Accepted Manuscript

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PII:	S1010-6030(15)30322-1		
DOI:	http://dx.doi.org/doi:10.1016/j.jphotochem.2016.03.009		
Reference:	JPC 10163		
To appear in:	Journal of Photochemistry and Photobiology A: Chemistry		
Received date:	14-12-2015		
Revised date:	6-3-2016		
Accepted date:	8-3-2016		

Please cite this article as: P.J.Tejkiran, M.S.Brahma Teja, P.Sai Siva Kumar, Pranitha Sankar, Reji Philip, S.Naveen, N.K.Lokanath, G.Nageswara Rao, D-A-*rmpi*-D synthetic approach for thienyl chalcones ndash NLO ndash a structure activity study, Journal of Photochemistry and Photobiology A: Chemistry http://dx.doi.org/10.1016/j.jphotochem.2016.03.009

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Title: D-A-π-D SYNTHETIC APPROACH FOR THIENYL CHALCONES –NLO- A STRUCTURE ACTIVITY STUDY (JPC 10163)

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GRAPHICAL ABSTRACT



Highlights

- Based on D-A- π -D SYNTHETIC APPROACH we could synthesize nine novel thienyl chalcones with high effective 3 photon absorption coefficient (3 PA) of order 10⁻²⁸ m³/W².
- Of these, T-CHL-NDM was found to have the highest 3PA coefficient of about $105.0 \times 10^{-28} \text{ m}^3/\text{W}^2$.
- Structure activity relationship based on the functional group vis-à-vis its NLO properties was established, and making minor modifications in the structure of the chalcones, desired 3PA values could be obtained.
- Structures of all compounds have been characterized by adequately.
- These compounds will be useful in various applications like optical devices, communications, etc.

Abstract: With the growing interest for organic molecules in Nonlinear Optical (NLO) applications, we have synthesized nine novel thienyl chalcones based on the D-A- π -D design. In order to establish the identity, these have been characterized in detail. Having followed the design based synthetic route, we have focused on two prime criteria for comparison; namely second harmonic generation (SHG) and non-linear absorption. In this work the role of the electron withdrawing groups, electron donating groups and extended conjugation, have been extensively studied vis-à-vis the NLO properties. The change in these properties by virtue of the molecular structure has been elucidated in this work as the structure activity relationship. Optical nonlinearity is studied using ultrafast (100 fs) laser pulses at 800 nm, employing the open aperture Z-scan technique. The compounds exhibit large effective three-photon absorption (3PA) coefficients, in the order of 10⁻²⁸ m³/W². These observations show that these compounds possess potential for application in all-optical limiting and switching devices.

Keywords: Thienyl chalcones; Z-Scan, nonlinear optical properties (NLO); three photon absorption; second harmonic generation (SHG).

1. Introduction

In the scenario of modern research, nonlinear optical (NLO) studies have assumed unquestionable importance, due to their applications in optical data storage, optical processing, optical computing, sensor protection, optical switching, and various other photonic technologies. Improved research has extended their application in THz wave generators, passive optical limiters, electro-optic modulators, and frequency converters.¹⁻⁴ The choice of the material in these applications is based on, response times in picoseconds or less, large nonlinear refractive and/or absorptive coefficients, and broad spectral response.⁵ Therefore determination of nonlinear properties and response times of the compounds is decisive. ¹ In the process of realizing this goal, organic compounds are chosen primarily due to their large diversity, and the flexibility they offer in the synthesis, strength of electron acceptor or donor groups ^{6, 6a-6c}, planarity in the molecule ⁷, the molecular symmetry, and extended conjugation stretches. ^{8,9} The susceptibilities of these molecules can be additionally enriched by increasing the length of conjugation. However, these changes result in the consequent decrease of the HOMO-first excited state energy gap.⁷ In order to obtain the best from these molecules, researchers have established various strategies to design organic molecules with enhanced nonlinear optical responses. These include synthesis and development of Acceptor-Donor-Acceptor (A-D-A), Donor-Acceptor- Donor (D-A-D), Donor-π- Donor (D-π-D) types of organic systems.² Chalcones exhibit intra-molecular charge transfer, and this allows for the use of design-based synthesis achieving the desired results. Molecules with similar structure allow for comparison with focus on the effect of substituents upon the properties under study. The Structure Activity Relation therewith allows to assign the change in the observed phenomena to the specific functional groups on the molecule.

