Strong two-photon absorptions in heteroleptic bis(phthalocyaninato) rare earth sandwich complexes

Ning Sheng ^{a*}, Bing Gu ^b, Boxiao Ren ^b, Yingying Wang ^a, Lijuan Han ^a, Jingxia Wang ^a, Houyong Cao ^a, Meihui Guan ^a, Xiurong Zhai ^a, Jingquan Sha ^{a*}

^a Department of Chemistry and Chemical Engineering, Jining University, Qufu, 273155, China

^b Advanced Photonics Center, Southeast University, Nanjing 210096, China

**Corresponding author: sns0215@163.com; shajq2002@126.com*

Abstract: A series of heteroleptic phthalocyaninato rare earth double-decker complexes owning large two-photon absorption cross-sections were reported. The third-order nonlinear optical properties of these heteroleptic phthalocyaninato complexes were experimentally investigated by the Z-scan technique with application of femtosecond (800 nm) pulse lasers. Due to the highly delocalized π -electron system and intense π - π interactions between the phthalocyaninato macrocycles, all complexes were revealed to exhibit large two-photon absorption cross-sections with the value up to 1.83×10^5 GM, which are comparable to those efficient two-photon absorbing materials. 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 optoelectronic devices.

Keywords: Sandwich type phthalocyanine; Rare earth; Two-photon absorption; Heteroleptic; Donor- π -acceptor; Femtosecond-pulsed Z-scan technique

1. Introduction

Recently, organic two-photon absorption materials have attracted considerable attention due to their potential applications including three-dimensional optical memory, optical power limiting, two-photon photodynamic therapy (PDT) and fluorescence microscopy [1-6]. There is still a challenge in the design and synthesis of organic materials with large two-photon absorption (2PA) cross section. For example, two-photon photodynamic therapy is expected to provide a way of more selective treatment of cancers. However, in the past reports on two-photon PDT, 2PA cross section values of photosensitizers were less than 50 GM, and resulted in a low PDT efficiency under two-photon irradiation conditions [7-9]. Thus, it is important to explore novel material owning large 2PA cross sections.

Phthalocyanines are suitable candidates as two-photon absorption materials. In order to improve the 2PA cross-section, considerable efforts have been continuously devoted to synthesize novel phthalocyanine derivatives and reveal factors which influence the 2PA magnitudes of phthalocyanine derivatives [10-14]. As π -electron delocalization throughout a molecular framework plays an important role, many efforts have been focused on expanding the π -conjugated phthalocyanine ring. In fact, it is very effective to expand the π -conjugated phthalocyanines along the vertical direction of the plane of phthalocyanine ring because phthalocyanine can complex with rare earth ions to form sandwich type complexes [15-20]. This class of complexes shows many excellent optical and electronic properties because of the strong π - π interactions exhibiting in them. The third-order nonlinear optical (NLO)

properties of some sandwich type phthalocyanine metal complexes including bis(phthalocyaninato), bis(naphthalocyaninato) and mixed (phthalocyaninato)(porphyrinato) rare earth complexes were investigated using various method, most of them showed excellent third-order NLO properties compared with monomer phthalocyanine [21-25]. However, reports on the 2PA properties of sandwich type phthalocyaninato rare earth complexes are rare [26].

For the purpose of clarifying the relationship between the molecular structure and the 2PA properties of sandwich type phthalocyaninato rare earth complexes, a series of heteroleptic substituted phthalocyaninato rare earth double-decker complexes (Fig. 1) $M(III)(Pc)(OOPc)$ [$M = Yb$ (**1**), Y (**2**), Er (**3**), Ho (**4**); $H_2OOPc = 2,3,9,10,16,17,23,24$ -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 1.50×10^5 GM (**1**), 1.28×10^5 GM (**2**), 1.83×10^5 GM (**3**) and 1.26×10^5 GM (**4**) at the wavelength of 800 nm, which are comparable to those efficient two-photon absorbing materials [27,28]. Highly delocalized π -electron system and intense π - π interactions between the phthalocyaninato macrocycles are considered responsible for the large 2PA cross-sections. The optical limiting behavior of these complexes in chloroform was also investigated by using femtosecond laser pulses.

