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Z-scan study of nonlinear absorption in novel lanthanide bis-phthalocyanines

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ARTICLE INFO

Article history:

Received 19 July 2012

In final form 10 October 2012

Available online 22 October 2012

ABSTRACT

We report our results on the nonlinear absorption of novel sandwich lanthanide(III) double-decker complexes $^{\text{Bu}}\text{Pc}_2\text{Ln}$ ($^{\text{Bu}}\text{Pc}$ = 2,3,9,10,16,17,23,24-octabutyl-phthalocyaninate; Ln = Eu, Dy, Er, Lu) studied in tetrahydrofuran (THF) solution using open aperture z-scan technique with 350 ps laser pulses at 532 nm. All the compounds exhibit reverse saturable (RSA) absorption. With approaching to the focus a weak saturation of absorption was observed, while at the focus a strong decrease in transmittance took place. Employing the rate equations formalism we demonstrate RSA being mainly contributed by the triplet state absorption.

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1. Introduction

Among conjugated organic molecules possessing nonlinear optical (NLO) properties phthalocyanines and their metal complexes attract much attention owing to their thermal and chemical stability, structural flexibility and ease of preparation. The presence of the extensive π -electron conjugated system plays a key role in the manifestation of optical nonlinearities. Furthermore, structural flexibility of phthalocyanine molecules, which allows one to control the nature of central metal ion as well as the number and location of peripheral substituents, opens a way to construct new materials with required NLO properties [1]. Some materials with strong nonlinearity are capable of exhibiting the phenomenon known as optical power limiting (OL) effect, which is characterized by decrease in optical transmittance under the strong illumination. OL is mainly governed by three mechanisms [1,2]: nonlinear absorption (NLA), nonlinear refraction and nonlinear scattering. In the case of phthalocyanines NLA is the most prominent effect. If it is positive then a material exhibits RSA behavior which is characterized by a high transmittance at low intensities of the incident light and a decrease in a transmittance under high intensity or high fluence illumination. Phthalocyanine metal complexes and particularly bis-phthalocyanines are the typical representatives of such materials [2–4]. RSA appears when the excited state absorption is more intense than that of the ground state, which is opposite to the case of saturable absorption (SA). In phthalocyanines RSA can be reached with intense pumping in the transparent region of the linear absorption spectrum between B and Q bands, while pumping near the Q-band peak leads to SA [5]. Effective OL properties of

phthalocyanines allow their application as optical limiters for eye and sensor protection [2,6,7], optical modulators [8] and switches [9,10].

In this Letter, we present the study of RSA phenomenon in the THF solutions of novel sandwich lanthanide(III) double-decker complexes $^{\text{Bu}}\text{Pc}_2\text{Ln}$ ($^{\text{Bu}}\text{Pc}$ = 2,3,9,10,16,17,23,24-octabutyl-phthalocyaninate; Ln = Eu, Dy, Er, Lu) **1a–d** by the z-scan technique [11]. Structures of the compounds are presented in Fig. 1.

The UV/Vis absorption spectra of bis-phthalocyanines **1a–d** are presented in Fig. 2 and corresponding data are summarized in Table 1. There are three main absorption bands corresponding to Q, BV (blue valence) and B (Soret) electronic transitions, what is in a good accordance with the spectra of similar lanthanide bis-phthalocyanines [12,13].

Fig. 3 displays the molecular orbital diagram based on a combination of literature data [14–17] with transitions corresponding to B-, BV-, and Q-bands. The transition from the HOMO $2b_1$ to the LUMO $6e_3$ gives the main contribution to the Q-band (670 nm). The B-band (320 nm) corresponds to the transitions from deeper orbitals $4a_1$, $4b_2$, $3a_1$ and $3b_2$ to LUMOs $6e_3$ and $6e_1$, respectively. In turn, the transition from the deeper $5e_1$ to the SOMO $2a_2$ matches the BV-band excitation.

