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REGULAR ARTICLE

Novel acentric D-π-A-π-D nonlinear optical (2E, 4E)-[dimethylamino) phenyl]-1-(4methylphenyl)penta-2,4-dien-1-one crystal for second and third order nonlinear applications

S RAGHAVENDRA[a,*], T CHANDRA SHEKHARA SHETTY[b], C S CHIDAN KUMAR[c], S NAVEEN[d], SIDDEGOWDA CHANDRAJU[e], SHIVARAJ R MAIDUR[f], PARUTAGOUDA SHANKARAGOUDA PATIL[f], G S ANANTHNAG[g] and S M DHARMAPRAKASH[h]

[a]Department of Engineering Physics, Adichunchanagiri Institute of Technology, Chikkamagaluru 577102, India
[b]Department of Post Graduate Studies and Research in Physics, St Aloysius College (Autonomous), Mangaluru 575003, India
[c]Department of Engineering Chemistry, VidyaVikas Institute of Engineering and Technology, Visvesvaraya Technological University, Alanahalli, Mysuru, Karnataka 570028, India
[d]Institution of Excellence, University of Mysore, Manasagangotri, Mysuru 570 006, India
[e]Department of Sugar Technology and Chemistry, Sir M. Visvesvaraya PG Center, University of Mysore, Tubinakere, Karnataka 571402, India
[f]Department of Physics, K. L. E. Institute of Technology, Opposite Airport, Gokul, Hubballi 580030, India
[g]Department of Chemistry, B. M. S. College of Engineering, Bull Temple Road, Bengaluru 560019, India
[h]Department of Studies in Physics, Mangalore University, Mangalagangotri 574199, India
E-mail: raghuphotonics@gmail.com

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Abstract. A novel organic crystal namely (2E, 4E)-[dimethylamino) phenyl]-1-(4methylphenyl) penta-2, 4-dien-1-one has been grown successfully from the slow evaporation method. The single-crystal X-ray diffraction study revealed that the compound belongs to the orthorhombic crystallographic system with non-centrosymmetric P_{212121} space group with lattice parameters $\alpha = 7.1354(3)$ Å, $\beta = 11.2112(7)$ Å and 20.0744(11) Å. The thermal properties have been studied by using Thermo Gravimetric (TG) and Differential Scanning calorimetry (DSC). The second harmonic generation (SHG) efficiency of the compound is 2.9 times that of urea for Nd-YAG laser operating at wavelength 1064 nm. We also report the results of thermally induced third-order nonlinear optical (NLO) properties of NLO material investigated by Z-scan technique using continuous wave (CW) laser. The calculated values of $\chi_R^{(3)}$ (esu), $\chi_i^{(3)}$ (esu) and $\chi^{(3)}$ are of the order of 10^{-7}esu, 10^{-8} esu and 10^{-7} esu, respectively. The estimated value of the non-linear refractive index is found to be -4.21×10^{-8} cm^2/W. The compound also exhibits promising optical limiting properties at 532 nm wavelength.

Keywords. Acentric; nonlinear; crystal growth; Z scan; optical limiting.

1. Introduction

In the recent years, non-linear optics plays an important role in the recognition and development of many photon related applications such as optical data storage, optical signal processing, harmonic generators, optical limiting and optical switching, etc.[1–5] The nonlinear optical (NLO) property of organic material is governed by the delocalization of the electrons present in individual molecular chromophores with donor-π-acceptor conjugation and delocalization of these π-electron systems connecting the donor and

