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## Z-SCAN & OPTICAL LIMITING PROPERTIES OF HIBISCUS SABDARIFA DYE

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<b>Corresponding Author:</b>	Malek Maaza, PhD NRF Somerset West, western Cape Province SOUTH AFRICA
<b>Corresponding Author Secondary Information:</b>	
<b>Corresponding Author's Institution:</b>	NRF
<b>Corresponding Author's Secondary Institution:</b>	
<b>First Author:</b>	Malek Maaza, PhD
<b>First Author Secondary Information:</b>	
<b>Order of Authors:</b>	Malek Maaza, PhD Abdel Diallo, PhD Sid Zongo, PhD Patience Mthunzi, PhD Wole Soboyejo, PhD Siham Elqaradawi, PhD Seif Rehman, PhD
<b>Order of Authors Secondary Information:</b>	
<b>Abstract:</b>	The intensity-dependent refractive index $n_2$ and the nonlinear susceptibility $\chi^{(3)}$ of Hibiscus Sabdariffa dye solutions in the nanosecond regime at 532 nm are reported. More precisely, the variation of both $n_2$ and $\chi^{(3)}$ versus the natural dye extract concentration has been carried out by Z-scan and optical limiting techniques. The third-order nonlinearity of the Hibiscus Sabdariffa dye solutions was dominated by nonlinear refraction, which leads to strong optical limiting of laser.
<b>Suggested Reviewers:</b>	C Pradeep , PhD Head, Cochin University of Science and Technology, pradeep@photonics.cusat.edu World expert in the field  Marian Marciniak, PhD Director , Institut of Telecommunication M.Marciniak@itl.waw.pl World expert in Lasers & NLO  Papita Das Papita Das Saha, PhD Head, National Institute of Technology Durgapur papitasaha@gmail.com World expert in the field of NLO in natural dyes and their applications  Bouchta Sahraoui, PhD Director , Université d'Angers bouchta.sahraoui@univ-angers.fr Expert in the NLO field and materials for photonics

# Z-SCAN & OPTICAL LIMITING PROPERTIES OF HIBISCUS SABDARIFA DYE

**A. Diallo<sup>1-2</sup>, S. Zongo<sup>1-2</sup>, P. Mthunzi<sup>1-3</sup>, S. Rehman<sup>1-2</sup>, S.Y. Alqaradawi<sup>1-2</sup>, W. Soboyejo<sup>4</sup>, M.  
Maaza<sup>1-2</sup>**

<sup>1</sup>UNESCO-UNISA Africa Chair in Nanosciences/Nanotechnology, College of Graduate Studies,  
University of South Africa (UNISA), Muckleneuk ridge, POBox 392, Pretoria-South Africa,

<sup>2</sup>Nanosciences African Network (NANOAFNET), iThemba LABS-National Research Foundation, 1 Old Faure  
road, Somerset West 7129, POBox 722, Somerset West, Western Cape Province, South Africa,

<sup>3</sup>Council for Scientific and Industrial Research, P O Box 395, Pretoria 0001, South Africa,

<sup>4</sup>Mechanical & Aerospace Engineering, Faculty of Engineering, Princeton University, Princeton, NJ 08544,  
USA.

Corresponding author: Maaza@tlabs.ac.za

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## **Abstract**

The intensity-dependent refractive index  $n_2$  and the nonlinear susceptibility  $\chi^{(3)}$  of Hibiscus Sabdariffa dye solutions in the nanosecond regime at 532 nm are reported. More precisely, the variation of both  $n_2$  and  $\chi^{(3)}$  versus the natural dye extract concentration has been carried out by Z-scan and optical limiting techniques. The third-order nonlinearity of the Hibiscus Sabdariffa dye solutions was dominated by nonlinear refraction, which leads to strong optical limiting of laser.

## 1-INTRODUCTION

Similarly to the so called poled organic materials which are asymmetric organic molecules with a large molecular hyperpolarizability due to their electron delocalization along the conjugated backbone [1-2], specific natural dyes have been found to exhibit very attractive nonlinear optical (NLO) characteristics with nonlinear coefficients  $10^4$ – $10^6$  times higher than that of  $\text{CS}_2$ . This natural dye family includes Chlorophyll, red Carmine, Chinese tea and betanin, Hibiscus Sabdariffa as well as, recently, functionalized DNA [2-5]. Concerning the Hibiscus Sabdariffa dye which is the focus of this contribution, its NLO characteristics are due to the high population of delocalized  $\pi$ -electrons within their anthocyanin skeleton leading to a large 3<sup>rd</sup> harmonic generation and two-photon absorption phenomena including the appealing intensity dependent refractive index and optical limiting as it will be confirmed in this contribution.

