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Third-order nonlinear optical properties of sandwich-type mixed (phthalocyaninato)(porphyrinato) europium double- and triple-decker complexes

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ABSTRACT

The nonlinear optical (NLO) properties of sandwich-type mixed tetrapyrrole europium double- and triple-decker complexes Eu(Pc)(TPYRP) (**1**) and $Eu_2(Pc)_2$(TPYRP) (**2**) [Pc = unsubstituted phthalocyaninate, TPYRP = 5,10,15,20-tetrakis(1-pyrenyl)porphyrinate] were investigated by Z-scan experiments in $CHCl_3$ solution at 1064 nm wavelength, showing enhanced third-order NLO properties compared with metal free phthalocyanine, porphyrin, and pyrene. Strong intramolecular $\pi-\pi$ interaction and two-photon resonance are considered responsible for the large optical nonlinearity. The third-order NLO response of double-decker **1** is larger than that of triple-decker **2** probably associated with the unpaired electron in the former double-decker compound.

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]. Rare earth metal ions can bring these tetrapyrrole derivatives together to form a particularly interesting series of sandwich-type double- and triple-decker complexes. Due to the intramolecular $\pi-\pi$ interaction and the intrinsic nature of the metal centers, these novel complexes display characteristic features that cannot be found in their nonsandwich counterparts, enabling them to be used in different areas [3–11] such as field effect transistors, molecular magnets, molecular-based multibit information storage materials, receptors for metal ions and saccharides, and molecular solar cells. It is worth mentioning that sandwich-type tetrapyrrole metal complexes have got more and more attention as potential third-order NLO materials [9,12,13].

Shirk reported the third-order NLO properties of several homoleptic bis(phthalocyanines) rare earth complexes by means of DFWM [14], their second-order hyperpolarizability (γ) values were revealed about an order of magnitude larger than those of the typical mono-phthalocyanines. Other sandwich-type complexes such as $Sm(Pc)_2$ and $Eu(Nc)_2$ (Nc = naphthalocyanine) also showed higher γ values compared with mono-phthalocyanines according to DFWM measurements [15,16]. In addition, the third-order NLO properties of mixed (phthalcoyaniato)(porphyrinato) rare earth triple-decker complexes, including $Eu_2(Pc)(TPP)_2$, $Sm_2(Pc)(TPP)_2$, and $Sm_2(Pc)_2(TPP)$ (TPP = 5,10,15,20- tetraphenylporphyrinate) were also investigated using the femtosecond time-resolved optical Kerr gate method at 830 nm wavelength [17,18]. The enhancement of the optical nonlinearity was tentatively attributed to the introduction of lanthanide metal to the large π-conjugated system, strong intramolecular $\pi-\pi$ interaction, and two-photon resonance.

For the purpose of clarifying the relationship between the molecular structure and the enhanced optical nonlinearity of sandwich-type tetrapyrrole rare earth complexes, investigation over more sandwich-type phthalcoyaninato and/or porphyrinato rare earth complexes seems necessary. In the present paper, the third-order NLO properties of novel sandwich-type mixed

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(phthalocyaninato)(porphyrinato) europium double- and triple-decker complexes Eu(Pc)(TPYRP) (**1**) and $Eu_2(Pc)_2(TPYRP)$ (**2**) were measured using Z-scan method in picosecond regimes. The results showed that both sandwich-type complexes exhibit obvious NLO absorption and NLO refraction properties. The nonlinear refractive indexes n_2 were revealed to be 9.44×10^{-13} for **1** and 5.81×10^{-13} esu for **2** in $CHCl_3$ solution. The two-photon absorption coefficients β of **1** and **2** were 1.04×10^{-12} and 9.30×10^{-13} m/W, respectively. The third-order susceptibilities $\chi^{(3)}$ of **1** and **2** were therefore 1.54×10^{-13} and 1.00×10^{-13} esu, leading to the second-order hyperpolarizabilities γ of 1.04×10^{-30} and 0.41×10^{-30} esu for **1** and **2**, respectively. Obviously, all the values including n_2, β, $\chi^{(3)}$, and γ for double-decker complex **1** are larger than those for triple-decker complex **2** most probably due to the existence of unpaired electron in the former double-decker complex. At the end of this section, it is worth noting that the present result seems to represent the first example that both the NLO refractive effects and NLO absorption behavior were simultaneously studied for the sandwich-type complexes using Z-scan method.

