Optical limiting behaviour of linear fused ring dichloro-substituent chalcone isomers

Mundzir Abdullah¹, Dian Alwani Zainuri², Suhana Arshad², Ibrahim Abdul Razak², Heng Han Yann¹, Sabah M Mohammad¹, Siti Nur'Adiilah Mohd Shazlan¹

¹ Institute of Nano Optoelectronic Research and Technology (INOR), Universiti Sains Malaysia, 11800 USM Penang, Malaysia
² X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800, USM, Penang, Malaysia

*mundzir@usm.my

Abstract. The third-order nonlinear optical response of halogen anthracenyl chalcone isomers in dimethyl sulphonate (DMSO) as the solvent has been studied. Single beam Z-scan technique at 532nm of laser excitation wavelength is used to determine magnitude and sign of the nonlinear refractive index (n₂) and nonlinear absorption coefficient (β). The samples exhibited a self-focusing effect with a negative from the closed aperture z-scan analysis. The n₂ is observed to be 10⁻⁸ cm²/W. Open z-scan data showed reverse saturable absorptions with significant β for both samples. The magnitude of β is of the order of 10⁻⁴ cm/W. Optical limiting studies show a decrement in transmittance as a function of input fluence. Optical limiting action begins at as low as 20 kW/cm² of focal input intensity which is ideal for low powered continuous wave laser limiting applications. From the third-order nonlinear properties results, the compound is recommended for optoelectronic and photonics application.

1. Introduction

Any newfound materials with extremely high nonlinear absorption coefficient (β) value will be considered in the interested application area such as optical limiting (OL). These OL materials can be used for protecting optical instruments from intense light irradiation, laser mode-locking, and optical pulse shaping. An optical limiter ideally strong in absorbing intense laser beam and high in transmitting for low intensity laser irradiation [1] Much of the research on OL materials have focused upon the reverse saturable absorption and the multi-photon absorbance as the main mechanism of the OL [2]. For fundamental optical frequencies, at low incident intensity multi-photon absorption gives greater transmission just below the bandgap frequency. Up to date, the researchers have studied the OL performance of various inorganic and organic materials such as transition metal dichalcogenide[3–5], lead halide perovskite [1,6–10], phthalocyanines [2,11–13], carbon allotropes such as graphene [14], fullerene [15], carbon nanotubes [15,16], nanocomposite [17–20] etc. Large two-photon absorption coefficient were reported for these materials.

To study the relationships between molecular structure and the nonlinear absorption coefficient, we examined two anthracenyl chalcone isomers namely (E)-1-(antracen-9-yl)-3-(2,4-dichlorophenyl)prop-2-en-1-one and (E)-1-(antracen-9-yl)-3-(2,6-dichlorophenyl)prop-2-en-1-one. In an organic compound the features that show high nonlinear response consist of a strong electron door,
a highly polarizable π-conjugated bridged and a strong electron acceptor. A chalcone molecules with a π-conjugated system provides a large transfer axis with appropriate substituents groups on the two terminal aromatic rings. Moreover, organic molecules possessing an electron donor group and an electron acceptor group contribute to a large third-order optical susceptibility ($\chi^3$). Several organic molecular crystalline materials have also been identified as high-performance, third-order, optically nonlinear crystals, originate from a strong donor–acceptor intermolecular interaction. Organic crystals hold promise because of the large variety of such materials and the potential to synthesize molecules according to some design principles.

2. Experimental

2.1. Synthesis and crystal growth

The compound I and compound II were synthesized via Claisen Schmidt condensation methods. Whereby 9-acetylanthracene (0.5 mmol) and corresponding aldehydes: 2,4-dichlorobenzaldehyde (0.5 mmol) for compound I and 2,6-dichlorobenzaldehyde (0.5 mmol) for compound II were mixed. Each of the mixture and then dissolved in 20 mL methanol. Catalytic amount of NaOH (10 ml, 20%) was added into the solution dropwise with vigorous stirring. The reaction mixture was stirred for about 5–6 h at room temperature. The resultant crude products were filtered, washed successively with distilled water and recrystallized from acetone to get the corresponding chalcones. Figure 1 shows molecular structure of the compound I and II.