Hibiscus Sabdariffa Rosella is an annual shrub that grows in tropical and subtropical regions including West of Africa. The seedpods are enclosed in red fleshy calyces which are commonly used for making food and tea as well as for several bio and phytochemicals applications in relation to its antioxidant properties [6-8]. The calyx of Hibiscus Sabdariffa L. (Roselle) is originally of a deep red colour. This red colouring component is very soluble in  $\text{H}_2\text{O}$  and changes to fine red by HCl and by alkali to bluish green indicating the presence of anthocyanin cycles. The two major anthocyanin cycles are: delphinidin 3-xylosylglucoside (also called delphinidin 3-sambubioside or hibiscin) and cyanidin 3-xylosylglucoside (also called cyanidin 3-sambubioside or gossypicyanin). As illustrated in Figure 1, Hibiscus Sabdariffa's anthocyanin is glycosylated in the 3-position with the chemical structure given as: delphinidin-3-O-(2-O-d-xylopyranosyl)-d-glucopyranoside (R=OH,1), cyanidin-3-O-(2-O-d-xylopyranosyl)-d-glucopyranoside (R =H, 2) [9-10].

From nonlinear optical viewpoint, Henari et al have reported the first experimental observation of self-action phenomena, such as self-phase modulation and beam fanning in a Roselle-Hibiscus Sabdariffa solution for a fixed concentration. This natural dye has been found to be an attractive novel type of organic nonlinear media, with a large negative nonlinear refractive index of about  $n_2 \sim 1.0 \cdot 10^{-4}$  esu, likely from a thermal origin [3]. Relatively to Henari et al's pioneering work on NLO properties of Hibiscus Sabdariffa Roselle's dye under Argon laser radiations ( $\lambda = 514$  nm), this contribution reports on complementary z-scan as well as optical limiting properties of such natural dye solutions versus a wide concentration range with a doubled Q-switched Nd:YAG laser source in the nanosecond regime. More precisely, the coefficient of the intensity-dependent refractive index  $n_2$  ( $n = n_0 + n_2 I$ ), the 3<sup>rd</sup> order nonlinear susceptibility  $\chi^{(3)}$  ( $n_2 n_0^2 / 12 \pi^2 = \chi^{(3)}$ ) and the optical limiting thresholds are presented [11].

## 2-EXPERIMENTS & DISCUSSION

As mentioned previously, Hibiscus Sabdariffa-Roselle calyces contain high amounts of anthocyanins, especially delphinidin-3-sambubioside and cyanidin-3-sambubioside, and this up to 2.5 g/100 g DW [13-14]. Based on the work of Cisse et al related to the kinetics and modeling of the aqueous extraction of the

