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OPTICAL LIMITING EFFECT IN TWO PHTHALOCYANINES OBSERVED BY PICOSECOND PULSED LASER*

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Optical limiting (OL) properties of two phthalocyanines were investigated by using picosecond laser pulses at 532nm. The relative ratios k of the absorption cross section of the first singlet excited state to that of the ground state were approximately obtained by the analysis of the experimental results in which the reverse saturable absorption model of the three-energy-level scheme was employed. A significant comparison with fullerene C_{60} was presented for OL. The OL mechanisms have been analysed in detail.

Keywords: optical limiting, reverse saturable absorption, absorption
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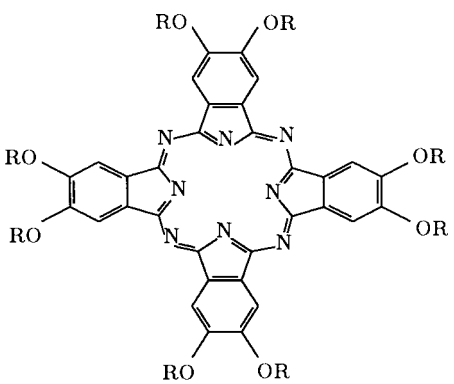
I. INTRODUCTION

Recently, the most frequently reported optical limiting (OL) materials have been fullerene C_{60} and their derivatives,[1−3] inorganic clusters[4−7] and such organic complexes as phthalocyanines.[8−13] In such systems, phthalocyanine (Pc) complexes are promising OL materials because they can be readily synthesized into metallophthalocyanine (MPc) complexes with more than 60 kinds of metal atoms. These yielded MPc complexes have two-dimensional highly conjugated delocalized π electronic systems and charges transferring of metal-conjugant bond. This makes MPc exhibit strong optical nonlinearities.

In this paper, we report on the ultra-fast OL responses in two phthalocyanines with different substituent groups of octa-dodecaoxyl long chains. We measure the ratio of the absorption cross section of the excited state to that of the ground state by fitting the experimental results with the reverse saturable absorption (RSA) model. The OL mechanisms are also discussed.

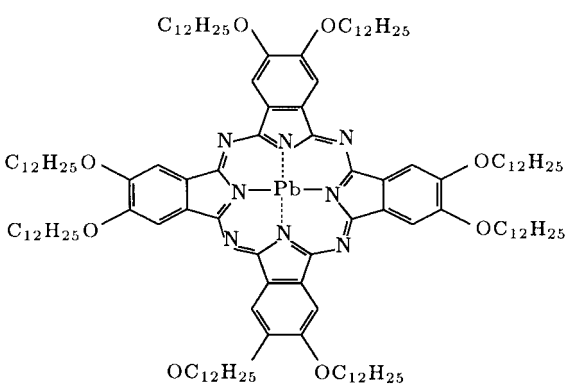
II. SAMPLES AND EXPERIMENTS

The two compounds, free-base phthalocyanine $(C_{12}H_{25}O_2)_8Pc$ and heavy-atom lead phthalocyanine $(C_{12}H_{25}O)_8PcPb$, were synthesized with a known procedure.[12] Their molecular weights are 2095.1 and



R=–$OC_{12}H_{25}$

(a)



(b)

Fig.1. Molecular structures of the two compounds: (a) $(C_{12}H_{25}O_2)_8Pc$ in toluene; (b) $(C_{12}H_{25}O)_8PcPb$ in toluene.

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2194.3, respectively, which were characterized by Uv-vis, IR, ^{1}H-NMR and element analysis. The molecular structures are shown in Fig.1. The corresponding Uv-vis absorption spectra are shown in Fig.2.

