Effect of peripheral ligands on the optical limiting property of homoleptic sandwich-type rare earth metal diphthalocyanines

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Abstract. The optical limiting property of sandwich-type rare earth metal diphthalocyanines, $Eu[Pc(R)_8]_2[R = n\text{-}C_7H_{15}, OC_5H_{11}]$, was investigated via fluence-dependent transmittance measurements. The measurements were performed using collimated 10-ns pulses generated from a frequency-doubled Nd:YAG laser at 532-nm wavelength. The results demonstrated that $Eu[Pc(OC_5H_{11})_8]_2$ exhibited better optical limiting behavior than $Eu[Pc(C_7H_{15})_8]_2$. This is attributed to the enhanced delocalization of the π-conjugated system in $Eu[Pc(OC_5H_{11})_8]_2$ because of the stronger electron-donating ability of alkoxy relative to that of alkyl.

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Optical limiting (OL) refers to a decrease of the optical transmittance of a material with increase of the incident light intensity, which is considered as a powerful protecting means for laser applications. These days, the increasing need for protecting human eyes and optical sensors from exposure to undesired intense laser beams has attracted considerable attention [1–5] to the development of OL materials. Phthalocyanines (Pcs) have been shown [6–9] to be one of the most promising OL materials for nanosecond 532-nm laser pulses. Due to their relatively low linear absorption and high ratio of excited-state to ground-state absorption cross sections in the range of 400–600 nm [7], the dominant mechanism in metal phthalocyanines (MPcs) for OL has been associated with reverse saturable absorption (RSA) [10], in which the OL for nanosecond laser pulses resulted from the strong triplet–triplet absorption and large absorption cross section ratio of triplet state to ground state.

The excellent propertiesof Pcs as candidates for OL applications originated not only from their extensive π-electron delocalization and their thermal and chemical stability, but also from their processability by either substituting the peripheral or axial side groups or changing the central metal ion. The peripheral [11] or axial [9] substitution could enhance

the solubility of Pcs and thus improve their usability. Heavy-metal atoms [2, 7] could facilitate intersystem crossing from the singlet state to the triplet state via spin–orbit coupling and thus reinforce the absorption of the triplet state by increased population. The latter is often referred to as the heavy-atom effect. Up to now, metal phthalocyanines which have been studied for their OL behavior [6–9] are all two-dimensional and with symmetry D_{4h} because the metal ions encompassed have a small radius.

As a new kind of phthalocyanine derivatives, sandwich-type metal diphthalocyanines, in which the large conjugated π systems are held in close proximity by metal ions of larger radius such as rare-earth metals and transition metals, have also been synthesized and found widespread applications in materials science, especially in electrochromism [12, 13], intrinsic molecular conductivity [14] and for their gas-sensing property [15]. However, to our knowledge, the OL properties of these double-decked complexes have not been reported. In this letter, sandwich-type rare earth metal europium diphthalocyanines $Eu[Pc(R)_8]_2[R = n\text{-}C_7H_{15}, OC_5H_{11}]$ were studied for their OL properties. In addition, the effect of different peripheral ligands was compared.

Double-decked molecular structures of the two europium diphthalocyanines, $Eu[Pc(R)_8]_2[R = n\text{-}C_7H_{15}, OC_5H_{11}]$, are shown in Fig. 1. Their synthesis process is referred to in [16]. The trivalent europium ion is sandwiched by two parallel but staggered Pc macrocycles. An unpaired electron is localized over the two Pc rings. The molecule can be represented as $HPc^{2-}Eu^{3+}Pc^{-}$. Due to the strong intermolecular $\pi-\pi$ interaction, MPcs in solution are prone to aggregation, especially in a solution with high concentration [17] or in a solvent having high polarity [11]. In order to suppress the aggregation, both MPcs were dissolved in chloroform with low concentrations and finally prepared in 5-mm-thick glass cells with identical linear transmittance of 74%. The concentrations of $Eu[Pc(C_7H_{15})_8]_2$ and $Eu[Pc(OC_5H_{11})_8]_2$ solutions are 0.86×10^{-5} M and 0.97×10^{-5} M respectively.