2. Materials and experimental method

2.1. Materials

The novel sandwich-type mixed (phthalocyaninato)(porphyrinato) europium double- and triple-decker complexes Eu(Pc)(TPYRP) (**1**) and $Eu_2(Pc)_2(TPYRP)$ (**2**) (Fig. 1) were prepared according to the previous method [19]. The sandwich nature of these two complexes has been confirmed by a wide range of spectroscopic methods including mass spectrum, ^1H NMR, electronic absorption, and infra-red (IR) spectroscopy in addition to the elemental analysis.

2.2. Method

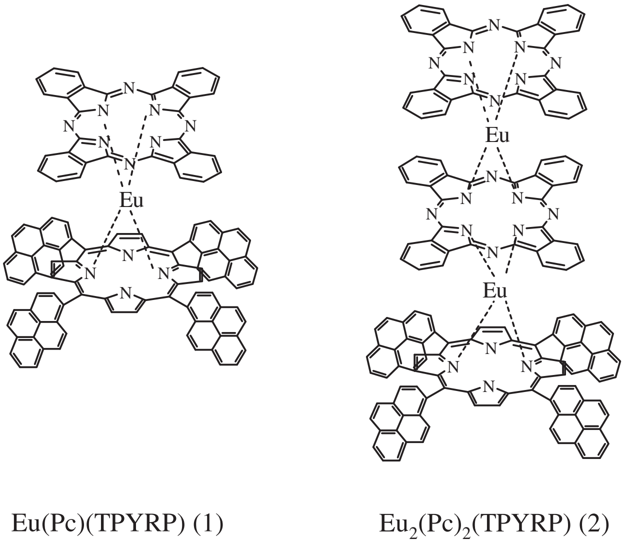
The Z-scan technique has been widely used to study the third-order NLO processes of many materials since it was reported by M. Sheik-Bahae in 1989 [20]. In the experiment, a focused GAUSSIAN light beam, propagating in the z-direction, is usually applied. A portion of the input beam is divided by a beam splitter and measured by a photo detector to determine the incident energy on the entrance face of the sample. The other beam propagated in the z-direction and passed through the sample. The sample is translated along the z-direction and with nonlinear refractive index causes an additional, depending on z, focusing (at positive n_2) or defocusing (at negative n_2) of the light beam. It changes the transmitted intensity of the beam passing through a finite aperture placed in the far-field when moving the sample along z (closed aperture Z-scan). For an open aperture Z-scan, the aperture was removed to collect the entire laser beam transmitted through the sample. The intensity of the transmitted beam through the sample was measured with closed and open aperture scheme using the photo detector fed to the digital power meter.

In the measurements, a mode-locked Nd: YAG laser system (PY61C-10, Continuum) was used at the wavelength of 1064 nm with the pulse width of 20 ps and the repetition rate of 10 Hz. The laser beam was focused with an $f = 15$ cm lens and the beam waist radius (w_0) was measured to be 40.0 μm and the corresponding Rayleigh length is 3.9 mm. The thickness of a quartz cell containing the sample is 1 mm which is less than the Rayleigh length of the laser beam.

3. Results and discussion

The electronic absorption spectra of the mixed ring europium double- and triple-decker complexes **1** and **2** recorded in $CHCl_3$ are shown in Fig. 2. Except for some more or less shift in corresponding absorption bands associated with the change in the tetra(pyrenyl) porphyrin ligand, sandwich-type complexes **1** and **2** display very similar electronic absorption spectra to other counterparts composed of tetra(aryl)porphyrin ligand, which can therefore be assigned in a similar manner [21–26]. It is worth noting that for the double-decker complex **1**, the band observed at 1330 nm with a shoulder at 1715 nm in its electronic absorption spectrum is attributed to the ring-to-ring charge transfer transition (RRCT) from Por^{2-} to Pc^{-}. This confirms the presence of a hole in the phthalocyanine macrocyclic ligand. However, no absorption band is observed in near IR region for the triple-decker complex **2**.

The third-order NLO properties of the mixed ring europium double- and triple-decker complexes **1** and **2** were investigated by Z-scan technique at 1064 nm with the pulse width of 20 ps and the repetition rate of 10 Hz. The samples were dissolved in $CHCl_3$ with the concentration of 0.72×10^{-4} mol/L for **1** and 1.19×10^{-4} mol/L for **2**, respectively. Before the measurements, the system was calibrated using CS_2 in a quartz cell as done according to Ref. [20].



Eu(Pc)(TPYRP) (1) $Eu_2(Pc)_2(TPYRP)$ (2)

Fig. 1. Schematic molecular structures of the sandwich-type double- and triple-decker complexes.