2. Materials and experimental method

2.1. Materials and measurements

The sandwich type heteroleptic substituted phthalocyaninato rare earth double-decker complexes $M(III)(Pc)(OOPc)$ [$M = Yb$ (**1**), Y (**2**), Er (**3**), Ho (**4**); $H_2OOPc = 3,4,12,13,21,22,30,31$ -octakis(octyloxy)phthalocyanine] were prepared according to previously reported methods [29,30]. The sandwich nature of these complexes has been confirmed by a wide range of spectroscopic methods [31-35]. The MALDI-TOF mass data and spectra of complexes **1-4** are shown in Table S1, Fig. S1-Fig. S4 in supporting information. Electronic absorption spectra were recorded with a Shimadzu UV-3600 spectrophotometer.

2.2. NLO Method

The 2PA properties of $Yb(Pc)(OOPc)$ (**1**), $Y(Pc)(OOPc)$ (**2**), $Er(Pc)(OOPc)$ (**3**), $Ho(Pc)(OOPc)$ (**4**) were measured by using an open-aperture Z-scan method which was pioneered by M. Sheik-Bahae in 1989 [36]. As shown in Fig. 2, a femtosecond-pulsed single-beam Z-scan technique was used in this experiment. The nonlinear optical properties of the samples were carried out by a single-beam Z-scan technique. The laser pulses used were generated by a Ti: sapphire regenerative amplifier (Coherent Inc.), operating at a wavelength of $\lambda = 800$ nm with a pulse duration of $\tau_f = 170$ fs and a repetition rate of $\nu = 1$ kHz. In the Z-scan measurements, the laser beam was focused by an achromatic lens with a focal length of $f = 200$ mm, producing the beam waist at the focus of $20.82 \mu m$. The Rayleigh length of the beam was estimated to be 1.70 mm. To perform Z-scan measurements, the sample was scanned across the focus along the z -axis using a computer-controlled translation

stage, while the transmitted pulse energies were completely probed by a detector, producing the open-aperture Z-scan trace. The measurement system was calibrated with a piece of CdS bulk crystal and the experimental uncertainty should be within $\pm 10\%$. The complexes were dissolved in CHCl_3 with the concentration of 10^{-3} mol/L contained in 2 mm thick quartz cell with the same excitation intensity of $I_0 = 118.5$ GW/cm². From the measured Z-scan trace, the nonlinear absorption index can be extracted by the formula as [37]:

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

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 heteroleptic substituted phthalocyaninato rare earth complexes Yb(Pc)(OOPc) (**1**), Y(Pc)(OOPc) (**2**), Er(Pc)(OOPc) (**3**), Ho(Pc)(OOPc) (**4**) recorded in CHCl_3 with the concentration of 2×10^{-6} mol/L are shown in Fig. 3. Their UV-Vis spectra are similar to those reported bis(phthalocyaninato)lanthanide(III) complexes [38-41]. The absorption spectra of these heteroleptic substituted phthalocyaninato rare earth double-decker complexes **1-4** show similar Soret bands with maxima around 362-365 nm and intense Q-band at

662-666 nm, in line with the results reported previously [29,31-33]. It is noteworthy that all of these complexes exhibit similar π -radical ($\text{Pc}^{\cdot-}$) related bands at 484-486 nm which is characteristic for double-decker rare earth (III) phthalocyaninato complexes, whereas there is no characteristic band at this position for monomeric phthalocynines.

3.2. 2PA properties

The 2PA properties of the heteroleptic phthalocyaninato rare earth double-decker complexes Yb(Pc)(OOPc) (**1**), Y(Pc)(OOPc) (**2**), Er(Pc)(OOPc) (**3**) and Ho(Pc)(OOPc) (**4**) were investigated by open-aperture Z-scan measurements. As shown in Fig. 4, all Z-scan traces display symmetrical valleys with respect to the focus, suggesting that all of complexes exhibit positive nonlinear absorption in nature. Furthermore, the experimental data are in good agreement with the theoretical fitting using Z-scan theory as described in the literature [37]. Z-scan measurements were conducted on the pure chloroform in 2 mm thick quartz cell in order to exclude the optical nonlinearity from the solvent. There was no peak and valley observed in the OA Z-scan traces even the input intensities more than 150 GW/cm^2 , therefore the nonlinear absorption on pure chloroform can be safely ignored.

As shown in Fig. 3, all complexes exhibit absorption band in the range of 330-700 nm, resulting in the highly transparent nature for their CHCl_3 solution around 800 nm. As a consequence, the nonlinear absorption effect measured at the wavelength of 800 nm is only able to originate from 2PA. By best fittings between the measured Z-scan traces and the Z-scan theory (see Eq. (1)) [37], the 2PA coefficients (β) of these sandwich type complexes were 0.039, 0.035 0.048 and 0.033 cm/GW respectively.

