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Ultrafast third-order optical nonlinearity of several sandwich-type phthalocyaninato and porphyrinato europium complexes*

Huang Wen-Tao(黄文涛)[a], Li Yan(李 焱)[a]†, Xiang Hong(向 红)[a], Yang Hong(杨 宏)[a], Gong Qi-Huang(龚旗煌)[a]‡, Huang Yan-Yi(黄岩谊)[b], Huang Chun-Hui(黄春辉)[b], and Jiang Jian-Zhuang(姜建壮)[c]

[a] *State Key Laboratory for Mesoscopic Physics and Department of Physics, Peking University, Beijing* 100871, *China*
[b] *State Key Laboratory of Rare Earth Material Chemistry and Application, College of Chemistry, Peking University, Beijing* 100871, *China*
[c] *Department of Chemistry, Shandong University, Jinan* 250100, *China*

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The third-order optical nonlinearity of two sandwich-type phthalocyaninato and porphyrinato europium complexes, including double- and triple-deckers ($Eu[Pc(OC_5H_{11})_8]_2$, $Eu_2(Pc)(TPP)_2$, Pc=phthalocyanine, TPP=5, 10, 15, 20- tetraphenylporphyrinate), was investigated by using the femtosecond time-resolved optical Kerr gate method at 830 nm wavelength. Their second-order hyperpolarizability is estimated to be 0.74×10^{-30}esu and 3.0×10^{-30}esu respectively. This exhibits an evident enhancement in comparison with 0.47×10^{-30}esu for one-decker Eu(Pc)(acac) (acac=acetylacetonate), which is also measured under the same conditions. The enhancement is attributed to the introduction of lanthanide metal to the large π-conjugated system, intermacrocycle interaction and two-photon resonance etc.

Keywords: ultrafast third-order optical nonlinearity, phthalocyanine, porphyrin
PACC: 4265, 4280W, 7820, 7855K

1. Introduction

Phthalocyanines and porphyrins are two classes of stable, robust and functional tetrapyrrole derivatives. They are well-known macrocyclic compounds with highly delocalized large π-electron system which endows them unique properties useful for catalysis, medicine, photovoltaic cells etc.[1−3] In addition, their capability of including many metallic ions makes them typical organometallic compounds with effective charge-transfer transitions between metal atom and ligand. Such metal-ligand bonding displays large molecular hyperpolarizability, which was caused by the transfer of electron density between the metal atom and the conjugated macrocycle. So they are considered to be promising candidates as usable nonlinear optical (NLO) materials with large third-order optical nonlinearity.[4−9] The diversity of central metal atoms and peripheral substituents offers ease of synthesizing and tailoring. Furthermore, three-dimensional structures can be formed by polymerization or by coordination of transition metals. The unique sandwich-type cofacial stack extending of their planar π-electron systems such as MPc_2 attracts great attention by introducing particularly intermacrocycle interaction.[10−15]

For instance, sandwich-type bis (phthalocyaninato or porphyrinato) metal complexes have been investigated as promising electrochromic display materials and optical limiting materials.[16−18] Also considered as potential third-order NLO materials, several lanthanide bis (phthalocyanines) and their anions have been systematically investigated years ago.[10] Their second-order hyperpolarizability (γ) enhanced more than 2 orders of magnitude comparing with γ

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†E-mail: li@pku.edu.cn
‡Corresponding author. E-mail: qhgong@pku.edu.cn

of metal-free monophthalocyanine. And a strong enhancement of γ with oligomer size n scaling as n^3 ($n = 1 - 3$) has been found when the γ of μ-oxo silicon phthalocyanine oligomers $(SiPcO)_n$ is studied.[11] Such unique cofacial stack extending of planar π-electron systems was considered models for studying structure relationships of third-order NLO property, particularly intermacrocycle interaction. Manas *et al* have theoretically analysed the effects of cofacial stack on γ, and suggested the experimental investigation on the third-order NLO property of triple-decker sandwich-type metallophthalocyanine.[19]

