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Chemical Physics Letters 374 (2003) 639–644

CHEMICAL PHYSICS LETTERS

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Large and ultrafast third-order optical nonlinearity of heteroleptic triple-decker (phthalocyaninato)(porphyrinato)Sm(III) complexes

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Received 3 January 2003; in final form 7 May 2003

Abstract

The third-order optical nonlinearity of two triple-decker mixed phthalocyaninato and porphyrinato Sm complexes, $Sm_2(Pc)_2(TPP)$ and $Sm_2(Pc)(TPP)_2$ (Pc = phthalocyanine; TPP = 5,10,15,20-tetraphenylporphyrinate), is investigated using the femtosecond time-resolved optical Kerr gate method at 830 nm wavelength. Their second-order hyperpolarizabilities are estimated to be 2.6×10^{-30} and 2.2×10^{-30} esu, respectively. Introducing of Lanthanide Sm to the large π-conjugated system, intermacrocycle interaction and two-photon resonance are considered responsible for the large optical nonlinearity.

1. Introduction

Over the past decade, tetrapyrrole derivatives such as phthalocyanines and porphyrins were intensively studied. As well-known macrocyclic compounds, they have highly delocalized large π-electron system that endows them many unique properties useful for catalysis, medicine, photovoltaiccells, etc. [1–3]. They are highly stable and versatile components, capable of including many metallic and nonmetallic ions in the ring cavity and incorporating a variety of peripheral substituents. Moreover, three-dimensional structures can be formed by polymerization or by coordination of transition metals. Such extending of molecular structure brings various researching attention. For instance, long rod-like arrays of porphyrines have been designed to investigate ultrafast intramolecular energy transfer as a model of light-harvesting antenna [4,5]. Sandwich-type bis(phthalocyaninato or porphyrinato) metal complexes have been considered promising electrochromic display

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doi:10.1016/S0009-2614(03)00785-1

materials and models for the 'special pair' in the reaction center protein of photosynthetic bacteria [6,7]. Moreover, optical limiting property has also been investigated for several homoleptic double-decked diphthalocyanines [8,9].

One interesting property of the tetrapyrrole derivatives is their great third-order optical nonlinearity attributed to their highly polarizable extended two-dimensional π-electron system [10–15]. And with the unique cofacial stack or linear extending of planar π-electron systems, MPc_2, $MNPc_2$, SiPcO oligomers and porphyrine polymer, etc. have been considered models for studying structure relationships of third-order nonlinear optical (NLO) property, particularly intermacrocycle interaction [16–21]. Shirk et al. [16] have systematically measured the second-order hyperpolarizability (γ) of Sc, Y and several lanthanide bis(phthalocyanines) and their anions. They found more than two orders of magnitude enhancement on the γ compared with that of metal-free monophthalocyanine. Chen et al. [18] have investigated the γ of μ-oxo silicon phthalocyanine oligomers $(SiPcO)_n$, and found that the γ was strongly enhanced with oligomer size n scaling as n^3 for $n = 1–3$. Then Manas et al. [22] theoretically analyzed the effects of intermacrocycle interactions on the γ of the cofacial phthalocyanine dimers and trimers. They also suggested the experimental research on the third-order NLO property of triple-decker sandwich-type metallophthalocyanine. While, only some double-decker metal bis(phthalocyanines) and bis(naphthalocyanines) have been studied till now [16,17].

In this Letter, the third-order NLO property of two triple-decker heteroleptic phthalocyaninato and porphyrinato Sm compounds, $Sm_2(Pc)_2(TPP)$ and $Sm_2(Pc)(TPP)_2$, was measured using femtosecond time-resolved optical Kerr gate method at 830 nm wavelength. Their second-order hyperpolarizabilities were estimated to be 2.6×10^{-30} and 2.2×10^{-30} esu, respectively. Although all the available second-order hyperpolarizabilities of cofacial phthalocyanines were obtained by degenerate four wave mixing (DFWM) around 1064 or 532 nm under picosecond or nanosecond excitation, a comparison is made. The relative large nonlinearity of our samples is analyzed.