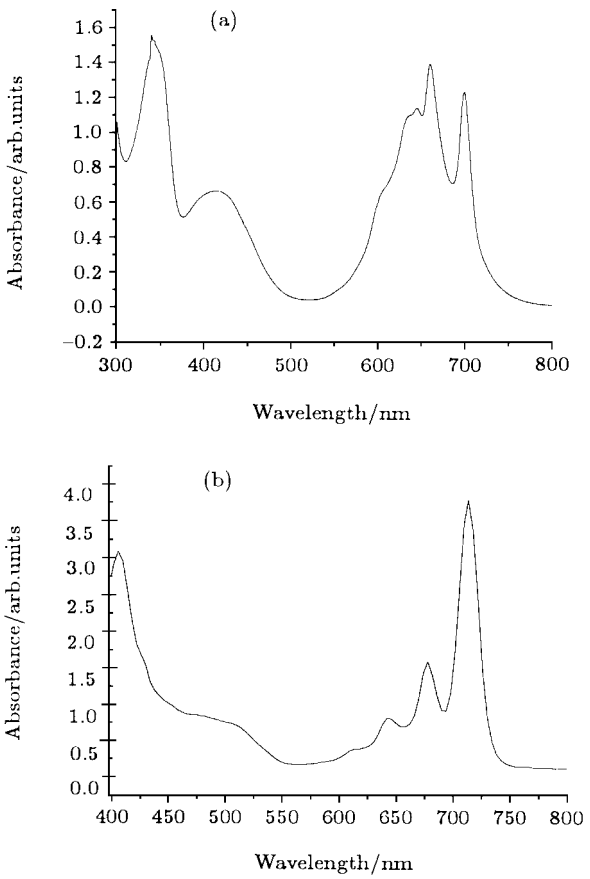


Fig.2. Ground-state absorption spectra of the two compounds: (a)$(C_{12}H_{25}O_2)_8Pc$ in toluene; (b) $(C_{12}H_{25}O)_8PcPb$ in toluene.

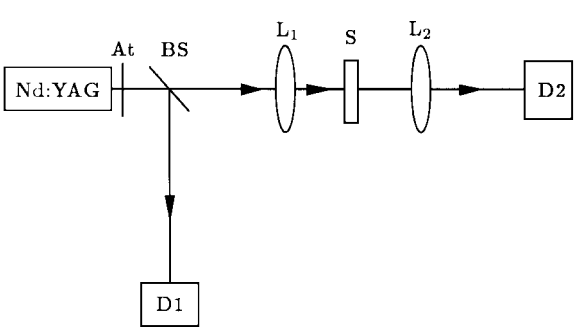


Fig.3. Experimental set-up for OL.

In the OL experiments, $(C_{12}H_{25}O_2)_8Pc$ and $(C_{12}H_{25}O)_8PcPb$ in toluene solutions were placed in quartz cells (5mm thick) and irradiated by laser pulses from a frequency-doubled, Q-switched, mode-locked continuum ns/ps Nd:YAG laser, which produces linearly polarized 21ps (FWHM) laser pulses at 532 nm with a repetition rate of 1 Hz. The spatial profile of the pulses is nearly Gaussian. The sample cell (S) was placed at the focus of a lens L_1 with a focal length of 30 cm, thus the changing transmission results solely from the nonlinear absorption, instead of nonlinear refraction. Both the incident and transmitted laser pulses were monitored simultaneously by using two energy detectors D1 and D2 (Rjp-735 energy probes, Laser Precision), respectively, as described in the experimental set-up shown in Fig.3. The linear transmission of the two samples placed in 5mm thick cells is 65%.

III. EXPERIMENTAL RESULTS AND THEORETICAL ANALYSIS

We have measured the OL effects of the two phthalocyanine compounds and that of C_{60} in toluene with an identical linear transmittance of 65% for comparison. The experimental data of the three samples are shown in Fig.4.

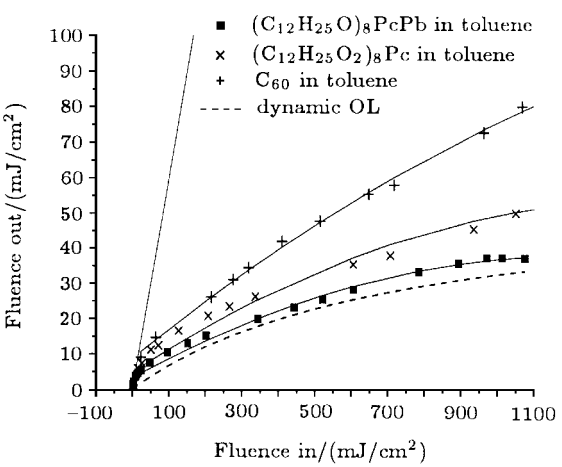


Fig.4. Comparisons of the OL results for $(C_{12}H_{25}O)_8$ PcPb and $(C_{12}H_{25}O_2)_8Pc$ in toluene solutions with that of C_{60} in toluene: solid curves are the corresponding theoretical fits; dashed curve is the dynamic result for $(C_{12}H_{25}O)_8PcPb$; the straight line is the linear result with a transmittance of 65%.

