Journal of Photochemistry and Photobiology A: Chemistry 316 (2016) 19–23

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Nonlinear dynamics and optical power limiting of nanoseconds pulses in naphthalocyanines and phthalocyanines with central metals gallium and indium

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ARTICLE INFO

Article history:
Received 1 July 2015
Received in revised form 6 September 2015
Accepted 3 October 2015
Available online 13 October 2015

Keywords:
Optical limiting
Naphthalocyanine
Phthalocyanine
Rate equation
Reverse saturable absorption

ABSTRACT

The optical dynamics of octa-(4-tert-butylphenoxy) substituted naphthalocyanines and phthalocyanines with different central metals (Ga, In) were investigated for 532 nm–7 ns laser pulses. In this work, we used numerical theoretical method with two-dimensional paraxial field equation and rate equations solving by Crank–Nicholson method. A five-level model was proposed to simulate the dynamical processes and the prominent optical limiting mechanism with long pulses is the sequential (singlet–singlet) × (triplet–triplet) two-photon absorption. The theoretical results indicate that both naphthalocyanines and phthalocyanines exhibit good optical limiting performances, which is attributed mainly to the reverse saturable absorption mechanism. The naphthalocyanines with larger difference of absorption cross sections and faster rate of the intersystem crossing transition between triplet and singlet states exhibit better optical limiting behaviour.

1. Introduction

Since the invention of laser in 1960s, the strong field laser has always been the focus of attention. Scientists have dedicated to develop high-intensity or short-width laser, which is widely used in medicine, military, informatics, manufacture and many other fields [1]. But the strong field laser is also dangerous to damage optical devices and human eyes. As a result, it is in great need of materials with good optical limiting (OL) properties for protection [2,3]. Among various mechanisms to realize OL dynamics, reverse saturable absorption (RSA) is mostly adopted in practice [4–6]. The obvious property of RSA materials is the absorption cross section of excited state is larger than that of ground state [7–9].

RSA is in fact two-step sequential two-photon absorption (TPA). It is the main OL mechanism when the duration of laser pulses interacting with medium is long, such as nanoseconds. In contrast, one-step coherent TPA is dominant for ultrashort pulses such as femtoseconds. The main reason is that one-step TPA is instantaneous in absorbing two photons while two-step TPA needs a finite response time [10–13]. For complex system with singlet and triplet states, when the width of pulses is comparable or longer than the effective population transfer time from ground to triplet state, the sequential (singlet–singlet) × (triplet–triplet) TPA will be the dominant channel [4].

In the past years, scientists are dedicated in finding and synthesizing better RSA materials. Materials with highly conjugated delocalized π-electron system are potent candidates, such as naphthalocyanines (Npcs) and phthalocyanines (Pcs) [14–22]. Photophysics of RSA on heavy-metal centered phthalocyanines, naphthalocyanines, and porphyrins are well studied for more than two decades [23–25]. Recently, Npcs and Pcs with metal-coordination bond are investigated in experimental studies and they exhibit different OL and photophysical properties due to different structures [26]. In our work, we studied the OL behaviours of Npcs and Pcs using a dynamical theory of the sequential TPA for nanosecond pulses. Our method is to solve the paraxial field equation numerically together with the rate equations using Crank–Nicholson method [27]. Our work mainly aims to study the OL effects by central heavy metals and the bulky substituted groups using new simulation methods. And we made a comparison of the OL behaviours between Npcs and Pcs.