*For correspondence

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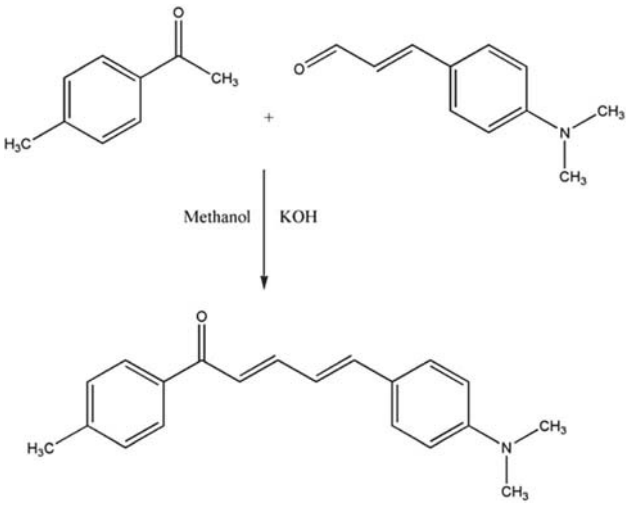
acceptor groups, leading to good NLO property.[6–8] Acentric (non-centrosymmetric) molecules possess highly delocalized conjugated π-electron systems interacting with a rightfully substituted electron donor (D) and acceptor (A) group's exhibit a high value of second-order polarizability.[9] The structural symmetry of the crystal plays a crucial role in NLO application. If the organic crystals are acentric, then they can possess NLO properties of even and odd orders and this strategy motivates the researchers in the design of new materials for second and third-order NLO materials.[10] The development of NLO devices depends strongly on the design of highly proficient NLO materials. Among these, organic compounds are more superior than inorganic materials in terms of ease of synthesis, fabrication of crystals in NLO devices and faster optical nonlinearities.[11] The inorganic material exhibit very poor optical nonlinearity, whereas organic materials are having high nonlinearity due to the presence of weak hydrogen and van der Waals bonds. This is also due to the presence of a high degree of delocalization of electrons in π- conjugated bridge.[12] To characterize these materials, Z-scan technique was proposed by Sheik-Bahae *et al.,* based on the spatial distortion of a laser beam, passed through an NLO material and this method is extensively used because of its simplicity and high sensitivity.[13,14] In order to protect human eyes and sensitive optical instruments from high energy laser, intense research is going on optical limiting effects.[15] We are interested in studying the NLA and NLR of our sample under CW laser. The nonlinearities observed are owing to the thermal lens effect when the sample was irradiated with a high power laser. This, in turn, has an application in protecting optically sensitive devices from high power lasers. This is further justified with the optical power limiting studies. In the present work we report the synthesis, crystal structure, spectral, thermal, second-order nonlinear optical property and thermally induced third-order nonlinearity including optical limiting application study of new organic crystal (2E,4E)-[dimethylamino)phenyl]-1-(4methylphenyl)penta-2,4-dien-1-one (DMAP4P) having elongated conjugation with donor and acceptor groups.

2. Materials and methods

2.1 *Synthesis and crystal growth*

The reagents and solvents for the synthesis were obtained from the Aldrich Chemical Co., India and were used without additional purification (Purity of reagents more than 95%). DMAP4P was synthesized as per the procedure reported earlier.[16,17] 4-Dimethyl amino cinnamaldehyde (0.01 mol) with purity 98% and 4′-methylacetophenone (0.01mol) was dissolved in 20 mL methanol (Scheme 1). A catalytic amount of NaOH solution was added to the above solution dropwise with rigorous stirring. The reaction mixture was stirred for about 5-6 h at room temperature. The progress of the reaction was monitored by TLC. The formed crude products were filtered, washed successively with distilled water and recrystallized from ethanol to get pure **DMAP4P**.



Scheme 1. Synthesis of **DMAP4P**.

Crystals suitable for X-ray diffraction studies were obtained from acetone solution by slow evaporation technique at room temperature. The purity of the compound was confirmed by thin-layer chromatography using Merck silica gel 60 F254 coated aluminum plates. To grow single crystals of DMAP4P, the slow evaporation technique at constant temperature method was employed. A saturated solution of the compound in acetone as solvent was prepared and warmed slightly to get a homogeneous mixture at room temperature. The solution was filtered to remove any undissolved impurities present and was kept undisturbed for 8 days. The mouth of the beaker was covered with filter paper to ensure slow evaporation. The defect-free seed crystals obtained in this way were used for growing bulk crystals.