Experiments for fluence-dependent transmittance measurements were performed using 532-nm wavelength, 10-ns laser pulses from a frequency-doubled Quantel Q-switched Nd:YAG laser. The experimental setup was similar to that

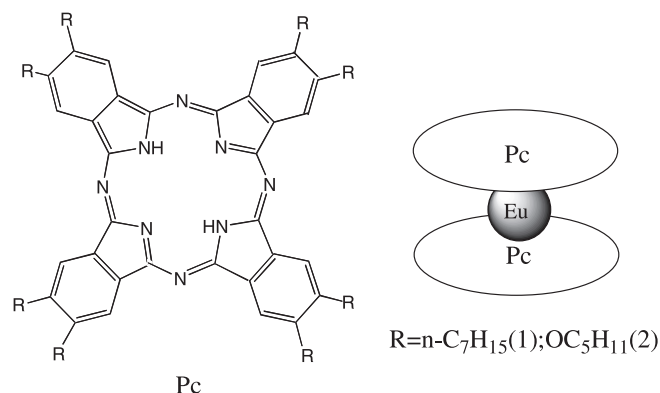*Corresponding author. (E-mail: qhgong@pku.edu.cn)

Fig. 1. Schematic diagram of molecular structures of Eu[Pc(C$_7$H$_{15}$)$_8$]$_2$ (1) and Eu[Pc(OC$_5$H$_{11}$)$_8$]$_2$ (2)

used in our previous work [18, 19], as shown in Fig. 2. The laser output was spatially filtered by a diaphragm and a nearly homogeneous light spot was obtained. Then, the laser beam was collimated to a smaller size by an inverted telescope system, which was formed by a convex lens ($f = 15$ cm) and a concave lens ($f = -5$ cm). Before entering the sample, the collimated laser beam was separated into two parts by a beam splitter, BS. The weak part was detected with an Rjp-735 energy probe (Laser Precision Corporation, USA) in order to monitor the incident laser energy. The strong part was transmitted into the glass cell, which was filled with the sample solution. The light spot on the sample was measured to be of 0.9-mm diameter by a razor method. The transmitted pulse energy was detected with another energy probe (Rjp-734, Laser Precision Corporation, USA). Compared with the light-spot dimension, the much larger acceptance area of the energy probes ensured the collection of all the energy of the pulse and thus the factor of nonlinear refraction was excluded. To avoid the influence of thermal effects, a single-pulse measurement was used so that each pulse of light was certain to encounter fresh molecules in the sample.

The experimental results of output–input characteristic (O–I) curves and the corresponding fluence-dependent transmittance (T–I) curves are shown in Figs. 3 and 4 respectively. It is evident that the transmittances of both solutions decrease remarkably with the increased laser intensity and thus the OL effect is proved. From the curves, the OL performance of Eu[Pc(OC$_5$H$_{11}$)$_8$]$_2$ is better than that of Eu[Pc(C$_7$H$_{15}$)$_8$]$_2$.

Generally, the OL ability of a sample can be evaluated with a limiting threshold, which is defined as the incident laser fluence at which the transmittance of the solution decreases to half of its linear transmittance. It is obvious that the smaller the limiting threshold, the better the OL perform-
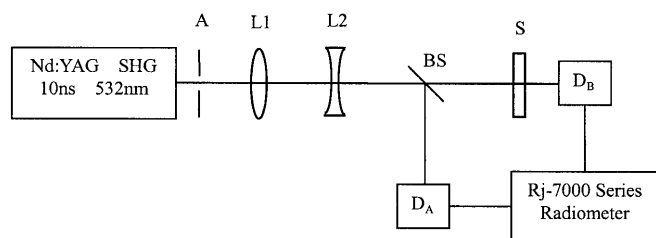