![Compound I and Compound II](image_url)

**Figure 1.** Molecular structure of Compound I and Compound II.

2.2. Linear absorption studies

Figure 2 shows the UV-Vis absorbance spectra of the compounds. The linear absorption coefficient, $\alpha$ at 532nm was calculated based on the absorbance value. The refractive index, $n$ of the alloy suspensions was measured using a digital refractometer (DR201-95, KRUSS).

2.3. Single beam z-scan technique for nonlinear characterization

Z-scan is performed by moving sample through focused Gaussian laser beam. As the sample approaches focal point the laser intensity increases, meanwhile the laser intensity decreases when the sample starts moving away from the focal point [9,10]. This technique is able to determine the magnitude and the sign of the nonlinear susceptibility ($\chi^3$). It can be used to measure both nonlinear refractions (NLR) and nonlinear absorption (NLA) too, by involving computation of intensity–dependent transmission.
Figure 2. UV-Vis absorption spectra of compound I and compound II.

A continuous-wave frequency-doubled diode pumped solid state (DPSS) laser (Coherent Verdi-V5) and with adjustable gain silicon amplified photodetector (PDA55, Thorlabs) are used for this study. At converging lens, \( f = 20 \text{cm} \), by using laser beam profiler (Beam Master) Gaussian beam-spot’s radius at focal point was measured to be 23 \( \mu \text{m} \). In a quartz cuvette, the sample was mounted into a precision motorized stage (LTS-300, Thorlabs) with a path length of 1mm which is smaller than Rayleigh length (3.12mm) - an essential prerequisite for z-scan thin sample analysis. The sample moment at the z-direction of the laser beam was controlling by computer. Simultaneously, the signal from PD1, PD2, and PD3 (photodetectors) were recorded by an oscilloscope. The signal from first photodetectors is used to eliminate power fluctuation. Meanwhile, PD2 represent open z-scan curve for NLA response and PD3 represent closed z-scan signal that contribute to NLR. Table 1 summarized the parameters of the z-scan setup used in the experiment.

| Parameters | Value  |
|------------|--------|
| \( f \)    | 20cm   |
| \( r_a \)  | 0.19cm |
| \( w_0 \)  | 0.0023cm |
| \( \lambda \) | 532nm |
| \( S \)    | 0.42   |

3. Results and discussion

Figure 3 shows the open aperture curve for compound I and II. Both compounds exhibit reverse saturable absorption indicated by the characteristic valley as shown in the figure, which suggested that the positive sign of the coefficient \( \beta \). The reduction in the transmittance within the Rayleigh range of the beam also may indicates the two-photon absorption phenomena that is desirable for optical limiting applications. This behaviour can be attributed to the intrinsic nonlinear properties at the molecular level. Both compounds possess a conjugated molecular system that is responsible for the
reverse saturable absorption. The compounds have high optical hyperpolarizability due to the nature of their π-bonding tail and the donor to acceptor (D-A) intramolecular charge transfer (ICT).

The magnitude of β can be obtained by line fitting of the open aperture curve according to the standard z-scan theory. The solid fitting line (shown in red) were in good agreement with the data points through Levenberg-Marquadt algorithm. The sign and the magnitude of the α and β are shown in Table 2. In our case, the higher linear absorption coefficient will translate into higher nonlinear absorption coefficient. This suggested the contribution of thermal nonlinearity during the z-scan measurement, since higher α will translates into higher localized thermalization at the beam waist.