An additional benefit of chalcones is that they have blue-light transmittance, and high propensity to crystallize in non-Centro symmetric structure. ^{11,11a,12} Chalcones being organic molecules cannot be used right away in applied photonic device applications as they get degraded or bleached when exposed to extreme optical signals. ¹³⁻¹⁵ In order to overcome this shortcoming, they can be either doped into a polymer matrix or made into a solution. ¹⁶ However the polymer matrix is cumbersome to formulate and hence solutions of the compounds were made and the nonlinear optical studies were conducted. The solvent of choice must essentially be transparent towards the laser signal, must possess high thermal and photochemical stability. ¹⁷⁻²⁰

Thienyl-chalcones which have a D-A- π -D molecular configuration are related to the class of organic chromophores, chalcones. ³ Apart from their optical properties, they have been used in numerous applications ranging from anti-cancer, radio-protective, cytotoxic ²¹ and anti-viral activities; as synthons for heterocycles, chemo- protective agents, phase two enzyme inducers, radical scavengers, and catalysts; and in nonlinear optics. ²²⁻²⁵ Thiophene containing polymeric compounds have been investigated, and are found to exhibit good nonlinear optical properties by the effective 3PA process. ²⁶ Owing to the numerous applications of thienyl-chalcones and high nonlinear optical activity ²⁷, in the present work we studied nine chalcones, and report their synthesis, characterization, and nonlinear optical properties. Optical nonlinearity is investigated using the Z-scan technique, employing ultrafast (femtosecond) laser pulses for excitation. The observed effective three-photon absorption and the consequent optical limiting behavior are discussed in detail. Second Harmonic Generation (SHG) of these compounds also has been investigated. Finally, we correlate the observed NLO enhancement to the presence of extended conjugation and different electron pumping and withdrawing groups substituted at different positions in the aromatic ring.

2. RESULTS AND DISCUSSION.

2.1. Characterization.

The compounds were synthesized by Claisen-Schmidt condensation ²⁸ and were characterized by UV-vis, IR, ¹H-NMR, ¹³C-NMR, and MS. The data is reported in Table-S in the supplementary data.

2.1.1. Linear Optical Properties.

UV-visible absorption spectra for all the compounds is shown in Fig.1 and the λ_{max} values are reported in Table-1. All the compounds were found to have two absorption maxima. The λ_{max} values for these α , β -unsaturated carbonyl compounds can be attributed to the π π^* transition of the carbonyl group. The spectra can be interpreted by taking the substitutions into consideration comparing with a non-substituted one i.e. T-CHL-B whose λ_{max} value stands at 320 nm. The λ_{max} value for the compound T-CHL-NDM at 428 nm is the highest among the others, due to the conjugation by the electron pumping nature of the N, N- dimethyl amino group. This is followed by T-CHL-SM, T-CHL-OH, and T-CHL-OM with λ_{max} values of about 363 nm, 356 nm, and 349 nm respectively. In all these compounds the absorption increases with increasing capacity of donating electrons. Due to the increase in the conjugation between both the rings,

the λ_{max} value for T-CHL-2T stands at 352 nm. Due to the nature of the iso-propyl group, which is a good electron donating group, T-CHL-ISO has a λ_{max} value of 331 nm. Whereas the λ_{max} value for T-CHL- Cl is 323 nm.

