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# Near IR Two Photon Absorption of Cyanines Dyes. Application to Optical Power Limiting at Telecommunication Wavelengths

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## ABSTRACT

The design and synthesis of symmetrical and unsymmetrical heptamethine cyanines is reported. These chromophores present significant two-photon cross section in the 1400-1600 nm spectral range. In addition, they display optical power limiting (OPL) properties. OPL curves were interpreted on the basis of two-photon absorption (2PA) followed by excited state absorption (ESA). Finally, these molecules present several relevant properties (nonlinear absorption properties, two-step gram scale synthesis, high solubility, good thermal stability), which could lead to numerous practical applications in material science (solid state optical limiting, signal processing) or in biology (imaging).

**Keywords:** cyanine, near infrared, two photon absorption, excited state absorption, optical power limiting.

## 1. INTRODUCTION

Systems displaying two-photon absorption (2PA) properties have been widely studied in the visible (400-1000 nm), for various applications in the field of material science (3D microfabrication, optical storage, optical power limiting) or in biology (imaging, photodynamic therapy).<sup>1</sup> With the development of frequency-tuneable pulsed laser in the near infrared (NIR) up to telecommunication wavelengths (1400-1600 nm), there is an increasing need for devices presenting 2PA properties in this spectral range. In this context, the challenge is to transpose the 2PA model widely studied in the visible to the NIR. To date, only a few studies report NLO properties in the NIR region; inorganic semiconductors (GaAs) are known to present a significant 2PA coefficient ( $\alpha_2$ ) at 1300 nm;<sup>2</sup> 2PA absorbing porphyrins were described, and the group of Marder reported dipolar polyenic chromophores, cyanines and squaraines.<sup>3</sup> In the meantime, three-photon absorbing (3PA) chromophores with additional OPL properties at 1300 nm were reported by the group of Prasad.<sup>4</sup> The first requirement for material displaying such properties is a significant NIR absorption (closed to 700-800 nm). We therefore focused on heptamethine cyanines, which are largely used for biological imaging due to their spectacular linear absorption around 800 nm.<sup>5</sup> In this article, we report on the synthesis of four organic dyes depicted Fig. 1. 2PA properties of these dyes in the NIR spectral range (1300-1600 nm) were determined using Z-scan technique in the femtosecond (fs) regime. Applications of these chromophores in OPL in the nanosecond (ns) regime will be shown.

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## 2. SYNTHESIS

Cyanine dyes are organic molecules in which a positive charge is delocalized between two heteroatoms through a polyenic backbone. In addition, the four target molecules **1-4** contain a cyclohexenyl ring functionalized by a *tert*-butyl moiety (Fig.1). The role of this carbocycle is to enhance the photostability of the dye and the additional *tert*-butyl group will increase the solubility and prevent aggregation. The starting material, bis-aldehyde **A** is easily accessible using the Vilsmeier reaction ( $\text{POCl}_3$ , DMF) on the commercially available 4-*tert*-butylcyclohexanone. Various methylene-functionalized group were condensed to the bis-aldehyde **A** using the Knoevenagel reaction to obtain symmetric or unsymmetric chromophores. Symmetric dyes **1-2** were synthesized using two equivalents of indoleninium salts **B** and **A** in ethanol in presence of an organic base (pyridine). The final molecules **1-2** were purified by simple recrystallisation from diethyl ether (70%). The dipolar product was synthesized one-pot in boiling butanol in presence of pyridine, by successive addition of the tricyanofurane **C** (TCF) and the indoleninium **B**. Purification by column chromatography afforded **3** and **4** in moderate yield (35%). These syntheses require only few steps and allow the synthesis of the dyes on gram scale. The four dyes were fully characterized using classical spectroscopic methods ( $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, mass spectroscopy...). Thermogravimetric analysis (TGA) showed that all chromophores are thermally robust, as indicated by their 10% weight loss decomposition temperature around 250°C.