The nonlinear absorptions of the three compounds can be described by the three-energy-level model illustrated in Fig.5. S_i denote the singlet electronic energy levels, N_i denote the molecular population densities of the associated levels, σ_{10} and σ_{21} are the ground-state and excited-state absorption cross sections, respectively, and τ_{01} is the first singlet excited-state lifetime.

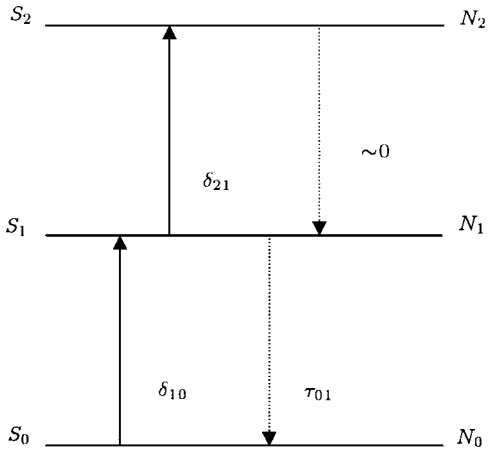


Fig.5. Molecular energy-level diagram.

The three-energy-level model is of interest for ultra-fast (21ps) pulses used in our experiments. The triplet states can essentially be neglected because even for heavy-metal phthalocyanines, intersystem crossing times are typically nanoseconds.[14] Therefore, we consider the following expression for the nonlinear absorption

$$\alpha_{nl} = N_0\sigma_{10} + N_1\sigma_{21}. \tag{1}$$

From the three-energy-level diagram, we can obtain the following rate equations to describe the changes in populations and irradiance

$$\mathrm{d}N_0/\mathrm{d}t = -N_0\sigma_{10}I/h\nu + N_1/\tau_{01}, \tag{2}$$

$$\mathrm{d}N_1/\mathrm{d}t = N_0\sigma_{10}I/h\nu - N_1/\tau_{01} - N_1\sigma_{21}I/h\nu + N_2/\tau_{12}, \tag{3}$$

$$\mathrm{d}N_2/\mathrm{d}t = N_1\sigma_{21}I/h\nu - N_2/\tau_{12}, \tag{4}$$

$$\mathrm{d}I/\mathrm{d}z = -\alpha_{nl}I, \tag{5}$$

where I is the irradiance, $h\nu$ is the photon energy, and z is the distance of propagation.

Note that the rate equation approximation is valid here for the relatively weak excitation.[15–17] The Rabi frequency ($\sim 10^{12}\mathrm{s}^{-1}$) is much smaller than the inverse rate of the phase ($\sim 10^{14}\mathrm{s}^{-1}$). In addition, the pulse duration (21ps) is much longer than the dephasing times, so coherent transient effects can be neglected. The population of the short-lived S_2 can be neglected due to the very short lifetime ($\tau_{12} \sim 0$). Only for comparing the OL properties of the three samples is the steady-state approximation model employed for the above rate equations, hence $\mathrm{d}N_i/\mathrm{d}t$=0. Thus, the following nonlinear absorption is obtained by solving the above rate equations

$$\alpha_{nl} = \alpha_0(1 + \tau_{01}\sigma_{21}I/h\nu)/(1 + \tau_{01}\sigma_{10}I/h\nu), \tag{6}$$

where $\alpha_0 = \sigma_{10}N$ is the linear absorption coefficient and N is the total molecular population density. Equation (5) may now be written as