2. Method

The structures of Npcs and Pcs are shown in Fig. 1(a). Considering the propagation of long pulses in OL materials, the studied system can be simplified as a five-level model, including three singlet and two triplet states shown in Fig. 1(b). In

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http://dx.doi.org/10.1016/j.jphotochem.2015.10.006
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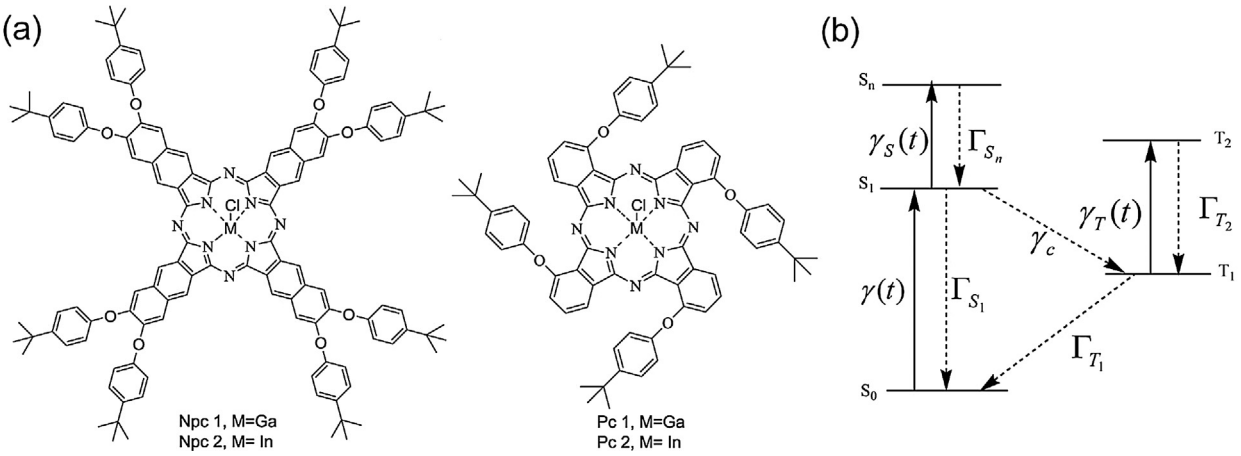

Fig. 1. (a) Structures of the naphthalocyanines and phthalocyanines in reference [26] and (b) the Jablonski diagram of a generalized five-level system.

this five-level scheme, there are two sequential TPA channels: $(S_0 \to S_1) \times (S_1 \to S_n)$ and $(S_0 \to S_1) \times (T_1 \to T_2)$. Following the experiment [26], the frequency of pulses in our simulation was tuned in the vicinity of one-photon transitions. So the two sequential TPA channels are enhanced but the nonresonant transition $(S_0 \to S_n)$ by coherent one-step TPA or one photon absorption is weak enough to be ignored. The total photon absorption cross section is [4,28]

$$\sigma_{\text{tot}} = \sigma_{S_0S_1}(\rho_{S_0} - \rho_{S_1}) + \sigma_{S_1S_n}(\rho_{S_1} - \rho_{S_n}) + \sigma_{T_1T_2}(\rho_{T_1} - \rho_{T_2}), \tag{1}$$

where σ_{mn} represents one photon absorption cross section of transition $m \to n$. The corresponding rate of one photon transition is

$$\gamma_{mn}(t) = \frac{\sigma_{mn} I(t)}{\hbar\omega} \frac{\Gamma_{mn}^2}{\Omega_{mn}^2 + \Gamma_{mn}^2}, \tag{2}$$

where ω is the laser frequency and Ω_{mn} is the detuning of the incident light frequency from the resonant frequency. Γ_{mn} is the width of transition spectrum. In liquids, it can reach $\hbar\Gamma = 0.1$ eV and small fluctuations did almost no effect to our results. So we assumed below in our simulation to be the same for different transitions, $\hbar\Gamma_{mn} = \hbar\,\Gamma = 0.1$ eV [29].