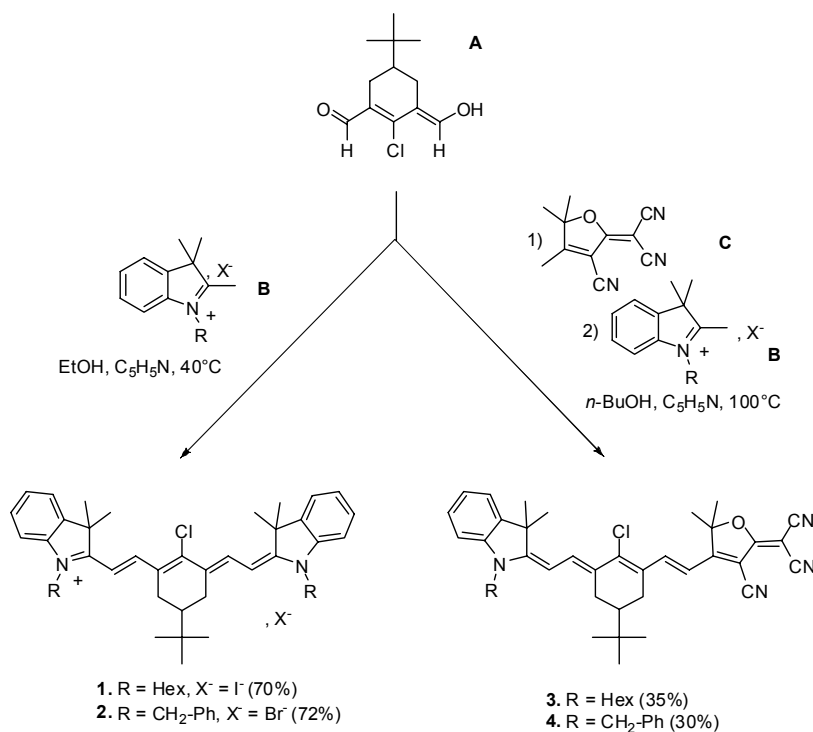


Fig.1. Synthesis of **1-4** chromophores

## 3. LINEAR OPTICAL PROPERTIES

The absorption spectra (one photon absorption, 1PA) of the chromophores were measured in dichloromethane (DCM). **1** and **2** present the typical spectrum of a cyanine dye: an intense and narrow transition in the NIR ( $\lambda_{\text{max}} = 791 \text{ nm}$ ,  $355\,000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  for **2**) and a less intense blue-shifted shoulder (Fig. 2 and Table 1).<sup>5</sup> The spectra of **3** and **4** also present two

bands in the NIR, but their relative intensity is quite similar ( $\lambda_{\max} = 810 \text{ nm}$ ,  $91\,000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  for **4**). All these compounds follow the Beer-Lambert law in concentration range comprised between  $10^{-4} \text{ L}\cdot\text{mol}^{-1}$  and  $10^{-6} \text{ L}\cdot\text{mol}^{-1}$ ; this result excludes the possibility of aggregation (cyanine dyes are known to aggregate) and may be connected to the presence of the multiple lateral substituents (benzyl, hexyl and *tert*-butyl, see Fig. 1). In addition, all chromophores display a broad red emission (Table 1).

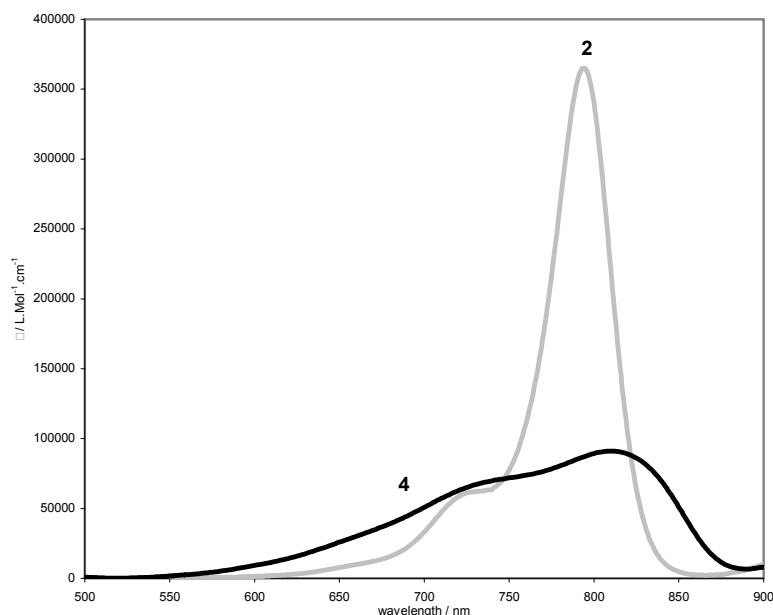


Fig. 2. UV-Vis-NIR absorption spectra for **2** and **4** in DCM.