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4 anthocyanins from the calyces, fresh calyces were collected and immersed in H<sub>2</sub>O solutions for a swift surface  
5 cleaning. The original collected calyces material were dried under sunny conditions at ambient temperature  
6 and then ground with an electric mill of ~1mm in mesh. 5 extracts were prepared in a fixed volume of de-  
7 ionised H<sub>2</sub>O for 48 h each (0.5 l, 25°C). The initial mass of the milled calyce powders were 0.5, 2, 4, 6 and 8g.  
8 The liquid extract samples which were filtered twice eliminate nano-scaled residual solids if any. The samples  
9 will be designed as S<sub>1/2</sub>, S<sub>2</sub>, S<sub>4</sub>, S<sub>6</sub> and S<sub>8</sub> where the subscript “i” in S<sub>i</sub> is the used mass during the extraction  
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17 Figure 2 reports the room temperature optical UV-VIS-NIR spectra of the 5 liquid solutions through a quartz  
18 cell of 10 mm in thickness. Excluding the slight absorption band centered around 962 nm which is due to H<sub>2</sub>O  
19 vibrational modes, 2 major regions can be distinguished; 200-≤500 nm and ≥ 500 nm. While the optical  
20 transmission of the concentrated samples is low in the 1<sup>st</sup> spectral region of 200≤ λ ≤500 nm, the less  
21 concentrated one i.e S<sub>1/2</sub> does exhibit a large absorption band (~347- ~513 nm) which is in fact a  
22 convolution of at least 3 peaks. These latter peaks can be assigned to π-π\* and σ- π\* transitions. While the  
23 optical transmission is nearly 90% for all samples above 500nm, there is a redshift in the cut-off wavelength  
24 as the concentration increases. Consequentially, and considering such optical transmission profiles, Hibiscus  
25 Sabdariffa solutions are, a priori, attractive materials for optical limiting applications for a wide variety of laser  
26 sources whose wavelengths lie in the visible region.  
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34 The linear refractive indices of these liquid solution samples were measured using an Abbe type refractometer  
35 while their UV-VIS-NIR spectra were recorded using a CECIL scanning spectrophotometer (model 2021). The  
36 nonlinearity optical properties, in addition to the optical limiting, were investigated by Z-scan technique which  
37 has the advantages of simplicity and high sensitivity, as well as enabling simultaneous measurement of the  
38 magnitude and sign of the nonlinear refractive index and the nonlinear absorption coefficient of the samples  
39 [15-16]. Basically, the method consists of translating a sample through the focus of a Gaussian beam and  
40 monitoring the changes in the far field intensity pattern (Figure 3). When the intensity of the incident laser  
41 beam is sufficient to induce nonlinearity in the sample, it either converges or diverges the beam, depending on  
42 the nature of that nonlinearity. By moving the sample through the focus, the intensity dependent absorption is  
43 measured as a change of transmittance through the sample (open aperture). The nonlinear refraction is  
44 determined by the intensity variation at the plane of a finite aperture placed in front of the detector (closed  
45 aperture), as the sample itself acts as a thin lens with varying focal length as it moves through the focal plane.  
46 A standard Q-switched Nd:YAG laser with a pulse width of 8 ns at 532 nm and a pulse repetition rate of about  
47 10 Hz was used as an excitation source. The laser beam with a Gaussian intensity profile, was focused by  
48 using a lens of focal length ~50 mm, into the sample solution contained in a ~1 mm standard quartz cuvette.  
49 The resulting beam spot at the focus was about 30 μm. The corresponding Rayleigh length, derived from the  
50 formula  $z_R = \pi w_0^2/\lambda$ , was found to be ~1.33 mm. Consequentially, and as the sample thickness of 1 mm is  
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4 less than the Rayleigh length, it can be treated as a thin medium and hence ensuring the validity of the Z-scan  
5 investigations. The Z-scan was performed at a laser power of 5mW, which resulted in an average fluence of  
6 7.1 GW/m<sup>2</sup>. The optical limiting measurements were performed keeping the sample at the focal point and  
7 varying the input energy while recording the output energy without placing the aperture in front of the  
8 detector. In order to avoid cumulative thermal effect, the data were collected in a single shot mode.  
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14 Figure 4 reports the closed aperture Z-scan measurements carried out at room temperature on the single  
15 beam set up (described in Figure 3) for the determination of the NLO the coefficient of the intensity-dependent  
16 refractive index  $n_2$  and the 3<sup>rd</sup> order nonlinear susceptibility  $\chi^{(3)}$  as well as the optical limiting investigations. In  
17 the Z-scan investigations [15-16], each Hibiscus Sabdariffa solution sample in a ~1 mm thickness quartz cell  
18 is scanned along the optical axis (z -direction) of the focused Gaussian laser beam, around its focus. The high  
19 intensity of the electromagnetic field in this region induces on the sample a non-linear lensing of variable focal  
20 length. This causes a refractive divergence or convergence of the laser beam, depending on the sample  
21 position relative to the beam focus and the sign of the non-linearity. The resulting variations in the beam  
22 radius within the closed aperture and therefore the normalized transmission of the irradiance in the far field are  
23 able to give adequate information for the calculation of the refractive index non-linearities. More precisely, the  
24 normalized transmission of the irradiance in the far field is given approximately by  $\Delta T(z, \phi) = 1 - \Delta\phi_0 \times$   
25  $/[(x^2+1)(x^2+9)]$  with  $x = z/z_R$  and  $\Delta\phi_0$ , the on-axis phase change at the laser beam focus [15-16]. More  
26 precisely, the parameter  $\Delta\phi_0(t)$  is the on-axis phase shift induced to the beam by the refractive non-linearities  
27 of the material, and hence it is related to the refractive index change at the focus  $\Delta n_0(t) = n_2$  by the relation  $n_2$   
28  $= \lambda |\Delta\phi_0| / (2\pi L_{\text{eff}} I_0)$  with where  $I_0$  is the intensity of the laser beam at focus ( $z = 0$ ),  $\lambda$  is the laser source  
29 wavelength,  $L_{\text{eff}}$  is the effective thickness of the sample ( $L_{\text{eff}} = [1 - \exp(-\alpha L)] / \alpha$ ,  $L$  is the of the sample  
30 thickness length while  $\alpha$  is the linear absorption coefficient). Moreover, and due to the mathematical  
31 formulation of the normalized transmission  $\Delta T(z, \phi)$  which presents an asymmetry versus  $z$ ,  $n_2$  is directly  
32 related to the difference between the normalized peak, and valley transmittances,  $\Delta T_{p-v} = T_p - T_v$ . Such a  
33 quantity is given by  $\Delta T_{p-v} = 0.406 (1 - S)^{0.25} |\Delta\phi_0|$  [17]. Figure 4 reports such characteristic asymmetric profiles  
34 of the various Hibiscus Sabdariffa liquid solutions for the Q-switched Nd:YAG laser radiations (532 nm). It  
35 can be observed that the difference peak-to-valley transmission  $\Delta T_{p-v}$  as well as the corresponding peaks' width  
36 increase with the dye concentration. The dashed line superposed on the  $S_8$  z-scan profile is a typical simulation  
37 curve allowing the determination of  $n_2$  and  $\chi^{(3)}$  of the various Hibiscus Sabdariffa liquid solutions and hence  
38 their concentration evolution. Table 1 summarizes the corresponding values while Figure 5 reports their  
39 variation with the concentration. Accordingly, one could then generalize the remark by Henari et al on the  
40 large value of  $n_2$  of the Hibiscus Sabdariffa dye solution that they have investigated for a fixed concentration  
41 (The concentration by weight of their sample solution was  $2.02 \cdot 10^{-2}$ ). The current  $n_2$  values are all larger by  
42 one order of magnitude than the value reported for the Chinese tea and thermotropic liquid crystals [18-19],  
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and much larger, indeed than that the reported values for photorefractive crystals, liquid crystals, and fullerenes [20-21]. Both the  $n_2$  and  $\chi^{(3)}$  obtained values are equivalent to those of Rekha and Ramalingam obtained on Carmine ( $C_{22}H_{20}O_{13}$ ) and Safranin O ( $C_{20}H_{19}N_4Cl$ ) natural dye solutions with a similar, yet a CW Nd-YAG laser source emitting at 532 nm [2,22]. As illustrated in Figure 5, there is an increasing trend for the values of  $n_2$  and  $\chi^{(3)}$  as the concentration increases. This should be attributed to the fact that the dye molecules' population increases with the concentration and therefore more thermally agitated particles resulting in an enhanced effect. The negative sign of the closed z-scan profiles is indicative of the dominance of the thermo-optic effect. Moreover, as a similar behaviour is observed in a continuous mode (CW Nd:YAG), the observed optical nonlinearity of the various Hibiscus Sabdarifa dye solutions is likely to be of a thermal origin indeed, arising from the temperature dependence of the refractive index. The phase of the propagating beam would be distorted due to the presence of this thermal lens. Moreover, based on Figure 4, one could deduce that the peak-valley difference for all investigated samples is  $\geq 14$  mm i.e. nearly 10 times Rayleigh range and hence confirming the presence of the thermal component; it is well established indeed that a peak-to-valley separation larger than  $1.7 z_R$  is an indication of a Kerr type of nonlinearity [17]. As it was concluded in the above mentioned natural dyes of Carmine and Safranin O, the organic dyes in solvent will have a tendency to form non-fluorescent dimers optimizing the conversion of the absorption energy into heat [23]. With increasing dye concentration there is an increase in dimer concentration. Such dimers are expected to absorb light inducing eventually a rise in the temperature of the medium. If the observed nonlinearity in the various Hibiscus Sabdariffa-H<sub>2</sub>O solutions is of a Kerr type in the nanosecond regime, it would certainly be of an additional nature in the pico and sub-pico regimes. As pointed out by Zhang et al and He et al [24-25] in their studies of Chinese tea dye solutions with both a He-Ne and a CW mode locked Nd:YAG (532 nm, 70ps) lasers, the large observed nonlinearity was attributed to the pull of higher refractive index molecules into regions of high optical density by light pressure as well as to their reorientation and redistribution in the tea dye solution.