3. Characterization

3.1 *FTIR spectroscopy*

Figure 1 shows the FT-IR spectrum of **DMAP4P**. The spectrum consists of an absorption band at 1643 cm^{-1} corresponding to C=O stretching. The C–H stretching and C=C stretching vibrations are found at the absorption bands 3090 cm^{-1} and 1549 cm^{-1}, respectively. The different functional groups and their corresponding characteristic peaks are assigned with wave numbers are presented in Table 1.

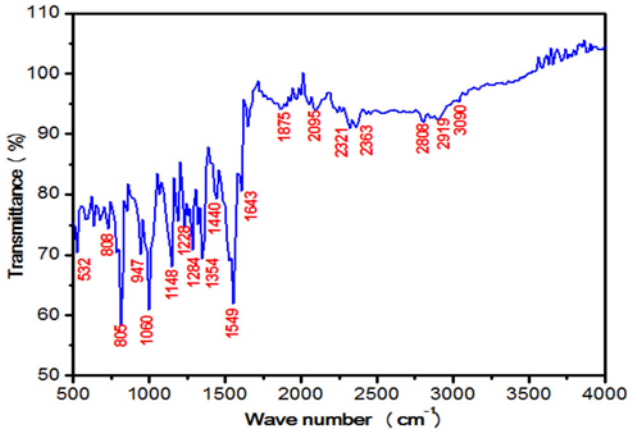


Figure 1. The FTIR spectrum of **DMAP4P**.

Table 1. Assignment of vibrational frequencies.

Wave number (cm^{-1})	Assignment
3090	aromatic C–H stretching vibration
2919	C–H stretching vibration
1643	C=O stretching vibration
1549	C=C stretching vibrations
1440	aromatic C=C stretching vibrations
1228, 1060	aromatic C–H in-plane bending vibrations
1148	C–N stretching
805, 947	C–H out of plane bending bands

3.2 *NMR spectroscopy*

^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of **DMAP4P** crystals were recorded using Bruker AV 400 NMR spectrometer in $CDCl_3$ solution. TMS was used as an internal standard. The ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra are presented in supplementary information. Chemical shifts are presented in terms of ppm (parts per million). Proton resonance multiplicities in ^{1}H NMR are designated as singlet (s), doublet (d) and multiplet (m). The characteristic peaks observed for ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of DMAP4P crystals were described as: ^{1}H NMR (400 MHz, $CDCl_3$): δ7.89 (d, 2H, J = 8.0 Hz, H-ArCH_3), 7.66-7.60 (m, 1H, propenone), 7.39 (d, 2H, J = 8.8 Hz, H-Ar$N(CH_3)_2$), 7.27 (d, 2H, J = 8.0 Hz, H-ArCH_3), 6.81-7.01 (m, 3H, propenone), 6.67 (d, 2H, J = 8.6 Hz, H-Ar$N(CH_3)_2$), 3.00 (s, 6H, -$N(CH_3)_2$), 2.42 (s, 3H, ArCH_3).

$^{13}C\{^{1}H\}$ NMR(400MHz, $CDCl_3$): δ 189.9 (-C(O)-), 151.0, 145.9, 142.9, 142.7, 136.0, 129.1, 128.9, 128.3, 124.1, 122.6, 122.4, 111.9 (Aromatic and propenone C), 40.1 (-OCH_3), 21.5 (-$N(CH_3)_2$).

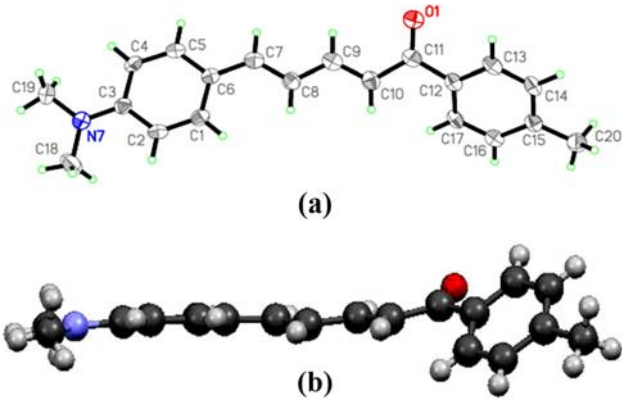


Figure 2. (**a**) ORTEP diagram of the **DMAP4P**, showing 30% probability displacement ellipsoids and the atom-numbering scheme. (**b**) Crystal structure showing the deviation of the 4-methylphenyl ring from the plane of the 4-methylaminephenly ring.