We have previously reported the measurement of the second-order hyperpolarizability of two triple-decker mixed phthalocyaninato and porphyrinato Sm complexes, $Sm_2(Pc)_2(TPP)$ and $Sm_2(Pc)(TPP)_2$. [20] In this paper we studied the third-order NLO property of three samples with the same metallic ions by using femtosecond time-resolved optical Kerr gate method at 830 nm wavelength, including a heteroleptic triple-decker $Eu_2(Pc)(TPP)_2$, a double-decker $Eu[Pc(OC_5H_{11})_8]_2$ and a one-decker Eu(Pc)(acac). Their second-order hyperpolarizabilities were estimated to be 3.0×10^{-30}esu, 0.74×10^{-30}esu and 0.47×10^{-30}esu respectively.

2. Experiments

2.1. Materials

The $Eu_2(Pc)(TPP)_2$, $Eu[Pc(OC_5H_{11})_8]_2$ and Eu(Pc)(acac) were synthesized by Jiang *et al*, and the detail process was reported elsewhere.[21,22] Their molecular structures have been confirmed by the ^{1}H NMR spectra, and many similar double- and triple-decker compounds with varied metallic ions have been synthesized and studied by the ^{1}H NMR spectra, mass spectra, IR and resonance Raman spectra, electronic spectra etc.[23,24] We present a schematic picture of the structure of $Eu_2(Pc)(TPP)_2$ and $Eu[Pc(OC_5H_{11})_8]_2$ in Fig.1. $Eu_2(Pc)(TPP)_2$ was concluded as (TPP) Eu (Pc) Eu (TPP) with the original planar Pc/TPP ring rotated around the axis determined by two metallic atoms and slightly curved because of the strong intermacrocycle interaction.[21,25,26]

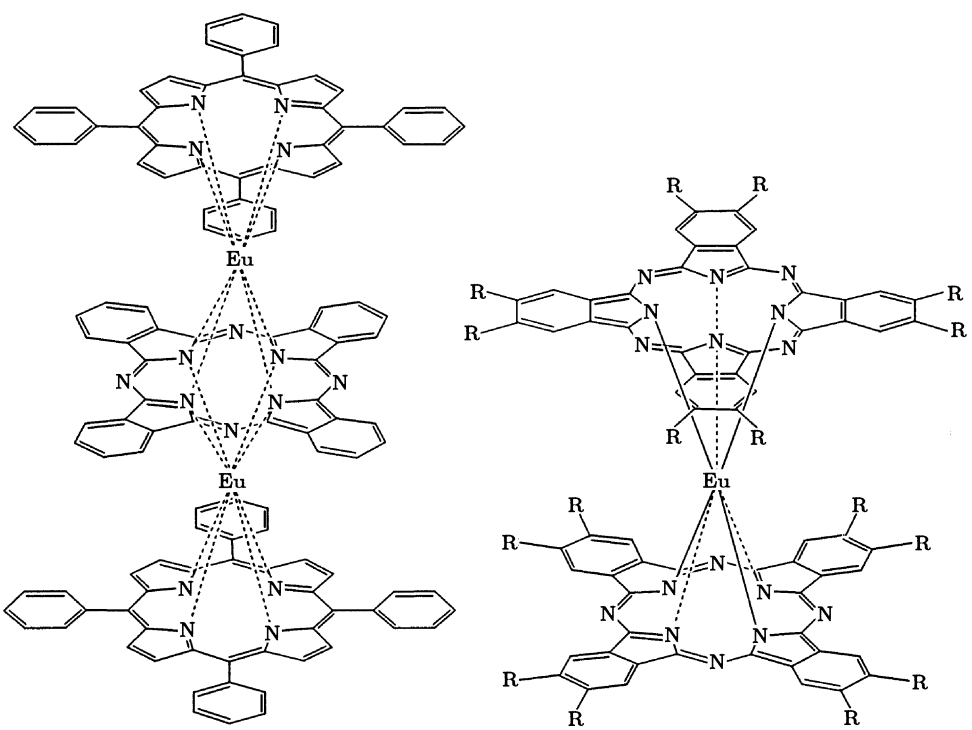


Fig.1. A schematic picture of the molecular structures of $Eu_2(Pc)(TPP)_2$ (left) and $Eu[Pc(OC_5H_{11})_8]_2$ (right) (R=$OC_5H_{11})_8$).