2.1.2. FT-IR, NMR, & Mass spectra.

In the FT-IR spectrum of T-CHL-B the $v_{C=0}$ is observed at 1650 cm⁻¹ which is characteristic of chalcones. ²⁵ The frequency of this band decreased as the electron donating nature of the substituent on the benzene ring increased and the lowest value of 1630 cm⁻¹ is seen in the case of T-CHL-NDM due to the powerful electron donating ability of -N(Me)₂.³⁰ The pmr spectra of these compounds were completely analyzed and the data is given in Table-S. Proton H-1 which is highly deshielded is observed at ~ $\delta 7.80 - 8.14$ as a double doublet with an ortho and meta coupling (J = 3.6 - 4.0 Hz and 0.8 - 1.2 Hz). H-2 is seen as a double doublet at $\delta 7.17 - 7.34$ with two ortho couplings (J = 4.8 - 5.2 and 3.6 - 4.0 Hz). H-3 signal appeared at ~ δ 7.66 – 7.94 as a dd (J=4.8-5.2 and 0.8-1.2 Hz). The two olefinic protons H-6 (δ 6.99 – 7.56) and H-7 (δ 7.62 – 7.97) signals appeared as doublets with a large coupling constant (J = 13 – 16 Hz) indicating the trans double bond. ³¹ In case of chalcones with the substituent at para position on the benzene ring the ortho and meta protons gave a pair of doublets with a J value of 7.2 - 8.4 Hz. In T- CHL-B and TCHL-CNA the ortho-protons are seen as 2-H doublet, meta-protons 2-H triplet and para-proton 1-H triplet. In the PMR spectrum of T-CHL-CAN four olefinic proton signals were observed. The CH₃Oin T-CHL-MO and protons of S—CH₃ in T-CHL-SM are seen as singlets at $\delta 3.05$ (3H) and $\delta 2.52$ (3H) respectively. The OH proton in T-CHL-OH, which is D_2O exchangeable, is observed as a singlet at $\delta 10.1$. In T-CHL-NDM, the two methyl groups of $-NMe_2$ gave a singlet at $\delta 3.04$ (6H). The ¹³CNMR spectra of these chalcones indicated the presence of C=O by the signal at ~ δ 182. Other signals as expected for the thienyl group, olefinic carbons and the aryl ring are observed in sp² C region of δ 111 to 162 as given in Table-S.

2.1.3 Single Crystal XRD of T-CHL-ISO.

The details of the crystal structure and data refinement are given in supplementary data (Table-S1). The list of bond lengths and bond angles of the non-hydrogen atoms is given in (Table S2 and Table S3)

respectively. The space group was found to be P 21/c; with cell dimensions a = 9.3268(2) Å, b = 10.3323(2) Å, c = 27.8159(5) Å, α = 90.00°, β = 91.6770(10)°, γ = 90.00°. Figure 2 represents the ORTEP of the molecule with thermal ellipsoids drawn at 50% probability. There are two molecules in an asymmetric unit and the molecule is non-planar. This non planarity is confirmed by the dihedral angle values of 9.76(14)° and 26.43(13)° between the two aromatic rings. The thiophene ring is affected by the π -conjugation. This can be explained by the longer C = S bonds values for S1A-C2A = 1.720(3) Å, S1B-C2B = 1.724(3) Å, S1A-C5A = 1.696(3) Å, S1B-C5B = 1.702(3) Å. The olefinic double bond is in E-configuration and is CSP2 hybridized. This is evident from the bond length values for C8A-C9A = 1.335(4) Å and C8B-C9B = 1.338(4) Å.

