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Third-order nonlinear optical properties of a series of porphyrin-appended europium(III) bis(phthalocyaninato) complexes

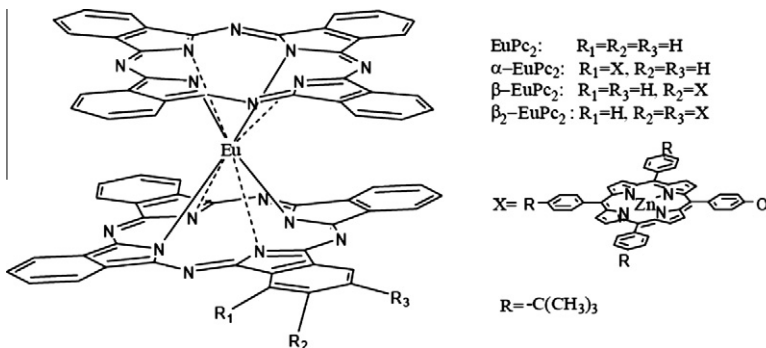
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HIGHLIGHTS

- ▶ Third-order nonlinear properties of porphyrin-bisphthalocyanines were investigated.
- ▶ Porphyrin-bisphthalocyanines are good materials with nonlinear optical properties.
- ▶ The enhanced nonlinearities are induced by high electron density and charge transfer.

GRAPHICAL ABSTRACT

Third-order nonlinear optical properties of a series of phthalocyanine–porphyrin complexes containing a sandwich-type bis(phthalocyaninato) europium(III) core and one or two zinc(II) porphyrin unit(s) were investigated by Z-scan techniques at 1064 nm. The second-order molecular hyperpolarizabilities of these complexes are in the order of 10^{-30} esu.



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ABSTRACT

The third-order nonlinear optical properties of a series of phthalocyanine–porphyrin complexes containing a sandwich-type bis(phthalocyaninato) europium(III) core and one or two zinc(II) porphyrin unit(s) were investigated by Z-scan techniques at 1064 nm. The second-order molecular hyperpolarizabilities of these complexes are in the order of 10^{-30} esu. The enhanced nonlinear properties are induced by the high delocalization of the electrons in the sandwich molecular structure, which may result in charge transfer between the central metal and the phthalocyanine ligands.

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Introduction

Phthalocyanine and phthalocyanine-like compounds with large delocalized π -conjugated electron system have potential applications in the field of nonlinear optics because of their specific electronic absorption, large optical nonlinearity, high thermal and environmental stability, facile preparation and easy modification

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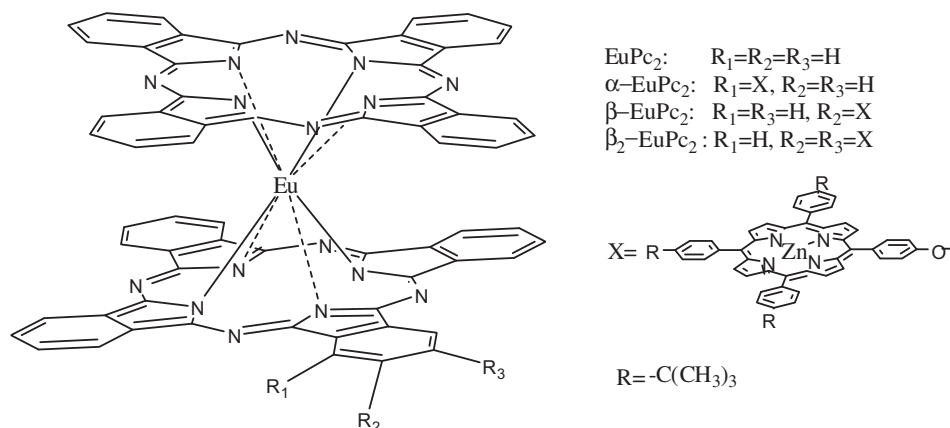


Fig. 1. The molecular structures of the porphyrin-appended europium(III) bis(phthalocyaninato) complexes.