3.3 *X-ray crystallography*

Crystal having dimensions of 0.29 mm × 0.28 mm × 0.27 mm was selected and mounted on a Bruker APEX-II CCD diffractometer with a fine-focus sealed tube graphite-monochromated Mo $K\alpha$ radiation of wavelength 1.54178 Å at 296 K in the range of $4.5 \leq \theta \leq 64.6°$. The crystal data was processed with SAINT and corrected for absorption using SADABS.[18] The structures were solved by the direct method using the program SHELXTL[19] and were refined by program SHELXL 2013.[20,21] The *ORTEP* diagram of the DMAP4P, with atom labelling scheme drawn at 30% probability displacement ellipsoid is shown in Figure 2(a). The molecule is composed of a dimethylamine phenyl and a 4-methyl-benzene ring and the dihedral angle between the mean planes of these rings is 47.93(17)° indicating a twist of the 4-methylbenzene (C12–C17) ring from the mean plane of the 4-dimethylaminobenzene (C1–C6) ring (Figure 2(b)). No classical hydrogen bonds were found for the present structure. The molecules are stacked into two-dimensional layers (Figure 3) *via* C–H···π interactions involving the centroids of C1–C6 and C23–C17 benzene rings. The bond length and bond angles agree with the literature values[16] and are comparable with those reported earlier.[17,22]

3.4 *Linear optical absorption studies*

UV visible absorption spectrum was recorded using Shimadzu 1800 UV-Visible spectrophotometer in the solution phase using DMF as a non-interactive solvent medium (Concentration 0.02 M, Optical Path length 1 cm). Figure 4 shows the UV Visible absorption

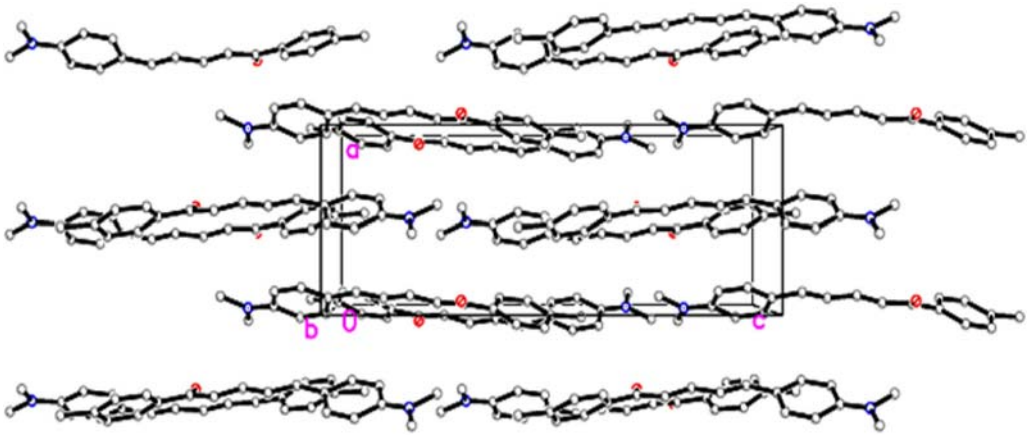


Figure 3. Packing of molecules (I) viewed along the *b* axis. All H atoms are omitted for clarity.