**Table 1:** Major derived nonlinear parameters of the Z-scan and optical limiting studies

<b>Sample</b>	<b>Conc.</b> <b>(g/l)</b>	$\Delta T_{p-v}$	$n_2$ <b>(<math>10^{-4}</math> esu)</b>	$\chi^{(3)}$ <b>(<math>10^{-6}</math> esu)</b>	<b>&lt;Saturated output power&gt;</b> <b>(mW)</b>	<b>&lt;Threshold input power&gt;</b> <b>(mW)</b>
<b>S<sub>1/2</sub></b>	0.5	0.12	1.31	05.77	2.67	31.69
<b>S<sub>2</sub></b>	2	0.15	1.63	07.18	2.70	22.86
<b>S<sub>4</sub></b>	4	0.19	2.07	09.12	2.14	20.38
<b>S<sub>6</sub></b>	6	0.23	2.50	11.16	1.86	18.96
<b>S<sub>8</sub></b>	8	0.34	3.70	16.52	1.66	14.60

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8 During the z-scan investigations, and high peak intensities closer to the focus ( $z^{\pm} \sim 0\text{mm}$ ), one could observe  
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10 diffraction type pattern with concentric ring structures which are likely to be caused by self-phase modulation  
11 as in the case of Henari et al. Hence for the optical limiting studies which were conducted on the 5 Hibiscus  
12 Sabdariffa solutions, the 1 mm quartz cell containing the dye solution was placed away from the focus. Figure  
13 6 shows the corresponding optical limiting profiles within the range of 0-40 mW for the laser beam input  
14 power. One could distinguish 2 typical regions; in the first one i.e. linear regime, the output power varies  
15 linearly with the input power according to Lambert-Beer law while for the second region, the output power  
16 goes through a plateau. The value of this latter is very low relatively to the input power and seems not to  
17 exceed 3.0 mW for an input as high as 40 mW. The values of the threshold input power for the various dye  
18 solutions have been estimated as 31.69, 22.86, 20.38, 18.96 and 14.60 mW for  $S_{1/2}$ ,  $S_2$ ,  $S_4$ ,  $S_6$  and  $S_8$   
19 respectively (Table 1). Consequentially, the optical limiting effect is enhanced and the transmittance decreases  
20 with increasing the concentration as more molecules per unit volume participate in the laser-dye cycles  
21 interaction during nonlinear absorption. The trend of Figure 6 clearly indicates that the optical limiting  
22 behaviour of the Hibiscus Sabdariffa Roselle originates from reverse saturable absorption. It is noteworthy to  
23 notice that the observed optical limiting in of the Hibiscus Sabdariffa solutions is similar to that of synthetic  
24 long conjugated organics with different  $\pi$ -electron conjugation bridge structures as reported by Guang et al  
25 [27].  
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### 39 **3-CONCLUSION**