Fig. 3. Output–input characteristics of Eu[Pc(C$_7$H$_{15}$)$_8$]$_2$ (*open circles*) and Eu[Pc(OC$_5$H$_{11}$)$_8$]$_2$ (*solid circles*) in chloroform solutions of 74% linear transmittance at 532 nm

ance. It can be learned from the T–I curves that the limiting thresholds of Eu[Pc(OC$_5$H$_{11}$)$_8$]$_2$ and Eu[Pc(C$_7$H$_{15}$)$_8$]$_2$ are 1.2 J/cm^2 and 1.8 J/cm^2 respectively. The former is 1.5 times lower than the latter.

A five-level model [20, 21] is usually used to fit the optical limiting results for RSA. At higher incident laser fluence, a phenomenological model for nonlinear absorption proposed by Golovlev et al. [22] can describe the optical limiting behavior of fullerene C$_{60}$ more perfectly than the five-level model [23]. Considering the same dominant mechanism for optical limiting in C$_{60}$ and MPcs and the higher incident laser intensity used in our experiments, the phenomenological model is used to fit our experimental results. In this model, the absorption cross section σ is expressed in the form of a series expansion of the laser fluence Φ:

$$\sigma(\Phi) = \sigma_0 + \mu_1\Phi + \mu_2\Phi^2 + \cdots \qquad (1)$$

Retaining the first two terms of this expansion and putting (1) into Beer's law, the laser fluence propagating equation in the medium can be obtained, and then by integration the expres-

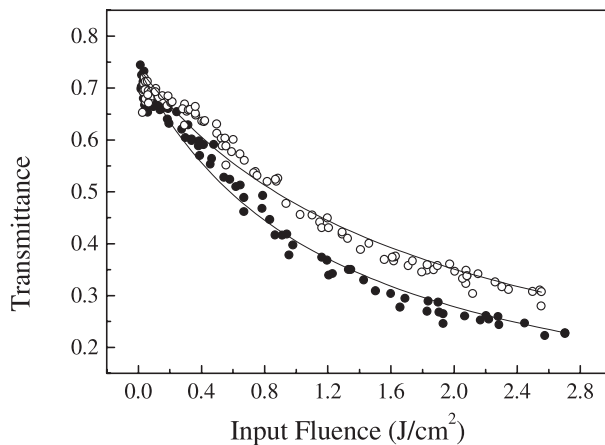**Fig. 2.** Experimental setup used for fluence-dependent transmittance measurements

Fig. 4. Fluence-dependent transmittance of Eu[Pc(C$_7$H$_{15}$)$_8$]$_2$ (*open circles*) and Eu[Pc(OC$_5$H$_{11}$)$_8$]$_2$ (*solid circles*) in chloroform solutions of 74% linear transmittance at 532 nm

sion of output laser fluence can be easily found:

$$\Phi_{\mathrm{out}} = T_0\Phi_{\mathrm{inp}}/\lfloor 1 + (1 - T_0)\,\Phi_{\mathrm{inp}}/\Phi_{\mathrm{nln}}\rfloor \qquad (2)$$

So the transmittance is obtained as follows:

$$T = T_0/\lfloor 1 + (1 - T_0)\,\Phi_{\mathrm{inp}}/\Phi_{\mathrm{nln}}\rfloor \qquad (3)$$

where $T_0 = \exp(-\sigma_0 N_0 L)$ is the linear transmittance, Φ_{inp} and Φ_{out} are the input and output laser fluences respectively and $\Phi_{\mathrm{nln}} = \sigma_0/\mu_1$. It can be seen from (2) and (3) that in this model the optical limiting performance of a sample can conveniently be assessed by only the value of Φ_{nln}. The smaller magnitude of Φ_{nln} denotes the better optical limiting performance of the sample.