Similar conformation was reported in earlier studies.¹⁵ The bond angle values for O7A-C6A-C2A = $119.8(2)^{\circ}$, O7B-C6B- C2B = $120.6(2)^{\circ}$, C2A-C6A-C8A= $117.8(2)^{\circ}$, C2B-C6B- C8B= $116.9(2)^{\circ}$ and O7A-C6A-C8A = $122.4(2)^{\circ}$, O7B-C6B-C8B = $122.5(2)^{\circ}$, about C6 indicates that the carbon atom is in a distorted trigonal plane which is due to steric hindrance of the oxygen atom. Similar conformation was observed in the molecule of 1-(2'-thiophen)-3-(2,3,5-trichlorophenyl)-2-propen-1-one. ³² Classic hydrogen bonds are not observed in the crystal structure except for a weak C–H... π interaction that may help to stabilize the structure. The packing of the molecule when viewed down along the b axis indicates that the molecules are arranged in a zigzag manner to form a three- dimensional structure (Figure.3). The CCDC number for the molecule is **1414507**.

2.2. Nonlinear optical properties.

2.2.1. SHG measurement.

In SHG-active crystals, it is interesting to note that the arrangement of molecules inside the crystal is critical to yield large effective nonlinearity, besides the non-centrosymmetric crystal structure. Hydrogen bonds, parallel stacking and p–p interaction favour high second harmonic generation efficiency in nonlinear materials. ³³ In addition, an optimized alignment of the molecular dipoles with hb = 0 (where hb is the angle between the charge transfer axis and the crystallographic b-axis) will establish a net macroscopic second order polarization in the crystal by adding the dipole moments of each molecule, maximizing the SHG efficiency.

Good SHG values are shown by compounds with an extensive conjugation within the system. Both electron donating and withdrawing groups play a crucial role in enhancing the conjugation. In the current scenario the π -electrons of both the benzene and thiophene rings are in cross conjugation with the carbonyl group. Measured SHG efficiency of the samples with respect to urea are listed in Table-1. Among all the compounds reported in this work, T- CHL-2T shows a value which is 52 times higher that of urea. ²⁴ This enhancement can be attributed not only to the conjugation, but also to the symmetry involved. This is followed by T-CHL-OM, T-CHL- NDM, T-CHL-ISO and T-CHL-CNA with 0.94, 0.45, 0.29, and 0.27 times efficiency respectively, with respect to urea. However other T-CHL-B, T-CHL-OH, T-CHL-SM, and T-CHL-Cl showed zero SHG activity. The behavior of the first three can be attributed to the electron pumping nature of the substituents whereas that of the last one is due to the increased extended conjugation between the carbonyl and the aromatic ring. Whereas the electron pumping ability of the groups are in the order N, N-dimethyl amino > methoxy > isopropyl, the SHG activity is not in the same order. This is due to the methyl groups present on the groups distorting the packing in the crystal structure.

A low SHG efficiency of 0.8 times urea has been reported for a chalcone derivative CMC and 0.15 times that of urea for 4NP3AP due to an un-optimized alignment of molecular dipoles in their crystal structure. ³⁴

2.2.2 Nonlinear absorption measurement.

The synthesized molecules possess a D-A- π -D type of arrangement. The compounds have the thiophene moiety as the donor followed by carbonyl group as an acceptor, and a π -bond and a phenyl group with a substituent at the other end as donor. All compounds show strong optical limiting behavior as shown in Fig. 4, where the sample transmittance decreases with increase in the pump fluence.

We found that the measured data numerically fits best to a three-photon absorption (3PA) type nonlinearity, in which the sample transmission (T) can be described by the nonlinear transmission equation-1 26 ,

$$T = \frac{(1-R)^2 \exp(-\alpha L)}{\left(\sqrt{\pi}\right) p_0} \left[\int_{-\infty}^{+\infty} \ln\left[\sqrt{1+(p_0)^2 \exp(-2t^2)} + p_0 \exp(-t^2)\right] dt \right]$$
(1)

where α is the linear absorption coefficient, L is the sample length, and R is the Fresnel reflection coefficient of the sample-air-interface. p_0 is given by

$$\left[2\gamma(1-R)^2 {I_0}^2 L_{eff}\right]^{1/2}$$
 (2)

where γ is 3PA coefficient, and I₀ is the incident intensity. L_{eff} is given by