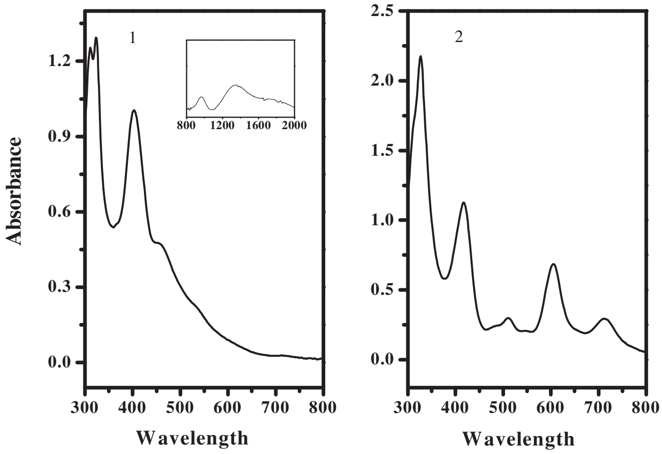


Fig. 2. The electronic absorption spectra of Eu(Pc)(TPYRP) (**1**) and $Eu_2(Pc)_2(TPYRP)$ (**2**) in $CHCl_3$. Inset is the near IR spectra of Eu(Pc)(TPYRP) (**1**).

Measurements on the pure solvent $CHCl_3$ in the cell were also performed under the same measurement conditions to verify that the valleys and the peaks in the Z-scan curves originate from the material instead from the solvent or the quartz cell.

The NLO absorption components were evaluated by Z-scan experiment under an open aperture configuration. The NLO absorption data can be well represented by equations which describe a third-order NLO absorption process [27]. Fig. 3 depicts the NLO absorptive properties of **1** and **2**. The curves of **1** and **2** demonstrate a positive nonlinear absorption which is regarded as the two-photon absorption (TPA) [28]. Black dots are the experimental data and the solid curves are the theoretical fitting using Z-scan theory described in literature [27]. It is obvious that the theoretical curves qualitatively reproduce well the general pattern of observed experimental data. This fact suggests an effective third-order characteristic for experimentally detected NLO effects. The two-photon absorption coefficients β of **1** and **2** were calculated to be 1.04×10^{-12} and 9.30×10^{-13} m/W, respectively.

The NLO refractive effects were assessed by dividing the normalized Z-scan data obtained under closed aperture configuration by the normalized Z-scan data obtained under the open aperture configuration. Fig. 4 displays the NLO refractive properties of **1** and **2**. The NLO refractive indexes n_2 were calculated to be 9.44×10^{-13} for **1** and 5.81×10^{-13} esu for **2** in $CHCl_3$ solution. The third-order susceptibilities $\chi^{(3)}$ of **1** and **2** were therefore to be 1.54×10^{-13} esu and 1.00×10^{-13} esu. The second-order hyperpolarizability values can be obtained from the equation:

$$\gamma = \frac{\chi^{(3)}}{L^4 N}$$

where $L = (n^2 + 2)/3$ is the local field correction factor, the refractive index of the solvent, n, is taken to be 1.44, N is the number density of the solute molecules in solution. Their second-order hyperpolarizabilities γ were calculated to be 1.04×10^{-30} and 0.41×10^{-30} esu, respectively.

In order to reveal the third-order nonlinearity of **1** and **2**, some related values of monomeric compounds including Pcs, Pors, and pyrene together with some sandwich-type tetrapyrrole rare earth complexes reported previously were also listed in Table 1. Of course, it is quite hard to judge in a definite manner the most excellent third-order optical material among all the sandwich-type complexes because of the data collected by different technique and different wavelength for different sample. However, comparison over all the data in Table 1 clearly reveals that sandwich-type tetrapyrrole rare earth complexes show obviously larger third-order NLO response over the monomeric phthalocyanine and porphyrin counterparts. This is also true for the two sandwich-type complexes **1** and **2** with their third-order nonlinearity about three orders higher relative to the monomeric phthalocyanine and porphyrin compounds. In addition, according to our previous experimental results conducted on the same experimental conditions as in the present case, no obvious NLO absorption was revealed for the metal free porphyrin (4-I)tris(4-OC_8H_{17})$PorH_2$ and pyrene [29]. Interestingly, these two compounds show similar NLO refractive effect to the two sandwich mixed (phthalocyaninato)(porphyrinato) europium complexes **1** and **2**, Table 1.