40 This contribution reported on the variation of the z-scan and optical limiting properties of Hibiscus Sabdariffa  
41 Roselle extract dye solutions versus concentration in the nanosecond regime. The obtained  $n_2$  values are all  
42 larger by one order of magnitude than the values reported for the thermotropic liquid crystals, photorefractive  
43 crystals, liquid crystals, and fullerenes. Both the  $n_2$  and  $\chi^{(3)}$  obtained values are of the same order than those  
44 obtained on other natural dye extracts such Carmine ( $C_{22}H_{20}O_{13}$ ) and Safranin O. The negative sign of the  
45 closed z-scan profiles as well as the spatial z-extension of the corresponding peak/valley are indicative of the  
46 dominance of a thermo-optic effect and hence the thermal origin of the observed optical nonlinearity which is  
47 of reverse saturable absorption type in view of the optical limiting trend. It is suggested to perform identical  
48 studies in the femtosecond regime with a beam shaped laser source[26].  
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## **6. FIGURE CAPTIONS**

### **Figure 1:**

Structure of Hibiscus sabdariffa anthocyanins: delphinidin-3-O-(2-O--d-xylopyranosyl)-\_d glucopyranoside (R = OH, 1), cyanidin 3-O-(2-O-\_dxilopyranosyl)--d-glucopyranoside (R =H, 2).

### **Figure 2:**

UV-VIS-NIR optical transmittance of the various Hibiscus Sabdariffa Roselle dye extract solutions contained in 10 mm quartz cell.

### **Figure 3:**

Z-scan arrangement for the closed aperture measurements of the various Hibiscus Sabdariffa Roselle dye extract solutions contained in 1 mm quartz cell.

### **Figure 4:**

Closed aperture Z-scan measurements of the various Hibiscus Sabdariffa Roselle dye extract solutions contained in 1 mm quartz cell. The Rayleigh length is about 1.33 mm.

### **Figure 5:**

Variation of the nonlinear refractive index  $n_2$  and the 3<sup>rd</sup> order nonlinear optical susceptibility  $\chi^{(3)}$  of the Hibiscus Sabdariffa Roselle dye extract solutions; Q-switched Nd:YAG radiation at 532 nm with a pulse width of 8 ns and pulse repetition rate of about 10 Hz.

**Figure 6:**

Optical limiting profiles of the various Hibiscus Sabdariffa Roselle dye extract solutions contained in 1 mm quartz cell. To avoid the observed diffraction caused by self-phase modulation, the quartz cell containing the dye solution was placed away from the focus.

