



Full length article

# Nonlinear optical properties and excited state dynamics of sandwich-type mixed (phthalocyaninato)(Schiff-base) triple-decker complexes: Effect of rare earth atom

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## ABSTRACT

The third-order nonlinear optical properties of two di-lanthanide (Ln = Tb and Dy) sandwich complexes with mixed phthalocyanine and Schiff-base ligands were studied using Z-scan technique at 532 nm with 20 ps and 4 ns pulses. Both complexes exhibit reverse saturable absorption and self-focusing effect in ps regime, while the second-order hyperpolarizability decreases from Dy to Tb. Interestingly, the Tb triple-decker complexes show larger nonlinear absorption than Dy complexes on ns timescale. The time-resolved pump-probe measurements demonstrate that the nonlinear optical response was caused by excited-state mechanism related to the five-level model, while the singlet state lifetime of Dy complexes is 3 times shorter than that of Tb complexes. Our results indicate the lanthanide ions play a critical role in the photo-physical properties of triple-decker phthalocyanine complexes for their application as optical limiting materials.

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## 1. Introduction

Phthalocyanines (Pcs) and their derivatives have received long-term research interests as nonlinear optical (NLO) materials not only because of their large conjugated  $\pi$ -electron system, but also owing to their exceptional structural flexibility and chemical stability [1–5]. The versatility of Pc synthetic organic chemistry has led to a large variety of sandwich-type double- and/or triple-decker rare earth complexes differing in tetrapyrrole deck number, axial ligands, etc. Due to the strong intra-molecular  $\pi$ - $\pi$  interactions and the presence of the heavy lanthanide metal ion, these sandwich-type complexes can display intriguing electrochemical and magnetic properties, enabling them to be used in single molecular magnets, field effect transistors, solar cell, etc [6–10]. Recently, the sandwich-type lanthanide phthalocyanines complexes have also received considerable attention as NLO materials [11–23]. Previous results demonstrate that the sandwich-type complexes have higher second-order hyperpolarizability ( $\gamma$ ) value than the monophthalocyanines [14,18,22,24,25]. And the centric metal atom pre-

sent additive tunability of the NLO properties for these phthalocyanine complexes [20,26–28]. Despite these efforts, however, the understanding of structure-property relationship for the sandwich-type multi-decker complexes remains ambiguous due to the complicated factors involved.

Recently, a new kind of sandwich-type rare earth complexes with mixed phthalocyanine and schiff base ligands has been reported [29–32]. Due to the strong coupling between two lanthanide ions, the rare earth atom is found to play an important role in the single-molecule magnets properties of these multikis (phthalocyaninato) Ln compounds [29,30]. However, reports concerning the effect of lanthanide ions on the NLO properties of these mixed (phthalocyaninato)(schiff-base) complexes are rare. Meanwhile, the photo-physical mechanism of these sandwich-type complexes remains un-explored. Therefore, a detailed investigation on the NLO properties and photo-physical mechanism of these triple-decker complexes is highly desired.

In this letter, the third-order nonlinear optical properties of two sandwich-type triple-decker di-lanthanide (Ln<sub>2</sub> = Tb-Tb or Dy-Dy) complexes with mixed phthalocyanine and Schiff-base ligands were investigated using Z-scan technique at 532 nm. Our purpose is to clarify the relationship between lanthanide ion and NLO prop-

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erties of mixed (phthalocyaninato)(Schiff-base) sandwich-type complexes with the same phthalocyanine ligands. The ps Z-scan results clearly shown that the NLO coefficients are higher for the Dy triple-decker complexes under 20 ps pulse excitation. However, Tb complex showed larger reverse saturable absorption than Dy complex in ns time regime. The ps time-resolved pump-probe results revealed that the Dy complex has larger ratio between excited and ground state absorption, while the singlet state lifetime for Dy complex is found to be three times shorter than that for Tb complex. Our results verify that these rare earth complexes are promising candidate for nonlinear optical applications such as optical limiter and all-optical switch.

## 2. Experiment

All the reagents were commercially available and used without further purification. The half-sandwich lanthanide complex  $[\text{Ln}(\text{Pc})(\text{acac})]$  ( $\text{Ln} = \text{Tb}$  and  $\text{Dy}$ ,  $\text{Pc} = \text{phthalocyaninate}$ ,  $\text{acac} = \text{acetylacetonate}$ ) and chiral Schiff base ligand  $\text{H}_2\text{L}$  were prepared according to the published procedure [33,34]. The sandwich-type mixed (phthalocyaninato)(Schiff-base) triple-decker complexes was synthesized according to the procedures reported in our pervious literature [31], as shown in Fig. 1. Elemental analysis was carried out with a Elementar Vario MICRO analyzer. IR spectra were recorded on a Vector22 Bruker spectrophotometer with KBr pellets. UV-vis spectra were obtained with a UV-3600 spectrophotometer.

The nonlinear optical properties of the triple-decker complexes were investigated by a single-beam Z-scan technique. The laser source were a mode-locked Nd:YAG laser (PL2143B, EKSPLA) and a Q-switched Nd:YAG laser (Continuum Surelite II-10). Both laser operate at wavelength of 532 nm with repetition rate of 10 Hz, with a pulse duration (FWHM) of 20 ps and 4 ns, respectively. The experimental configuration has been described in detail elsewhere [32,35]. The sample solution was contained in a 2-mm quartz cuvette. The incident laser beam was focused by a 400-mm focal length lens into the quartz cuvette. The beam waist at the focal plane was  $\sim 27 \mu\text{m}$ , giving a Raleigh length of  $\sim 3 \text{ mm}$ . The incident and transmitted energies were detected simultaneously by an energy meter (Laser Probe Corporation, Rj-7620). The experiments were performed with sample dissolved in neat  $\text{CH}_2\text{Cl}_2$  with concentrations of  $3 \times 10^{-4} \text{ M}$ . The Z-scan system was calibrated using the benchmark Kerr liquid  $\text{CS}_2$ , and the thin sample approximation is verified.

