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Crystalline perfection, third-order nonlinear optical properties and optical limiting studies of 3, 4-Dimethoxy -4′-methoxychalcone single crystal

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ABSTRACT

Transparent good quality single crystals of organic nonlinear optical material, 3, 4-Dimethoxy -4′-methoxychalcone (DMMC) were grown by slow evaporation solution growth technique in acetone at ambient temperature. The lattice parameters were estimated from powder X-ray diffraction. The crystalline perfection has been evaluated by high resolution X–ray diffractometry (HRXRD). The UV–vis-NIR absorption spectrum reveals that the crystal is transparent between 440 nm and 900 nm for optical applications. The fluorescence spectrum shows a peak at about 482 nm and indicates that the crystal has a blue fluorescence emission. The third order nonlinear optical properties of solution of DMMC in N, N-Dimethylformamide (DMF) solvent has been investigated using Z-scan technique with femtosecond (fs) Ti:sapphire laser pulses at 800 nm wavelength. The calculated values of nonlinear refractive index, nonlinear absorption coefficient, and the magnitude of third-order susceptibility are of the order of -7.7×10^{-14}cm^2/W, 1.7×10^{-9} cm/W and 6.7×10^{-12} e.s.u. respectively. The two photon absorption (2PA) cross section and molecular second-order hyperpolarizability values obtained is of the order of 10^{-49} cm^4 s/photon/molecule and 2.8×10^{-31} e.s.u. respectively. The crystal shows optical-limiting (OL) effects for femtosecond laser pulses at 800 nm. The results suggest that the nonlinear properties investigated for DMMC are comparable with some of the reported chalcone derivatives and can be desirable for nonlinear optical applications.

1. Introduction

To protect sensitive optical elements or human eyes for laser-induced damage, researchers have concentrated on optical limiting (OL) effects [1–4]. The OL effects can be enhanced by appropriate design of nonlinear optical materials, including organic molecular [4–6], hybrid materials [7–8], nanomaterials [9–10], quantum dots [11], and two-dimensional materials [12]. As an interesting type of nonlinear optical materials, the chalcones (1, 3-diaryl-2-propen-1-ones) have been received much attention due to their notable second and third –order nonlinear optical responses [13–17]. Interestingly, these types of compounds exhibit the enhancement of optical nonlinearities attributed to the introduction of electron donor and electron acceptor on either side of aromatic rings to the large π-conjugated system, strong intermolecular interaction, as well as 2PA resonance [18–20]. However, the full understanding on the ultrafast optical nonlinearities and applications in nonlinear photonics devices of these compounds are still incomplete. Because of the substantial importance of chalcones, we have been synthesized and examined the NLO properties of a series of chalcone derivatives experimentally and show encouraging outcomes in future applications such as nonlinear frequency conversion and optical limiters [20–25]. One such synthesized and grown bulk chalcone crystal, 3, 4-dimethoxy-4′-methoxychalocne (DMMC) crystallizes in monoclinic system with a noncentrosymmetric space group P21, and possess second harmonic generation efficiency (15 times higher than urea) [21]. As a part of extensive characterization, we present in this report the investigation of the powder X–ray diffraction, high-resolution X-ray diffraction (HRXRD), transmission cutoff and fluorescence properties. We also present our experimental investigation into the third order optical nonlinearities in DMF solution of 3, 4-Dimethoxy-4′-methoxychalcone using Z-scan techniques with femtosecond laser pulses. We have unambiguously determined all the nonlinear parameters in DMMC molecule, including the two-photon absorption (2PA) cross-section, second-order

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hyperpolarizability, and excited-state absorption (ESA) cross-section.