FIGURE 1

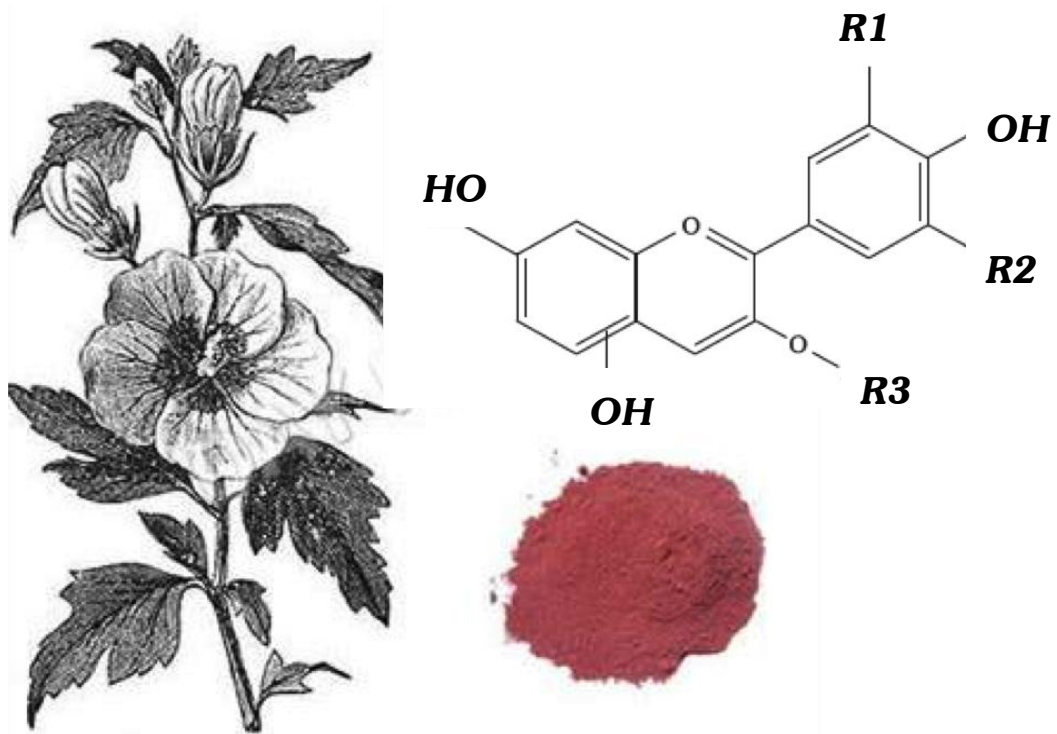


FIGURE 2

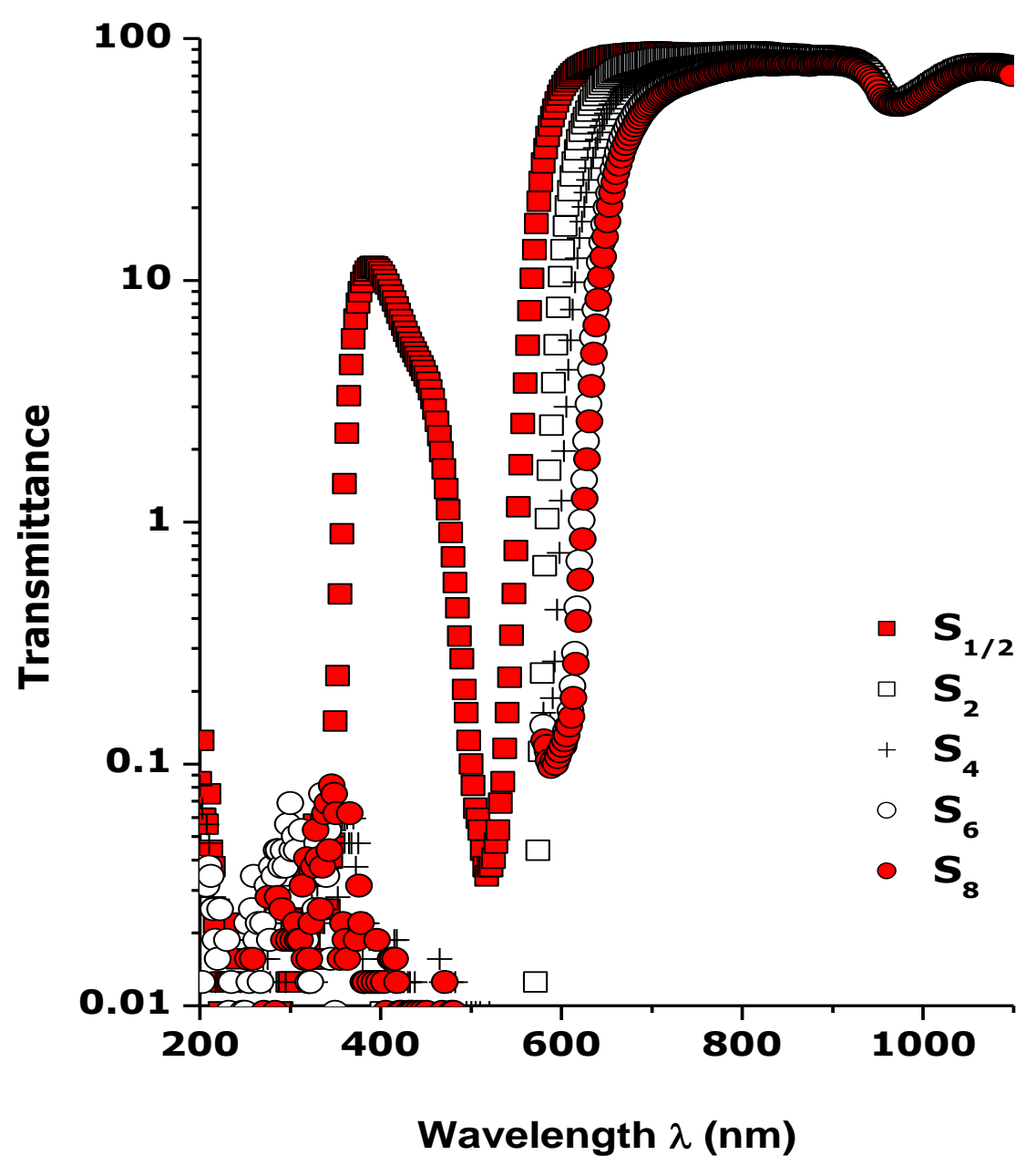