The photo-physical mechanism of the sandwich-type complexes were measured using time-resolved pump probe method

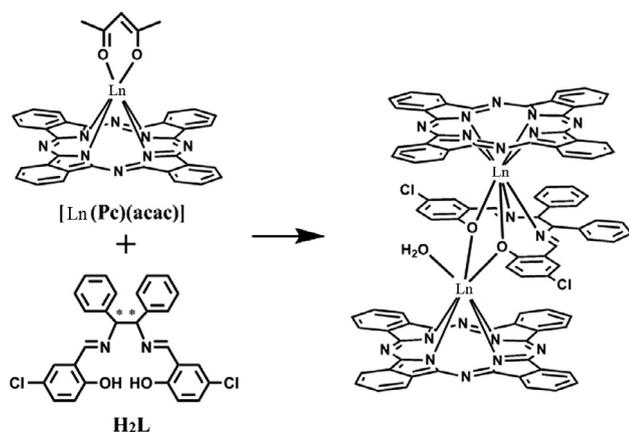


Fig. 1. Synthetic procedure of sandwich-type di-lanthanide ( $\text{Ln} = \text{Tb}$ ,  $\text{Dy}$ ) triple-decker complexes with mixed phthalocyanine and Schiff-base ligands.

at 532 nm. The excitation source was the same laser used in ps Z-scan experiments. The system configuration has been provided in our previous work [36]. The output beam was split into two parts with a 10:1 intensity ratio by a beam splitter. The strong pump beam was time-delayed using a computer-controlled translation stage (physik instrumente, M531). The polarizations of pump and probe beam were set to be perpendicular to each other. The pump and probe beams were focused into the sample cuvette using a 400-mm focal-length lens with a spot size of  $190 \mu\text{m}$  and  $26 \mu\text{m}$ , respectively. The energy of probe beam was recorded by a dual-channel energy meter (Laser Probe Corporation, Rj-7620) which transferred the digitized signals to a computer via GPIB interface.

## 3. Results and discussion

The UV-vis absorption spectra of sandwich-type di-lanthanide triple-decker complexes in  $\text{CH}_2\text{Cl}_2$  is illustrated in Fig. 2. It is found that the spectra of both sandwich-type complexes display typical features of the monomeric metal phthalocyanine with a strong Q band at around 670–685 nm and a medium Soret band at about 341 nm. The absorption spectrum of Dy complex is different from that of Tb complex in the Q-band region, indicating that the dysprosium ion states strongly mix with the ligand  $\pi$ -orbitals [37,38]. Compared to previous report, the absorption peaks related to pure Schiff-base are absent [39], hence the Schiff-base has no significant impact on the optical response of the mixed ligand triple-decker complexes. The absence of new absorption band indicates the weak intra-molecular interaction between the phthalocyanine and Schiff-base ligands and the non-aggregation nature of sandwich-type complexes in  $\text{CH}_2\text{Cl}_2$ .

Fig. 3 shows the ps Z-scan curves of sandwich-type di-lanthanide triple-decker complexes with and without far field aperture at 532 nm. The linear transmittance  $T_0$  of di-terbium and di-dysprosium complexes solution were measured to be 63% and 68%, respectively. The peak laser irradiance at the focal plane was  $I_0 = 1.2 \text{ GW/cm}^2$ . The solvent  $\text{CH}_2\text{Cl}_2$  was measured under identical experimental conditions and found to has negligible nonlinear response. The open aperture curves exhibit a strong transmission decrease, indicating the presence of reverse saturable absorption (RSA). And the normalized closed aperture curves show a large valley-to-peak configuration, suggesting that the nonlinear refractive index  $n_2$  is positive. We use the standard Z-scan theory to calculate the effective two-photon absorption coefficient  $\beta$  and

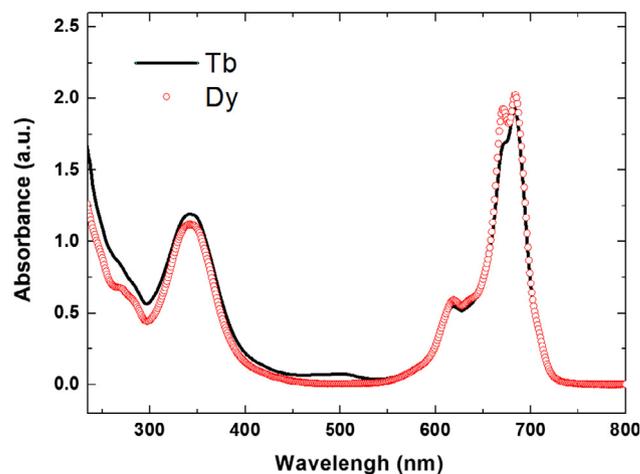


Fig. 2. UV-vis absorption spectra of the sandwich-type di-dysprosium and di-terbium triple-decker complexes in  $\text{CH}_2\text{Cl}_2$  at a concentration of  $1 \times 10^{-5} \text{ M}$ .

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