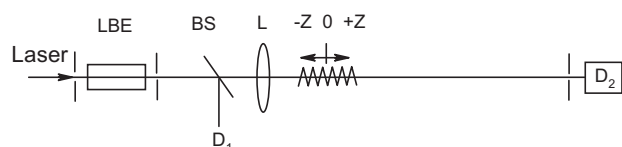


Fig. 2. Z-scan experimental setup at 1064 nm.

of their physical and chemical properties by molecular design [1–4]. The nonlinear optical properties of organic molecular systems have been actively studied both theoretically and experimentally over past years because of their large nonlinear optical susceptibility with short response time and the feasibility of controlling hyperpolarizability by modification of molecular electronic structure [4,5]. Usually, large nonlinear optical properties are always accompanied with highly conjugated large π -system or extended aromatic core of the molecular structure [6,7]. However, comparing with the actually applications of inorganic materials, up to date, search for new organic materials with large nonlinear optical properties, fast response time and studying on the factors affecting the nonlinear optical properties of these organic compounds as nonlinear optical materials are still necessary.

Recently, we have reported the synthesis, characterization, and photophysical properties of a series of porphyrin-appended europium(III) bis(phthalocyaninato) complexes [8]. Three novel phthalocyanine–porphyrin complexes containing a sandwich-type bis(phthalocyaninato) europium(III) core and one or two zinc(II) porphyrin unit(s) were synthesized, they were simplified as α -EuPC₂, β -EuPC₂, and β_2 -EuPC₂ hereinafter (Fig. 1). Considering the large π -system and extended aromatic core of the porphyrin-appended europium(III) bis(phthalocyaninato) complexes, it could be expected that these complexes may produce large nonlinear optical properties. To assess a material for the nonlinear application, the nonlinear refractive and nonlinear absorptive index of the material should be characterized, which could be investigated by Z-scan technique [9–13]. In this paper, the results showed that the porphyrin-appended europium(III) bis(phthalocyaninato) complexes did have very large nonlinear refractive and nonlinear absorptive index, which indicated that these compounds may be promising candidates as third-order nonlinear optical materials. And also, the mother complex europium(III) bisphthalocyanine(EuPC₂) was discussed as a model.

Experimental section

The complexes α -EuPC₂, β -EuPC₂, β_2 -EuPC₂ and EuPC₂ were dissolved in THF, for the large nonlinear refractive and large nonlinear

absorptive signal, the concentration of the complex was in the range of 2×10^{-4} mol/L. The sample and the reference were injected into a 1 mm cell, which matched the requirements for a thin sample used in the standard Z-scan procedure [9,10]. Briefly, as shown in Fig. 2, a Nd:YAG laser with a Gaussian temporal and spatial profile was used as laser source (Continuum surelite II, 1064 nm and 7 ns FWHM). The Gaussian-type laser incident pulse traveling along the Z axis was expanded by a laser beam expander (LBE) and split by a beam-splitter (BS). Two photodetectors were equipped to monitor the input pulse energy (D₁) and the output pulse energy (D₂), respectively. The laser intensity at the focal point in the experiment was $(1.7 \pm 0.2) \times 10^{13}$ W/m². The transmittance of the sample was recorded for each position along the Z axis. Carbon disulfide (CS₂) was used as reference in order to minimize the systemic error. The nonlinear refractive index of CS₂ has been measured before and the value is $(3.1 \pm 0.2) \times 10^{-18}$ m²/W [14]. The error of the measurements for the nonlinear refractive and nonlinear absorptive index was c.a. 20%. The main contributions to the errors arose from the laser power fluctuations, the influence of non-stability of laser parameters, optical instruments and some other consecutive measurements. Also, the experiment was repeated with pure solvent (THF) and no significant feature was observed in either the open or the closed Z-scan procedure.

Results and discussion

Z-scan theories on nonlinear process

The nonlinear refraction index $n(I)$ of NLO material is expressed in terms of nonlinear refractive index n_2 by the following expression,

$$n(I) = n_0 + n_2 I \quad (1)$$

where n_0 is the linear index of refraction, I is the intensity of the laser beam.