2. Experiment

Synthesis and purification procedures of compounds **1a–d** were published elsewhere [18,19]. Linear absorption UV/Vis spectra (Fig. 2) were recorded in the solution of THF with a conventional spectrophotometer in a 2 mm quartz cuvette. Molar concentration of the sample solutions was of $\sim 5 \times 10^{-5}$ M.

Z-scan technique that had been generally developed earlier [11] was utilized for the THF solutions of compounds **1a–d**. The scheme of the experimental setup is shown in Fig. 4. A small portion of laser

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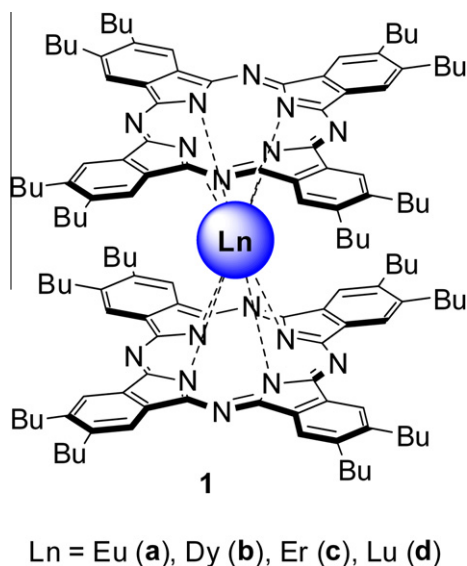


Fig. 1. Schematic structure of lanthanide double-decker phthalocyanine complexes.

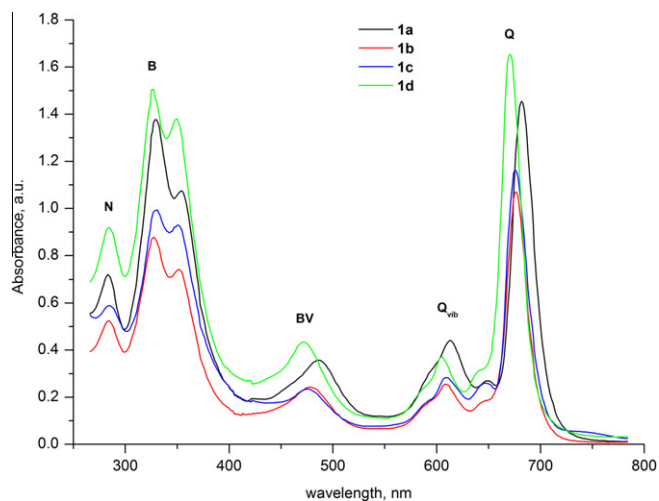


Fig. 2. UV/Vis electronic absorption spectra of compounds **1a–d** in THF solution.

irradiance after the beam splitter was directed to the photodetector D_1 for the input energy monitoring. In order to decrease the energy fluctuations of an input pulse we used a 10% programmable gate for D_1 photodetector. If the energy exceeded the gate range then such a measurement was ignored. The light transmitted through the splitter was focused with a lens and impinged on a thin cuvette with a phthalocyanine solution. The light energy transmitted through the sample was registered with the photodetector D_2 . The sample moved along the laser beam and the ratio D_2/D_1 was registered for each sample position relative to the beam

