

# Linear and nonlinear optical absorption characterization of natural laccaic acid dye

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**Abstract** We report on the optical performances of laccaic acid dye in solution at different concentrations and dye–poly(methyl methacrylate) composite thin films. The linear spectral characteristics including optical constants, i.e. refractive index ( $n$ ) and extinction coefficient ( $k$ ), were carried out in a comprehensive way through absorbance, fluorescence and ellipsometric studies. The nonlinear optical parameters such as nonlinear absorption coefficient  $\beta_{\text{eff}}$  (or  $\beta_2$ ), the imaginary third-order susceptibility ( $\text{Im}[\chi^{(3)}]$ ) and the imaginary part of second-order hyperpolarizability ( $\gamma$ ) of the samples were evaluated using the open-aperture Z-scan technique with a laser pulse duration of 10 ns at 532 nm wavelength. The corresponding numerical values of these parameters were of  $10^{-10}$ ,  $10^{-11}$  and  $10^{-32}$  order, respectively. Two-photon absorption was revealed

to be the main driving physical mechanism in the nonlinear response. This suggests that laccaic acid dye can be a potential candidate for NLO materials application.

## 1 Introduction

With the extensive use of sensitive spectrophotometers and high-power lasers in many different applications, much interest is being directed towards the search for materials with linear and nonlinear optical (NLO) applications. Organic materials [1], including natural dyes [1–3] with large NLO responses, are of major interest for their potential applications in optical signal-processing devices, upconversion lasers [4], optical limiting for photo-sensors and human eyes protection from intense laser irradiation [5–8]. Additionally, materials with NLO properties such as broadband spectral response and fast response time are of great importance for realizing optical data storage [9, 10], two-photon microscopy [11] and three-dimensional optical storage micro-fabrication [12]. The design of devices of such typical applications requires physical mechanisms such as multiphoton absorption, nonlinear refraction and reverses saturable absorption, in which strong absorption at the excited state plays a key role. Thus, optical techniques such as absorption, fluorescence and ellipsometric spectroscopy are important tools for the optical properties characterization, while the Z-scan technique [13, 14] is employed for nonlinear absorption (NLA) and nonlinear refraction (NR) properties investigation. Through these techniques, a large number of organic compounds with a conjugated  $\pi$ -electron system have been investigated [16–17]. This includes natural dyes such as anthocyanin, *Bixa orellana*, chlorophyll, carotenoids, betanines [18–21], *Hibiscus sabdarifa* [22]. Recently, Pramodini et al. [23] investigated

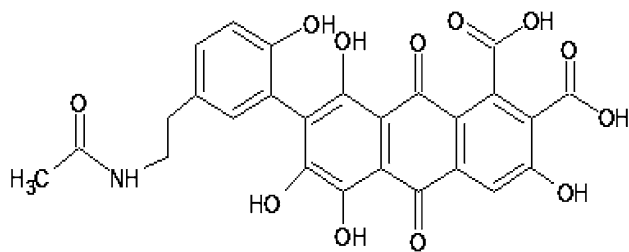
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the NLO and optical properties of anthraquinone dyes and found reverse saturable absorption (RSA) response type. In conjugated organic materials, RSA associated with two-photon absorption (2PA) is the most likely NLO physical mechanism related to the creation of excited states of molecules whose absorption cross sections are larger than that of the ground state. In this paper, we report the linear and nonlinear absorption properties of laccaic acid dye belonging to the family of chromophores with anthraquinone structure based [24, 25].