The nonlinear absorption index $\alpha(I)$ is expressed in terms of linear absorptive index α and nonlinear absorptive index β by the following expression.

$$\alpha(I) = \alpha + \beta I \quad (2)$$

The n_2 and β value of the sample can be readily obtained by Z-scan experiment, simply comparing the observed peak to valley change in the normalized transmittance of CS₂ with that of the sample obtained under the identical conditions using the following equation [15,16]:

$$n_{2,S} = n_{2,CS_2} \frac{\Delta T_{P-V,S}}{\Delta T_{P-V,CS_2}} \cdot \frac{I_{0,CS_2}}{I_{0,S}} \cdot \frac{L_{eff,CS_2}}{L_{eff,S}} \quad (3)$$

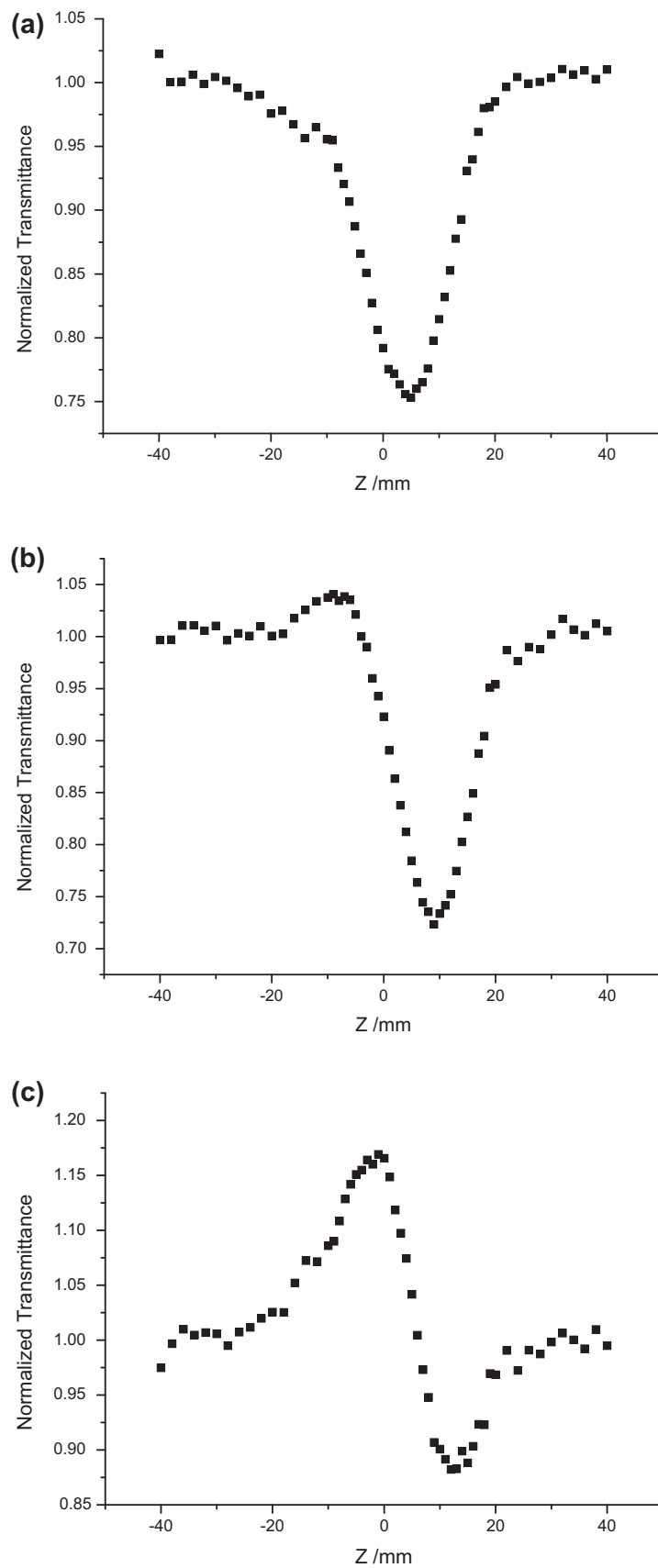


Fig. 3. (a) Open aperture Z-scan data of β_2 -EuPc₂, (b) Closed aperture Z-scan data of β_2 -EuPc₂, and (c) Result of the division of closed/open aperture Z-scan data of β_2 -EuPc₂.