As a result, the third-order optical nonlinearity of these two sandwich-type mixed tetrapyrrole europium complexes is strongly enhanced over monomeric phthalocyanines, porphyrins, and pyrene. According to the previous theoretical and experimental results, several factors have been considered to be responsible for the enhancements of the third-order optical nonlinearity. In the present case, strong $\pi-\pi$ interaction between the two or three tetrapyrrole ligands in both double-decker **1** and triple-decker **2** is believed to play an important role in contributing to the improved NLO properties of these two compounds relative to monomeric counterparts [12,30]. In addition, the two-photon absorption is considered to be another factor for leading to the large γ values of **1** and **2** since both complexes exhibit electronic absorption band at 532 nm which is the double-frequency wavelength of 1064 nm employed in our experiment. Nevertheless, these two sandwich-type complexes provide the structure with a highly delocalized π-electron system, which induces improved third-order NLO response.

Theoretical investigation revealed that the γ of $(SiPcO)_3$ trimer is larger than that of $(SiPcO)_2$ dimer [30]. This is in agreement with the DFWM experimental result in the fact that the increase in the number of interacted conjugated macrocycles induces an improved NLO property. As a consequence, the γ value of triple-decker $Eu_2(Pc)_2(TPYRP)$ (**2**) seems ought to be larger than that of double-decker Eu(Pc)(TPYRP) (**1**) because of the three $\pi-\pi$ interacted tetrapyrrole rings in the former compound versus the two ones in the latter one. However, as described above, all the values obtained for double-decker **1** including n_2, β, $\chi^{(3)}$, and γ are larger than those of triple-decker **2** as exemplified by the γ value of $Eu_2(Pc)_2(TPYRP)$ (**2**) (0.41×10^{-30} esu) versus that of Eu(Pc)(TPYRP) (**1**) (1.04×10^{-30} esu). This result seems to be inconsistent with the previous research result but could be attributed to the presence of unpaired electron in the double-decker **1**, which might leads to enhancement of the third-order nonlinear response since the presence of unpaired electron can increase both resonance effects and delocalization effects.

Shirk recorded the γ values of a series of bis(phthalocyaninato) complexes of Sc, Y, and several lanthanides as well as their anions at

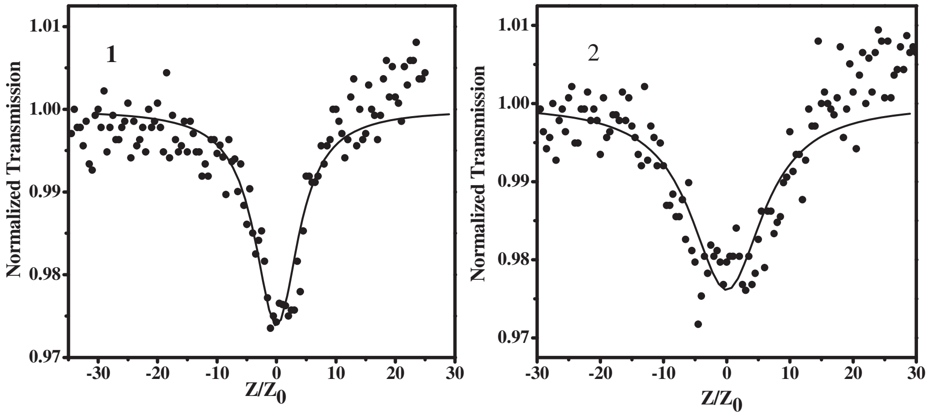


Fig. 3. *Z*-scan data for compounds **1** and **2** in $CHCl_3$ solution obtained under an open aperture configuration. The black dots are the experimental data and the solid curves are the theoretical fit.

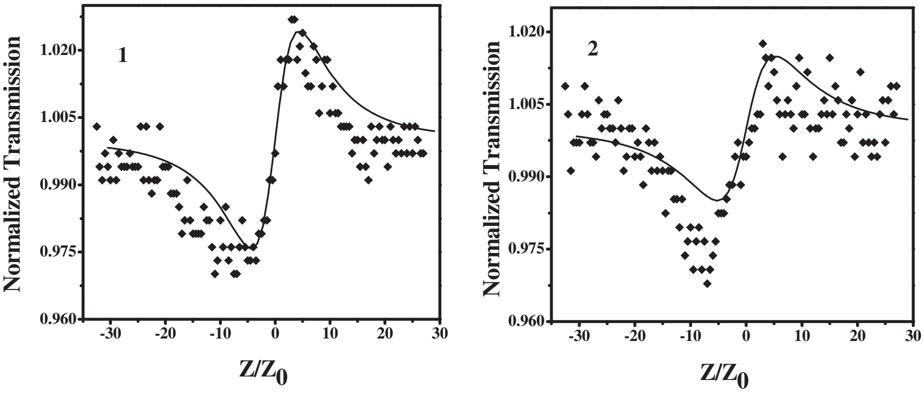


Fig. 4. *Z*-scan data for **1** and **2** in $CHCl_3$ solution obtained by dividing the normalized *Z*-scan data measured under a closed aperture configuration by the normalized *Z*-scan data obtained under the open aperture configuration. The black dots are the experimental data, and the solids curves are the theoretical fit.