![Figure 3](image1.png)

**Figure 3.** Open z-scan curve of Compound I to Compound II.

| Compound | Linear | Nonlinear |
|----------|--------|-----------|
|          | α (cm⁻¹) | β (cm/W) | Im χ³ (esu) |
| I        | 0.034   | 4.74E⁻⁰⁵ | 9.36E⁻⁰⁷ |
| II       | 0.044   | 1.96E⁻⁰⁴ | 3.86E⁻⁰⁶ |

Close-aperture z-scan curves for Compound I and II are shown in Figure 4. During the laser excitation, a spatial distribution of temperature is formed within the beam waist due to localized absorption of the beam propagating through the samples. This creates spatial variation of linear refractive index which is known as thermal lensing. In general, the nonlinear refraction can be originated from electronics, molecular and thermal effects. In the present case, the nonlinear refraction is dominated by the thermal effects resulting due to the absorption of 532nm continuous wave radiation. This creates peak and a valley in the transmittance curve as shown in Figure 4. The peak followed by a valley characteristic suggest the self-defocusing nature of the compounds i.e. the negative nonlinear refractive index, n². The nonlinear refractive index was calculated using the line fitting based on the close aperture z-scan theory. The fitting line (shown in red) in Figure 4 forms a good agreement with the experimental data, from which the magnitude of n² are calculated for both compounds. Table 3 shows the magnitude of n, n², and the real part of the third-order optical susceptibility, Re χ³. Compound II shows superior nonlinear refraction behaviour.

![Figure 4](image2.png)

A tremendous increase in the use of CW lasers in routine life necessitates the demand for optical limiters that caters the low powered laser regime. The optical limiting actions of the compounds were studied by changing the laser excitation power at the same z-scan experimental parameters. The optical limiting behaviour of the compounds are shown in Figure 5. At low input power, the output for both samples increase linearly obeying the Beer Lambert’s law and beyond a critical power, the limiting action starts to initiate represented by the stagnant in the output signal. The onset-limiting threshold of Compound I and II was measured at 20 kW/cm² and 23 kW/cm² respectively. A different threshold value benefit for different application such as low threshold value is required for low-intensity applications e.g: safety goggles and glass windows. Variation in the third-order optical
nonlinearity and the optical limiting action between compound I and II due to change I the molecular structure has shown the possibility of tailoring the nonlinear optical properties for specific limiting applications.

Figure 4. Closed z-scan curve of Compound I to Compound II.

Table 3. The linear and nonlinear refractive index of the compounds.

| Compound | Linear | Nonlinear |
|----------|--------|-----------|
|          | n      | $n_2$ (cm/W) | Re $\chi^3$ (esu) |
| I        | 1.4696 | -3.68E-08  | 2.02E-06   |
| II       | 1.4683 | -2.77E-08  | 1.51E-06   |

Figure 5. Optical limiting behaviour of Compound I and Compound II.

4. Conclusion
Open z-scan reveals positive $\beta$ coefficient which indicates reverse saturable absorption. Close z-scan shows negative $n_2$, indicates self-defocusing action. The Re $\chi^3$ and Im $\chi^3$ are in the order of $10^6$ and $10^7$, respectively. Both samples exhibit good optical limiting with action begins from 20 kW/cm$^2$. The results of this study showed that chalcones seem to be promising optical limiting candidates for future photonic and optoelectronic applications.

Acknowledgement
The authors thank Research Creativity and Management Office (RCMO), Universiti Sains Malaysia (USM) for the research facilities and the funding through Bridging Research Grant Scheme No. 304.CINOR.6316529 to conduct this work.
References

[1] Tutt L W and Boggess T F 2015 Two-photon absorption and broadband optical limiting with bis-donor stilbenes Opt. Lett. 22 1843

[2] Sadigh M K, Zakerhamidi M S S, Khadem Sadigh M and Zakerhamidi M S S 2017 Third order nonlinear responses of Basic Blue 55 molecules in polar solvents Optik 130 743–9

[3] Dong N, Li Y, Feng Y, Zhang S, Zhang X, Chang C, Fan J, Zhang L and Wang J 2015 Optical limiting and theoretical modelling of layered transition metal dichalcogenide nanosheets Sci. Rep. 5 1–10