Furthermore, the 2PA coefficient was converted into the 2PA cross-section with the value of σ_{2PA} according to the formula $\sigma_{2PA} = \hbar\omega\beta/N$, $\hbar\omega$ is the incident photon energy, and N is the number density of sample in solution. At the wavelength of 800 nm, the σ_{2PA} value is $1.50 \times 10^{-45} \text{ cm}^4 \cdot \text{s} \cdot \text{photon}^{-1}$ for complex **1**, $1.28 \times 10^{-45} \text{ cm}^4 \cdot \text{s} \cdot \text{photon}^{-1}$ for complex **2**, $1.83 \times 10^{-45} \text{ cm}^4 \cdot \text{s} \cdot \text{photon}^{-1}$ for complex **3** and $1.26 \times 10^{-45} \text{ cm}^4 \cdot \text{s} \cdot \text{photon}^{-1}$ for complex **4** respectively. According to $1 \text{ GM} = 10^{-50} \text{ cm}^4 \cdot \text{s} \cdot \text{photon}^{-1}$, the values of σ_{2PA} are estimated to be $1.50 \times 10^5 \text{ GM}$ for complex **1**, $1.28 \times 10^5 \text{ GM}$ for complex **2**, $1.83 \times 10^5 \text{ GM}$ for complex **3** and $1.26 \times 10^5 \text{ GM}$ for complex **4**.

For comparative reason, some recently reported excellent 2PA materials based on phthalocyanine and phthalocyanine derivatives including sandwich type phthalocyaninato rare earth double-decker complexes [26], pentapyrrolic expanded porphyrins [42], $\text{H}_2\text{ImPor-ZnPc}$ [43] and push-pull phthalocyanines [44] have been listed in Table 1. As shown in Table 1, all the sandwich type complexes **1-4** exhibit large 2PA cross sections. Their σ_{2PA} values are even in the same order of magnitude with other excellent 2PA materials reported previously, indicating that they are excellent candidates for 2PA materials. Several factors can be considered to explain the enhancement of the third-order optical nonlinearity of organic materials according to the previous theoretical and experimental results. Firstly, strong π - π interaction in sandwich type complexes plays an important role in contributing to the enhanced 2PA properties, which have been confirmed in our previous work [26]. In double-decker phthalocyaninato rare earth complexes, the two phthalocyaninato rings were sufficiently close to result in an effective π - π interaction, thus the electrons can

delocalize in the whole expanded double-decker π -electron system. In addition, π -electronic delocalization has been found to improve the 2PA magnitudes [44]. For the rare earth (III) double-decker complexes, all the neutral complexes not only possess sufficient suitable orbital but also possess sufficient electrons originated from the phthalocyaninato ring and rare earth ions. All of these situations make the complex with highly delocalized electron density. In general, the unique electronic structure and molecular structure of these complexes can provide highly delocalized π -electron system, which enhances the third-order NLO response.

As shown in Table 1, the 2PA cross-sections of heteroleptic substituted phthalocyaninato rare earth double-decker complexes Yb(Pc)(OOPc) (**1**), Y(Pc)(OOPc) (**2**), Er(Pc)(OOPc) (**3**), Ho(Pc)(OOPc) (**4**) are larger than those of homoleptic substituted phthalocyaninato rare earth complexes we reported previously. Previous reports indicated that the π - π interaction between the two phthalocyaninato rings becomes stronger with the decrease of the rare earth atomic radius. The complexes Yb(Pc)(OOPc) (**1**), Y(Pc)(OOPc) (**2**), Er(Pc)(OOPc) (**3**), Ho(Pc)(OOPc) (**4**) exhibit stronger π - π interaction due to the small ionic radii of Yb(III), Y(III), Er(III) and Ho(III) which belong to heavy rare earth elements. Accordingly, the 2PA cross-sections of these complexes were effectively enhanced because of the strong π - π interaction in sandwich type complexes. However, we found that the σ_{2PA} value of homoleptic substituted Lu(OOPc)₂ owning the smallest ionic radius is less than the σ_{2PA} value of heteroleptic substituted complexes **1-4**, this can be attributed to the symmetry of molecule. As shown in Fig. 1, the hydrogen atoms of the unsubstituted

phthalocyaninato ring serve as electron-acceptor and the eight octyloxy groups of the other phthalocyanine ring serve as electron-donor to form a D- π -A system in the heteroleptic substituted complex. Since organic molecules with electron donor and electron acceptor groups that are connected by a large conjugated π -electron system have high nonlinear effects [45,46], these heteroleptic substituted complexes **1-4** showed more excellent 2PA properties compared with that of homoleptic substituted phthalocyaninato rare earth complexes.