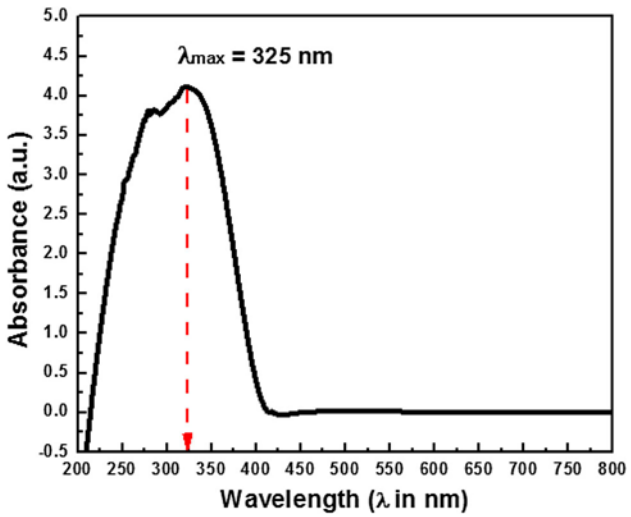


Figure 4. UV-Visible Spectrum of **DMAP4P**.

spectrum of **DMAP4P**. In general, organic molecules belonging to chalcones family absorb light in UV region and transmit light in the rest of the region. **DMAP4P** showed good transparency in the entire visible region (430 to 800 nm). Maximum absorption found in the UV-Visible region may be due to the π-π* transition, it could be attributed due to the presence of chromospheres carbonyl group[23] in the chalcones. Cut off wavelength (λ_{cw}) is found to be at 418 nm. Beyond λ_{cw} **DMAP4P** exhibits very poor absorption. Transparency in the visible region can be made useful **DMAP4P** in nonlinear optical device applications.

3.5 *Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)*

The thermal stability of DMAP4P was studied by the TGA and DSC techniques. The TGA-DSC for **DMAP4P** has been recorded using SDTQ-600 simultaneous TGA-DSC analyzer at the heating rate of 10 °C/min. An alumina crucible plate was used for heating the sample and measurement were recorded in a nitrogen atmosphere in the temperature range between room temperature to 700 °C. The TGA–DSC curves of **DMAP4P** are shown in Figure 5. The DSC curve shows that the melting point of DMAP4P is 160 °C. Weight loss is observed after 300 °C. Also, it is clear from the TGA curve that there is no phase transition before the melting point. The sharp melting point peak demonstrates good crystallinity and purity of the sample.[24]

3.6 *Second-order nonlinear optical properties*

The second harmonic generation (SHG) efficiency measurement was carried out using Kurtz and Perry technique, to evaluate the SHG efficiency of NLO materials.[25,26] A Q-switched Nd:YAG laser delivering the energy of 6 mJ/pulse at the wavelength 1064 nm

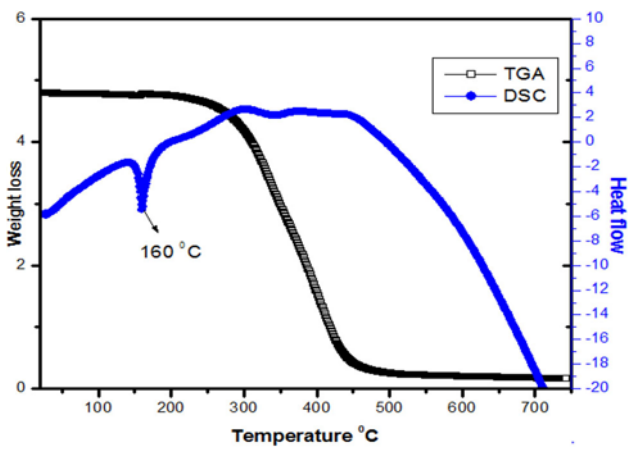


Figure 5. TGA DSC curve.

was used as a light source of fundamental laser light. The standard urea crystals which are powdered to have particle size comparable to that of DMAP4P crystals were used as the reference. The grown **DMAP4P** crystals were tightly packed in a microcapillary tube in the form of fine powder and mounted in the path of laser beam. It was observed that the **DMAP4P** crystal emitting green light indicating second harmonic generation phenomena. The SHG signal measured for standard urea was 4 mV while that for **DMAP4P** was 11.5 mV. Thus, the SHG efficiency of **DMAP4P** was 2.9 times that of urea. Ravindrachari *et al.,* synthesized and characterized similar chalcones with lower conjugation and reported their NLO activity. *Viz* 1-(4-Chloro phenyl)-3-(4-dimethylamino phenyl) prop-2-en-1-one is crystallized in centrosymmetric P21/c space group showed weak SHG efficiency with respect to urea[27] and 1-(4-methylphenyl)-3-(4-N,N dimethyl amino phenyl)-2-propen-1-one[28] crystal is crystallized with non-centrosymmetric space group P_{212121} showed SHG efficiency 0.8 times that of urea. **DMAP4P** crystal is having good SHG efficiency compared to reported crystals. The high value of conversion efficiency may be attributed to an elongated structure of **DMAP4P** crystals.