$$\mathrm{d}I/\mathrm{d}z = -\alpha_0[(I_S + kI)/(I_S + I)]I, \tag{7}$$

where a saturation irradiance $I_S = h\nu/\sigma_{10}\tau_{01}$ is defined. Integrating from 0 to L (sample optical length), we obtain the transmittance

$$T = I(L)/I(0) = \mathrm{e}^{-\alpha_0 L}[(I_S + kI(L))/(I_S + kI(0)]^{1-1/k}, \tag{8}$$

where the ratio $k = \sigma_{21}/\sigma_{10}$. Therefore, from Eq.(6) if $k > 1(\sigma_{21} > \sigma_{10})$, then $\alpha_{nl} > \alpha_0$, namely, increasing the irradiance causes a decreasing transmittance (e.g. RSA).

The transmitted irradiance $I(L)$ is evidently an implicit function of the incident irradiance $I(0)$ in Eq.(8), thus we can only obtain a numerical solution of $I(L)$ by the numerical calculation. In practice, we measure the energy transmittance T_e in our experiments, not the irradiance transmittance T. We approximately analyse the OL experimental results of $(C_{12}H_{25}O)_8PcPb$, $(C_{12}H_{25}O_2)_8Pc$ and C_{60} in toluene solutions by using Eq.(8). Of course, the analysis is rough, but it is significant for the relative comparison of the above three samples in OL behaviours in relatively weak excitation (the maximum of the incoming irradiance is less than $50\mathrm{GW/cm}^2$ for OL experiments). The approximate fits are shown in Fig.4. Apparently, the fits agree well between theory and experimental results. We find that the fitting values k of the above three samples are 7.4, 6.6 and 5.6, respectively, corresponding to taking the saturable irradiance values I_S of 1.8×10^9, 3.5×10^9 and $5.0 \times 10^9\mathrm{W/cm}^2$, respectively, at which the transmittance reduces to 0.2. Therefore, it is interesting to take the above saturable irradiance values, emphasizing that only k has relative meaning.

For analysing the OL difference under picosecond and nanosecond pulse excitations, we compare the obtained k of 7.4 with 8.97 (ratio k_T of the absorption cross section of the effective triplet excited state to that of the ground state), which we obtained by the four-energy-level model[18] using 8ns laser pulses for $(C_{12}H_{25}O)_8PcPb$ in toluene solution. We can obtain two estimations as follows: (1) RSA results mainly from the first singlet excited-state absorption by the picosecond pulse excitation and the first triplet

excited-state absorption by the nanosecond pulse excitation; (2) $k_T > k$ can be caused by the relatively large absorption cross section of the first triplet excited state with respect to that of the first singlet excited state in $(C_{12}H_{25}O)_8PcPb$ toluene solution.

In terms of the saturable irradiance values I_S of 1.8×10^9 and $3.5 \times 10^9 W/cm^2$ for $(C_{12}H_{25}O)_8PcPb$ and $(C_{12}H_{25}O_2)_8Pc$, we can also estimate that the values τ_{01} are 0.31 and 0.15ns by using $I_S = h\nu/\sigma_{10}\tau_{01}$ and $T_0 = e^{-\sigma_0 NL}$, respectively. The large τ_{01} implies that S_1 can populate a great number of molecules which contribute to RSA. There are scarce data for $(C_{12}H_{25}O)_8PcPb$ and $(C_{12}H_{25}O_2)_8Pc$, so we can but compare τ_{01} (0.31ns) of $(C_{12}H_{25}O)_8PcPb$ with those of PbPc with different molecular structures, for example, with 0.35 of tetra(t-butyl)PbPc.[19] The different τ_{01} may be due to their different molecular structures.

As a result of $\tau_{01} > \tau_p$ (pulse width), the steady-state results obtained above are apparently rough. Thus, it is necessary to give a dynamic analysis for the OL results by using Eqs.(1)–(4), and assuming $N_2 \sim 0$, $\tau_{12} \sim 0$. The dynamic result of the OL in $(C_{12}H_{25}O)_8PcPb$ is shown in Fig.5 (see the dashed curve) by using the lifetime $\tau_{01} \sim 0.31$ns and the ratio $k \sim 7.4$. Apparently, there is a small discrepancy between the steady-state and dynamic-state analyses. Despite this, k still possesses the relative meaning as mentioned above.

