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Nonlinear transmission properties of chloroindium phthalocyanines for picosecond pulse trains

Quan Miao[a,*], Zhaoyang Sang[b], Min Liang[a,c], Rengang Song[a,c], Erping Sun[a], Yan Xu[a,c]

[a] College of Electronics, Communication and Physics, Shandong University of Science and Technology, Qingdao, 266590 Shandong, People's Republic of China
[b] College of Science, China University of Petroleum (East China), Qingdao, 266580 Shandong, People's Republic of China
[c] College of Electrical Engineering and Automation, Shandong University of Science and Technology, Qingdao, 266590 Shandong, People's Republic of China

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ABSTRACT

We studied the optical dynamics and propagating properties of two chloroindium phthalocyanines with α- and β-alkoxyl substituents interacting with picosecond pulse trains. The pulse train contains 35 picosecond subpulses with 12 ns spacing, and the width of each subpulse is 100 ps. We applied a five-level model to simulate the interaction by solving two-dimensional paraxial field equation coupled with rate equations. Photophysical parameters of molecules are extracted from the experiment and we employed Crank–Nicholson numerical method to get accurate and credible results. The sequential (singlet-singlet) × (triplet-triplet) two-photon absorption is the vital optical limiting channel for long pulse trains. Our work indicates that chloroindium phthalocyanine with β-alkoxyl substituent shows better optical limiting behaviors for picosecond pulse trains, which is opposite with the result for one single nanosecond laser.

1. Introduction

Nowadays, understanding and application of light have reached to a whole new level. Many kinds of light sources could interfere with optical or electrical instruments and even the eyes. Especially the laser intensity gets a dramatic improvement [1], which will cause great potential damage. Therefore, scientists have carried out many researches in finding and synthesizing optical limiting (OL) materials [2,3] to do the protection. Up to now, reverse saturable absorption (RSA) is commonly acknowledged as the crucial feature in OL materials [4–9].

Metal phthalocyanines with highly conjugated delocalized π-electron system are the most excellent optical limiters [10–18]. During the interacting of the materials with long duration laser pulses, the main RSA channel is the (singlet-singlet) × (triplet-triplet) sequential two-photon absorption (TPA) [4,19–23]. The key lies on the heavy metals in increasing the population of the triplet state via spin-orbit coupling through intersystem crossing, following with the consequent enhanced (triplet-triplet) absorption. In various kinds of metal phthalocyanines, the most common heavy metal atoms are In, Ga, Sn, Pb, etc. [24–26]. In addition, the locations and species of the substituted groups can affect the OL behaviours of metal phthalocyanines [27,28].

Many experimental works focused on different OL influences of heavy metal atoms. However, an experimental group synthesized two indium phthalocyanines α-InPcCl and β-InPcCl with different substitute locations [29]. The emphasis of their work is locations of the substituted groups instead of the heavy metal atoms. Their results showed that molecules with same substituted groups at different positions exhibit quite distinct change of the OL behaviours. They investigated the interactions between the complexes with one single nanosecond pulse and found that α-InPcCl performed a better OL effect than β-InPcCl. In contrast, we applied picosecond pulse trains in this work and our results show that β-InPcCl has better OL properties. The paraxial field equation together with the rate equations were solved in the simulation by Crank–Nicholson method [30].

2. Method

We showed in Fig. 1 the molecular structures of α-InPcCl and β-InPcCl. Here we studied the propagation of picosecond pulse trains with long duration in OL materials, so it is convenient to compress the phthalocyanine complexes to a five-level scheme shown in Fig. 2 [23]. In the simulations we supposed that the incidence frequency of pulse trains is in the vicinity of one-photon transitions in alignment with the experiment [29]. Considering the interaction between RSA materials and long duration pulses, $(S_0 \rightarrow S_1) \times (S_1 \rightarrow S_n)$ and $(S_0 \rightarrow S_1) \times (T_1 \rightarrow T_2)$ are two major sequential TPA channels in the scheme [31,32].