3.7 *Nonlinear absorption, refraction and optical limiting study*

The thermally induced optical nonlinearity and optical limiting measurements of **DMAP4P** were carried out by Z-Scan technique by using continuous wave, Diode-Pumped Solid State (DPSS) laser operates at 532 nm wavelength with the output power 200 mW. Z-scan is a simple and sensitive single-beam method for determining both the nonlinear absorption coefficient (β) and nonlinear refractive index (n_2) of a given material and which gives information about sign and type of the optical nonlinearity.[13] The solution for the **DMAP4P** crystals was prepared using DMF solvent with 0.01M concentration. A quartz cuvette (1 mm path length) was used to place the sample solutions. The laser beam was focused by the convex lens having 28.6 cm focal length. The sample was scanned along its optical axis (-Z to +Z) under a computer-controlled translation stage. The open and closed aperture transmission data were simultaneously indicated by a dual-channel energy meter. Figures 6 and 7 show open and closed aperture Z-Scan plots at the concentration 0.01M under continuous wave regime. In the present experiment, open aperture Z-scan was also conducted with a pure solvent, however, within the limit of

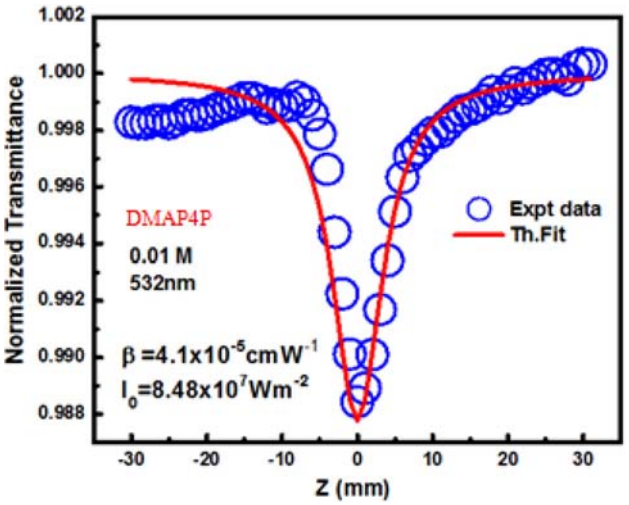


Figure 6. Open aperture curve for **DMAP4P**. Solid line is fitted to Eq. (1), with $\beta_{eff} = 4.1 \times 10^{-5}$ cm/W.

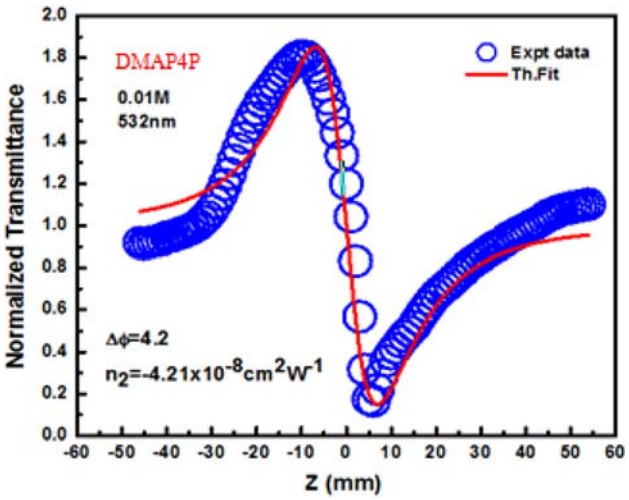


Figure 7. Nonlinear refraction curve DMAP4P. Solid line is a fit of data to Eq. (2) with $\Delta = 4.2$.