#### 4. TWO PHOTON ABSORPTION PROPERTIES

2PA spectra were measured by using an open aperture Z-scan method between 1200 and 1600 nm with a fs-optical parametric amplifier pumped by a Ti:sapphire regenerative amplifier laser operating at 1 kHz as a light source.<sup>6</sup> The basic theory for the analysis of the open-aperture Z-scan and the nonlinear transmittance measurements are the same. When a material absorbs light by only 1PA and 2PA processes and when the cascading processes can be ignored, the transmission of the sample can be computed using the following equation (1):

$$\frac{dI}{dz} = -\alpha_1 I - \alpha_2 I^2 \quad (1)$$

in which  $I$  is the optical intensity,  $z$  is the propagation axis coordinate and  $\alpha_1$  and  $\alpha_2$  are the 1PA (linear) and 2PA coefficients respectively. In our case, since the solution doesn't absorb the incident light,  $\alpha_1 \approx 0 \text{ cm}^{-1}$ , and the equation (1) becomes:

$$\frac{dI}{dz} = -\alpha_2 I^2 \quad (2)$$

Considering the propagation of a collimated laser beam with a Gaussian distribution in time and space through a media displaying only a 2PA, the nonlinear transmittance  $T_{nl}$  can be expressed by equation (3),

$$T_{nl} = \frac{1}{\sqrt{\pi}\alpha_2 L I} \int_{-\infty}^{\infty} \ln(1 + \alpha_2 L I e^{-u^2}) du \quad (3).$$

With this equation, we have a relation between  $T$ ,  $\alpha_2$  and laser parameters; finally, 2PA cross section  $\sigma_{2PA}$  is calculated from the convention:

$$\sigma_{2PA} = \frac{h\nu}{N} \alpha_2 \quad (4)$$

where  $N$  is the number density of molecules and  $h\nu$  is the photon energy at the operating wavelength.