2. Experimental procedure

2.1. Material synthesis

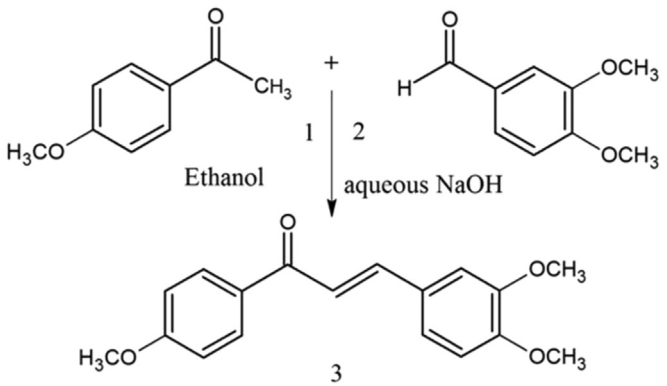
All chemicals used in this work were of analytical grade and used as supplied. DMMC was synthesized by the previously reported the standard method, Claisen–Schmidt condensation reaction, from 3, 4- dimethoxybenzaldehyde and 4′-methoxyacetophenone in ethanol [21]. The resulting crude solid was collected by filtration, dried, and purified by repeated crystallization from acetone. The molecular structure of DMMC is displayed in the Scheme 1.

2.2. Solubility and crystal growth

DMMC crystals were grown by slow evaporation solution growth technique. The resultant DMMC was crystallized using various solvents. Among the various solvents such as acetone, ethanol, methanol, chloroform, hexane and DMF, the acetone was found to be the best solvent to grow good quality crystals. To grow large sized crystals, the recrystallized DMMC was dissolved with acetone and kept for crystallization at room temperature. Non-hygroscopic light yellowish transparent crystals with maximum size of 1.8 cm × 0.65 cm × 0.4 cm (Fig. 1) were harvested from the mother solution after 12 days. The crystals obtained are stable at room temperature.

2.3. Characterization

The grown crystal was characterized by Powder X-ray diffraction using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) at a scan speed of 1°/min. The data was collected using Ni filtered Cu-target tube at room temperature. The diffraction pattern was indexed by Powder X software. The absorption spectrum was measured using a Perkin-Elmer UV–vis-NIR spectrometer (Lamada-900) in the range of 300–900 nm at room temperature. The fluorescence spectrum was measured at room temperature using the Edinburgh Analysis Instruments FLS920 spectrophotometer with Xenon lamp as a light source. To reveal the crystalline perfection of the grown crystals, a multi-crystal X-ray diffractometer (MCD) developed at NPL [26] has been used to record high-resolution diffraction curves (DCs). Before recording the diffraction curve to remove the non-crystallized solute atoms remained on the surface of the crystal and also to ensure the surface planarity, the specimen was first lapped and



Scheme 1. Chemical structure (3) and synthesis scheme of 3,4-Dimethoxy -4′-methoxychalcone.

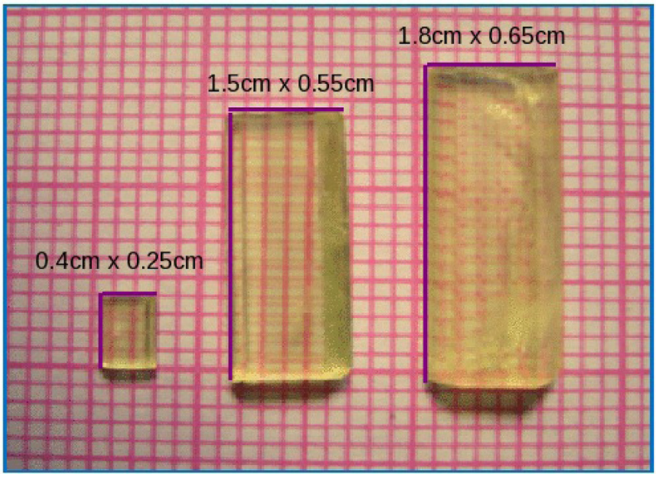


Fig. 1. Grown crystals of DMMC.

chemically etched in a non preferential etchant of water and acetone mixture in 1:2 volume ratio. This process also ensures to remove surface layers, which may sometimes form for e.g. a complexing epilayer may form on the surface of the crystal due to organic additives [27].