intensity used during the experiment, no NLA was observed, which indicates that only the solute (i.e., **DMAP4P** compound) contributes nonlinearity. Figure 6 gives information about two-photon absorption with reverse saturation and Figure 7 gives information about negative nonlinear refraction due to the self-defocusing effect. The experimental open aperture data was fit theoretically using the relation.[29]

$$T(Z) = 1 - \frac{\beta I_0 L_{eff}}{2\sqrt{2}\left(1 + Z^2/Z_0^2\right)} \quad (1)$$

Where I_0 is the intensity at the focus, T(z) is the normalized transmittance, L_{eff} is the effective length of the sample. The measured two-photon absorption coefficient for DMAP4P sample was found to be 4.1×10^{-5} cm/W. In order to measure phase shift

Table 2. Comparison of third-order NLO property of reported NLO materials.

NLO materials	Wavelength (nm)	NLA coefficient β (cm W^{-1})	NLR Index n_2 (cm^2/W)	Nonlinear susceptibility $\chi^{(3)}$ (esu)	References
FAMFC	532	35.8×10^{-4}	-0.18×10^{-8}	0.21×10^{-6}	33
3CAMC	532	0.50×10^{-5}	-0.23×10^{-8}	0.2×10^{-6}	34
Graphene Oxide (GO)	532	17×10^{-9}	1.2×10^{-13}	5.7×10^{-12}	35
Graphene Oxide-Ag	532	45.4×10^{-9}	5.7×10^{-12}	16×10^{-12}	35
(G/MoS_2)3.9/PMMA		282×10^{-9}	–	–	36
2APF	632.8	–	-2.49×10^{-8}	–	37
F3NC	532	1.2×10^{-6}	-1.31×10^{-8}	1.13×10^{-6}	38
1-carboxymethyl)quinolin-1-ium chloride	635	5.89×10^{-4}	-3.81×10^{-8}	–	39
DMAP4P (present work)	532	4.1×10^{-6}	-4.21×10^{-8}	2.41×10^{-7}	

($\Delta\phi_0$) the experimentally obtained closed aperture data was fitted theoretically fitted with the equation

$$T(Z) = 1 - \frac{(4X\Delta\phi_0)}{(X^2+1)(X^2+9)} \quad (2)$$

Where $X = Z/Z_0$. Nonlinear refractive index can be calculated by using the relation $\Delta\Phi_0 = kn_2I_0L_{eff}$ where $k = 2\pi/\lambda$ called wave vector.

Nonlinear absorption coefficient (β) and nonlinear refractive index n_2 are related to the real and imaginary part of third-order nonlinear optical susceptibility χ(3) through the relations

$$\chi_R^{(3)}\,(\text{esu}) = \frac{cn_0^2}{120\pi^2} n_2\,(\text{m}^2/\text{W}) \quad (3)$$

$$\chi_i^{(3)}\,(\text{esu}) = \frac{c^2n_0^2}{240\omega\pi^2}\beta(\text{m/W}) \quad (4)$$