$$\left[1 - exp(-2 \propto L)\right] /_{2 \propto} \qquad (3)$$

The calculated values of the 3PA absorption coefficient (γ) are given in Table-1. Since the samples have some weak absorption at 800 nm (linear transmission is 85%) the 3PA process will be resonantly enhanced. In view of the absorption spectra which show enhanced absorption at the two-photon wavelength of 400 nm and at the three-photon wavelength of 266.6 nm, the following three processes can occur: (i) genuine 3PA which happens without the aid of real intermediate levels; (ii) genuine 2PA which is followed by one-photon absorption; (iii) three sequential, individual one-photon absorption events. Genuine 3PA will be the weakest of the above three processes. Therefore the nonlinear absorption in this case is an *effective* 3PA process, so that we call γ the *effective* 3PA coefficient.

We observed that the 3PA coefficient of T-CHL-B can be enhanced by modifying the benzene ring. The enhancement is reflected in the γ value of this compound (8.5 x 10⁻²⁸ m³/W²). Three types of structural changes were effected; (1) introducing substituents at para position in the benzene ring, (2) extending the π -system in between the carbonyl group and the benzene ring, and (3) replacing the benzene ring with a 5-membered heterocyclic ring. In the first type of the structural change, a variety of substituents like chloro, iso-propyl, methoxy, hydroxyl, methylthio and N,N-dimethyl amino are studied. The effect of substituents on γ is represented graphically in Fig. 5.

When a chloro group is introduced at the para position on the benzene ring, the γ value of T-CHL-ClB (10.0 x10⁻²⁸ m³/W²) is not much enhanced. The reason for this is that the –I effect dominates the +R-effect shown by the chloride group.

When an iso-propyl group is introduced at the same position, the γ value (14.5 x10⁻²⁸ m³/W²) increases due to the reason that this group donates electrons through +I-effect. Other groups introduced are methoxy, methylthio, N, N-dimethyl amino, and hydroxyl. The γ values for these substituents are in the order N, N-dimethyl amino (105.0 x10⁻²⁸ m³/W²)> methylthio (68.0 x10⁻²⁸ m³/W²)> methoxy (49.9 x10⁻²⁸ m³/W²)> hydroxyl (40.0 x10⁻²⁸ m³/W²). This is due to the fact that both methoxy and hydroxyl groups are electron withdrawing by –I effect but donate electrons by +R effect. In the case of methylthio and N, N-dimethyl amino groups –I effect is weak whereas +R effect is more dominating. Groups with a better electron donating capability may increase the γ value.

In the second type of structural change made, the π -system is extended by using cinnamaldehyde instead of a substituted benzaldehyde and the γ value (25.0 x 10⁻²⁸ m³/W²) increased by two-fold. In the third type of structural modification, thenaldehyde is used instead of benzaldehyde. As the latter is better electron donating than the benzene ring, the γ value (30.55 x 10⁻²⁸ m³/W²) increases almost by three fold. Thus the study reveals that the nonlinear absorption property of a compound is directly proportional to the electron donating ability of the substituted groups. A.N.Prabhu et al. in their studies have also reported similar findings. ³⁵

