



A series of homoleptic bis(phthalocyaninato) rare earth sandwich complexes with large two-photon absorption cross-section



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ABSTRACT

The third-order nonlinear optical properties of a series of homoleptic substituted phthalocyaninato rare earth double-decker complexes were experimentally investigated by the Z-scan technique at the wavelength of 800 nm. All complexes were revealed to exhibit large two-photon absorption cross-sections. The measured two-photon absorption values of these complexes remain constant at different laser intensities, indicating nonlinearity is originated from pure two-photon absorption behavior. In addition, the two-photon absorption cross-section of these complexes increases along with the decrease of the rare earth atomic radius, suggesting that intense intramolecular π - π interaction between the phthalocyaninato macrocycles improves the third-order nonlinear optical properties. The optical limiting behavior of these complexes in chloroform was also investigated by using femtosecond laser pulses. The excellent two-photon absorption properties and optical limiting performance indicate their good application potential in photonic and optoelectronic devices.

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1. Introduction

Phthalocyanines and porphyrins are versatile functional pigments with a wide range of applications not only because of their large π -electron system with two-dimensional conjugated electronic molecular structure, but also because of their exceptional chemical and thermal stability together with versatile functionalization at the peripheral positions and various possibilities of the central metal ion [1,2]. These macrocycles can complex with large metal ions including rare earths, actinides, and some early transition metals and main group elements to form sandwich type complexes [3]. This class of complexes, with either a double- or triple-decker structure, usually exhibits strong π - π interactions resulting in intriguing electronic and optical properties. These unique features together with other characteristics enable them to function as useful materials for a wide range of applications in the fields of molecular electronics [4], organic field effect transistors [5], molecular information storage materials [6] and single

molecular magnets [7,8]. Recently, the sandwich type tetrapyrrole metal complexes have attracted more and more attention as potential third-order nonlinear optical (NLO) materials [9]. Several bis(phthalocyanines) [10,11] and bis(naphthalocyanine) [12] rare earth complexes showed higher second-order hyperpolarizability (γ) values compared with mono-phthalocyanines. In addition, the third-order NLO properties of mixed (phthalocyaninato)(porphyrinato) rare earth complexes [13–15] were also investigated either using the femtosecond time-resolved optical Kerr gate experiments or the Z-scan method, their γ values were revealed to be about an order of magnitude larger than those of the typical mono-phthalocyanines and mono-porphyrins.

Phthalocyanines and porphyrins, owning high two-photon absorption (2PA) cross-sections have been attracted considerable attention due to their potential applications including three-dimensional memory, optical power limiting and two-photon photodynamic therapy [16–19]. In order to improve the 2PA cross-section, considerable efforts have been continuously devoted not only to synthesize novel phthalocyanine derivatives [20–22] and porphyrin derivatives [23–25], but also to reveal factors which influence the 2PA magnitudes of phthalocyanine derivatives and porphyrin derivatives. However, many investigations made in this field seem to focus on the 2PA properties of either monomeric

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tetrapyrrole derivatives or the assemblies of tetrapyrrole derivatives. In contrast, reports on the 2PA properties of sandwich type tetrapyrrole rare earth complexes have, to our knowledge, never been investigated systematically.

For the purpose of clarifying the relationship between the molecular structure and the 2PA properties of sandwich-type tetrapyrrole rare earth complexes, a series of homoleptic substituted phthalocyaninato-rare earth double-decker complexes (Fig. 1) $M(\text{III})(\text{OOPc})_2$ [$M = \text{Ce}$ (1), Sm (2), Lu (3); $\text{H}_2\text{OOPc} = 3,4,12,13,21,22,30,31$ -octakis(octyloxy)phthalocyanine] have been experimentally investigated by the use of the Z-scan technique at the wavelength of 800 nm. All complexes exhibit extremely large 2PA cross-sections up to 3.5×10^4 GM (1), 9.3×10^4 GM (2) and 1.2×10^5 GM (3) at the wavelength of 800 nm, which are comparable to those efficient two-photon absorbing materials [26,27]. Highly delocalized π -electron system and intense π - π interactions are considered responsible for the large 2PA cross-sections. The 2PA coefficients of these complexes were measured under different laser intensities. It is shown that the values of 2PA of these complexes remain constant at different levels of laser intensities, indicating nonlinearity is originated from the 2PA process. In addition, the 2PA cross-section of these complexes increases along with the decrease of the rare earth atomic radius, suggesting that intense intramolecular π - π interaction between the phthalocyaninato macrocycles improves the third-order nonlinear optical properties. The optical limiting behavior of these complexes in CHCl_3 was also investigated by using femtosecond laser pulses.

2. Materials and experimental method

2.1. Materials and measurements

The sandwich-type homoleptic substituted phthalocyaninato-rare earth double-decker complexes $M(\text{OOPc})_2$ [$M = \text{Ce}$ (1), Sm (2), Lu (3); $\text{H}_2\text{OOPc} = 3,4,12,13,21,22,30,31$ -octakis(octyloxy)phthalocyanine] were prepared according to previously reported methods [28,29]. The sandwich nature of these complexes has been confirmed by a wide range of spectroscopic methods including mass spectrometry, ^1H NMR, electronic absorption, and infra-red (IR) spectroscopy in addition to the elemental analysis [30–34]. Electronic absorption spectra were recorded with a Shimadzu UV-3600 spectrophotometer.