## 2 Experimental details

The laccaic acid (Mw 537) was purchased from Kremer Pigmente Company (Kremer GmbH) in Germany. The molecular structure of laccaic acid dye shown in Fig. 1 presents an anthraquinone based. Four grades of 0.007, 0.014, 0.02 and 0.03 g were weighted and dissolved in 25 ml of acetone in containers. The solutions were thereafter filtered from residue. The initial concentrations were of  $5.11 \times 10^{-4}$ ,  $1.02 \times 10^{-3}$ ,  $1.44 \times 10^{-3}$  and  $2.02 \times 10^{-3}$  mol/l. For spin-coating purpose, 0.2 g of PMMA (Mw  $\approx$  550,000) powder weighted was mixed with 12 ml of each initial concentration and stirred for 1 h at 45 °C. The final concentration of the mixture was about 0.016 g/ml. Four thin films were therefore prepared at different rpm. The UV–Vis absorption spectra of both solution and thin film samples were recorded in the spectral range of 190–2500 nm using a LAMBDA 950 UV–VIS–NIR spectrophotometer. Fourier transform infrared (FTIR) spectrum of laccaic acid powder was recorded through a Bruker Vertex 70 FTIR unit with a spectral range of 200–4000  $\text{cm}^{-1}$  for qualitative analysis. Fluorescence emission peaks were also recorded under an excitation wavelength of 523 nm using a QuantaMaster™ system. The optical constants refractive index  $n$  and extinction coefficient  $k$  of the thin films were estimated through the Tauc–Lorentz model using a spectroscopic ellipsometer Jobin–Yvon (UVSEL–NIR) in air at room temperature. The nonlinear optical response was examined through the fluence-dependent transmittance measurements using the standard



**Fig. 1** Chemical structure of lac dye under investigation

open-aperture (OA) Z-scan technique employing a CW Nd:YAG laser with 10-ns pulses at 532 nm wavelength. In this particular experiment of Z-scan, the samples were mounted at the focal point during the fluence-dependent transmittance measurement while moving along the propagating direction of the laser beam.