The incident shape of pulse train is assumed to be

* Corresponding author.
E-mail address: qmiao2013@yahoo.com (Q. Miao).

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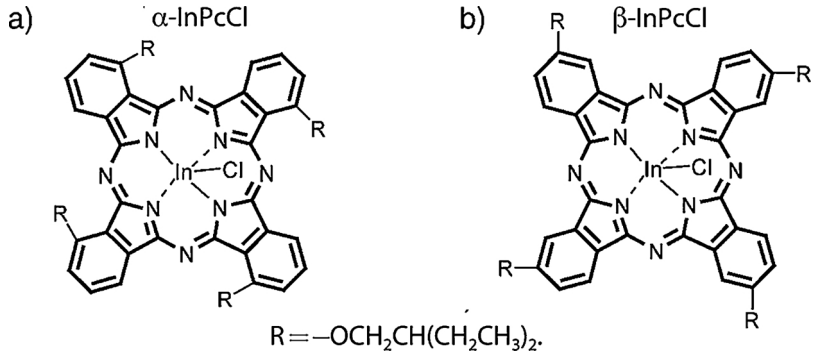

Fig. 1. Structures of chloroindium phthalocyanines with α- and β-alkoxyl substituents [29].

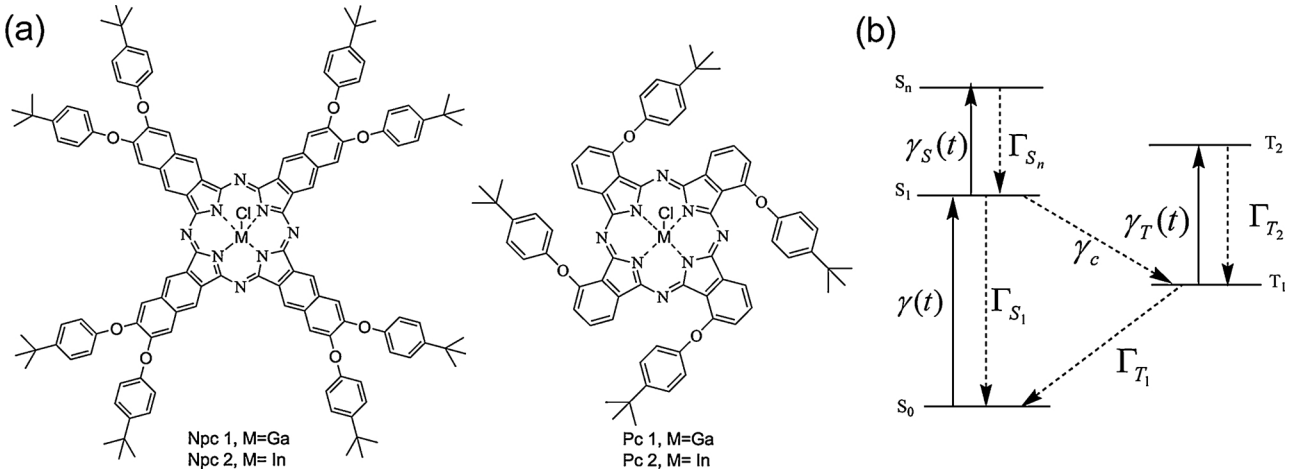

Fig. 2. The Jablonski diagram of a generalized five-level system.

$$I(t) = \sum_{n=0} I_n(t), \quad n = 0, 1, \ldots, n_{\text{tot}} - 1. \tag{1}$$

Here $n = 0, 1, 2, \ldots$ is the sequence number of subpulses, and n_{tot} is the total.

The paraxial equation of each subpulse is described depending on propagation distance z and time t [33]

$$\left(\frac{\partial}{\partial z} - \frac{1}{c}\frac{\partial}{\partial t}\right) I_n(t) = -N \sum_{j>i} \sigma_{ij}(\rho_i - \rho_j) I_n(t), \tag{2}$$

where N is material concentration, c is the speed of light in vacuum, and i and j are the state labels. σ_{ij} is absorption cross-section in transition from low state to high one, and ρ_k represents population of state k.