The experimental results were fitted with (2) for Fig. 3 and (3) for Fig. 4. It can be learned from the best fitting results, which are shown in Figs. 3 and 4 with solid curves, that the values of Φ_{nln} of $Eu[Pc(OC_5H_{11})_8]_2$ and $Eu[Pc(C_7H_{15})_8]_2$ are $0.3\,\mathrm{J/cm^2}$ and $0.45\,\mathrm{J/cm^2}$ respectively. The former is smaller than the latter. This result is congruous with what we found above that the limiting threshold of $Eu[Pc(OC_5H_{11})_8]_2$ is 1.5 times lower than that of $Eu[Pc(C_7H_{15})_8]_2$. This congruency demonstrates that the optical limiting performance of samples can be qualitatively compared with the ratio Φ_{nln}.

The nonlinearities of organic materials predominantly originate from their π-conjugated system. The peripheral ligands of MPcs that have strong electron-donating or electron-accepting abilities can increase the intramolecule electron transfer, and thus can heighten the delocalization of the π-conjugated system and probably improve the nonlinearities of MPcs. It has been demonstrated [20, 24] that the peripheral ligands, having stronger electron-donating ability, can raise the second-order hyperpolarizabilities of MPcs. Here, this superiority of $Eu[Pc(OC_5H_{11})_8]_2$ over $Eu[Pc(C_7H_{15})_8]_2$ for optical limiting can also be attributed to the stronger electron-donating competence of alkoxy than alkyl, which can be seen from the following UV-Vis spectra.

The ground-state absorption spectra of $Eu[Pc(C_7H_{15})_8]_2$ and $Eu[Pc(OC_5H_{11})_8]_2$ both in chloroform with identical linear transmittances of 74% at 532 nm and with concentrations of $0.86 \times 10^{-5}\,\mathrm{M}$ and $0.97 \times 10^{-5}\,\mathrm{M}$ respectively are shown in Fig. 5. Both of them exhibit more complex UV-Vis absorption than the planar MPc monomer [7]. This complexity results mainly from the π–π interaction between the two Pc rings of the diphthalocyanines, which is a Pc dimer in nature. This would lead to a splitting of the degenerate molecular orbitals of each monomer. Besides, considerable charge transfer [25] between the two Pc rings due to the smaller intermacrocycle distance may also contribute to the extra absorption peaks in the diphthalocyanines.

In addition, the absorption of $Eu[Pc(OC_5H_{11})_8]_2$ exhibits a slightly blue-shifted Q-band and a stronger shoulder at 590 nm compared with that of $Eu[Pc(C_7H_{15})_8]_2$. These demonstrate an enhancement of the π–π interaction between the two Pc rings in $Eu[Pc(OC_5H_{11})_8]_2$, because the blue shift of the Q-band has been reported in Pc dimers both theoretically and experimentally [11, 26]. This enhancement of the π–π interaction between the two Pc rings in $Eu[Pc(OC_5H_{11})_8]_2$ relative to $Eu[Pc(C_7H_{15})_8]_2$ can be associated with the stronger electron-donating ability of alkoxy than alkyl, which heightens the π-conjugation effect in one
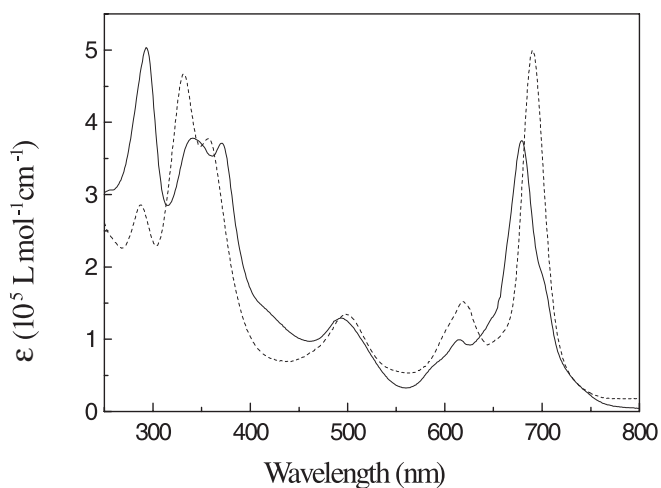

