)* matrix. The thicknesses of the films were measured by a spectroscopic ellipsometry method and found to be ~11 μm.

2.2. Z-scan and degenerate four-wave mixing measurements

Z-scan and degenerate four-wave mixing (DFWM) experiments [22–24] were performed using a nanosecond Nd:YAG laser at 532 nm. The intensity of the laser beam was kept at 1.2 GW cm^{-2} for Z-scan measurements. The forward folded boxcar geometry was implemented in the DFWM experiments.

3. Results and discussions

3.1. Spectral analysis

The UV–Vis spectrum of the complex is shown in figure 1(b). In the spectrum of the RuL, many bands appear in the range 250– 490 nm. The bands in the region 230–350 nm and 390–500 nm corresponds to intraligand π–$\pi*$ charge transfer transitions (ILCT) and d–d forbidden transitions.
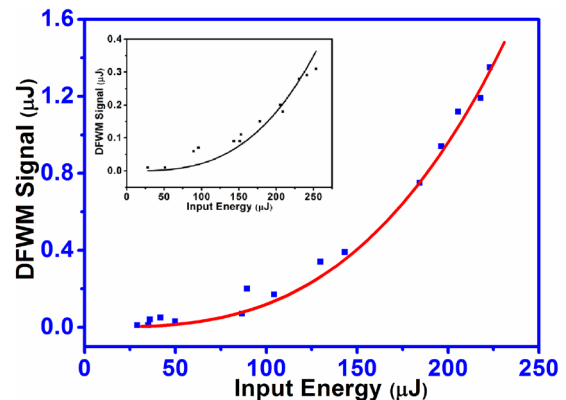
Figure 4. DFWM signal of RuL:solution at a concentration of 1×10^{-3} mol l^{-1}. The inset shows the DFWM signal of CS$_2$.

3.3. NLO measurements

The nonlinear absorption coefficient (β_{eff}) of the Ru complex in solution and film form was determined from the open aperture Z-scan traces shown in figures 2(a) and (b), respectively. The imaginary part of $\chi^{(3)}$ of the complex was determined using the relations available in the literature [22, 25]. The obtained values of β_{eff} and Im $\chi^{(3)}$ are tabulated in tables 1 and 2. The absorption phenomenon in the complex
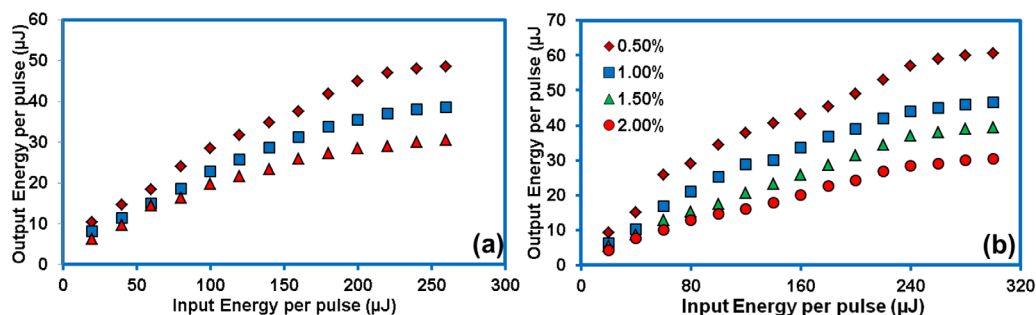
Figure 5. Optical power limiting response of (a) RuL:solution and (b) RuL:film at the various concentrations indicated in the inset.
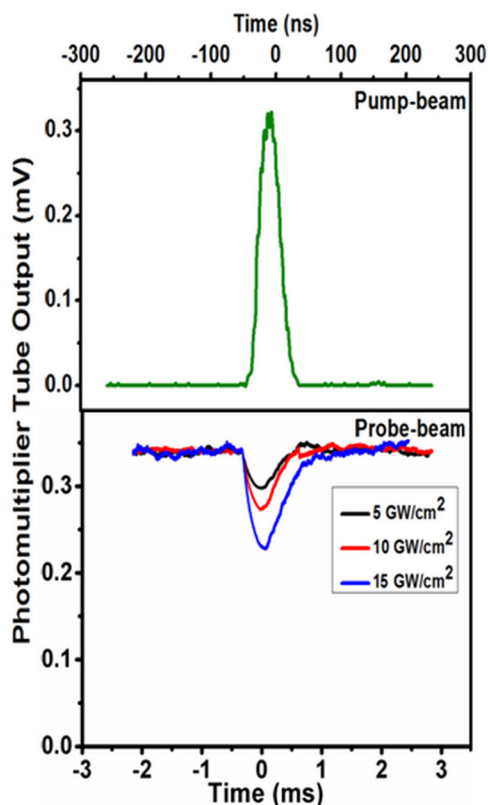