Table 1
Nonlinear refractive properties of the complexes.

Sample	Concentration (mol/L)	n_2 (m ² /W)	$\chi_R^{(3)}$ (m ² /V ²)	γ_R	
				m ⁵ /V ²	esu
EuPc ₂	2.20×10^{-4}	-5.40×10^{-18}	-3.78×10^{-20}	-0.921×10^{-43}	-6.60×10^{-30}
α -EuPc ₂	2.16×10^{-4}	-5.90×10^{-18}	-4.14×10^{-20}	-1.03×10^{-43}	-7.35×10^{-30}
β -EuPc ₂	2.16×10^{-4}	-5.79×10^{-18}	-4.06×10^{-20}	-1.01×10^{-43}	-7.21×10^{-30}
β_2 -EuPc ₂	2.08×10^{-4}	-4.93×10^{-18}	-3.46×10^{-20}	-0.890×10^{-43}	-6.37×10^{-30}
CS ₂	16.6	3.10×10^{-18}	2.91×10^{-20}	5.05×10^{-49}	3.62×10^{-35}

Table 2
Nonlinear absorptive properties of the complexes.

Sample	Concentration (mol/L)	β (m/W)	$\chi_I^{(3)}$ (m ² /V ²)	γ_I	
				m ⁵ /V ²	esu
EuPc ₂	2.20×10^{-4}	3.27×10^{-11}	1.94×10^{-20}	4.72×10^{-44}	3.38×10^{-30}
α -EuPc ₂	2.16×10^{-4}	1.88×10^{-11}	1.11×10^{-20}	2.76×10^{-44}	1.98×10^{-30}
β -EuPc ₂	2.16×10^{-4}	1.24×10^{-11}	0.738×10^{-20}	1.83×10^{-44}	1.31×10^{-30}
β_2 -EuPc ₂	2.08×10^{-4}	2.23×10^{-11}	1.33×10^{-20}	3.42×10^{-44}	2.45×10^{-30}

where the subscripts *S* and CS₂ refer to sample and reference, respectively. ΔT_{p-v} is the peak to valley normalized transmittance difference in the corrected Z-scan data, I_0 is the radiation intensity at the focal point, L_{eff} is the sample's effective length. The nonlinear absorptive index β can be estimated from the equation below [17],

$$\beta = \frac{2\sqrt{2}\Delta T_{\max}}{I_0 L_{eff}} \quad (4)$$

where ΔT_{\max} is the difference between the normalized transmittance at $z = 0$ and $z \rightarrow \infty$ of the open aperture Z-scan.

Nonlinear refractive and nonlinear absorptive properties of the series of EuPc₂

In our experiments, the Z-scan signals were similar for all these samples. Fig. 3a showed closed Z-scan data of β_2 -EuPc₂ obtained on the Z-scan experimental apparatus ($S = 0.11$). The closed-aperture scheme allowed the determination of both the sign and the value of nonlinear refractive index (n_2). The peak-valley pattern of the normalized transmittance curve in the figure indicated that β_2 -EuPc₂ had a negative sign for the nonlinear refraction and exhibited self-defocusing behavior. The results of open aperture Z-scan of the sample in the same condition shown in Fig. 3a was used for the measurements of nonlinear absorptive index (β). After correction for the energy fluctuations, we then divided the data of closed aperture (Fig. 3b) by that of open aperture (Fig. 3a) in order to get the corrected normalized Z-scan curve, as shown in Fig. 3c. This gave a very good approximation of the transmittance due to only the refractive part n_2 of the nonlinear response. From the value of β and n_2 , the other optical parameters, including the real and imaginary part of the third-order susceptibility ($\chi_R^{(3)}$, $\chi_I^{(3)}$), the real and imaginary part of the second-order molecular hyperpolarizability (γ_R , γ_I), could be estimated [18] and were summarized in Tables 1 and 2, including the nonlinear refractive property of the reference (CS₂) for comparing.