To view the nonlinear absorption efficiency of the present materials in perspective, it is worthwhile to refer to the nonlinear absorption coefficient values reported in literature for similar molecules. The effective 3PA coefficient value reported in literature for poly {2, 2'-(3,4-didodecyloxythiophene-2,5-diyl)bis[5-(2-thienyl)-1,3,4-oxadiazole]}, a polymer, is quite high at 4.8 x 10⁻²² m³/W². ²⁵ For the chalcone 'VFC', with 780 nm irradiation, the dominant absorption was 2PA at lower fluences (2PA coefficient = $3.11 \times 10^{-13} \text{ m/W}$) and 2PA induced excited state absorption at higher fluences ($\gamma = 1.51 \times 10^{-27} \text{ m}^3/\text{W}^2$). ⁵ For the chalcones 3TF, 3TC, and 3TM, γ is in the range of $10^{-28} \text{ m}^3/\text{W}^2$. ³⁶ On the other hand the γ value reported for thiazole based compounds is in the order of $10^{-31} \text{ m}^3/\text{W}^2$. ¹³ Z-scan at 532 nm of stilbazolium derivatives DASPI, ASPI, FeVPI, and FeSPI gave γ values in the order of $10^{-31} \text{ m}^3/\text{W}^2$. ³⁷ For conjugated TTF-Quinone molecules, the γ values are reported to be much lower, in the order of $10^{-46} \text{ m}^3/\text{W}^2$. ³⁸ The 3PA coefficient for a multi-branched chromophore in femto second regime was found to be 3.32×10^{-25}

cm⁶ GW⁻². ³⁹ Also the co-crystals studied by E. D. D'silva shows less third order NLO properties compared with that of the individual compounds. ⁴⁰ It should be noted that since coefficients for *effective* nonlinear absorption in a material are dependent on the excitation wavelength, excitation intensity and sample concentration, reported values can vary in a wide range.

3. CONCLUSIONS

In summary, we present the Thienyl chalcones, with their structure ascertained by the XRD of a representative member. From the studies carried out it is evident that- (1) the substituents on the molecule play a role in the optical properties, which is established via the Structure Activity Relation and (2) the electronic distribution has a profound effect on the NLO properties; thus supporting the design based synthetic route. The presence of electron donating groups or extended conjugation enhances the NLO properties. The large magnitudes of the NLO coefficients obtained highlight their prospective advantage in applications such as second order frequency conversion, optical switching, optical limiting, and photonic devices.

4. **EXPERIMENTATION**

4.1 Synthesis

All the compounds covered under this study were prepared by Claisen-Schmidt Reaction. ²⁸ The starting materials used, 2-acetylthiophene and the various aldehydes were purchased from Sigma-Aldrich Chemical Company (India) with a stated purity of greater than 98%, and were used as such without any further purification. A solution of ethanol (12.25 ml) - water (20 ml) was prepared under inert atmosphere and 2.2g of sodium hydroxide were taken in a round bottomed flask. The corresponding aldehydes (0.043 mol) and (0.043 mol) of 2-acetythiophene were added to the solution at 5°C under nitrogen atmosphere. The reaction mixture was stirred at room temperature and completion of the reaction was ascertained by Thin Layer Chromatography. Upon completion of the reaction, the mixture was cooled for 12 hours. The physical state of all the products was solid. The solid was filtered and washed free of alkali.

Recrystallization was carried out using distilled methanol. The reaction times, yields and the melting points of the recrystallized products were determined and are reported in Table-2.

4.2 Single Crystal growth and XRD analysis.

The single crystal growth of the compound T-CHL-ISO was done using the slow evaporation growth technique at room temperature. The recrystallized compound was used to grow single crystals using a variety of solvents ranging over methanol, ethanol, acetone, chloroform and some mixtures. Single crystals from methanol were found to be best. A block shaped single crystal of dimensions $0.3 \times 0.27 \times 0.25$ mm of the title compound was chosen for X-ray diffraction study. The X-ray intensity data were collected at a temperature of 296 K on a Bruker Proteum2 CCD diffractometer equipped with an X-ray generator operating at 45 kV and 10 mA, using CuK_a radiation of wavelength 1.54178 Å. Data were collected for 24 frames per set with different settings of φ (0° and 90°), keeping the scan width of 0.5°, exposure time of 2 s, the sample to detector distance of 45.10 mm and 2 θ value at 46.6°. A complete data set was processed using SAINT PLUS. ⁴¹ The structure was solved by direct methods and refined by full-matrix least squares method on F2 using SHELXS and SHELXL programs. ⁴² All the non-hydrogen atoms were revealed in the first difference Fourier map itself. All the hydrogen atoms were positioned geometrically and refined using a riding model.