FIGURE 3

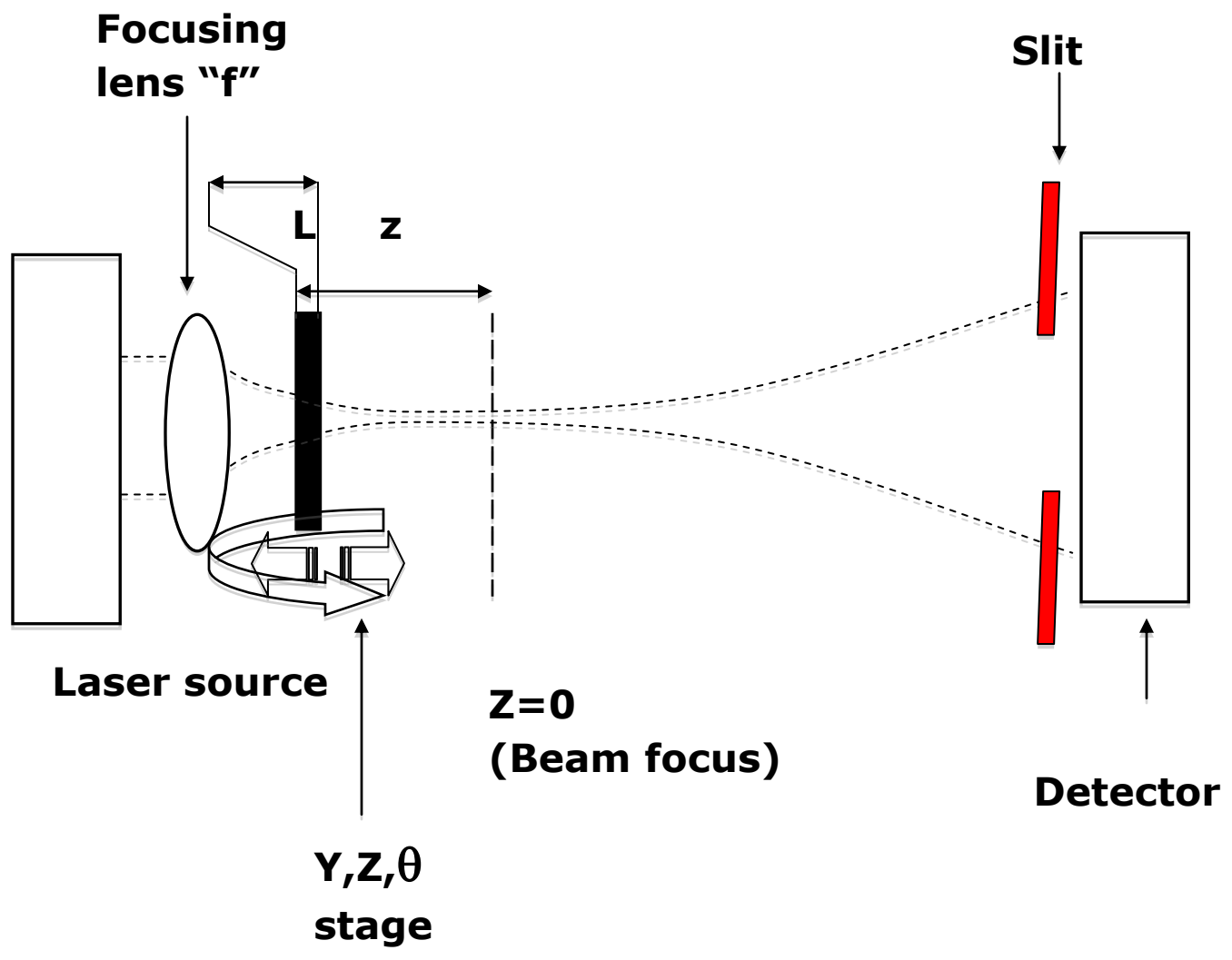


FIGURE 4