2.2. Experimental setup

The standard optical Kerr gate method was employed to study the ultrafast NLO response of sample solutions at 830nm, with the femtosecond laser pulses generated from a Ti:sapphire oscillator (Mira 900F, Coherent, USA). Detailed apparatus configuration has been described in our previous reports.[27−29] In brief, the laser output pulse was split into a strong pump and a weak probe pulse train with a ratio of 10:1 and 45° polarization difference. Two beams were carefully adjusted parallel and focused by a convex lens to overlap spatially in the sample solution filled in a 1mm-thickness glass cell. After the interaction, with the pump beam blocked, the probe beam was collimated into an analyser (polarizer) whose transmission axis was strictly perpendicular to its original polarization. Only the generated orthogonal signal and optical Kerr effect (OKE) signal passed and were detected by a photodiode after the analyser. A motor-driven optical delay line was used in the optical path of the pump beam to obtain time-resolved signal. In order to obtain good signal/noise ratio, the pump and probe beams were chopped at different frequencies and the signal was amplified at the sum frequency by a lock-in amplifier (SR830, Stanford, USA). A computer was used to control the step motor and monitor the measurement. By replacing the sample cell with a 0.3mm-thick BBO crystal, we can determine the zero delay point and obtain the autocorrelation signal of the system. We got 120fs for the full width at half-maximum of the laser pulses at 830nm.

3. Results and discussion

The linear absorption spectra of our sample solutions (Eu_2 (Pc) $(TPP)_2$, $Eu[Pc(OC_5H_{11})_8]_2$ and Eu(Pc)(acac)) in chloroform were shown in Fig.2, which were measured by Agilent 8453 UV–visible spectroscopy system. The solutions were contained in a 1mm-path-length cuvette with concentrations of 4.6×10^{-5}M for Eu_2 (Pc) $(TPP)_2$, 7.0×10^{-5}M for $Eu[Pc(OC_5H_{11})_8]_2$ and 23.3×10^{-5}M for Eu (Pc) (acac). The absorptions at *ca* 350 and 680 nm can be attributed to the B bands and Q bands of Pc rings respectively. The former is clear for all three solutions, but the latter totally disappears or shifts for Eu_2 (Pc) $(TPP)_2$, which indicates strong intermacrocycle interaction. For Eu_2 (Pc) $(TPP)_2$, the absorption *ca* 420 nm can be attributed to the B bands of TPP ring, and its relative intensity to the peak *ca* 350 is 2:1 corresponding to the TPP: Pc ration in this complex.[21] The absorptions at 830 nm can be neglected for all samples.

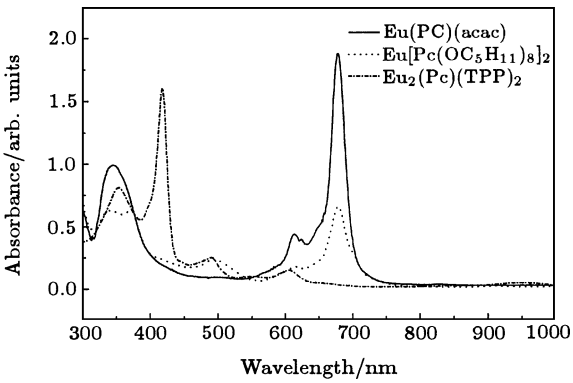


Fig.2. Absorption spectra of $Eu_2(Pc)(TPP)_2$, $Eu[Pc(OC_5H_{11})_8]_2$ and Eu(Pc)(acac) in chloroform from 300 nm to 1000 nm.