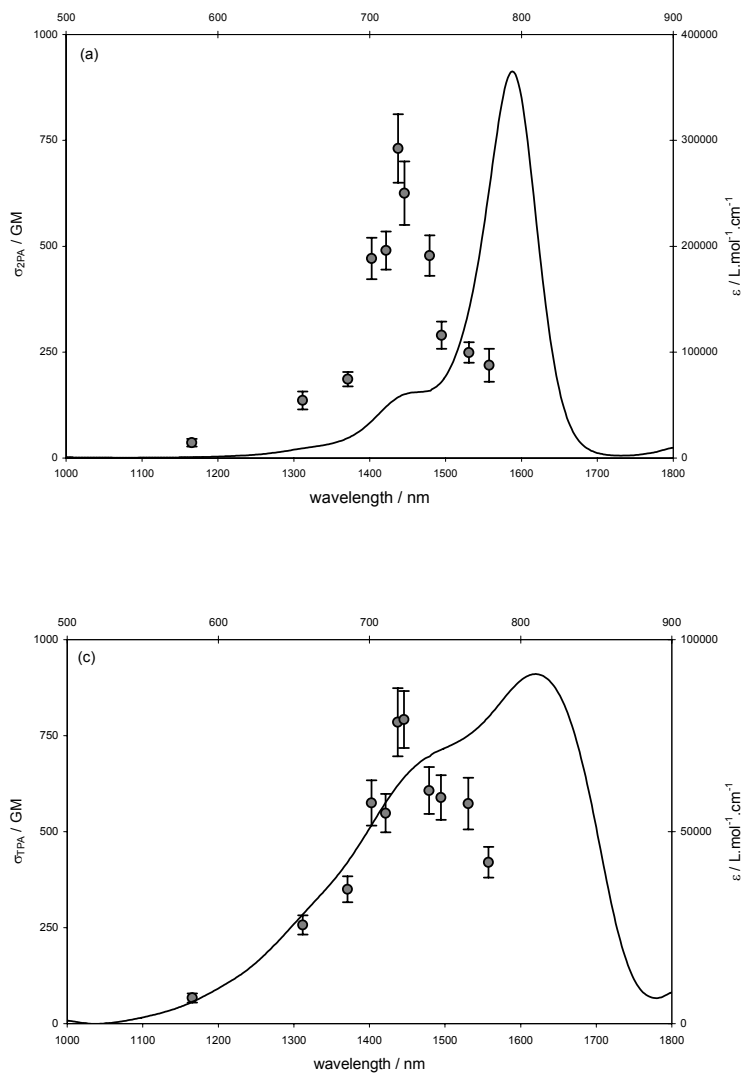


Fig.3. 2PA spectra measured by fs-Z-scan method (filled circle) and 1PA spectra in upper abscissa (□) of compounds **2** (a), **4** (b) in DCM solution.

Fig. 3 shows the comparison of 2PA and 1PA spectra in wavelength doubled scale, for compounds **2** and **4**. Both compounds present significant 2PA absorption in the 1300-1500 nm range (Fig. 3 and Table 1). The 2PA spectrum of the noncentrosymmetric dipolar compound **4** matches the wavelength-doubled scale 1PA absorption (Fig. 3b). The case of **2** (Fig. 3a) is different; the 2PA spectrum is blue-shifted with respect to the 1PA spectrum, and seems to match the weakest band. Generally, it is well known that the selection rules for centrosymmetric molecules are complementary between 1PA and 2PA: a 1PA-allowed transition is forbidden for 2PA and vice-versa.<sup>7</sup> It is not clear to date why the 2PA peak overlaps with the weakest 1PA band; two assumptions can be considered coincidence between the transition energies to 1PA- and 2PA-allowed excited states, or breaking of the centrosymmetry due to vibronic coupling or other reasons. The maximum two photon cross-sections  $\sigma_{2PA}^{\max}$  reported in Table 1 are comprised between 700 and 800 GM.  $\sigma_{2PA}^{\max}$  values obtained in the case of polymethine dyes **2**, **4** compare well with that of related compounds briefly described in the literature.<sup>3b</sup> The value of  $\sigma_{2PA}^{\max}$  for the dipolar chromophore **4**, is slightly higher ( $\sigma_{2PA}^{\max} = 792 \pm 74$  GM at 1445 nm) than  $731 \pm 74$  GM at 1437 nm for **2**, but remains lower than those reported for other dipolar compounds featuring a longer  $\pi$ -conjugated backbone ( $\sigma_{2PA}^{\max} = 1500$  GM at 1440 nm)<sup>3a</sup> or  $\sigma_{2PA}^{\max} = 2100$  GM at 1300 nm for the related squaraine.<sup>3c</sup>

Table 1. Photophysical data in DCM solution

Compound	$\lambda_{\max}$ / nm	$\epsilon_{\max}$ / L.Mol <sup>-1</sup> .cm <sup>-1</sup>	$\lambda^{(2)}$ / nm <sup>a</sup>	$\sigma_{2PA}^{\max}$ / GM <sup>b</sup>	$\lambda_{\text{em}}$ / nm <sup>c</sup>
<b>1</b>	791	355000	-	-	-
<b>2</b>	794	350000	1437	731	817
<b>3</b>	831	112000	-	-	-
<b>4</b>	810	91000	1445	792	845

<sup>a</sup> Maximal 2PA wavelength obtained by fs Z-scan technique; <sup>b</sup> Maximal 2PA cross-section measured by fs Z-scan technique; <sup>c</sup> Maximal emission wavelength.