2.4. Nonlinear optical measurements

The nonlinear optical (NLO) properties of the DMMC in DMF solution were measured by using standard Z-Scan technique, which gives the information about nonlinear absorption and nonlinear refraction coefficients [28–31]. In this technique the sample is scanned through the focal plane of a tightly focused Gaussian beam [31]. Meanwhile, the changes in the far-field intensity pattern with and without aperture are monitored. Z-scan technique has great advantages due to its simplicity and high sensitivity; it can simultaneously measure both sign and magnitude of nonlinear refraction index and nonlinear absorption. The experimental setup is shown in Fig. 2. Experiments were performed using fs pulses from a Ti: sapphire oscillator (repetition rate ~80 MHz, pulse duration of ~150 fs, maximum average power of ~4 W). The Z-scan experiments are done with typically 10-20 mW input power with corresponding pulse energy being 0.2–0.3 nJ. The pulses were tunable in the wavelength region of 680–1060 nm. The sample was scanned along the Z-direction through the focus of the beam passed through a 100 mm focal length lens. The input beam was spatially filtered to attain a pure Gaussian profile in the far field. The sample was placed on a 10 μm resolution translation stage and the data was collected manually using power meter detector (Field-Max, Coherent). The transmitted intensity was recorded as a function of the sample position. The beam waist (ω_0) estimated at the focus was ~21 μm with a corresponding Rayleigh range of ~1.64 mm. The closed aperture scan was performed at intensity where the contribution from the higher order nonlinear effects is negligible (the value of $\Delta\phi$ estimated was found to be $< \pi$). The experiments were performed at 800 nm. Solution of the recrystallized DMMC was prepared using DMF solvent with 0.01 M concentration.

3. Results and discussion

3.1. Powder X-ray diffractometer

The recorded powder X-ray diffraction pattern is shown in Fig. 3. The presence of well defined reflections (peaks) in the

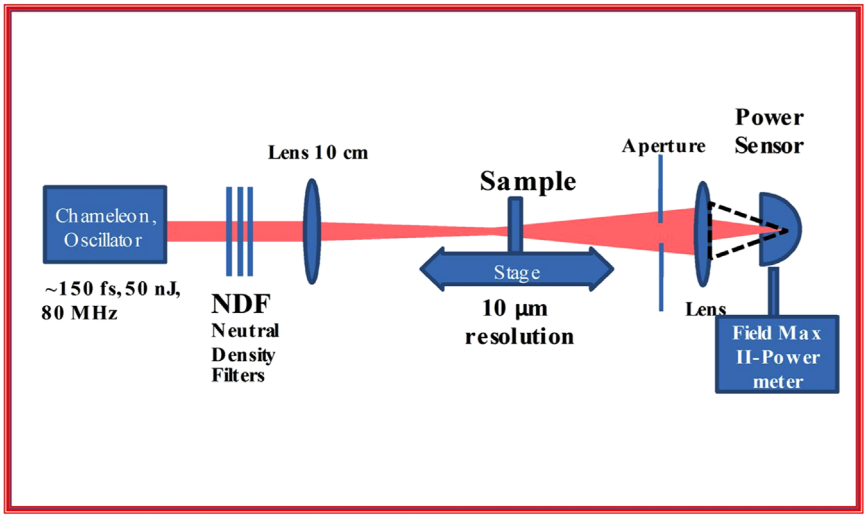


Fig. 2. Z-Scan experimental setup to measure the NLO parameters.

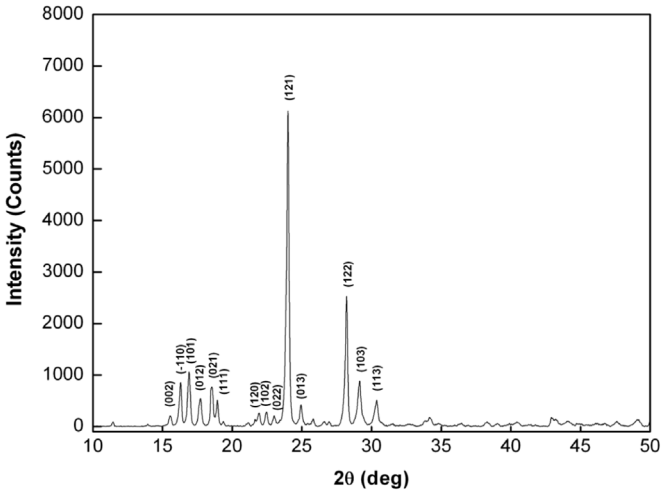


Fig. 3. Powder X-ray diffraction pattern of DMMC.