Usually, during Z-scan experiments, the measurement data will fluctuate with the change of different Z position for the system errors, especially for the little change of laser intensity. But in our case, the signals were so strong that the measurement data were very smoothly, in the open aperture and closed aperture Z-scan process, which indicated that all the samples had very large nonlinear refractive and nonlinear absorptive properties. We noticed

that the γ_R and γ_I were in the order of 10^{-30} esu for all the europium(III) bisphthalocyanine complexes, the connecting position of the porphyrin chromophore onto the double-decker and the number of porphyrin moieties did affect little for the nonlinear optical parameters. And these values were larger than the published data of any traditional metal phthalocyanines which located in the range of 10^{-32} – 10^{-33} esu [19]. Shirk et al. have reported that the γ values of some metal bisphthalocyanine were in the order of 10^{-31} esu [20]. Gong et al. have published that the γ values of any double- and triple-deckers europium phthalocyanine were also in the order of 10^{-30} esu using femtosecond time-resolved optical Kerr gate method at 830 nm wavelength [21]. Recently, Zhang et al. also published that a copper phthalocyanine–ferrocene dyad had a large γ value in the order of 10^{-30} esu, and concluded that the large γ value came from the formation of intramolecular charge-transfer and the enhancement delocalized the large π system [22].

The electronic absorption spectra of all the complexes are very similar, which were the sum of the spectra of europium(III) bisphthalocyanine and different porphyrin component [8]. All the spectra show the absence of strong electronic interaction between the two components, meant that the high delocalized conjugated π -system in the part of EuPc₂ was maintained whether it was connected one or two porphyrin part(s) or not. In the molecular structures of these compounds, all adopted a slightly distorted square-antiprismatic structure around the metal europium(III) center, the two phthalocyanine rings were close enough that resulted a significant and effective π – π interaction. The metal europium(III) formed eight coordination bonds with the eight isoindole nitrogen atoms of the two phthalocyanine ligands, besides that, the complexes had an unpaired *n* electron in one of the macrocyclic ligands, which made the europium(III) bisphthalocyanine also had high density of *n* electron [23–26]. All of these situations made the complex with highly delocalized electron density. Moreover, the central metal atom, europium(III), had a valence of +3, and charge neutrality required three other electrons to be shared between the ligand rings. The europium atom, with an atomic electron configuration of $4d^{10}5s^25p^64f^6$ had sufficient unoccupied orbitals. So, the charge transfer from metal to ligand might be occurred and even be enhanced owing to the electron enrichment of ligand and electron poverty of central metal. And vice versa, the electron transfer process from the porphyrin moieties to the sandwich-type bisphthalocyanine core (in case of α -EuPc₂, β -EuPc₂ and β_2 -EuPc₂) would also

enhance the delocalized high electron density of the complexes [8]. This would also make some enhancement of the third-order nonlinear optical properties. We believe that the enlarged π -system in double-deckers phthalocyanines have not only all the physical and chemical merits of usual phthalocyanines used as nonlinear optical materials, but also much more enhanced nonlinear optical refractive and nonlinear optical absorptive properties. These sandwich-type bisphthalocyanine compounds would be more promising candidates for application than the mono-phthalocyanine. Other researches on the practice use in film and solid state are in progress.

Conclusions

The third-order nonlinear optical properties of a series of phthalocyanine-porphyrin complexes containing a sandwich-type bis(phthalocyaninato) europium(III) core and one or two zinc(II) porphyrin unit(s) were investigated by Z-scan techniques at 1064 nm. The real part and imaginary part values of the second-order molecular hyperpolarizability (γ_R, γ_I) all located in the order of 10^{-30} esu, which were 2–3 order larger than mono-phthalocyanines. The enhanced nonlinear properties were induced by delocalized high density of electron of the sandwich molecular structure and the sufficient unoccupied orbits of the central metal, between which may occur charge transfer. We believe this kind of sandwich-type phthalocyanines are promising candidates for the practical application in the field of nonlinear optical materials.

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