## 5. OPTICAL POWER LIMITING

The high solubility of these compounds in DCM (concentrations closed to 100 g.mol<sup>-1</sup> were used, Table 2) allows performing OPL experiments in the NIR spectral range. Nonlinear transmittance measurements were carried out in the 1200-1600 nm range using a tripled Q-switched Nd:YAG laser pumping an optical parametric oscillator (7 ns pulse, 10 Hz). For all samples, variations of the nonlinear transmittance vs the incident laser energy at a given wavelength present the characteristic behavior of an optical limiter: a good transmission at low energy ( $T > 0.9$ ) that significantly decreases at higher energy (Fig. 4). Similar OPL curves were obtained for each molecule **1-4**. Although experimental points were limited due to the weak power of the incident laser, an attenuation of 40% of the incident laser beam (incident energy  $3 \cdot 10^{-4}$  J) could be reached (Fig. 4). It must be noted that experimental concentrations used for OPL experiments (Table 2) were not maximal and that more efficient transmission attenuation could therefore be readily reached. It is important to note that the OPL curves are strongly concentration dependant.<sup>8</sup>

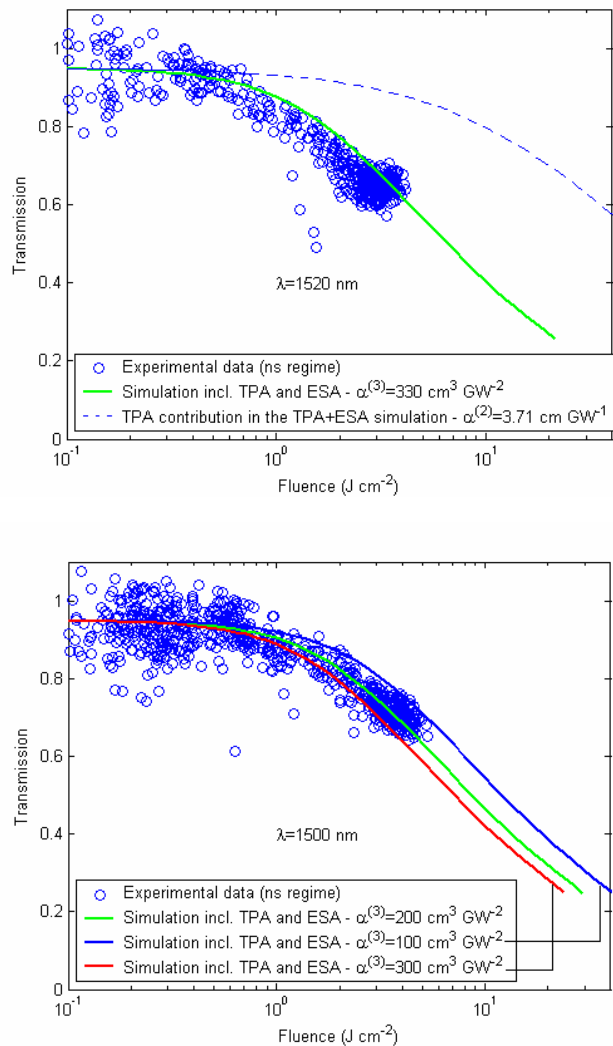


Fig. 4. Nonlinear transmittance of **4** (up) in concentrated dichloromethane solution (experimental data points and theoretical simulations using simplified 2PA model (----) or complete model including 2PA and ESA (—)). Nonlinear transmittance of **4** (bottom) with theoretical simulations using different  $\alpha_3$  coefficients.

Since the theoretical treatments for the open-aperture Z-scan and the nonlinear transmittance measurements are the same as mentioned above, the obtained OPL curve was first analyzed with the equation (3) assuming that only the 2PA process is involved in the observation. The simulation curves (dashed lined curve of Fig. 4 (up)), with the two-photon absorption coefficient  $\alpha_2^{calcd}$ , calculated according to (4) with the concentrations of the OPL samples and using the  $\sigma_{2PA}$  value determined from the fs Z-scan experiments, exhibit a large deviation from the experimental points. Such a large difference was already observed in the nanosecond regime.<sup>9</sup> When the pulse duration is comparable or longer than the lifetime of the excited state of the molecule, high-order phenomena like 2PA-induced excited state absorption (ESA) become non negligible, as illustrated in Fig. 5.