3.3. Optical power limiting

Optical limiting is a nonlinear effect consisting of a decrease in the transmittance of the nonlinear optical material under high-intensity illumination [47]. Because of the intensity dependent transmittance feature, the optical-limiters are useful for sensors against hazardous sources of light and protecting human eyes. The optical limiting behavior of complexes Yb(Pc)(OOPc) (**1**), Y(Pc)(OOPc) (**2**), Er(Pc)(OOPc) (**3**), Ho(Pc)(OOPc) (**4**) were investigated since they have large 2PA cross-sections. The concentrations of them were kept constant at 10^{-3} mol/L. The experiments were performed using cuvette with 2 mm path-length. The pump source for optical power limiting, as well as the 2PA cross-section measurements, was a focused ultra short pulsed laser beam from a Ti: sapphire laser. This beam was focused by a converging lens with the focal length of 15 cm. The transmittance of the solutions of complex **1-4** dependent on different peak intensity I_0 from 1 to 140.7 GW/cm^2 are shown in Fig. 5. Obviously, all the solutions of complexes have high transmittance when the lower incident light intensity ($1\text{-}25 \text{ GW/cm}^2$) increases. However, the solutions of the

complexes display obvious optical power limiting effects when the incident light intensity increases to about 25 GW/cm². It is obvious that these heteroleptic substituted complexes with higher 2PA cross-section values exhibit a better optical limiting performance. In addition, the optical limiting ability of these two-photon absorbing material is in agreement with the magnitude of their 2PA cross-sections, the complex Er(Pc)(OOPc) (**3**) exhibit the best optical limiting behavior with the largest cross-section 2PA value of 1.83×10⁵ GM.

4. Conclusions

In summary, a series of heteroleptic phthalocyaninato rare earth double-decker complexes owning large two-photon absorption cross-sections were experimentally investigated by the Z-scan technique with application of femtosecond pulse lasers. Due to the highly delocalized π -electron system and intense π - π interactions, all complexes were revealed to exhibit large two-photon absorption cross-sections with the value up to 1.83×10⁵ GM, which are comparable to those efficient two-photon absorbing material. The experimental results confirm that construction of highly delocalized expanded π -electron system as well as D- π -A system is an effective method to improve the 2PA properties. These sandwich type complexes are considered to be useful in nonlinear photonic devices.

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Table 1 2PA parameters of selected phthalocyanine compounds reported recently.

<i>Compounds</i>	σ_{2PA} (GM)	<i>Technique</i>	λ (nm)	<i>Solvent</i>	<i>Reference</i>
Ce(OOPc) ₂	3.5×10^4	Z-scan fs	800	CHCl ₃	26
Sm(OOPc) ₂	9.3×10^4	Z-scan fs	800	CHCl ₃	26
Lu(OOPc) ₂	1.2×10^5	Z-scan fs	800	CHCl ₃	26
Yb(Pc)(OOPc)	1.5×10^5	Z-scan fs	800	CHCl ₃	this work
Y(Pc)(OOPc)	1.28×10^5	Z-scan fs	800	CHCl ₃	this work
Er(Pc)(OOPc)	1.83×10^5	Z-scan fs	800	CHCl ₃	this work
Ho(Pc)(OOPc)	1.26×10^5	Z-scan fs	800	CHCl ₃	this work
Pentapyrrolic expanded porphyrins	3300 ± 100	Z-scan fs	800	CH ₂ Cl ₂	42
H ₂ ImPor-ZnPc	1.6×10^4	Z-scan fs	800	CHCl ₃	43
Push-pull phthalocyanines	$(1-3) \times 10^3$	fluorescence method fs	815-850	CCl ₄	44

Figure Captions

Fig. 1. The molecular structures of heteroleptic bis(phthalocyaninato) rare earth complexes Yb(Pc)(OOPc) (**1**), Y(Pc)(OOPc) (**2**), Er(Pc)(OOPc) (**3**), Ho(Pc)(OOPc) (**4**).

Fig. 2. Schematic diagram of experimental Z-scan set-up.