2. Materials and experimental method

2.1. Materials

The $Sm_2(Pc)_2(TPP)$ and $Sm_2(Pc)(TPP)_2$ were synthesized by Jiang et al. [23,24]. The molecular structures of these two heteroleptic (phthalocyaninato)(porphyrinato)metal complexes, as shown in Fig. 1, have been confirmed by the ^{1}H NMR spectra [24]. Many similar 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, EPR spectra and cyclic voltammetry, etc. [25–27]. Associated with other theoretical calculations, the molecular structures of our samples were concluded as (Pc)Sm(Pc)Sm(TPP) and (TPP)Sm(Pc)Sm(TPP), with the original planar Pc/TPP ring slightly curved and the adjacent rings rotated with respect to each other on the axis determined by the metallic atoms [23,24,28,29].

2.2. Method

The ultrafast NLO response of our samples in chloroform was measured by the standard optical Kerr gate method with femtosecond laser pulses generated from a Ti:sapphire laser (Mira 900F, Coherent, USA) at 830 nm. The laser output was split into a strong pump beam and a weak probe beam with intensity ratio of 10:1. The polarization of the probe beam was set 45° with respect to the linear polarization of the pump beam. A motor-driven optical delay line was inserted into the optical path of the pump beam to obtain time-resolved signal. Two beams were carefully adjusted parallel and then focused by a convex lens to overlap spatially in the solution filled in a 1-mm-thickness glass cell. After that the pump beam was blocked, and the probe beam was collimated into an analyzer (polarizer) whose transmission axis was strictly perpendicular to its original polarization. A photodiode was inserted just after the analyzer to detect the generated orthogonal signal, optical Kerr effect (OKE) signal. To obtain good signal/noise ratio, the pump and the probe beams were chopped at different frequencies, and the signal was amplified at the sum frequency by a