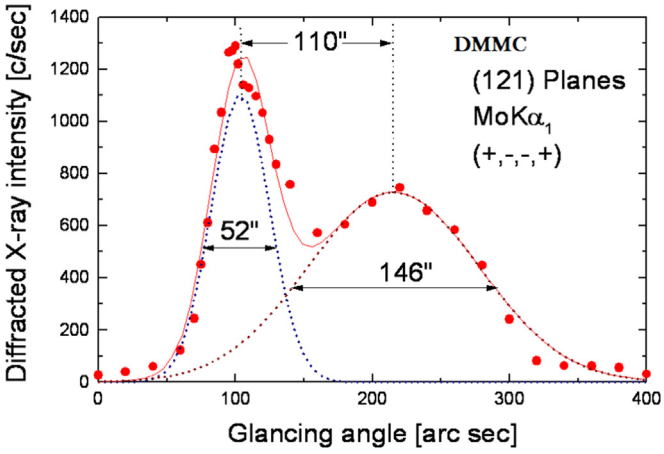


Fig. 4. Diffraction curve recorded for DMMC single crystal for (121) diffracting planes by employing the multicrystal X-ray diffractometer with MoKα_1 radiation.

pattern, announces the existence of periodically ordered atomic planes in the grown crystal. The DMMC crystal belongs to the monoclinic system, and the calculated lattice parameters are in good agreement with the reported literature values [21].

3.2. Multicrystal X-ray diffractometer

Fig. 4 shows the high-resolution diffraction curve (DC) recorded for DMMC specimen crystal using (121) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer with MoKα_1 radiation. As seen in the figure, the curve is not having a single diffraction peak. The solid line, which follows well with the experimental points (filled circles), is the convoluted curve of two peaks using the Gaussian fit. The additional peak depicts an internal structural low angle (tilt angle >1 arc min but less than an arc degree) boundary [32] whose tilt angle (misorientation angle between the two crystalline regions on both sides of the structural grain boundary) is 110 arc sec from its adjoining region. The FWHM (full width at half maximum) of the main peak and the very low angle boundary are 52 and 146 arc sec, respectively. Though the specimen contains a low angle boundary, the relatively low angular spread of around 400 arc sec of the diffraction curve and the low FWHM values show that the crystalline perfection is reasonably good. The entrapment of impurities or solvent molecules could be responsible for the formation of these grain boundaries which may be segregated at the boundaries during the growth process. It may be mentioned here that such a low angle boundary could be detected with well-resolved peak in the diffraction curve only because of the high-resolution of the multicrystal X-ray diffractometer used in the present studies. The influence of such minute defects on the NLO properties is very insignificant. However, a quantitative analysis of such unavoidable defects is of great importance, particularly in case of phase matching applications.

3.3. Absorption and emission spectra

Electronic absorption spectrum of the DMMC was measured in DMF solution (Fig. 5.). The cutoff wavelength ($\lambda_{cut-off}$) of absorption was found to be at 440 nm. The maximum absorption observed at 405 nm is assigned to n–π^* transition and this transition may be attributed to C=O group excitation and aromatic ring excitation in the molecule. It is highly transparent in the near infrared range and hence, one may expect strong 2PA effects with laser radiation at 800 nm [22].

The fluorescence spectrum of solution of DMMC crystals in DMF was recorded at room temperature. The sample was excited at 380 nm and is shown in Fig. 5. A strong broad emission band peaking at 482 nm is observed. The result indicates that the crystal

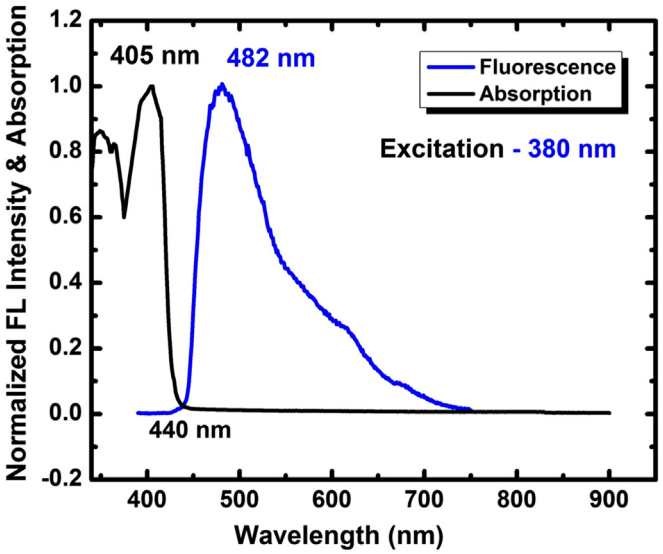


Fig. 5. Normalized electronic absorption and fluorescence emission spectra of DMMC in DMF at room temperature.