We can also obtain the theoretical explanation of the strong RSA in Pc or MPc by their ground-state and excited-state absorption spectra for the strong OL behaviours in the three samples. The ground-state absorptions of $(C_{12}H_{25}O)_8PcPb$ and $(C_{12}H_{25}O_2)_8Pc$ in the region of 450–600nm is very weak (see Fig.2). Moreover, we find that CuPc in chloroform,[20] AlPc-F and GaPc–Cl both in pyridine[21] have ground-state absorption spectra similar to $(C_{12}H_{25}O)_8PcPb$ and $(C_{12}H_{25}O_2)_8Pc$. And almost all MPc have similar stronger excited-state absorption in the region of 450–600nm.[22,23] The different centre metal atom causes only a small change.[24] Therefore, RSA in MPc can be observed at this wavelength region. Besides, the ground-state absorption of C_{60} molecules is also very weak. While the singlet and triplet first excited-state absorptions are quite strong in the region of 400–600nm.[25] Similarly, RSA is expected at the wavelength of 532nm.

RSA is one of the main mechanisms for OL, and it is significant for the search of nonlinear optical materials with RSA. According to the rate-equation model, RSA can be characterized by the ratio k of the absorption cross section of the excited state to that of the ground state, and the ground-state saturable intensity I_S. Strong OL demands a large k but a small I_S. On the other hand, in terms of structures and chemical bonding of molecules, highly conjugated delocalized π electronic systems have a strong nonlinear response to electromagnetic interactions. Thus, the stronger OL effects of Pc than those of C_{60} can be understood clearly by their molecular structures.

As is well known, the C_{60} molecule is a three-dimensional π-electron conjugated system, while MPc are delocalized two-dimensional π-electron conjugated systems. Moreover, the nonlinear optical properties can be weakened with increasing dimensions of conjugated systems.[26,27] Therefore, $(C_{12}H_{25}O)_8PcPb$ and $(C_{12}H_{25}O_2)_8Pc$ show stronger OL effects than C_{60}. The rigid structural framework of Pc leads to a small geometric change on excitation and a concentration of intensity into the $S_1 \leftarrow S_0$ (0, 0) vibronic transition, resulting in a strong narrow band absorption (Q(0) band). Thus, the Pc can exhibit a low saturation intensity, depending on the relevant relaxation rate, which may induce very strong excited-state absorptions in a weak linear absorption spectrum range. It should be noted that $(C_{12}H_{25}O)_8PcPb$ and $(C_{12}H_{25}O_2)_8Pc$ have a significant difference in their OL behaviours despite the identical molecular structure, which comes from the increase of k and τ_{01} by introducing metal lead. Especially, the transmittances decrease from 60% to about 3.5% as the incident fluences increase from 0 to $1 J/cm^2$ for $(C_{12}H_{25}O)_8PcPb$. This implies a large nonlinear attenuation factor of 17 (7.5 for C_{60} in toluene), for which the larger k is mainly responsible.

It should also be noted that the solubility of phthalocyanines in organic solvents is improved greatly, because of the alkoxy groups attached on the ring of phthalocyanine in the two compounds. The optical nonlinearities of the two phthalocyanines can be enhanced furthest in organic solvents (e.g. toluene). Besides, no optical damage has been discovered as the incident irradiance reaches $4.8 \times 10^{10} W/cm^2$ corresponding to the fluence of $1 J/cm^2$.

IV. CONCLUSIONS

The ultra-fast OL performances of the two novel phthalocyanines with the substituent group of octadodecaoxyl long chains have been investigated by 21 ps

laser pulses at 532nm. The experimental results show that the OL properties of the two compounds are much stronger than those of C_{60} in toluene. The OL mechanisms are analysed, and a theoretical model of RSA considering only the first singlet excited-state absorption is established. The fits of the experimental results yield the ratios of the absorption cross section of the first singlet excited state to that of the ground state for samples. Further investigation of the lead phthalocyanine using nanosecond pulses will be reported elsewhere.

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