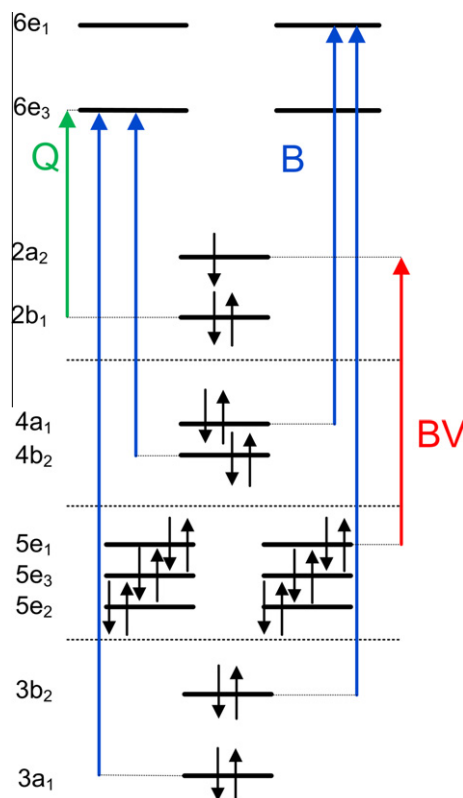


Fig. 3. Frontier molecular orbital diagram for the general Pc_2Ln radical (in D_{4d} symmetry) and the excitations assigned to the Q, B, and BV bands according to Refs. [14–17].

waist. The position of the beam waist was referred to $z = 0$. The transmittance T , which had been registered as the ratio D_2/D_1 , was then normalized by the value of the linear transmittance T_{lin} obtained far from the beam waist. The experiment resulted in the z -scan curves which were yielded by plotting the transmittance T versus the sample position z .

The z -scan experiment was carried out at $\lambda = 532$ nm using the second harmonic of a Nd:YAG laser operating in the TEM_{00} mode with the pulse duration of $\tau_p = 350$ ps (halfwidth at e^{-1} intensity) and the repetition rate of 5 Hz. The beam was tightly focused by a 15 cm focal distance lens. The GAUSSIAN beam radius ω_0 at the focus (halfwidth at e^{-2} intensity) was of 25–30 μm . The energy of the pulse was $E_0 = 38$ μJ . Intensity of the GAUSSIAN pulse as the function of spatial coordinates and time is given by the following formula

$$I(t, r, z) = I_{00} \left(\frac{\omega_0^2}{\omega^2(z)} \right) \exp \left(-\frac{t^2}{\tau_p^2} \right) \exp \left(-\frac{2r^2}{\omega^2(z)} \right)$$

where $\omega(z)$ is the beam radius at the distance z from the beam waist

$$\omega(z) = \omega_0 \left[1 + \frac{z^2}{z_0^2} \right]^{\frac{1}{2}}$$

Table 1
UV/Vis electronic absorption data for double-decker complexes **1a–d** in THF.

	λ_{max} [nm] (I/I_{max})					
	N	B (Soret)		BV (π -radical)	Q_{vib}	Q
1a	283 (0.496)	329 (0.947)	354 (0.739)	486 (0.245)	613 (0.303)	682 (1.000)
1b	283 (0.490)	328 (0.820)	351 (0.694)	478 (0.227)	609 (0.239)	676 (1.000)
1c	284 (0.507)	330 (0.855)	350 (0.800)	475 (0.202)	609 (0.244)	675 (1.000)
1d	284 (0.556)	327 (0.911)	349 (0.835)	472 (0.263)	605 (0.225)	671 (1.000)

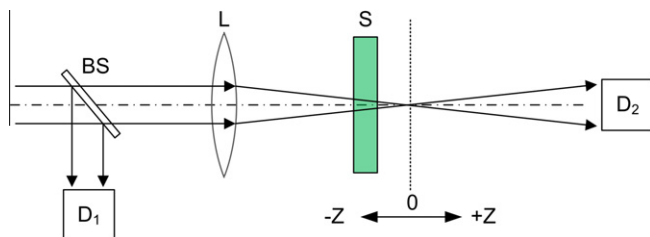


Fig. 4. Scheme of the open-aperture z-scan setup. BS, beam splitter; L, lens; D₁ and D₂, photodetectors; S, sample.

and z_0 is the Rayleigh length:

$$z_0 = \frac{\pi \omega_0^2}{\lambda}$$

The z-scan measurements were performed with samples dissolved in THF having the concentration of 5×10^{-5} M in a 3-mm thick quartz cuvette. Chosen concentration allowed us to avoid aggregation of the phthalocyanines in solution. We also passed 100 measurements at each point in order to decrease the influence of the fluctuation of the laser parameters such as pulse-to-pulse radius and energy fluctuations.