Fig. 5. UV-Vis spectra of $Eu[Pc(C_7H_{15})_8]_2$ (*dashed line*) and $Eu[Pc(OC_5H_{11})_8]_2$ (*solid line*) both in chloroform with identical linear transmittances of 74% at 532 nm and with concentrations of $0.86 \times 10^{-5}\,\mathrm{M}$ and $0.97 \times 10^{-5}\,\mathrm{M}$ respectively

Pc ring and then strengthens the π–π interactions between the two Pc rings.

The substitution of peripheral ligands has been shown [11] to improve the OL ability of MPcs by enhancing their solubility through suppressing molecule aggregation. Here the augmentation of electron-donating competence of peripheral ligands is also shown to strengthen the optical limiting ability of MPcs efficiently. Thus a new way of improving the optical limiting performance of MPcs through the substitution of peripheral ligands is demonstrated. This is important for future applications.

In addition, it is worth noting that by changing the size of the metal center, the ring–ring separation and then the π–π interaction between the two Pc rings in the diphthalocyanines have been shown [27, 28] to be altered. This therefore provides another entry to improve the nonlinearities of these sandwich-type complexes. Further studies of this influence on their OL properties are deserved.

The UV-Vis spectra of $Eu[Pc(OC_5H_{11})_8]_2$ in chloroform solutions with different concentrations were measured by us
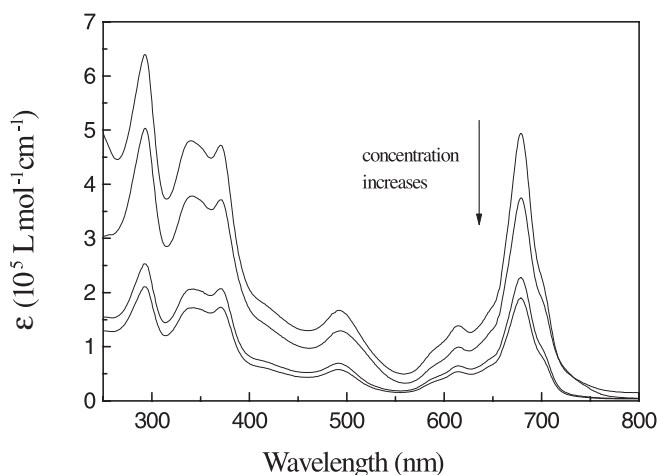

Fig. 6. UV-Vis spectra of $Eu[Pc(OC_5H_{11})_8]_2$ in chloroform (1×10^{-6}, 1×10^{-5}, 2.5×10^{-4}, and 5×10^{-4} M)

and shown in Fig. 6. The decrease of the molecular extinction coefficient in solution with higher concentration reflects the evidence of aggregation. As an important character of the phthalocyanines, aggregation would add complexity to the concentration dependence of the optical limiting performance of the MPcs. A detailed investigation is in progress.

In summary, the optical limiting performance for 532-nm, 10-ns laser pulses of sandwich-type homoleptic lanthanide europium diphthalocyanines, $Eu[Pc(R)_8]_2[R = n\text{-}C_7H_{15}, OC_5H_{11}]$, was first reported. Besides, comparison under identical conditions showed that $Eu[Pc(OC_5H_{11})_8]_2$ has a remarkable superiority over $Eu[Pc(C_7H_{15})_8]_2$ for optical limiting due to the stronger electron-donating ability of alkoxy than that of alkyl. This leads to another important way of improving the optical limiting performance of MPcs.

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