We considered the incident laser pulses as $\mathbf{E}(\mathbf{r}, t) = \boldsymbol{E}(\mathbf{r}, t)\cos(\mathbf{k}\cdot\mathbf{r} - \omega t)$ with intensity $I = c\varepsilon_0|\mathcal{E}|^2/2$. Using the slowly varying envelope approximation (SVEA) [29], Maxwell's equations are reduced to the paraxial equation with photon absorption cross section in the following form,

$$\left(\frac{\partial}{\partial z} + \frac{n_0}{c}\frac{\partial}{\partial t} - \frac{i}{2k}\Delta_\perp\right)\boldsymbol{E} = -\frac{N\sigma_{\text{tot}}}{2}\boldsymbol{E}. \tag{3}$$

Here $k = n_0\omega/c$, N is the concentration of molecules and n_0 is the refraction index which we assume $n_0 \approx 1$. The transverse Laplace operator in cylindrical coordinates is written as

$$\Delta_\perp = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2}. \tag{4}$$

During the laser pulses propagation, the dynamical populations of singlet and triplet states obey the rate equations,

$$\begin{aligned}
&\frac{\partial}{\partial t}\rho_{S_0} = -\gamma(t)(\rho_{S_0} - \rho_{S_1}) + \Gamma_{S_1}\rho_{S_1} + \Gamma_{T_1}\rho_{T_1},\\
&\left(\frac{\partial}{\partial t} + \Gamma_{S_1} + \gamma_c\right)\rho_{S_1} = \Gamma_{S_n}\rho_{S_n} - \gamma_S(t)(\rho_{S_1} - \rho_{S_n}) + \gamma(t)(\rho_{S_0} - \rho_{S_1}),\\
&\left(\frac{\partial}{\partial t} + \Gamma_{S_n}\right)\rho_{S_n} = \gamma_S(t)(\rho_{S_1} - \rho_{S_n}),\\
&\left(\frac{\partial}{\partial t} + \Gamma_{T_2}\right)\rho_{T_2} = \gamma_T(t)(\rho_{T_1} - \rho_{T_2}), \quad \sum_k \rho_k = 1,
\end{aligned} \tag{5}$$

where γ_c is the rate of intersystem crossing (ISC) transition $S_1 \to T_1$. $\gamma(t)$, $\gamma_S(t)$ and $\gamma_T(t)$ are the populated rates to excited states via one-photon transitions $S_0 \to S_1$, $S_1 \to S_n$ and $T_1 \to T_2$, respectively. Γ_{S_1}, Γ_{S_n}, Γ_{T_1} and Γ_{T_2} are the decay rates of the states S_1, S_n, T_1 and T_2, respectively. In this system, the nonradiative decays between excited states S_n, T_2 and lower excited states S_1,T_1 with rates of $1\ \text{ps}^{-1}$ are the dominant channels, so we ignored the slow decay channels $S_n \to S_0$ and $S_1 \to S_0$ in our simulation.

The incident pulse was assumed to be the lowest order mode TEM_{00} of the transverse electromagnetic mode, which is isotropic in the transverse direction and is formed as a Gaussian beam [30]. The boundary conditions to solve the paraxial equation (3) are therefore written as

$$\begin{aligned}
&r\mathcal{E}(r, z, T) = 0 \quad for \quad r = 0, R,\\
&\mathcal{E}(r, z_0, T_0) = E_0(T_0)\frac{\omega_0}{\omega(z_0)}\exp\left(-\frac{r^2}{\omega^2(z_0)}\right)\exp\left(\imath k\frac{r^2}{2R(z_0)} - \imath\zeta(z_0)\right),\\
&R(z) = z\left[1 + \left(\frac{l_0}{z}\right)^2\right], \zeta(z) = \arctan\left(\frac{z}{l_0}\right).
\end{aligned} \tag{6}$$

Here $T_0 = t - n_0z_0/c$, and $T = t - n_0z/c$. $l_0 = \pi\omega_0^2/\lambda$ is the Rayleigh length, $\omega(z) = \omega_0\sqrt{1 + (z/l_0)^2}$ is the beam width at the focal distance z and $R \approx 5\omega(z)$. We also assumed the temporal shape of the initial pulse has the form of Gaussian

$$E_0(t) = E_0\exp\left(-2\left(\frac{t - t_0}{\tau}\right)^2\ln 2\right), \tag{7}$$

where τ is the full width at half-maximum (FWHM). To keep consistent with the experiment [26], we performed our simulation using $\tau = 7.0$ ns, $t_0 = 2.5\tau$ and $\omega_0 = 1$ mm.