Table 1
Optical parameters of selected NLO compounds.

Compound	n_2, (esu)	β, (m/W)	γ, (esu)	$\chi^{(3)}$, (esu)	λ (nm)	Technique	Reference
ZnTPP			9.00×10^{-32}		1064	OKE [a]	[31]
T(4-methoxyl) PPZn			0.10×10^{-32}		1064	OKE	[31]
$(C_8H_{17})_2NCOCH_2OPcNi$			2.47×10^{-32}		1064	EFISH [b]	[32]
$(C_8H_{17})_2NCOCH_2OPcCu$			3.94×10^{-32}		1064	EFISH	[32]
(4-I)tris(4-OC_8H_{17}) $PorH_2$ [c]	1.17×10^{-12}				1064	Z-scan	[29]
Pyrene	1.07×10^{-12}				1064	Z-scan	[29]
Eu(Pc)(TPYRP) (**1**)	9.44×10^{-13}	1.04×10^{-12}	1.04×10^{-30}	1.54×10^{-13}	1064	Z-scan	This work
$Eu_2(Pc)_2$(TPYRP) (**2**)	5.81×10^{-13}	9.30×10^{-13}	0.41×10^{-30}	1.00×10^{-13}	1064	Z-scan	This work
$Eu(Pc)_2$			0.22×10^{-30}		1064	DFWM [d]	[14]
$Eu[Pc(OC_5H_{11})_8]_2$			0.74×10^{-30}		830	OKE	[17]
$Eu_2(Pc)(TPP)_2$			3.00×10^{-30}		830	OKE	[17]
$Sm_2(Pc)_2$(TPP)			2.60×10^{-30}		830	OKE	[18]
$Sm_2(Pc)(TPP)_2$			2.20×10^{-30}		830	OKE	[18]

[a] OKE, Optical Kerr gate method.
[b] EFISH, Electric field-induced second harmonic generation.
[c] (4-I)tris(4-OC_8H_{17})$PorH_2$, 5-(4-iodophenyl)-10,15,20-tris(4-octyloxyphenyl)porphyrin.
[d] DFWM, Degenerate four-wave mixing.

1064 nm using DFWM method [14]. The results showed that γ values of $Sc(Pc)_2$, $Lu(Pc)_2$, and $Yb(Pc)_2$ are larger than other rare earth analogs. The peak wavelength of the intervalence transition of $Sc(Pc)_2$, $Lu(Pc)_2$, and $Yb(Pc)_2$ is 1190, 1380, and 1390 nm, respectively. The γ value of $Sc(Pc)_2$ is the largest among the three compounds because the peak wavelength of the intervalence transition of this compound is closer to the probe wavelength of 1064 nm. Usually, in addition to the highly delocalized electronic structure, the resonance effects may provide a new degree of freedom for charge redistribution under the influence of an optical field, thereby improving the nonlinear response. In a similar manner, in the present case for the double-decker Eu(Pc)(TPYRP) (**1**), the band around 1330 nm attributed to intervalence transition is partly overlapped with the probe wavelength of 1064 nm, which in turn results in an enhanced γ value for this compound. As for the triple-decker $Eu_2(Pc)_2$(TPYRP) (**2**), there is no absorption band observed in near IR region close to 1064 nm, leading to a relatively smaller γ value in comparison with **1**. Future research will focus on the double-decker sandwich-type complexes with the intervalence transition overlapped around 1064 nm.

4. Conclusion

Briefly summarizing above, we have studied both NLO refractive effects and NLO absorption behavior of novel sandwich-type mixed (phthalocyaninato)(porphyrinato) europium double- and triple-decker complexes Eu(Pc)(TPYRP) and $Eu_2(Pc)_2$(TPYRP) using Z-scan method. In comparison with monomeric phthalocyanine, porphyrin, and pyrene, both these two double- and triple-decker complexes showed large third-order nonlinearity due to the strong intramolecular π–π interaction and two-photon resonance. Nevertheless, the presence of the near IR absorption band locating at 1330 nm, which partly overlaps the probe wavelength of 1064 nm, remarkably improves the third-order NLO because of the resonance effects. The experimental results confirm that construction of complexes with strong intramolecular π–π interactions and resonance effects is one of the useful strategies to develop novel organic NLO materials.

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