3. Results and discussion

Z-scan curves obtained in the study are presented in Fig. 5 for all samples **1a–d**. To interpret the obtained data we used the five-level model which describes processes of excitation and relaxation in the molecule. The scheme of the model is shown in Fig. 6. The ground state is signed as S_0 and corresponds to the ground singlet state with fully occupied π -orbital $2b_1$. Pumping at 532 nm mainly affects the excitation $2b_1 \rightarrow 6e_3$ near the Q-band. Absorption of the photon at 532 nm leads to the transition of the electron to the vibronic sublevel of the first excited singlet state S_1 . The lifetime of the vibronic level is of subpicosecond range [20], so one can treat only the direct transition $S_0 \rightarrow S_1$. The electrons from S_1 can relax either to the ground state, with the decay time τ_0 , or to the triplet state T_1 via intersystem crossing, with the time τ_{ISC} . Under the influence of the incident radiation excited electrons at states S_1 and T_1 can transit to the upper excited states S_n and T_n , respectively. We neglected the two-photon absorption due to the excited state absorption gives the most prominent contribution to NLA in the case of phthalocyanines [3,21]. The population dynamics of all mentioned states is described by system of rate equations [22,23]:

$$\begin{aligned} \frac{dN_0}{dt} &= -\sigma_0 N_0 \frac{I}{\hbar \omega} + \frac{N_{S_1}}{\tau_0} + \frac{N_{T_1}}{\tau_{T_1}} \\ \frac{dN_{S_1}}{dt} &= \sigma_0 N_0 \frac{I}{\hbar \omega} - \sigma_1 N_{S_1} \frac{I}{\hbar \omega} - \frac{N_{S_1}}{\tau_0} - \frac{N_{S_1}}{\tau_{ISC}} + \frac{N_{S_2}}{\tau_{S_2}} \\ \frac{dN_{S_2}}{dt} &= \sigma_1 N_{S_1} \frac{I}{\hbar \omega} - \frac{N_{S_2}}{\tau_{S_2}} \\ \frac{dN_{T_1}}{dt} &= -\sigma_2 N_{T_1} \frac{I}{\hbar \omega} + \frac{N_{S_1}}{\tau_{ISC}} + \frac{N_{T_2}}{\tau_{T_2}} - \frac{N_{T_1}}{\tau_{T_1}} \\ \frac{dN_{T_2}}{dt} &= \sigma_2 N_{T_1} \frac{I}{\hbar \omega} - \frac{N_{T_2}}{\tau_{T_2}} \end{aligned}$$

where N_i is the population of the i -th state, σ_0 is the ground state absorption cross-section, σ_1 is the first excited singlet state absorption cross-section, σ_2 is the first excited triplet state absorption cross-section, τ_i is the lifetime of the i -th state and τ_{ISC} is the intersystem crossing lifetime. The lifetimes of S_n and T_n are less than one picosecond and, therefore, these levels can be treated as unpopulated for relatively long laser pulses, as in the case of our study.