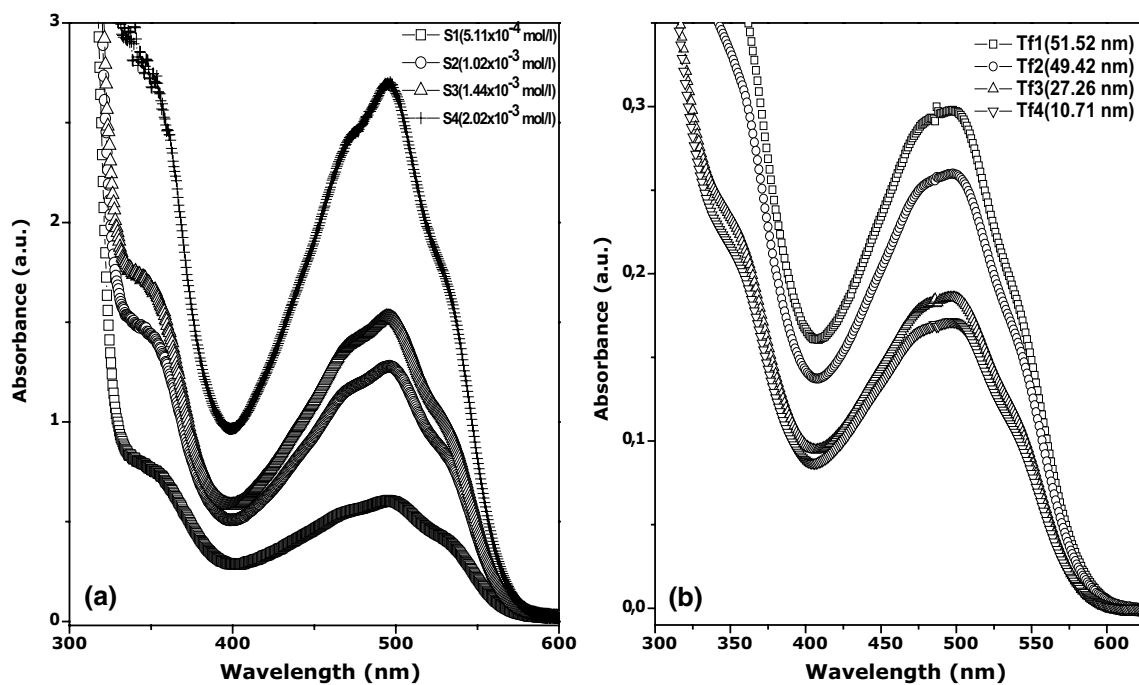
## 3 Results and discussion

### 3.1 Absorption and vibrational spectroscopy

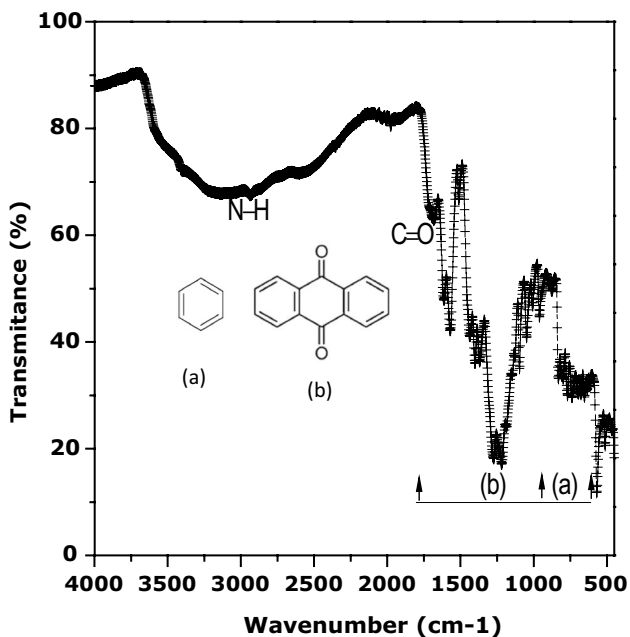
The electronic absorption spectra in both solution and spin-coated thin film samples are presented in Fig. 2a, b, respectively. The absorbance peaks in the liquid samples showed a convolution of peaks at three components at 467, 496 and 530 nm, attributed to the electronic  $\pi \rightarrow \pi^*$  transitions [25]. On the other hand, the thin films present sharp peaks at 485 nm. As shown in Fig. 1, laccaic acid dye contains electron-donating substituents (hydroxyl groups) and carbonyl groups as the acceptors. It is such typical donor–acceptor structure which leads to the electron density transfer through the delocalization mechanism. As a result, the spectral changes are due to the relaxation processes following  $\pi \rightarrow \pi^*$  interband absorption associated with the mobility of the electrons and holes and their highly delocalization. Moreover, the weak absorption signature observed between 325 and 380 nm could be attributed to the  $n \rightarrow \pi^*$  electronic transition in the C=O functional group. The FTIR spectrum of the laccaic acid dye is depicted in Fig. 3. The peak observed at 3117  $\text{cm}^{-1}$  was assigned to the N–H stretching [25]. The absorption signature observed between 3650 and 3000  $\text{cm}^{-1}$  can be assigned to the phenolic OH and OH of the carboxylic acid groups. The vibration modes observed between 1728 and 1000  $\text{cm}^{-1}$  correspond to the anthraquinone-ring-based stretching with the presence of C=O, OH and NHC=O functional groups. The peaks at 1274 and 1200  $\text{cm}^{-1}$  were assigned to the –C–O stretching of primary alcoholic group (–CH<sub>2</sub>–OH) and COOH group [25–27], respectively. The series of weak bands observed between 2000 and 1700  $\text{cm}^{-1}$  can be attributed to simple aromatic group. The C–H bending vibration observed between 850 and 670  $\text{cm}^{-1}$  can be used to sustain the presence of aromatic compound. The intramolecular H bonds resulting from the functional groups may induce a shift of each normal vibration band, making a difficult and complete interpretation of the vibrational modes of the laccaic acid molecule.