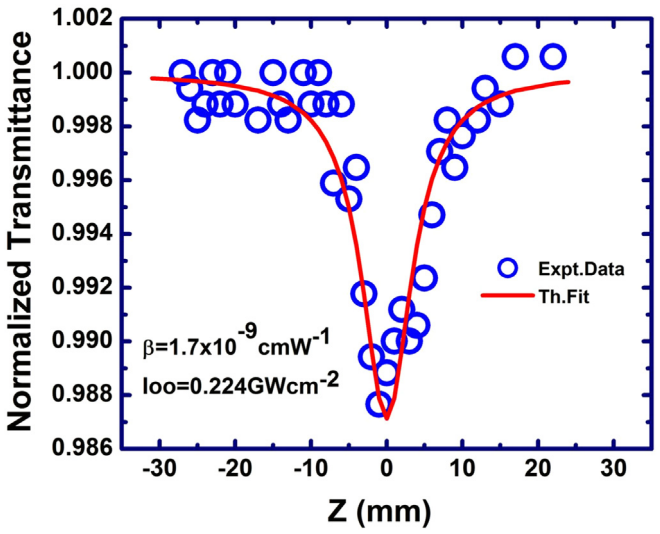


Fig.6. Open aperture Z-scan curve of DMMC in DMF solution for 2PA. Solid line is a theoretical fit to the experimental data.

has a blue fluorescence emission and may used in the fabrication of blue light emitting diodes (LEDs). One of the main explanations of fluorescence effect is the appearance of intramolecular charge transfer (ICT) states. The intramolecular charge transfer from donor to the acceptor gives rise to a large variation of the dipole moment, which clearly explains the charge transfer interaction between the methoxy (OCH_3) group and carbonyl (C=O) group through the π-conjugated system [20]. The π-electron cloud moment from donor to acceptor can make the molecule highly polarized through the single-double path when it changes from the ground state into the excited state. Thus it reveals the origin of fluorescence band at 482 nm. More detailed experiments are in progress to investigate the relation between structure of the compound and the fluorescence peak with a view of better understanding how the fluorescence affects the nonlinear properties and optical limiting performance.

3.4. Nonlinear optical properties

In the Z-scan experiment, the nonlinear transmission of compounds without aperture (open aperture) was measured in the far-field as the sample was moved through the focal point. This allows us to determine the nonlinear absorption coefficient β. The open aperture curve of DMMC is shown in Fig. 6. Here, the transmission is symmetric with respect to focus ($z=0$), where it reaches a minimum value, showing an intensity dependent absorption effect. The experimental data was fitted with the theoretical formula for two photon absorption. The presence of valley in open aperture scans indicates strong reverse saturation absorption (RSA) at peak intensities. The corresponding normalized transmission as a function of sample position in open aperture condition is given by,

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

Where, β is the two photon absorption coefficient which is found to be 1.7×10^{-9} cm W^{-1} from the open aperture fit, $L_{eff}=\frac{(1-exp^{-\alpha L})}{\alpha}$ is the effective length of the sample, here α is linear absorption coefficient and L is thickness of the sample. I_0 is the intensity of the laser beam at the focus; Z is the distance of the sample from focus and $Z_0=\pi\omega_0^2/\lambda$ is the Rayleigh range which is found to be ~1.64 mm with beam waist radius ω_0 ~21 μm.