Figure 6. All-optical switching response of RuL:film at a concentration of 1 wt.% with various pump intensities as indicated in the inset. The response time of the material is a few μs at a pulse repetition rate of 10 Hz.

can be explained by a five-level energy model, shown in figure 2(c) [26, 27]. Exposure of the molecule to the laser leads to the transition $S_1 \leftarrow S_0$ $(v = 0)$ and is characterized by absorption cross section σ_0. From state S_1, the molecule can undergo transition $S_2 \leftarrow S_1$. The transition $S_2 \leftarrow S_1$ will not deplete the population in S_1 since atoms excited to S_2, decay to S_1 $(v = 0)$ within picoseconds. They can be transferred from $S_1(v = 0)$ to $T_1(v = 0)$ through intersystem crossing, where transitions to triplet state T_2 occur [25, 26]. The molecules in the excited state S_1 can be further excited to the higher energy states S_2 and, similarly, from state T_1 to T_2 with absorption cross section of σ_S and σ_T, respectively. If σ_T or $\sigma_S > \sigma_0$, then the absorption process is termed reverse saturable absorption (RSA). For the ns laser pulses triplet–triplet transitions make significant contribution to the observed nonlinear absorption [28].

The effective absorption cross-sections σ_{exc} and σ_g of the complex were obtained using the relation available in the literature [25] and the values are given in tables 1 and 2. The larger value of σ_{exc} compared to σ_g indicates a RSA process [29, 30]. The decrease of β_{eff} with on-axis intensity I_0, in figure 2(d), further confirms the RSA process. In addition, multi-photon excitations may also give some contribution to the observed effect [31].

The nonlinear refractive index n_2 was obtained from the pure nonlinear refraction Z-scan traces shown in figures 3(a) and (b), respectively. The samples exhibit negative nonlinearity. The peak–valley satisfies the condition of $\Delta Z \tilde{\ } 1.7 \Delta Z_0$ which confirms the third-order process [32]. The real part of susceptibility $\chi^{(3)}$ was determined using the relation given in the literature [25]. The obtained values of n^2 and Re $\chi^{(3)}$ are reported in tables 1 and 2, respectively. The second-order hyperpolarizability γ_{h} of the complex were obtained using the relation $\chi^{(3)} = \gamma_{\mathrm{h}} f^4 N$, and found to be 1.725×10^{-30} esu where N is the density of molecules, f is the local field factor given by $f = (n_2 + 2)/3$ [33].

The DFWM experiments were performed to determine the $\chi^{(3)}$ value of the Ru complex. Figure 4 shows the variation of DFWM signal with pump energy, the solid curve is the cubic fit to the experimental data. The obtained value for the Ru complex is 1.015×10^{-12} esu. The $\chi^{(3)}$ values of Ru complex films are comparable with that for polydiacetylene thin film [34] and the values of γ_{h} reported are comparable with stilbazolium derivatives [35] and silicon naphthalocyanine [36]. Here the Ru complex with the salen ligand is a combination of aliphatic and aromatic diimine bridges. The N_2O_2 tetradentate ligands impart strong ligand fields leading to square-planar geometries and low-spin ground states for the metal complexes inducing a high degree of covalence within the metal-ligand bonds [17, 18].