After ten cycles of refinement, the final difference Fourier map showed peaks of no chemical significance and the residuals saturated to 0.0480. The geometrical calculations were carried out using the program PLATON.⁴³ The molecular and packing diagrams were generated using the software MERCURY.⁴⁴

4.3 Instrumentation.

Single crystal X-ray diffraction pattern of the reported sample was recorded using Bruker Proteum2 CCD diffractometer. ¹HNMR spectra were obtained on VARIAN 400 MHz, ¹³CNMR on VARIAN 100 MHz using TMS as the internal standard and CDCl₃ as solvent. For mass spectra AGILENT 6430 Triple Quad LC/MS was employed. The FT-IR spectra were recorded in the range of 400-4000cm⁻¹ using KBr pellets employing Thermo-Nicolet Avatar 370 spectrophotometer. UV-Vis spectra in methanol were recorded in the wavering range 200-600 nm using Shimadzu 2450 spectrophotometer.

4.4 Nonlinear Optical measurements.

4.4.1 Nonlinear absorption measurement.

The absorptive optical nonlinearity of the samples was studied using the open aperture Z-scan technique. Pulses of 100 fs duration (FWHM) at 800 nm obtained from a regeneratively amplified mode-locked Ti: Sapphire laser, operating at a pulse repetition rate of 10 Hz, were used for excitation. A fast mechanical shutter suitably synchronized to laser emission was used in the beam path to allow single pulses to pass through, so that the experiment could be performed in the single-shot mode. In this way the effective sample irradiation rate was reduced to about one pulse in five seconds, so that the possibility of sample heating during measurement could be avoided. The laser pulses were divided by a beam splitter, and the reflected part was used as a reference to monitor fluctuations in the incident pulse energy. The transmitted part, which had an energy of about 5 micro joules, was focused using a converging lens (focal length = 10.75 cm) to achieve continuous variation in the incident intensity along the beam axis (z-axis), with maximum intensity at the focal point (z=0). Each sample was appropriately diluted so that the linear transmission was 85% at the excitation wavelength, when taken in a 1 mm cuvette. The sample cuvette was mounted on an automated linear translation stage so that the sample could be moved to any desired position along the z-axis with respect to the focal point. By keeping the incident laser energy constant, light transmission through the sample was measured as a function of the sample position.

4.4.2. Powder SHG measurement.

SHG efficiency measurement was carried out using the conventional Powder (Kurtz and Perry) SHG technique with Nd:YAG laser (1064 nm, 8 ns) for excitation. The pulse energy was 6 mJ; and the pulse repetition rate was 10 Hz. The beam was optically steered to be incident on the microcrystalline powder samples which were tightly packed in a glass capillary. A dichroic mirror was used to remove the fundamental from the generated second harmonic (532 nm), which was detected by a sensitive photomultiplier tube (PMT). The PMT converts the SHG signal to an electrical signal, which was then displayed on an oscilloscope. Finely ground urea crystals with uniform particle size were used as reference for the SHG experiment.

Acknowledgements

The authors dedicate the work to the founder chancellor of Sri Sathya Sai Institute of Higher Learning, Bhagawan Sri Sathya Sai Baba. We thank Prof. S. S. Rajan (Dept. of Biosciences, SSSIHL) and Prof. J Sashidhara Prasad (Former Vice Chancellor, SSSIHL) for their valuable suggestions. We are grateful to the Institution of Excellence, Vijnana Bhavana, University of Mysore, India, for providing the singlecrystal X-ray diffractometer facility. Pranitha Sankar is grateful to the Australia-India Strategic Research Fund (AISRF) for a junior research fellowship. We also thank our fellow researchers R S Sai Siddhardha and Swayamsiddha Kar.