We followed the standard reference measurement to obtain the third-order NLO susceptibility $\chi^{(3)}$ of a sample solution.[27−30] The following equation

$$\chi_S^{(3)} = \chi_R^{(3)} \left(\frac{I_S}{I_R}\right)^{1/2} \left(\frac{n_S}{n_R}\right)^2 f(\alpha) \qquad (1)$$

is used to calculate $\chi^{(3)}$. The subscripts, S and R, represent the parameters of the sample solution and the reference CS_2 respectively. I is the intensity of the obtained OKE signal. n is the refractive index. $f(\alpha)$ is an absorption correction factor, which equals one when the corresponding absorption can be neglected. The n of CS_2 is 1.62 and its $\chi^{(3)}$ was estimated to be 1.0×10^{-13} esu in femtosecond time scale.[31] We can use the n of chloroform at 20°C (n =1.446) as the refractive index of the solution since the concentration of sample is very dilute.

The typical OKE response of $Eu_2(Pc)(TPP)_2$ in chloroform is shown in Fig.3. We measured the signal of the pure solvent under the same condition, which was very small and subtracted in calculation. We also measured the signal of the pure CS_2 under identical condition for comparison. According to Eq.(1), the third-order NLO susceptibility for the solution of $Eu_2(Pc)(TPP)_2$ at 4.6×10^{-5}M is deduced to be 2.8×10^{-13}esu. From the figure, we notice that the NLO response of the solution is the same time scale as the pulse duration and no decay process appeared. It is believed that such an instantaneous response in femtosecond time scale can be predominantly attributed to the delocalization of electrons.[32]

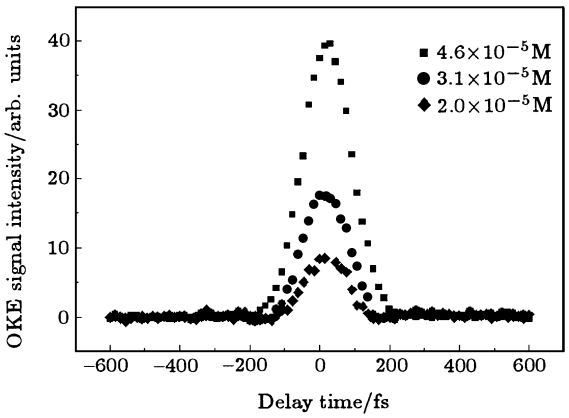


Fig.3. The optical Kerr effect response of the solution of $Eu_2(Pc)(TPP)_2$ dissolved in chloroform at concentrations of 4.6×10^{-5}M, 3.1×10^{-5}M and 2.0×10^{-5}M.

In order to verify the linear dependence of the measured $\chi^{(3)}$ on the solution concentration, the OKE signals of the sample at different concentrations have been measured. We give the data in Fig.4 with $Eu_2(Pc)(TPP)_2$ as a representative. The linear fit of the three values of $\chi^{(3)}$ (2.8×10^{-13}esu, 1.9×10^{-13}esu, and 1.3×10^{-13}esu) on the concentrations (4.6×10^{-5}M, 3.1×10^{-5}M and 2.0×10^{-5}M) is excellent. The fitted line is very close to origin. It concludes that our experimental measurement is reliable and the followed equation,

$$\gamma = \chi^{(3)}/NL, \tag{2}$$

can be introduced to estimate the second-order hyperpolarizability (γ) of the sample molecule. Here N is the number density of the sample molecule and L is the local field correction factor given by $[(n^2+2)/3]^4$. The calculated γ is 3.0×10^{-30}esu for $Eu_2(Pc)(TPP)_2$. And the γ of $Eu[Pc(OC_5H_{11})_8]_2$ and Eu(Pc)(acac) are deduced to be 0.74×10^{-30}esu and 0.47×10^{-30}esu by the same routine respectively.