To determine the sign and magnitude of nonlinear refraction

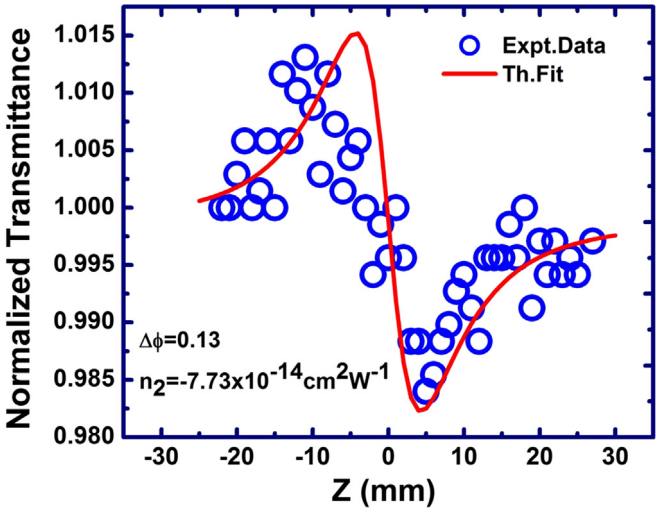


Fig.7. The closed aperture Z-scan curve of DMMC using fs laser pulses at 800 nm wavelength and 80 MHz repetition rate. The circles are the experimental data and solid line is the corresponding theoretical fitting.

simultaneously, closed aperture Z-scan was performed by placing an aperture in front of the detector (closed aperture). The closed aperture Z-scan curve is shown in Fig. 7. To obtain a pure nonlinear refraction curve, we have divided closed aperture data from the open aperture data and the obtained curve exhibit peak-valley characteristic indicating negative nonlinear refraction (self defocusing) effect with the on-axis *peak intensity of* $I_0=0.22$ GWcm^{-2}. The change in the normalized transmittance between the peak and valley (ΔT_{pv}) can be empirically determined by relating to the induced phase distortion $\Delta\phi_0$ for a third order nonlinear refractive process in the absence of NLA is given according to Sheik-Bahae et al. [28].

$$\Delta T_{pv}=0.406(1-S)^{0.25}|\Delta\phi_0| \quad (2)$$

Where, S is the aperture transmittance which we have taken 0.4 in our experiment for good approximation. To obtain the nonlinear refraction coefficient n_2, we fit the transmission curve by the well-established formula and the normalized transmittance is given by,

$$T(Z)=1-\frac{(4X\Delta\varphi_0)}{[(X^2+1)(X^2+9)]} \quad (3)$$

Where, $X=Z/Z_0$ and $\Delta\phi_0$ is the on-axis nonlinear phase shift and I_0 is the peak intensity at the focus, $k=2\pi/\lambda$ is the wave vector. Then the third order nonlinear refraction index n_2 can be easily calculated by knowing $\Delta\phi_0$ from the closed aperture Z-scan graph by using the relation $\Delta\Phi_0=kn_2I_0L_{eff}$. The value of n_2 for DMMC is found to be -7.7×10^{-14} cm^2 W^{-1}.

The nonlinear refractive index n_2 and nonlinear absorption coefficient β are related to the real and imaginary part of third order nonlinear optical susceptibility $\chi^{(3)}$ through the following relations respectively [33,34].

$$\chi^{(3)}=\chi_R^{(3)}+i\chi_I^{(3)} \quad (4)$$

$$\chi_R^{(3)}(\text{esu})=\frac{cn_0^2}{120\pi^2}n_2(\text{m}^2/\text{W}) \quad (5)$$

$$\chi_I^{(3)}(\text{esu})=\frac{c^2n_0^2}{240\pi^2\omega}\beta(\text{m/W}) \quad (6)$$

Where, n_0 is the linear refraction index and c is the velocity of light in vacuum, β and n_2 are the nonlinear absorption and refraction coefficients and ω is the angular frequency of the light field. The calculated values of $\chi_R^{(3)}$(esu) and $\chi_I^{(3)}$(esu) are -6.616×10^{-12} esu and 0.926×10^{-12} esu, respectively. These values show that the DMMC has a large nonlinear optical susceptibility, which compares favorably with the nonlinearities of some chalcones [35–36] (Table 1).

The nonlinear induced polarization per molecule is described by the microscopic susceptibilities known as the hyperpolarizability. For third order effects the corresponding hyperpolarizability γ_h (second order hyperpolarizability) is related to the third order susceptibility $\chi^{(3)}$ by the equation,

$$\gamma_h=\frac{x^{(3)}}{[(1/3)(n_0^2+2)]^4N} \quad (7)$$

Where, N is the number of molecules per cm^3.