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Fig. 1: UV-Vis absorption plot: a) T-CHL-B, b) T-CHL- SM, c) T-CHL-ClB, d) T-CHL-ISO, e) T-CHL-OM, f) T-CHL-2T, g) T-CHL-OH, h) T-CHL-NDM, i) T-CHL-CAN



Fig. 2: ORTEP of the molecule with thermal ellipsoids drawn at 50% probability



Fig. 3: Packing of the molecules when viewed down along the b axis exhibiting zigzag arrangement.



Fig. 4: Open aperture Z-scan curves measured for the samples, and the corresponding optical limiting behaviour (calculated from the Z-scan data). Solid lines are numerical fits to the data points using Eq. (1).



Fig.5: Graphical representation of the effect of substituents on the *effective* three photon absorption coefficient (γ).

Table-1: UV- Visible absorption maxima, SHG efficiency and effective 3PA absorption coefficients of thienyl- chalcones.

Code	Linear Absorption	SHG values vs.	Effective 3PA coefficient
	(λ _{max} , nm)	Urea	(γ, m³/W²)
T-CHL-B	320	0*	8.5 x 10 ⁻²⁸
T-CHL-CI	323	0*	10.0 x 10 ⁻²⁸
T-CHL-ISO	331	0.29	14.5 x 10 ⁻²⁸
T-CHL-CAN	352	0.27	25.0 x 10 ⁻²⁸
T-CHL-2T	350	52 [*]	30.6 x 10 ⁻²⁸
T-CHL-OH	356	0	40.0 x 10 ⁻²⁸
T-CHL-OM	349	0.94	49.9 x 10 ⁻²⁸
T-CHL-SM	363	0*	68.0 x 10 ⁻²⁸
T-CHL-NDM	428	0.45	105.0 x 10 ⁻²⁸

*24

	$1 \underbrace{4 \atop S} \underbrace{4 \atop O} 0 \underbrace{6 \atop 7} \varphi$				
Code	Ф- Group	IUPAC Name	Reaction Time(hrs)	Yield (%)	Melting Point (°C)
T-CHL-CAN	3 m 9	2,4-Pentadien-1-one, 5-phenyl-1- (2-thienyl)-, (2E,4E)-	16	95.0	101.8 - 102.8
T-CHL-2T	9 10 8 s	2-Propen-1-one, 1,3-di-2-thienyl-, (2E)-	24	89.2	99.4 - 100.3
Code	R-Group	IUPAC Name	Reaction Time(hrs)	Yield (%)	Melting Point (°C)
T-CHL-B	-H	2-Propen-1-one, 3-phenyl-1-(2- thienyl)-, (2E)-	16	83.6	82.2 - 82.6
T-CHL-Cl	-Cl	2-Propen-1-one, 3-(4-chlorophenyl)-1- (2-thienyl)-, (2E)	16	76.2	132.2 - 132.9
T-CHL-ISO	-CH(CH ₃) ₂	2-Propen-1-one, 3-[4-(1-methylethyl) phenyl]-1-(2-thienyl)-,(2E)-	48	90.8	51.4 - 52.2
T-CHL-OH	-OH	2-Propen-1-one, 3-(4-hydroxyphenyl)- 1-(2-thienyl)-, (2E)-	24	65.6	166.7 - 167.3
T-CHL-OM	-O (CH ₃)	2-Propen-1-one, 3-(4- methoxyphenyl)-1-(2-thienyl)-, (2E)-	24	80.2	83.6 - 84.2
T-CHL-SM	-S(CH ₃)	2-Propen-1-one, 3-[4- (methylthio) phenyl]-1-(2-thienyl)- ,(2E)-	24	79.7	86.6 - 87.4
T-CHL- NDM	-N (CH ₃) ₂	2-Propen-1-one, 3-[4-(dimethyl amino)phenyl]-1-(2-thienyl)-,(2E)	16	91.4	93.3 - 95.3

Table 2: Reaction Time, Yield, and Melting Points of the Thienyl chalcones.