Fig. 3. The electronic absorption spectra of heteroleptic bis(phthalocyaninato) rare earth complexes Yb(Pc)(OOPc) (**1**), Y(Pc)(OOPc) (**2**), Er(Pc)(OOPc) (**3**), Ho(Pc)(OOPc) (**4**) recorded at room temperature. The concentrations were held at 2×10^{-6} mol/L.

Fig. 4. Z-scan data for Yb(Pc)(OOPc) (**1**), Y(Pc)(OOPc) (**2**), Er(Pc)(OOPc) (**3**), Ho(Pc)(OOPc) (**4**) obtained under an open-aperture configuration with the same excitation intensity of $I_0 = 118.5$ GW/cm². The concentration of them is 10^{-3} mol/L. The dots are the experimental data while the solid curves are the theoretical fit using Eq. (1).

Fig. 5. Ultrafast optical limiting for chloroform solution of sandwich type complex **1-4** as a function of the input irradiances under the excitation of laser pulses at the wavelength of 800 nm wavelength with 170 fs excitation. The scatters are the experimental data, while the solid lines are the numerical simulations with the parameters from the Z-scan measurements.

Fig. 1 The molecular structures of heteroleptic bis(phthalocyaninato) rare earth complexes Yb(Pc)(OOPc) (**1**), Y(Pc)(OOPc) (**2**), Er(Pc)(OOPc) (**3**), Ho(Pc)(OOPc) (**4**).

Fig.2 Schematic diagram of experiental Z-scan set-up.

Fig. 3 The electronic absorption spectra of heteroleptic bis(phthalocyaninato) rare earth complexes Yb(Pc)(OOPc) (1), Y(Pc)(OOPc) (2), Er(Pc)(OOPc) (3), Ho(Pc)(OOPc) (4) recorded at room temperature. The concentrations were held at 2×10^{-6} mol/L.

Fig. 4 Z-scan data for Yb(Pc)(OOPc) (**1**), Y(Pc)(OOPc) (**2**), Er(Pc)(OOPc) (**3**), Ho(Pc)(OOPc) (**4**) obtained under an open-aperture configuration with the same excitation intensity of $I_0 = 118.5 \text{ GW/cm}^2$. The concentration of them is 10^{-3} mol/L . The dots are the experimental data while the solid curves are the theoretical fit using Eq. (1).

Fig. 5 Ultrafast optical limiting for chloroform solution of sandwich type complex **1-4** as a function of the input irradiances under the excitation of laser pulses at the wavelength of 800 nm wavelength with 170 fs excitation. The scatters are the experimental data, while the solid lines are the numerical simulations with the parameters from the Z-scan measurements.

Supporting Information

Strong two-photon absorptions in heteroleptic bis(phthalocyaninato) rare earth sandwich complexes

Ning Sheng ^{a*}, Bing Gu ^b, Boxiao Ren ^b, Yingying Wang ^a, Lijuan Han ^a, Jingxia Wang ^a, Houyong Cao ^a, Meihui Guan ^a, Xiurong Zhai ^a, Jingquan Sha ^{a*}

^a Department of Chemistry and Chemical Engineering, Jining University, Qufu, 273155, China

^b Advanced Photonics Center, Southeast University, Nanjing 210096, China

**Corresponding author: sns0215@163.com; shajq2002@126.com*

Supporting Information

Table S1 Mass spectroscopic data for complexes **1-4**.

Figure S1 The MALDI-TOF mass spectrum of complex **1**.

Figure S2 The MALDI-TOF mass spectrum of complex **2**.

Figure S3 The MALDI-TOF mass spectrum of complex **3**.

Figure S4 The MALDI-TOF mass spectrum of complex **4**.

Table S1 Mass spectroscopic data for complexes **1-4**.

Complex	Formula	M^+ (m/z)	calcd. for (M^+)
1	$C_{128}H_{160}N_{16}O_8Yb$	2222.9	2223.8
2	$C_{128}H_{160}N_{16}O_8Y$	2139.9	2139.6
3	$C_{128}H_{160}N_{16}O_8Er$	2218.0	2218.0
4	$C_{128}H_{160}N_{16}O_8Ho$	2215.9	2215.7

Figure S1 The MALDI-TOF mass spectrum of complex **1**.

Figure S2 The MALDI-TOF mass spectrum of complex **2**.

Figure S3 The MALDI-TOF mass spectrum of complex **3**.

Figure S4 The MALDI-TOF mass spectrum of complex **4**.