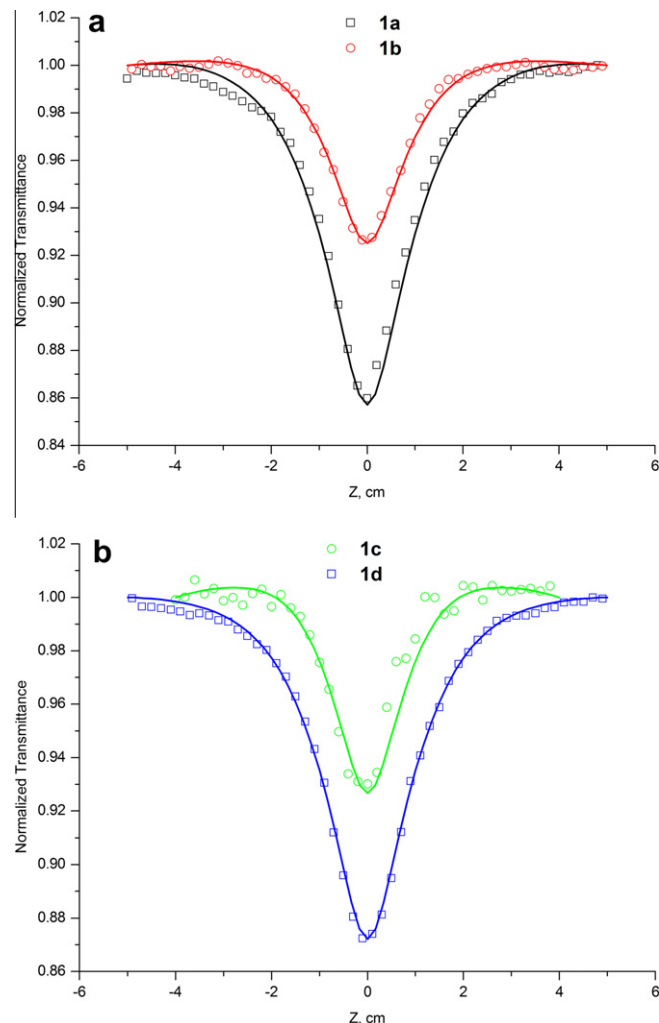


Fig. 5. Open aperture z-scan curves for samples **1a–d**. Experimental values (dotted lines) and corresponding theoretical approximations (solid lines).

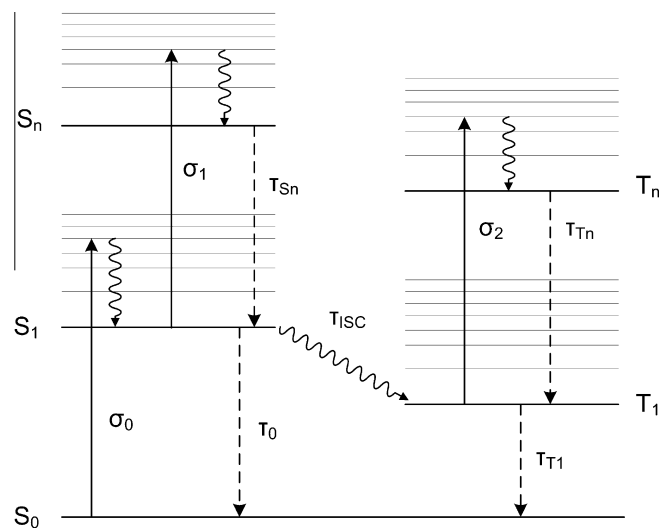


Fig. 6. Jablonski diagram of excitation (solid lines) and relaxation (dashed and jagged lines) processes in a molecule.

The lifetime of the triplet state T_1 is quite large (of microseconds or even more) since it is forbidden by multiplicity, hence the decay

Table 2
Summary of the photophysical parameters of compounds **1a–d**.

	1a	1b	1c	1d
τ_0 , ns	2.0	2.0	2.0	2.0
τ_{ISC} , ns	2.6	2.9	3.0	2.6
σ_0 , 10^{-17} cm ²	4.7	2.6	2.9	4.5
σ_1 , 10^{-17} cm ²	1.8	0.9	1.0	1.6
σ_2 , 10^{-17} cm ²	22.0	14.5	20.0	16.5
σ_2/σ_0	4.7	5.6	6.9	3.7

process $T_1 \rightarrow S_0$ can be neglected. With such assumptions these five rate equations are reduced to the system of three equations considering only populations of S_0 , S_1 and T_1 states. The absorption in the sample is governed by the Beer's law

$$\frac{dl}{dz} = -\sigma_0 I_G - \sigma_1 I_{S_1} - \sigma_2 I_{T_1}$$

where z' is the coordinate inside the sample. The first term describes the absorption of the ground state and the other two describe the absorption of excited singlet and triplet state, respectively. The transmittance of the pulse is determined by the following expression

$$T(z) = \frac{\int_{-\infty}^{\infty} dt \int_0^{\infty} I_{out}(r, z, t) r dr}{\int_{-\infty}^{\infty} dt \int_0^{\infty} I_{in}(r, z, t) r dr}$$

where I_{in} and I_{out} are the intensities of incident and transmitted pulses, respectively. Calculating transmittance for each z -position yields the z -scan curve.