During the interaction process, we used rate equations to describe the dynamical populations of five levels [23],

$$\begin{aligned}
&\tfrac{\partial}{\partial t}\rho_{S_0} = -\gamma(t)(\rho_{S_0} - \rho_{S_1}) + \Gamma_{S_1}\rho_{S_1} + \Gamma_{T_1}\rho_{T_1},\\
&\left(\tfrac{\partial}{\partial t} + \Gamma_{S_1} + \gamma_c\right)\rho_{S_1} = \Gamma_{S_n}\rho_{S_n} - \gamma_S(t)(\rho_{S_1} - \rho_{S_n}) + \gamma(t)(\rho_{S_0} - \rho_{S_1}),\\
&\left(\tfrac{\partial}{\partial t} + \Gamma_{S_n}\right)\rho_{S_n} = \gamma_S(t)(\rho_{S_1} - \rho_{S_n}),\\
&\left(\tfrac{\partial}{\partial t} + \Gamma_{T_2}\right)\rho_{T_2} = \gamma_T(t)(\rho_{T_1} - \rho_{T_2}), \quad \textstyle\sum_k \rho_k = 1.
\end{aligned} \tag{3}$$

Here γ_c is the transition rate of intersystem crossing (ISC) $S_1 \rightarrow T_1$. And Γ_{S_1}, Γ_{S_n}, Γ_{T_1}, Γ_{T_2} denote the decay rates of the states S_1, S_n, T_1 and T_2 respectively. Also $\gamma(t)$, $\gamma_S(t)$, $\gamma_T(t)$ represent the populated rates from low states to higher ones via one photon absorption $S_0 \rightarrow S_1$, $S_1 \rightarrow S_n$, $T_1 \rightarrow T_2$ respectively. These populated processes can be expressed as following

$$\gamma_{ij}(t) = \frac{\sigma_{ij} I(t)}{\hbar\omega}, \tag{4}$$

Here ω is the incident frequency of laser pulses, and Planck constant $h = 6.626 \times 10^{-34}$, $\hbar = h/(2\pi)$.

We assumed each initial subpulse has temporal shape of rectangular form as following [33,34]

$$I_n(r) = I_0 \exp\left[-\left(\frac{n\Delta - t_0}{\tau_e}\right)^2 \ln 2\right] \exp\left[-\left(\frac{r}{r_0}\right)^2 \ln 2\right]. \tag{5}$$

Half width at half-maximum (HWHM) of the envelope $\tau_e = 10\Delta/3$ and $t_0 = [(n_{tot} - 1)\Delta + \tau]/2$. We set beam width $r_0 = 2$ mm. Usually, the pulse trains used in experiments are picosecond pulses separated by nanosecond separation [9,35,36]. The single pulse duration is 3.5 ns (HWHM) in experiment [29], so we supposed there are 35 subpulses with 12 ns spacing, and each subpulse with duration of 100 ps. In the simulation, $\Delta = 12$ ns, $\tau = 100$ ps, and $n_{tot} = 35$, then the total duration of pulse trains is 35×100 ps $= 3.5$ ns.

The total energy transmittance during the OL process is calculated as following

$$\mathcal{T}(L) = \frac{J(z_0 + L)}{J(z_0)}, \tag{6}$$

where the initial position of the pulse train $z_0 = 0$ and L is the propagation thickness of laser pulses. $J(z)$ is the total pulse energy at z, which can be written as

$$J(z) = 2\pi \int_0^R \int_0^\infty I(t, r, z) r \, \mathrm{d}r \, \mathrm{d}t, \tag{7}$$

where $I(t, r, z)$ is the instantaneous laser intensity.

3. Results and discussion

In experiment, α-InPcCl and β-InPcCl were synthesized and