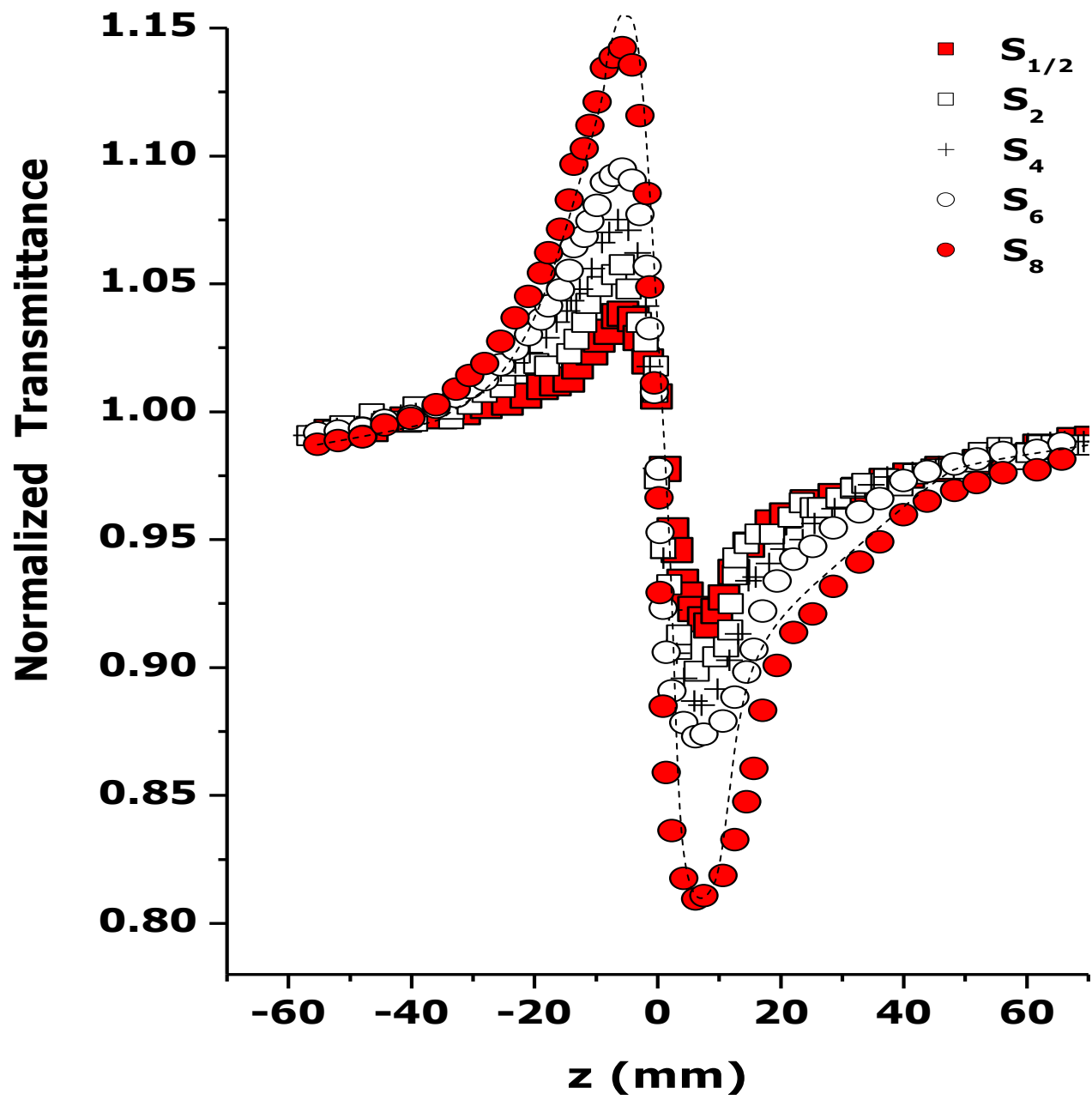


FIGURE 5

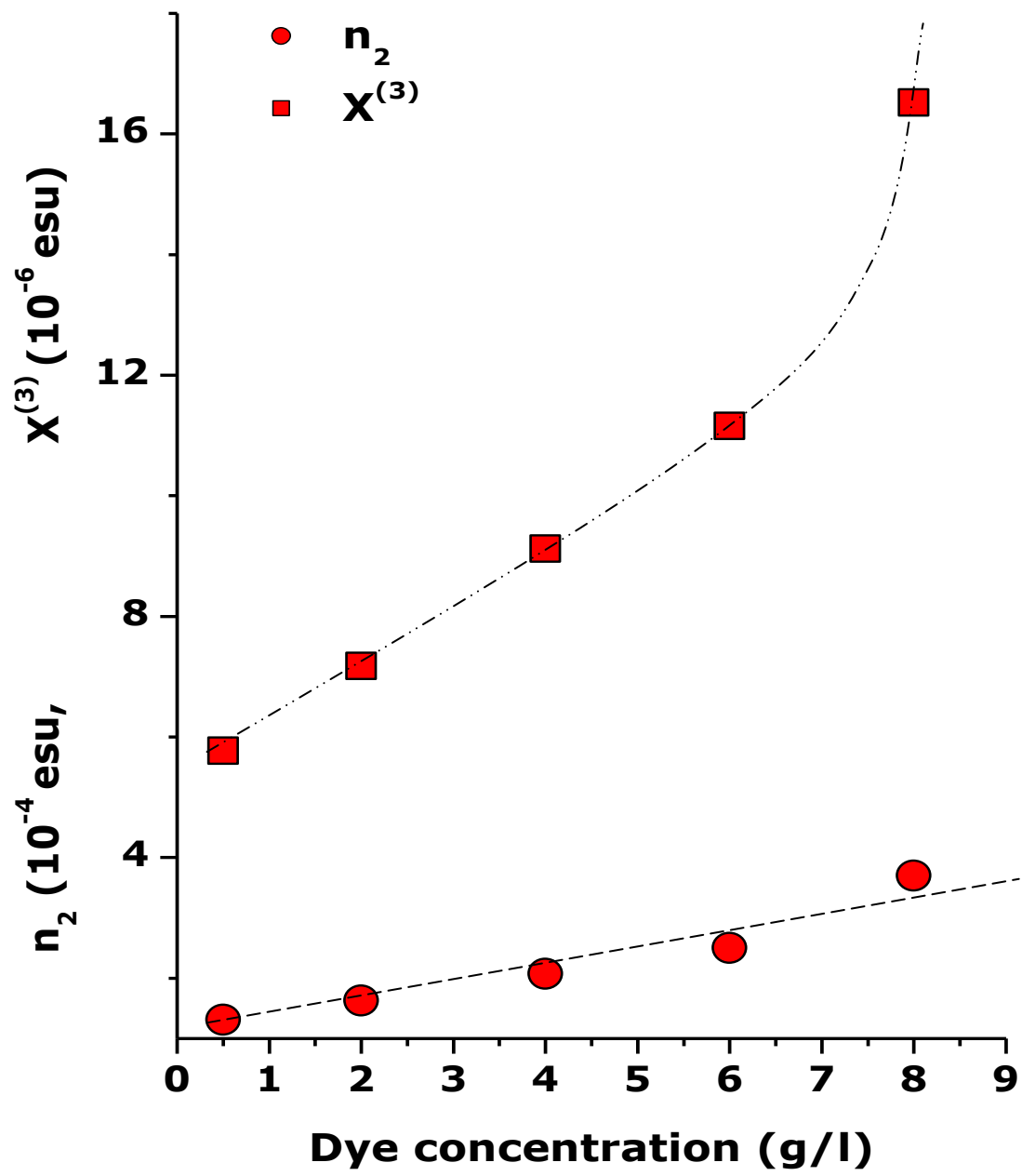




FIGURE 6