### 3.2 Fluorescence

Room-temperature fluorescence studies were carried out in both solutions and thin films as shown in the corresponding



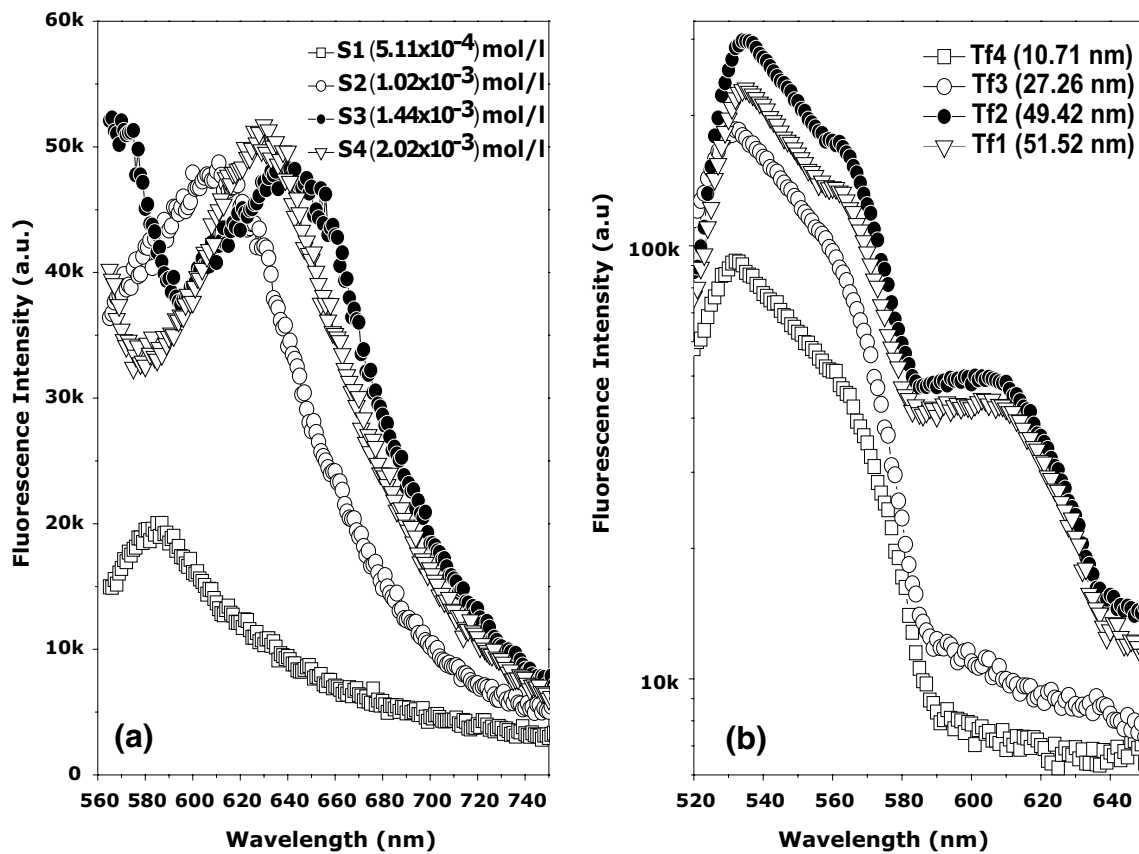
**Fig. 2** UV-visible absorption spectrum of **a** laccaic acid dye solution at different concentrations and **b** laccaic acid dye-PMMA composite thin film at different thicknesses



**Fig. 3** FTIR spectrum of laccaic acid in acetone with 10<sup>-3</sup> M concentration

spectra in Figs. 4a and 5b, respectively. The visible absorption spectra can be interpreted as an allowed  $\pi \rightarrow \pi^*$  interband transition yielding electrons and holes in the conduction and valence bands, respectively [28, 29]. With