3.4. All-optical power limiting and switching studies

Superior optical power limiting materials are required in applications such as optical sensors [37, 38]. Optical power limiting of the Ru complex was evaluated by placing the samples at the focus in the Z-scan experiment and measuring the transmitted energy at various input energy. The limiting performance of the complex is shown in figures 5(a) and (b). The clamping levels of the output energy (μJ) for the Ru complex in solution are ~48, ~38 and ~30 with limiting thresholds (μJ) of 135, 120 and 110, at concentrations (mol l^{-1}) of 2.5×10^{-4}, 5×10^{-4} and 10×10^{-4}, respectively. For Ru

complex thin films, the output energy (μJ) is clamped at ~60, ~46, ~39 and ~30 with limiting thresholds (μJ) of 100, 80, 60 and 40, at concentrations (wt.%) of 0.5, 1.0, 1.5 and 2.0, respectively. The clamping levels depicted by the Ru complex are greater than those reported in literatures [39, 40] indicating the superior power limiting performance of the complex in the nanosecond domain. Optical power limiting studies show that the Ru complex possesses high photo-thermal stability up to an intensity of 6.20 GW cm^{-2} in solution and up to 7.17 GW cm^{-2} in thin film which indicates that doping of the complex in a polymer matrix enhances the photo-thermal stability.

All-optical switching was carried out using a standard pump–probe technique [41]. The intensities of the pump beam were chosen to be 5, 10 and 15 GW cm^{-2}. Optical switching behaviour of the complex is depicted in figure 6. Modulations of the probe were noted to be 12, 20 and 33% for pump-beam intensities of 5, 10 and 15 GW cm^{-2}, respectively. Optical switching indicates that one can fabricate an optical inverter or NOT gate. The higher probe modulation at higher intensity is due to the larger population in triplet state [43]. The switching response times were in the range of a few micro seconds. Slow switching time observed in the complex is due to the forbidden relaxation of the triplet state to the ground state [44].

4. Conclusions

In summary, the third-order NLO parameters of the Ru metal–organic complex were investigated by employing the nanosecond Z-scan and DFWM technique. Open and closed aperture Z-scan results indicate that the Ru complex displays RSA and negative nonlinear refractive index, respectively. The real and imaginary parts of third-order NLO susceptibility $\chi^{(3)}$ were of the order of 10^{-11} esu. Optical switching measurements show that the Ru complex possesses a switching response in the range of a few microseconds and can be used to fabricate an optical inverter or NOT gate. The complex also exhibits good power limiting performance based on the RSA process with low limiting threshold for 7 nanosecond laser pulses at 532 nm wavelength. Photo-thermal stability of the Ru complex increased from 6.20 to 7.17 GW cm^{-2} when the complex was doped into the polymer matrix, indicating the effect of doping on photo-thermal stability. Hence, the Ru metal–organic complex investigated here is a potential candidate for use in optoelectronic device applications.

Acknowledgments

References

[1] Kajzar F and Swalan J D 1996 *Organic Thin Films for Waveguiding Nonlinear Optics* (New York: Gordon and Breach)

[2] Kuzyk M G and Dirk C W 1998 *Characterization Techniques and Tabulations for Organic Nonlinear Optical Materials* (New York: Dekker)

[3] Moloney J V 1998 *Nonlinear Optical Materials* (New York: Springer)

[4] Videnichev D A and Belousova I M 2014 *Appl. Phys.* B **115** 401

[5] Couris S, Koudoumas E, Ruth A A and Leach S 1995 *J. Phys. B: At. Mol. Opt. Phys.* **28** 4537

[6] Riggs J E, Walker D B, Carroll D L and Sun Y A P 2000 *J. Phys. Chem.* B **104** 7071

[7] Poornesh P, Umesh G, Hegde P K, Manjunatha M G, Manjunatha K B and Adhikari A V 2009 *Appl. Phys.* B **97** 117

[8] Manjunatha K B, Dileep R, Umesh G, Satyanarayan M N and Ramachandra Bhat B 2014 *Opt. Mater.* **36** 1054

[9] Green M L H, Marder S R, Thompson M E, Bandy J A, Bloor D, Kolinsky P V and Jones R J 1987 *Nature* **330** 360

[10] Kolev T Z, Kityk I V, Ebothe J and Sahraoui B 2007 *Chem. Phys. Lett.* **443** 309

[11] Bures F, Cermakova H, Kulhanek J, Ludwig M, Kuznik W, Kityk I V, Mikysek T and Ruzicka A 2012 *Eur. J. Org. Chem.* **2012** 529

[12] Mata J A, Peris E, Asselberghs I, Van Boxel R and Persoons A 2001 *New J. Chem.* **25** 299

[13] Mata J A, Peris E, Asselberghs I, Van Boxel R and Persoons A 2001 *New J. Chem.* **25** 1043