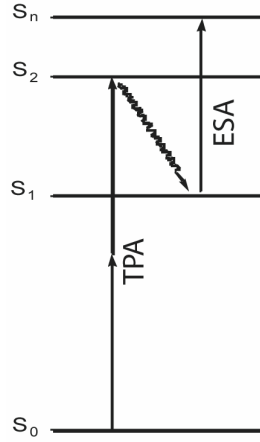


Fig. 5. Description of the 3PA process

In this context, the 2PA model can't be used to match the OPL curve and higher-order effect must be taken into account following eq. (5):

$$\frac{dI}{dz} = -\alpha_1 I - \alpha_2 I^2 - \alpha_3 I^3 \quad (5)$$

in which  $\alpha_3$  is the 3PA coefficient. Any nonlinear absorption process with the same order as 3PA, such as the 2PA-induced ESA process, is included in  $\alpha_3$ . The OPL curves were fitted using the extended equation (5). The  $\alpha_3$  coefficient is determined by numerical resolution of equation (5) always assuming a Gaussian temporal and spatial incident intensity distribution, as depicted in relationship (6), since the equation (5) does not give a simple analytical formulation for  $T_{nl}$  such as the equation (3) when both  $\alpha_2$  and  $\alpha_3$  are non zero:

$$I(z=0, r, t) = \frac{E}{\pi^{3/2} \tau \omega_0^2} e^{-\frac{t^2}{\tau^2}} e^{-\frac{2r^2}{\omega_0^2}} \quad (6)$$

where  $E$  is the total energy,  $\tau$  is the HW1/eM pulse duration, and  $w_0$  is the HW1/e<sup>2</sup>M beam size.

Simulations of experimental data using the  $\alpha_3$  approach are represented in the Fig. 4 and are in agreement with experimental curves. The 3PA coefficients at 1500 nm are comprised between 190 and 330 cm<sup>3</sup>.GW<sup>-2</sup> for 2-4. Fig. 4 (bottom) illustrates, in the case 2 the precision in the  $\alpha_3$  determination from equation (6), in which three fits are represented using  $\alpha_3 = 100, 200$  or  $300$  cm<sup>3</sup>.GW<sup>-2</sup>. Clearly the curves displaying  $\alpha_3 = 100$  and  $\alpha_3 = 300$  cm<sup>3</sup>.GW<sup>-2</sup> represent upper and lower acceptable limits for the experimental data fitting, and therefore the  $\alpha_3$  value could be estimated to  $200 \pm 100$  cm<sup>3</sup>.GW<sup>-2</sup>, 2PA coefficients  $\alpha_2^{calcd}$  at the telecommunication wavelengths of 1500 nm are comprised between 2 and  $5 \cdot 10^{-11}$  m.W<sup>-1</sup>, which is twice lower than those measured for the reference inorganic material GaAs at 1300 nm.<sup>2</sup> However as pure 2PA is not the only process involved in the OPL properties, this relative weakness is overcome thanks to the ESA process.



Table 2: 2PA and 3PA data using different models.

compound	C <sup>a</sup> (g.L <sup>-1</sup> )	$\lambda^b$ (nm)	$\alpha_2^{calcd}$ cm.GW <sup>-1</sup>	$\alpha_3^d$ cm <sup>3</sup> .GW <sup>-2</sup>
<b>2</b>	96.5	1500	1.59	200
<b>4</b>	92.3	1440	5.02	190
<b>4</b>	92.3	1520	3.71	330

<sup>a</sup> experimental concentration used in optical limiting measurements; <sup>b</sup> maximal two-photon absorption wavelength; <sup>c</sup> from fs Z-scan measurement; <sup>d</sup> determined from OPL experiments using complete model.

## 6. CONCLUSION

Heptamethine dyes presenting 2PA in the 1400-1600 nm range were synthesized and fully characterized. Furthermore, these compounds present many relevant advantages for practical applications such as a two steps synthesis in a gram scale, a high solubility in organic solvents and a good thermal stability. At telecommunications wavelengths, these molecules display OPL properties in the ns regime. In this time regime, the OPL experiments were rationalized on the basis of a 3PA effect induced by 2PA (2PA-induced ESA). The existence of several sites allowing functionalization for further uses in a biological medium or for a grafting in solid matrices, should allow the investigation of these molecules for several different 2PA based applications in the NIR range.

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