ultraviolet or visible light, fluorophores in the dye molecule are excited to higher vibrational levels of the first or second singlet energy state. Therefore, the fluorescence emission occurs from the singlet electronic excited states to an allowable vibrational level in the electronic ground state [30]. Correlating the electronic absorption peaks to the emission peaks, a shift to longer wavelength can be observed. In other terms, the fluorescence emission peaks in both solution and thin film samples are red-shifted compared to those of the UV-Vis spectra. Although there is a similarity between the solution and thin film absorption spectra, a considerable difference between their fluorescence emission spectra can be observed. With increasing absorption, that is, with a decreasing energy difference between the excited and ground state, the number of options to get rid of the excited-state energy by radiationless deactivation increases. Hence, most known stable and bright fluorophores in the dye chromophore absorb and emit in the wavelength range between 300 and 700 nm [31]. Upon excitation to higher excited singlet states, molecules relax through internal conversion to higher vibrational levels of the first excited singlet state. If return transitions to the ground state ( $S_0$ ) usually occur to a higher vibrational level, which subsequently reaches thermal equilibrium, then both vibrational relaxation and internal conversion cause heating of the solvent as the dye molecules in a high vibrational level of the triplet state can lose energy through collisions with solvent molecules [31, 32], which emission response



**Fig. 4** **a** Fluorescence spectra of laccaic acid dye in solution at different concentrations and **b** thin films at different thicknesses of 51.52, 49.42, 27.26, 10.71 nm

would differ from that of thin film where the solvent is evaporated. Moreover, the extra peaks may arise from the host polymer which could blend the dye donor and acceptor systems, leading to the enhancement of the emission.

### 3.3 Linear optical parameters determination

Figure 5 shows spectroscopic ellipsometry data from the spin-coated thin films of laccaic acid dye–PMMA composite of 2000, 4000, 6000 and 8000 rpm. The corresponding thicknesses are of 51.52, 49.42, 27.26, 10.71 nm. The refractive index ( $n$ ) and extinction coefficient ( $k$ ), commonly called optical constants [33] were evaluated using Drude-Lorentz oscillator models in which the complex dielectric function is described by [33–35]:

$$\varepsilon_{\text{TL}} = \varepsilon_{r,\text{TL}} + i \cdot \varepsilon_{i,\text{TL}}$$