[14] Chao H, Li R H, Ye B H, Li H, Feng X L, Cai J W, Zhou J Y and Ji L N 1999 *Dalton Trans.* **21** 3711

[15] Long N J 1995 *Angew. Chem., Int. Ed.* **34** 21

[16] Evans O R and Lin W 2002 *Acc. Chem. Res.* **35** 511

[17] Lacroix P G 2001 *Eur. J. Inorg. Chem.* **2001** 339

[18] Bella S D 2001 *Chem. Soc. Rev.* **30** 355

[19] Gaudry J B, Capes L, Langot P, Marcén S, Kollmannsberger M, Lavastre O, Freysz E, Létard J F and Kahn O 2000 *Chem. Phys. Lett.* **324** 321

[20] Dai Z, Yue X, Peng B, Yang Q, Liu X and Ye P 2009 *Chem. Phys. Lett.* **317** 9

[21] Tedim J, Patrício S, Bessada R, Morais R, Sousa C, Marques M B and Freire C 2006 *Eur. J. Inorg. Chem.* **17** 3425

[22] Sheik-Bahae M, Said A A, Wei T H, Hagan D J and Van Stryland E W 1990 *IEEE J. Quantum Electron.* **26** 760

[23] Iliopoulos K, El-Ghayoury A, Derkowska B, Ranganathan A, Batail P, Gindre D and Sahraoui B 2010 *Appl. Phys. Lett.* **101** 261105

[24] Hales J M, Perry J W, Sun S-S and Dalton L R 2008 *Introduction to Organic Electronic and Optoelectronic Materials and Devices* (Boca Raton, FL: CRC Press)

[25] Poornesh P, Hegde P K, Umesh G, Manjunatha M G, Manjunatha K B and Adhikari A V 2010 *Opt. Laser Technol.* **42** 230

[26] Yim S H, Lee D R, Rhee B K and Kim D 1998 *Appl. Phys. Lett.* **73** 3193

[27] Giuliano C and Hess L 1967 *IEEE J. Quantum Electron.* **3** 358

[28] Zhang F J, Guo W F, Sun X B, Ren Q, Gao Y, Yang H L, Zhang G H, Chow Y T and Xu D 2007 *Laser Phys. Lett.* **4** 230

[29] Henari F Z, Blau W J, Milgrom L R, Yahioglu G, Philips D and Lacey J A 1997 *Chem. Phys. Lett.* **267** 229

[30] Przhonska O V, Lim J, Hagan D J and Van Stryland E 1998 *J. Opt. Soc. Am.* B **15** 802

[31] Guo S L, Xu L I, Wang H T, You X Z and Ming N B 2003 *Optik* **114** 58

[32] Albota K M *et al* 1998 *Science* **281** 1653

[33] Gong Q, Sun Y, Xia Z, Zou Y, Gu Z, Zhou X and Qiang D 1992 *J. Appl. Phys.* **71** 3025

[34] Tomaru S, Kenichi K, Kurihara T and Zembutsu S 1987 *Japan. J. Appl. Phys.* **26** 1657

[35] Sun W, Lawson C M, Gray G M, Zhan C and Wang D 2000 *Appl. Phys. Lett.* **78** 1817

[36] Sun W, Byeon C C, Mc Kerns M M, Lawson C M, Dong S and Wang D 1999 *Proc. SPIE* **3798** 107

[37] Perry J W *et al* 1996 *Science* **273** 1533

[38] Tutt L W and Boggess T F 1993 *Prog. Quantum Electron.* **17** 299

[39] Naseema K, Manjunatha K B, Sujith K V, Umesh G, Kalluraya B and Rao V 2012 *Opt. Mater.* **34** 1751

[40] Shettigar S, Umesh G, Chandrasekharan K, Sarojini B K and Narayana B 2008 *Opt. Mater.* **30** 1297

[41] Zhang G, Wang H, Yu Y, Xiong F, Tang G and Chen W 2003 *Appl. Phys.* B **76** 677

[42] Abdeldayem H, Frazier D O and Paley M S 2003 *Appl. Phys. Lett.* **82** 1120

[43] Singh C P, Bindra K S, Jain B and Oak S M 2005 *Opt. Commun.* **245** 407

[44] Henari F Z 2001 *J. Opt. A: Pure Appl. Opt.* **3** 188