In order to model the propagation of the pulse through the nonlinear sample numerically we followed the procedure presented in [22]. During numerical calculations the laser pulse was divided into 30 time intervals and 20 radial intervals. The sample was divided into 10 spatial intervals. Within each time interval the pulse intensity was assumed to be constant and the system of the rate equations was solved with the fourth order Runge–Kutta (RK) method. The time step for the RK method was chosen to be equaled one twentieth of the time interval. Further increase in the amount of subintervals did not lead to a drastic change of the theoretical curve, but increased the time of calculation. As can be seen from the figures we reached rather good fitting of the experimental data. The values σ_1 , σ_2 and τ_{ISC} were treated as adjustable input parameters during calculations. Their values were varied with the following steps: 0.1×10^{-17} cm² for σ_1 , 0.5×10^{-17} cm² for σ_2 and 0.1 ns for τ_{ISC} . The decrease in the variance step of input parameters also did not change the curve behavior significantly.

Fig. 5 shows that RSA takes place for the entire compounds **1a–d** under applied conditions. Table 2 summarizes the results obtained via numerical modeling. Values of the ground-state absorption cross-section σ_0 for all the samples **1a–d** were determined from the absorption spectra (Fig. 2). We also determined σ_0 for the samples via the direct measurement of the linear transmittance $T_{lin} = \exp(-\sigma_0 NL)$ far from the focus and found good agreement with the values obtained from the spectral data. The cross-section σ_0 appeared to be rather big in comparison with those known for similar compounds from literature [12,24]. For numerical calculations we took the singlet lifetime to be of 2 ns, as for Pc₂Lu from the Ref. [24].

It is common case for phthalocyanines that the absorption cross-section of S_1 state is bigger than that of the ground state S_0 . But according to our results the cross-section σ_1 is much smaller than σ_0 (see Table 2). This leads to the narrowing of the z -scan

curve. As can be seen from experimental and theoretical curves, while moving towards the focus, the samples exhibit rather weak saturation. This effect is the most noticeable for dysprosium (**1b**) and lutetium (**1d**) bis-phthalocyanines (Fig. 1). When the sample reaches the focus RSA takes place. According to absorption cross-section ratio of the excited triplet and ground states presented in Table 2 we suggest that such behavior of the curve is mainly determined by considerable triplet absorption.

4. Conclusions

In summary, the nonlinear absorption of four novel lanthanide(III) bis-phthalocyanine complexes was investigated in THF solution using the z -scan technique at 532 nm wavelength with 350 ps laser pulses. For all the compounds RSA process was observed. Owing to comparatively long pulse duration the contribution of the triplet state to RSA cannot be neglected. Therefore, in order to describe photoexcitation and relaxation processes we applied the five-level model. The narrowness of the z -scan curves showed that compounds exhibit a weak saturation near the focus. Experimentally determined values of the ground state absorption cross-section appeared to be much bigger than ones known for analogous compounds. Moreover, the defined values clearly evidence that the excited singlet state absorption cross-section σ_1 is smaller than the ground state one, σ_0 . Employing the five-level model we also assessed the values of the triplet state absorption cross-section, σ_2 , and the intersystem crossing lifetime, τ_{ISC} , while also determined the ratio σ_2/σ_0 . The biggest ratio, $\sigma_2/\sigma_0 \approx 6.9$, was obtained for the erbium bis-phthalocyanine complex **1c**. Taken together, these results allowed us to conclude that observed RSA behavior was caused by the considerable triplet state absorption.

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