The calculated γ_h value (Table 2) is comparable with the other chalcone derivatives [35–36]. Furthermore, the γ_h value of DMMC is greater than that of thiophene (dimer, trimer, tetramer, and pentamer), stilbazolium derivative and comparable with that of thiophene (hexamer) [37–38].

Using the open aperture Z scan data, the excited state absorption cross section σ_{ex} can be estimated by the following relation,

$$T=\frac{\ln\left[1+\frac{q_0}{1+x^2}\right]}{\left(\frac{q_0}{1+x^2}\right)} \quad (8)$$

Where, $x=z/z_0$, $q_0=\alpha_0\sigma_{ex}F_0L_{eff}/2h\nu$, $F_0=2E/\pi\omega_0^2$ is the fluence of the laser at the focus, hν is the energy of the incident photon, α_0 is the linear absorption coefficient, σ_{ex} is the excited state absorption cross section, the value obtained by the open aperture fit is in the order of 10^{-15} cm^2 for DMMC. The ground state absorption cross section σ_g calculated by the relation, $\sigma_g=\alpha_0/NC$, where N is the Avogadro's number and C is the concentration of the solution in mol/L. the value obtained is in the order of 10^{-16} cm^2, it can be seen from the obtained values that, excited state absorption σ_{ex} is larger than the value of σ_g, which is found to be in agreement with the condition for observing reverse saturation absorption.

Table 1
Measured linear absorption coefficient (α_0), 2PA coefficient (β), linear refractive index (n_0), nonlinear refractive index (n_2), real and imaginary part of third order nonlinear optical susceptibility $\chi^{(3)}$ for DMMC in DMF solution with concentration of 0.01 M at 800 nm wavelength and 80 MHz laser repetition rate.

α_0 (cm^{-1})	β (10^{-9} cmW^{-1})	n_0	n_2 (10^{-14} cm^{2}W^{-1})	Re $\chi^{(3)}$ (10^{-12} e.s.u.)	Im $\chi^{(3)}$ (10^{-12} e.s.u.)	$\chi^{(3)}$ (10^{-12} e.s.u.)
0.913	1.7	1.5	−7.7	−6.62	0.93	6.68

Table 2
Molecular 2PA cross section (σ_{2PA}), GSA cross section (σ_{GSA}), ESA cross section (σ_{EXA}), and second-order hyperpolarizability γ_h for DMMC in DMF solution (0.01 M) at 800 nm wavelength and 80 MHz laser repetition rate.

σ_{GSA} (10^{-16} cm^2)	σ_{EXA} (10^{-15} cm^2)	σ_{2PA} (10^{-49} cm^4 s photon^{-1}Molecule^{-1})	γ_h (10^{-31} esu)
1.51	4.1	7.01	2.76

For a molecular system, the 2PA cross section σ_{2PA} describes the efficiency of a particular molecule in the ground state to reach the excited state via a two photon absorption process, and it is defined as follows,

$$\sigma_{2PA}=\frac{h\nu\beta}{NC\times10^{-3}} \quad (\text{cm}^4\text{ s photon}^{-1}\text{ molecule}^{-1}) \quad (9)$$

Where, $h\nu$ is the energy of the incident laser pulse, N is Avogadro's number and C is concentration of the solution in mole per liter. σ_{2PA} is commonly given in a new SI unit (GM) defined as 1 GM$=10^{-50}$ cm^4 s photon^{-1} molecule^{-1} [39]. The measured σ_{2PA} value is in the order 10^{-49} cm^4 s photon^{-1} molecule^{-1}, which is in good agreement with the literature [39]. Excited state absorption data is of interest because on one hand it provides fundamental information about the nature of the lying excited states often inaccessible from the ground state, and on the other hand, it can provide important information to assess the lasing potential of the medium. The TPA cross section depends on type of functional group and its position on the aromatic ring of the chalcone molecule.