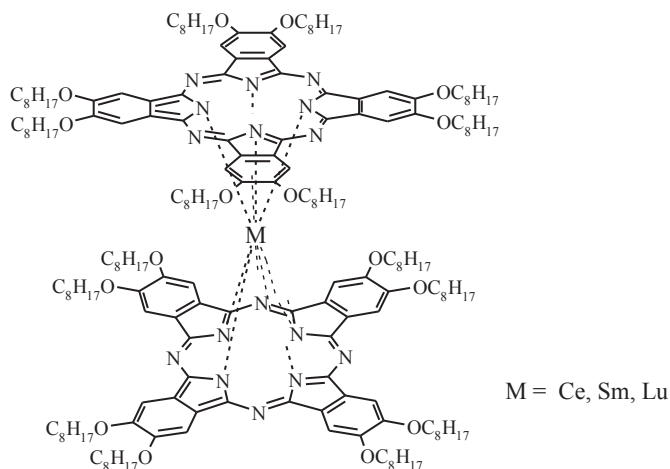


Fig. 1. The molecular structures of homoleptic bis(phthalocyaninato) rare earth complexes $\text{Ce}(\text{OOPc})_2$ (1), $\text{Sm}(\text{OOPc})_2$ (2) and $\text{Lu}(\text{OOPc})_2$ (3).

2.2. NLO method

The Z-scan technique has been widely used to study the third-order NLO properties of many materials since it was first pioneered by M. Sheik-Bahae in 1989 [35]. As shown in Fig. 2, a femtosecond-pulsed single-beam Z-scan technique was used in this experiment.

In the measurements, the laser source was a Ti:sapphire regenerative amplifier (Coherent Inc.), operating at a wavelength of 800 nm with a pulse duration of 170 fs and a repetition rate of 1 kHz. The laser pulses had near-Gaussian profiles in time and space. In the Z-scan experiments, the laser beam was focused by an achromatic lens with a 150 mm focal length, producing the beam waist at the focus of 15 μm (the Rayleigh range $z_0 = 1.12$ mm). To carry out Z-scans, the sample was scanned across the focus along the optical axis using a computer-controlled translation stage, while the transmitted pulse energies in the presence or absence of the far-field aperture were recorded by a detector, producing the open-aperture (OA) Z-scan traces. The measurement system was calibrated with a piece of cadmium sulfide bulk crystal and the results indicated that the experimental uncertainty should be within $\pm 10\%$. The samples were dissolved in CHCl_3 with the concentration of 5×10^{-4} mol/L contained in 1 mm thick quartz cell with the same excitation intensity of $I_0 = 114.8$ GW/cm². To exploit the application of the nonlinear absorption effect, the optical limiting experiments were performed by tuning the input pulse energies with a half wavelength plate and Glan-Taylor polarizer, by monitoring both the incident and the transmitted pulse energies simultaneously by two detectors. The experimental system was similar to that for the open-aperture Z-scan measurements except that the nonlinear sample was fixed at the focal plane of the converging lens. From the measured Z-scan trace, the nonlinear absorption index β can be extracted by the formula as [36]:

$$T(z) = 1 - 0.33839\psi_2 + 0.13326\psi_2^2 - 0.03446\psi_2^3 + 0.0377\psi_2^4, \quad (1)$$

where $\psi_2 = \beta I_0 L_{\text{eff}} / (1 + z^2/z_0^2)$, β is the 2PA coefficient, I_0 is the on-axis intensity of the Gaussian beam at the focus, 2PA coefficient, $L_{\text{eff}} = (1 - e^{-\alpha_0 L}) / \alpha_0$ is the effective sample length, α_0 is the linear absorption coefficient, and L is the physical thickness of the sample.

3. Results and discussion

3.1. Electronic absorption spectra

The electronic absorption spectra of the sandwich-type rare earth complexes $\text{Ce}(\text{OOPc})_2$ (1), $\text{Sm}(\text{OOPc})_2$ (2) and $\text{Lu}(\text{OOPc})_2$ (3) in the region of 330–800 nm recorded in CHCl_3 with the concentration of 2×10^{-6} mol/L are shown in Fig. 3. Their electronic absorption spectra were similar to those of other bis(phthalocyaninato)lanthanide(III) complexes and could be

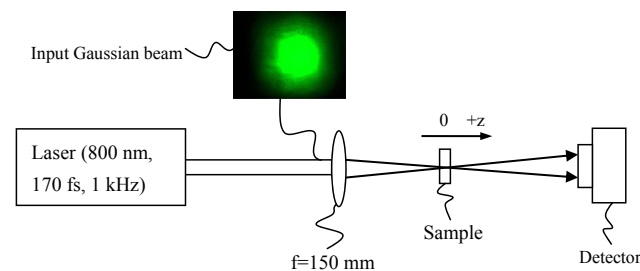


Fig. 2. Z-scan experimental setup.

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