[4] Zhou K G, Zhao M, Chang M J, Wang Q, Wu X Z, Song Y and Zhang H L 2015 Size dependent nonlinear optical properties of atomically thin transition metal dichalcogenide nanosheets Small 11 694–701

[5] Shi Y, Li H and Li L J 2015 Recent advances in controlled synthesis of two-dimensional transition metal dichalcogenides via vapour deposition techniques Chem. Soc. Rev. 44 2744–56

[6] Lu W-G, Chen C, Han D, Yao L, Han J, Zhong H and Wang Y 2016 Nonlinear Optical Properties of Colloidal CH 3 NH 3 PbBr 3 and CsPbBr 3 Quantum Dots: A Comparison Study Using Z-Scan Technique Adv. Opt. Mater. 4 1732–7

[7] Zhang F, Miao J-T, Fang Y, Sun R, Guo X-Z, Song Y-L and Ge J-F 2015 Aggregation induced convertible third-order nonlinear optical absorptions of the phenoxazinium containing films prepared by sol-gel method Dye. Pigment. 10 1–8

[8] Romanova E, Kuzytukin Y, Shiryaev V, Abdel-Moneim N, Furniss D and Guizard T B A S S 2004 Measurement of non-linear optical coefficients of chalcogenide glasses near the fundamental absorption band edge J. Non. Cryst. Solids 11 18–28

[9] Wei K, Xu Z, Chen R, Zheng X, Cheng X and Jiang T 2016 Temperature-dependent excitonic photoluminescence excited by two-photon absorption in perovskite CsPbBr 3 quantum dots Opt. Lett. 41 3821

[10] Liu W, Xing J, Zhao J, Wen X, Wang K, Lu P and Xiong Q 2017 Giant Two-Photon Absorption and Its Saturation in 2D Organic-Inorganic Perovskite Adv. Opt. Mater. 5 1601045

[11] Henari F Z 2001 Optical switching in organometallic phthalocyanine J. Opt. A Pure Appl. Opt. 3 188–90

[12] Viswanath V and Muneera C I 2017 Nonlinear Refraction Behaviour of Toluidine Blue O Dye-PVA Nanocomposite Films under CW Laser Light Excitation Opt. Laser Technol. 41 1

[13] Bankole O M and Nyokong T 2016 Nonlinear optical response of a low symmetry phthalocyanine in the presence of gold nanoparticles when in solution or embedded in poly acrylic acid polymer thin films J. Photochem. Photobiol. A Chem. 319–320 8–17

[14] Wang J, Hernandez Y, Lotya M, Coleman J N and Blau W J 2009 Broadband nonlinear optical response of graphene dispersions Adv. Mater. 21 2430–5

[15] Tutt L W and Boggess T F 1993 A review of optical limiting mechanisms and devices using organics, fullerenes, semiconductors and other materials Prog. Quantum Electron. 17 299–338

[16] Yusof Y and Johan M R 2014 Concentration-dependent properties of amorphous carbon nanotube/silica composites via the sol–gel technique Cryst. Eng. Comm. 16 8570–5

[17] Chen S-Q, Liu Z-B, Zang W-P, Tian J-G, Zhou W-Y, Song F and Zhang C-P 2005 Study on Z scan characteristics for a large nonlinear phase shift J. Opt. Soc. Am. B 22 1911

[18] Frare M C, Weber V, Signorini R and Bozio R 2014 Gold nanoparticles in a polycarbonate matrix for optical limiting against a CW laser Laser Phys. 24

[19] Lepeshkin N N, Kim W, Sazonov V P, Zhu J G, Armstrong R L, White C W, Zuhri R A and Shalaev V M 1999 Optical nonlinearities of metal-dielectric composites J. Nonlinear Opt. Phys. Mater. 8 191–210

[20] Abdullah M, Bakhtiar H, Islam S, Aziz M S A and Krishnan G 2019 3rd order nonlinearity and optical limiting properties of sol-gel based bromophenol blue dye immobilized in Silica-Titania nanohybrid J. Sol-Gel Sci. Technol. 89 361–9