$$\text{With } \chi^{(3)} = \chi_R^{(3)} + i\chi_i^{(3)} \quad (5)$$

Where c is the velocity of light in vacuum,$n_0$is the linear refraction index and ω is the angular frequency of the light field. The calculated values of third-order nonlinear susceptibilities $\chi_R^{(3)}$ (esu), $\chi_i^{(3)}$ (esu) and $\chi^{(3)}$ are found to 2.41×10^{-7}(esu), 0.99×10^{-8}(esu) and 2.4×10^{-7}(esu) respectively. The calculated value of index of nonlinear refraction for **DMAP4P** is found to be -4.21×10^{-8} cm^2/W. The obtained curve and theoretical fit show that nonlinear refractive index is negative i.e., peak is followed by a valley. H. Nadjari *et al.,* synthesized silver and gold nano-colloid, with ablation of their metal foil in pure water and observed negative nonlinear refraction.[30] The asymmetric nature of the curve in addition to the fact that the laser beam used in the present experiment is a continuous wave suggests that the nonlinear refractive index (NLR) observed is of thermal-origin. The self-defocusing effect is attributed to the thermal nonlinearity resulting from the absorption of the focused beam passing through DMAP4P sample, which results in the spatial distribution of the temperature and consequently, a spatial variation of the NLR that acts as a thermal lens, resulting in a phase distortion of the propagating beam.[31] The nonlinear induced polarization per molecule is explained by the microscopic susceptibilities known as the hyperpolarizability. Table 2 gives the third-order nonlinear optical parameters of material under present investigation and comparative list of third-order NLO property of reported NLO materials. To examine the viability of **DMAP4P** as optical limiters, the nonlinear transmission of the compound was verified as a function of input fluence (Figure 8). Optical limiters protect sensitive optical equipment and human eye from the high-intensity laser light.[32] In this scenario, the OL experiment was performed using an open aperture Z-Scan technique. The deviation of transmission from the linearity with increasing laser fluence indicates the occurrence of OL in **DMAP4P**. Also, the optical limiting behavior shows trends of thermal accumulation as evident from the deviation of the data to the fit indicating thermally induced nonlinearity. The calculated OL threshold value is found to be 5.32 kW/cm^2.

3.8 *Structure property relationship*

The Z-Scan result shows that the imaginary part of third-order nonlinear susceptibility is less than that of real part indicating that nonlinearity is non-resonant.[27] Third-order nonlinear optical property of compound increases with the introduction of strong donor and

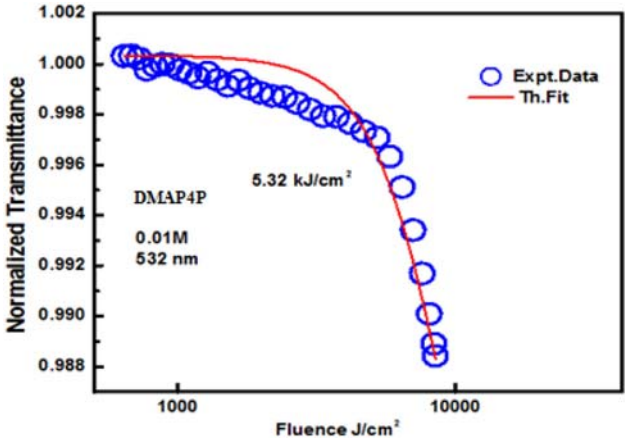


Figure 8. Optical limiting behavior of **DMAP4P**.

acceptor functional group which increases the delocalization of π-conjugated electrons from donor end to acceptor end.[40] In **DMAP4P** di methylamine group (H_3C-N-CH_3) is attached at phenyl ring and methyl group (CH_3) is placed at benzoil ring acts as two donors at the end. The carbonyl group (C=O) in the centre of the molecule acts as acceptor. In **DMAP4P** the asymmetric nature observed in the nonlinear curve due to the fact that the laser beam used in the present experiment is a continuous wave suggests that the nonlinear refractive index (NLR) observed is of thermal-origin. We have reported D-π-A-π-D and D-π-A-π-A type structures with lower conjugation length.[23,31] Present molecule belongs to D-π-A-π-D system with an elongated structure.

4. Conclusions

A new organic crystal **DMAP4P** has been synthesized and its crystal structure has been studied using single-crystal X-ray diffraction, its thermal behavior has been characterized by simultaneous TGA/DSC analysis. Third-order nonlinear optical properties have been studied using Z-Scan technique. Value of β, n_2 and optical limiting threshold values are calculated and compared with reported values. Our results show that **DMAP4P** exhibits good thermal stability and significant third-order nonlinear optical properties. Analysis of nonlinearity of the **DMAP4P** showed a self-defocusing (negative) nonlinearity phenomenon. A pre-focal transmittance maximum followed by a post-focal transmittance minimum valley in the Z-scan experiment is an indication of negative nonlinearity. The good transparency, high thermal stability high NLA and NLR coefficient makes **DMAP4P** a promising candidate for NLO applications.

Supplementary Information (SI)

Hydrogen bond geometry, selected bond length and bond angles and various hydrogen bonds present in the molecule are available at www.ias.ac.in/chemsci.

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