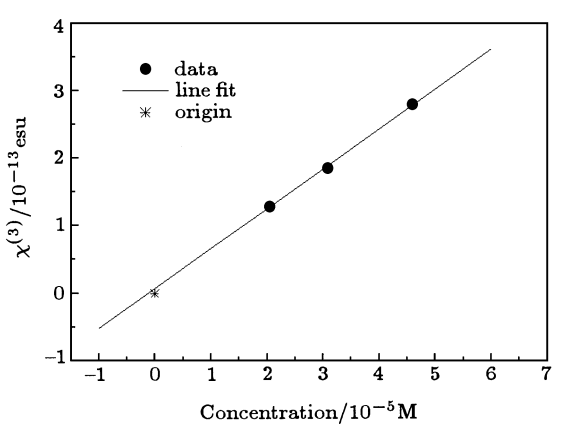


Fig.4. Linear concentration dependence of the third-order NLO susceptibility $\chi^{(3)}$ of $Eu_2(Pc)(TPP)_2$ in chloroform.

In our previous letter, we have suggested that the acceptable non-resonance γ for metal-free Pc and tetraphenylporphyrin is about 10^{-33}esu at 830 nm.[20] Although the differences of measurement systems and experimental conditions have made the measured susceptibilities hard to be compared with each other, it is obvious that the third-order optical nonlinearity of our complexes is strongly enhanced with 2–3 orders relative to the mono-layer metal-free Pc and TPP. We have previously reported the large second-order hyperpolarizability of triple-decker mixed phthalocyaninato and porphyrinato Sm complexes $Sm_2(Pc)_2(TPP)$ and $Sm_2(Pc)(TPP)_2$, which are 2.6×10^{-30}esu and 2.2×10^{-30}esu. Introducing of Lanthanide metal to the large π-conjugated system, we have concluded that intermacrocycle interaction and two-photon resonance are responsible for their large optical nonlinearity.[20] And these three factors also lead to the strong enhancement for $Eu_2(Pc)(TPP)_2$. The measured γ of $Eu_2(Pc)(TPP)_2$ is about 4 times as that of $Eu[Pc(OC_5H_{11})_8]_2$. Two-photon resonance is considered responsible for this enhancement based on the theoretical analysis of Manas *et al.*[19] They suggested a fourfold enhancement of the γ of $(SiPcO)_3$ trimer to $(SiPcO)_2$ dimer due to two-photon resonance. In absorption spectra of $Eu_2(Pc)(TPP)_2$, it shows evidence for two-photon resonance that the B band of TTP locates near 415 nm (the double-frequency wavelength of 830 nm). The measured γ of $Eu[Pc(OC_5H_{11})_8]_2$ is appreciably larger than other results for bis (phthalocyanines) which ranged between 0.10×10^{-30}esu and 0.50×10^{-30} esu. [10,15] Shirk *et al* gave 0.22×10^{-30} esu for $Eu(Pc)_2$ at 1064 nm by degenerated four-wave mixing. Such difference may come from the wavelength dispersion of γ and the influence of peripheral substituent. According to previous work on bis(phthalocyanines), introducing Lanthanide Eu and strong intermacrocycle interaction are responsible for the large nonlinearity of $Eu[Pc(OC_5H_{11})_8]_2$. The measured γ of Eu(Pc)(acac) is about 10 times as those for metallophthalocyanines with normal metals.[4,33] Despite the especial uncomplete f-shell of Lanthanide Eu, out planar position of Eu and acaca may be helpful in such enhancement. Nalwa *et al* have found a fourfold enhancement of nonlinearity for $VOPc(NH_2)_4$ to $CuPc(NH_2)_4$ and introduced the effect of such structure.[34] The γ of MoOPc was measured as 0.31×10^{-30}esu, which is close to our result.[15]

4. Conclusion

In summary, the third-order optical nonlinearities of a triple-decker mixed porphyrinato-phthalocyaninato Lanthanide compound Eu_2 (Pc) $(TPP)_2$, a double-decker Eu [Pc $(OC_5H_{11})_8]_2$ and a mono-layer Eu (Pc) (acac) were explored by using femtosecond optical Kerr gate method. Their instantaneous second-order hyperpolarizabilities were estimated to be 3.0×10^{-30}esu, 0.74×10^{-30}esu and 0.47×10^{-30}esu respectively. Mechanism for such large nonlinearity was discussed.

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