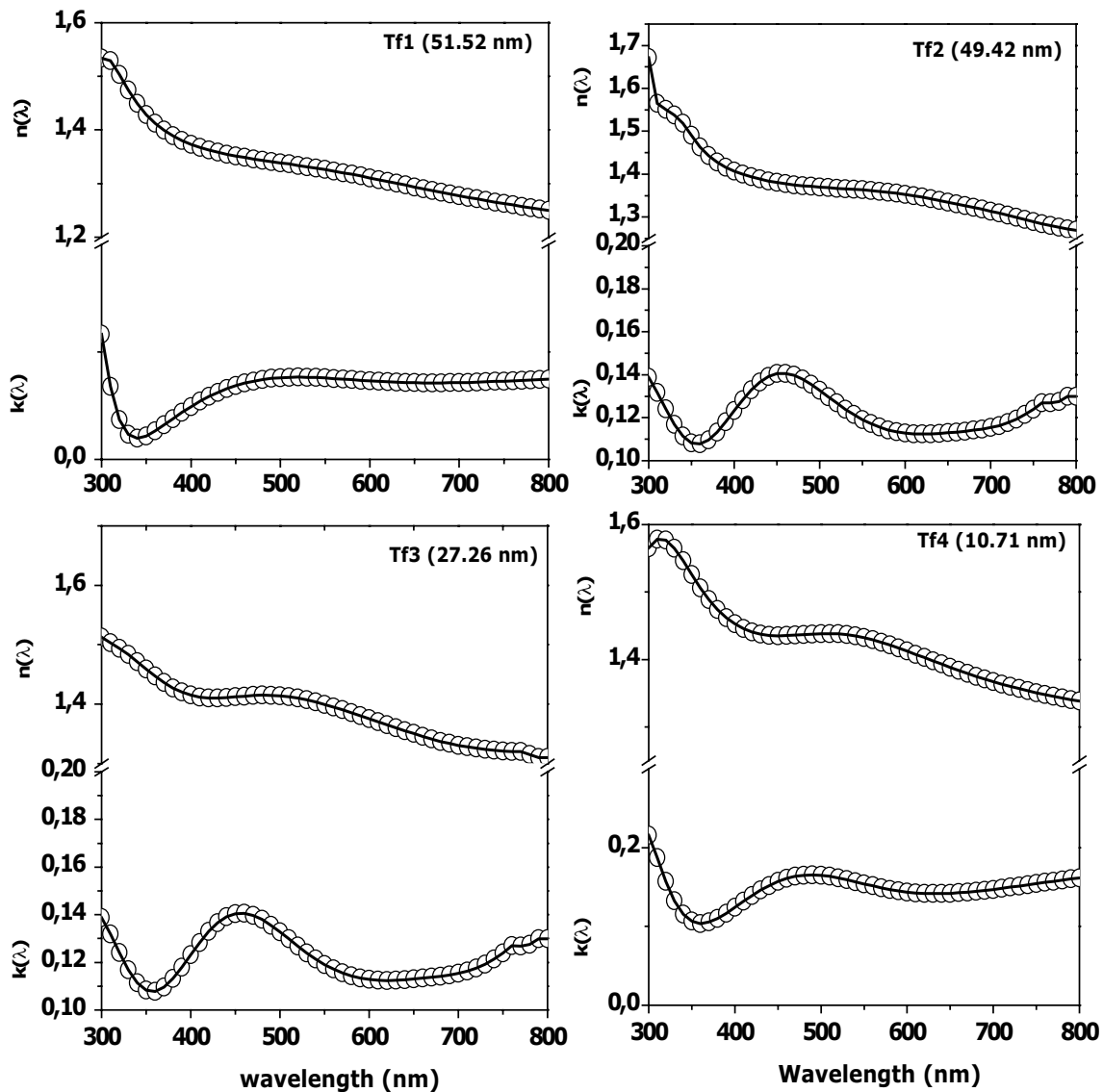
where

$$\varepsilon_{r,\text{TL}} = \varepsilon_{\infty} + \sum_{j=1}^N \frac{2}{\pi} \cdot P \int_{E_g}^{\infty} \frac{\xi \cdot \varepsilon_i(\xi)}{\xi^2 - E^2} d\xi \quad (1)$$

and

$$\varepsilon_{i,\text{TL}} = \begin{cases} \sum_{j=1}^N \frac{1}{E} \cdot \frac{A_j \cdot E_j \cdot C_j \cdot (E - E_g)^2}{(E^2 - E_j^2)^2 + C_j^2 E^2} & \text{for } E < E_g \\ 0 & \end{cases}$$

where  $\varepsilon_{\infty}$  is the high-frequency dielectric constant.  $P$  is the Cauchy principal part of the integral.  $E_j$  is the peak transition energy,  $E_g$  is the optical band gap,  $C_j$  is the brooding term, and  $A_j$  is proportional to the transmission probability matrix element. The derived dispersion relations of the linear refractive index and the extinction coefficient as a function of the wavelength are displayed in Fig. 5. It can be seen that the refractive index ( $n$ ) continuously decreases with the increased wavelength. However, the extinction coefficient for Tf1 increases from 345 up to 500 nm and becomes constant above 500 nm. For thin films Tf2, Tf3 and Tf4, the extinction coefficients are dominated by a peak in the near-visible/blue region of the spectrum. A closer inspection shows that the extinction coefficient spectra for Tf2 and Tf3 are the same, while their refractive indices spectra at longer wavelength differ. Above 600 nm, we can observe a relative increasing extinction coefficient ( $k$ ) (except in Tf1), whereas no absorption peak is observed in the UV–Vis absorption spectra. All these observations suggest that



**Fig. 5** Variation of linear refractive index and extinction coefficient as a function of the wavelength ( $\lambda$ ) of four thin films at different rpm of 2000, 4000, 6000 and 8000 with corresponding thicknesses of 51.52, 49.42, 27.26, 10.71 nm, respectively