The third-order NLO properties arise in DMMC is due to the strong delocalization of π-electrons. Generally, in π-conjugated molecules, the charge cloud formed by conjugated π-electrons has the capability of being strongly deformed under the effect of an external optical field. In the molecular structure of chalcone, the para position of benzoyl ring, and meta and para position of phenylene ring consists of OCH_3 group. The OCH_3 group is a donor group. The crystal containing methoxy and dimethoxy at the ends and an electron acceptor carbonyl group (C=O) at the middle forms a donor-π-acceptor-π-donor (D–π–A–π–D) system, where charge transfer takes place from the donor ends to the acceptor at the middle of the molecule leading to the nonlinearity.

3.5. Optical limiting (OL)

Optical limiting is a phenomena observed when the transmission of a medium decreases with increasing input laser intensity (or fluence). Optical limiters are useful for the protection of human eyes, optical elements and optical sensors from intense laser pulses. Fig. 8 illustrates the intensity-dependent transmission of DMMC in DMF solution as a function of input laser fluence (*i.e.* energy per unit area). The deviation of linear transmittance suggests the occurrence of optical limiting in DMMC. An important term in the optical limiting measurement is the limiting threshold. It is defined as the input fluence (or energy) at which the transmittance is 50% of the linear transmittance [40]. The optical limiting threshold value measured from deviation from linearity and the values of some other compounds are given in Table 3. The

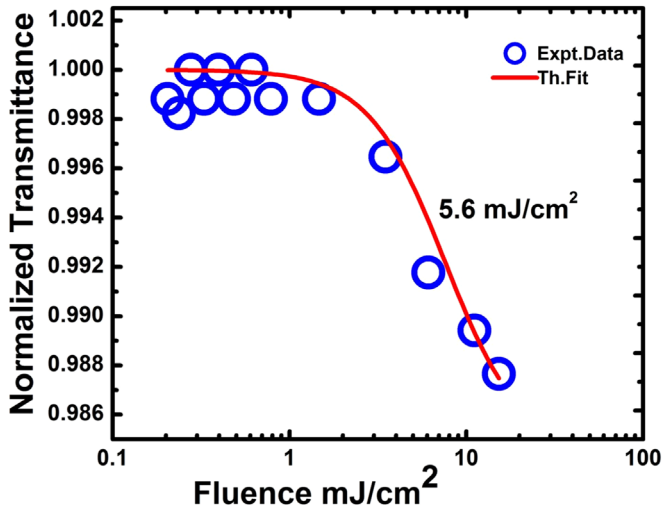


Fig.8. Optical limiting (OL) effect of DMMC in DMF solution as a function of input irradiance under the fs laser excitation. Solid line is theoretical fit to the experimental data.

Table 3
Optical limiting threshold values for different molecules at given laser parameters.

Name of the compound	Pulse width, wavelength	Threshold value (J/cm^2)	Reference
Oleylamine-capped gold nanoparticles	7 ns,1064 nm 7 ns, 532 nm	7.5 0.6	[41]
CNTs	7 ns, 1064 nm 7 ns, 532 nm	10.0 1.0	[41]
PC3	2 ps, 800 nm	11.2×10^{-2}	[42]
Ag PNC films	150 fs, 800 nm	3.8×10^{-2}	[43]
DMMC	150 fs, 800 nm	5.6×10^{-3}	Current work

results suggest that DMMC is the better candidate for the optical limiting application as it has a lower optical limiting threshold. The observed nonlinear absorption, which originates from two photon absorption, is responsible for the optical limiting property.

4. Conclusions

Organic nonlinear optical chalcone derivative DMMC crystallized by solvent slow evaporation technique using acetone solution. The unit cell parameters were calculated from powder X-ray diffraction pattern. The diffraction curve of the high resolution XRD results confirms the crystalline perfection. The crystal has maximum absorption peak at 405 nm in the electronic absorption spectrum and exhibits blue fluorescence emission at 482 nm. We have experimentally investigated the optical nonlinearities of DMF solution of 3, 4,-Drimethoxy-4′-methoxychalcone in the near infrared region. By performing open- and closed-aperture Z-scan experiments, we have observed third-order nonlinearities of this chalcone solution. We have determined all the nonlinear parameters in DMMC molecule, including the 2PA cross-section, second order hyperpolarizability and ESA cross-section. Two- photon absorption contributes to the observed optical-limiting effect for femtosecond laser pulses at 800 nm. The excellent photo physical properties of the DMMC chalcone are indicative of its feasible applications in photonic devices.

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