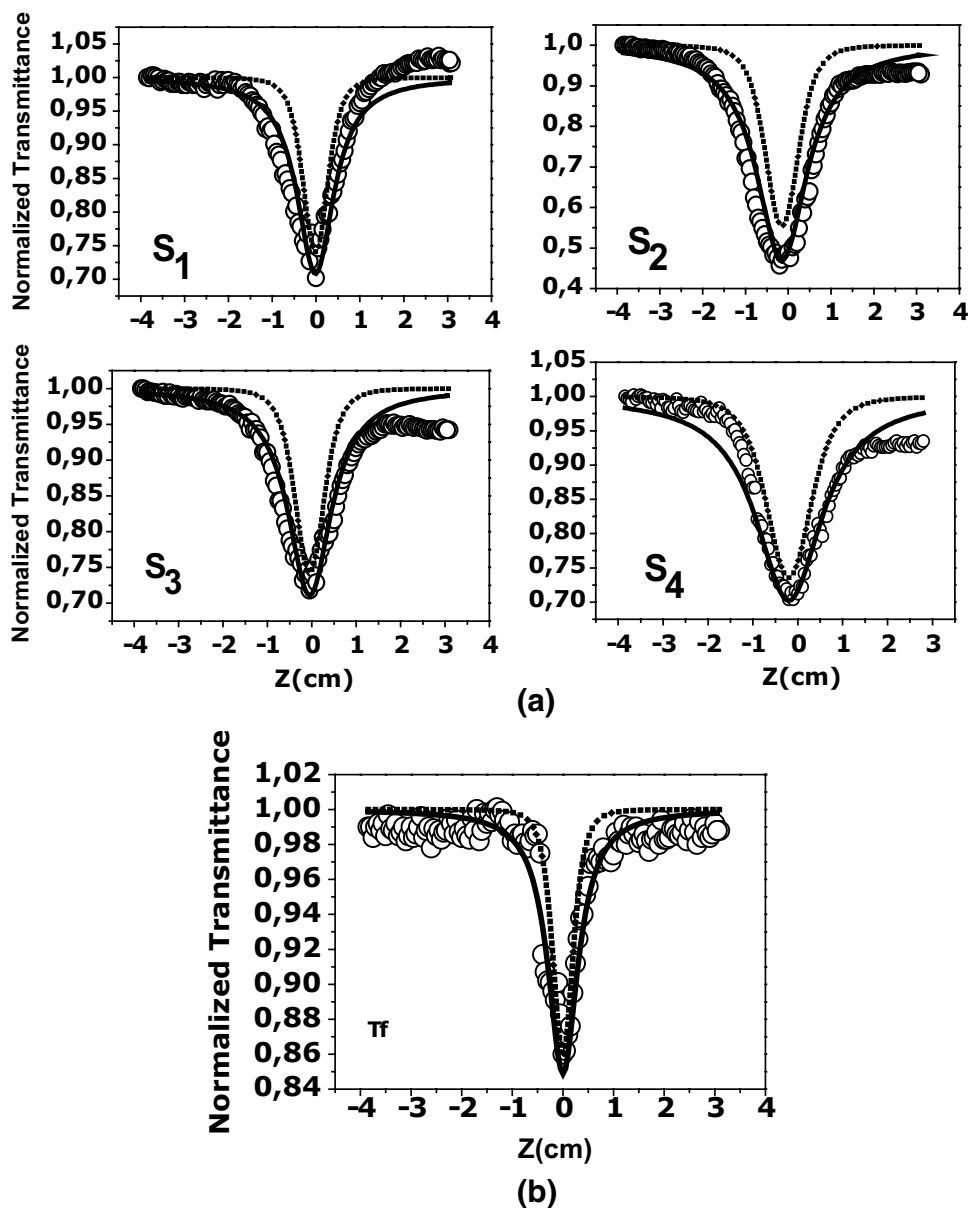
the electron-donating character of auxochromes of the laccaic acid dye and, hence the steric effects do not prevent the electronic  $\pi$ -stacking interactions with the backbone [36]. Moreover, there should also be a contribution of increased reflection losses caused by the changes in the refractive index. Another possible explanation could be associated with the substrate transparency. As the substrate is transparent, then it is possible for some of the light to be reflected from the back surface of the substrate into the detector [37], hence influencing the extinction coefficient results. From the plot of refractive index and coefficient of extinction versus the thickness (not shown here), the minimum and maximum values are 1.32 and 1.43 for the refractive index and 0.06 and 0.15 for the coefficient of extinction,

respectively. This shows that these parameters are thickness dependent.

### 3.4 Nonlinear optical absorption

The nonlinear absorption parameters were evaluated through the open-aperture Z-scan technique. Different processes such as two-photon absorption (TPA), saturable absorption (SA), reverse saturable absorption (RSA), transient absorption, free carrier interband absorption and nonlinear scattering are reported to be operative in the nonlinear absorption response. In the open-aperture Z-scan measurements, the Z-scan data exhibiting a peak shape will describe saturable absorption (SA) effect, while those showing a valley will be

**Fig. 6** Open-aperture Z-scan signature at 532 nm of laccaic acid dye solution ( $S_1$ – $S_4$ ) in (a) and dye–PMMA composite thin film (Tf) in (b). The *filled circles* represent the experimental data, while the *solid line* and the *dash-dot* are the fitted 2PA and 3PA, respectively



a signature of a reverse saturable absorption (RSA) process. Figure 6 shows the open-aperture Z-scan measurements on laccaic acid dye samples in solution and dye–PMMA composite thin film. It can be seen that the value of transmittance decays from the maximum absorbance value when the sample moves away from the pump beam focus. It can also be noticed that, as the input energy of the pumping beam increases, the transmittance value exhibits saturation far from the focus, in both negative and positive Z-position [38]. Therefore, one can accordingly deduce that the RSA process is likely to describe the observed nonlinear absorption of the laccaic acid dye. To confirm two or more photon absorption as main driving physical process, the experimental Z-scan data were fitted using the relation established by Sutherland [39]. The experimental data and numerical

**Table 1** Summary of numerical values of the nonlinear optical parameters of laccaic acid dye

Sample	$\beta_2 \times 10^{-10}$ (m/W)	$\text{Im}[\chi^{(3)}] \times 10^{-11}$ (esu)	$\gamma \times 10^{-32}$ (esu)
$S_1$	6.29	1.86	3.84
$S_2$	33.27	9.86	10.22
$S_3$	21.47	6.37	4.68
$S_4$	40.24	11.93	6.24
Thin film	$35.41 \times 10^{-1}$	10.49	$5.89 \times 10^{-1}$

simulations are shown in Fig. 6. The NLA coefficient ( $\beta_2$ ), the imaginary part of the third-order susceptibility ( $\text{Im}[\chi^{(3)}]$ ) and the second-order hyperpolarizability ( $\gamma$ ) were evaluated, which the numerical are summarized in Table 1.

Based on the fitting model [39–41], 2PA is found to be more consistent. Therefore, we propose 2PA as main physical mechanism process involved in the nonlinear response of our dye material. From the interesting NLA results observed, laccaic acid dye could be potential for applications such as optical limiters and optical data storage devices.

## 4 Conclusion

We have investigated the linear and nonlinear optical properties of laccaic acid dye. From the absorption spectroscopy analysis, it was found that the linear properties are concentration and thickness dependent. Nonlinear optical parameters  $\beta_2$ ,  $\text{Im}[\chi^{(3)}]$  and  $\gamma$  calculated through the open-aperture (OA) Z-scan technique were of  $10^{-10}$ ,  $10^{-11}$  and  $10^{-32}$  order, respectively. The achieved values of  $\gamma$  in the solutions were of 10<sup>-1</sup> order of magnitude compared to that of anionic 3-dicyanomethylen-5,5-dimethyle-1-[2-(4-hydroxyphenyl)ethenyl]-cyclohexene (**1**) in Ref. [42]. The study also reveals two-photon absorption to be consistent physical mechanism describing the nonlinear optical response of the laccaic acid dye. These results suggest that our material could be interesting candidate for photonic nonlinear applications.

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