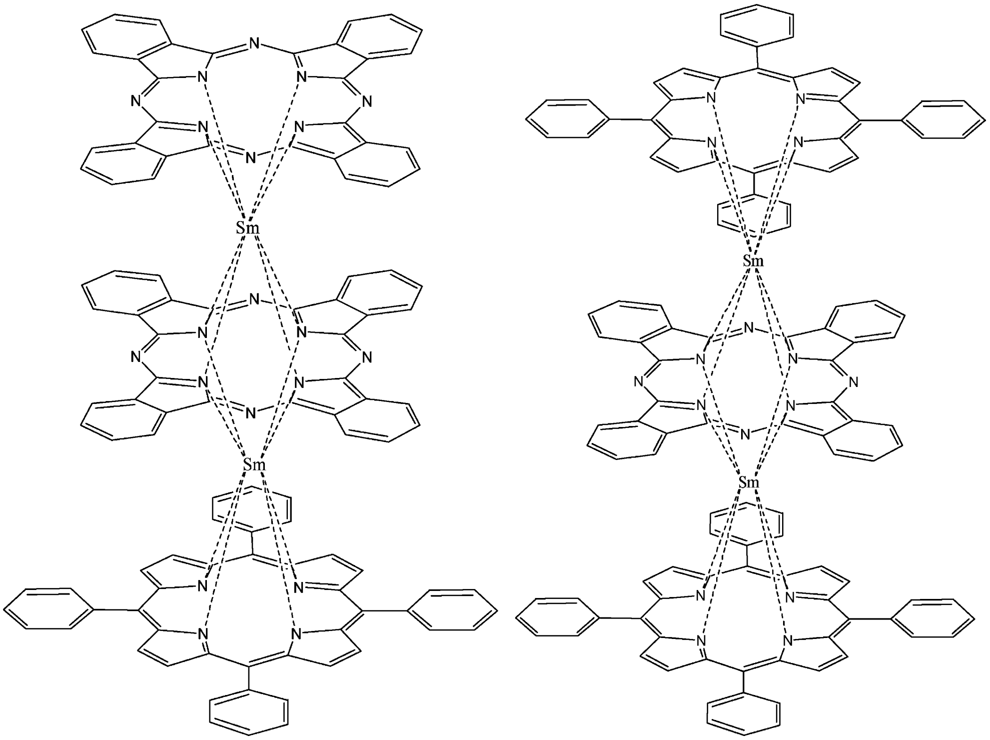

Fig. 1. A schematic picture of the molecular structures of $Sm_2(Pc)_2(TPP)$ (left) and $Sm_2(Pc)(TPP)_2$ (right).

lock-in amplifier (SR830, Stanford, USA). A computer was used to control the step motor, monitor the measurement and collect the data. By replacing the sample cell with a 0.3-mm-thickness BBO crystal, we can determine the zero delay point and obtain the autocorrelation signal of the system. The pulse duration was deduced to be 120 fs. More detailed apparatus configuration has been described in our previous Letters [30,31].

3. Results and discussion

The linear absorption spectra of our samples ($Sm_2(Pc)_2(TPP)$ and $Sm_2(Pc)(TPP)_2$) in chloroform was measured by Agilent 8453 UV–Vis spectroscopy system, as shown in Fig. 2. The solutions were contained in a 1-mm-path-length cuvette with concentrations of 5.0×10^{-5} M for $Sm_2(Pc)_2(TPP)$ and 4.6×10^{-5} M for $Sm_2(Pc)(TPP)_2$. The absorptions at ca. 350 and 415 nm can be attributed to the B bands of Pc and TPP macrocycles, respectively. And their relative intensity is corresponding to the Pc:TPP ratio in the complex. Other remaining absorption bands are attributed to the Q bands of the macrocycles while the contributions from Pc and

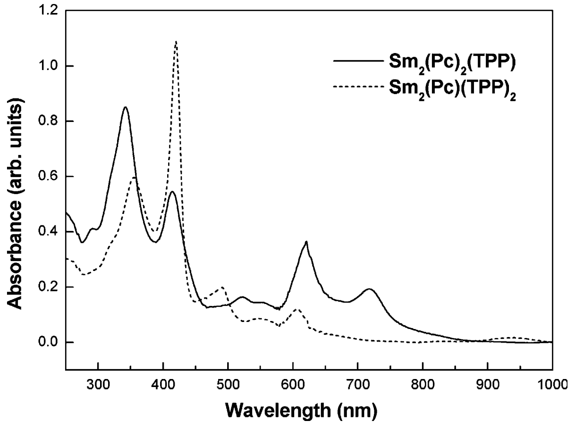

Fig. 2. Absorption spectra of $Sm_2(Pc)_2(TPP)$ and $Sm_2(Pc)(TPP)_2$ in chloroform from 250 to 1000 nm.

TPP are mixed someway [23,24]. The absorption coefficients of the solutions are evaluated to be 0.502 and 0.091 cm^{-1} at 830 nm for $Sm_2(Pc)_2(TPP)$ and $Sm_2(Pc)(TPP)_2$, respectively.

The standard reference measurement was followed to obtain the third-order NLO susceptibility $\chi^{(3)}$ of a sample [30–33]. The following equations:

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

$$f(\alpha) = \frac{\alpha l}{(1 - e^{-\alpha l})e^{-\alpha l/2}}, \tag{2}$$

are used to calculate the value of $\chi^{(3)}$. The subscripts, S and R represent the parameters of the solution and the reference, respectively; I denotes the intensity of the obtained OKE signal; n is refractive index; $f(\alpha)$ is an absorption correction factor, where α is the linear absorption coefficient of the solution and l is the interaction length. CS_2 was selected as the reference for its excellent and stable third-order nonlinear optical response. 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 [34]. Since the concentration of the sample is very low, we can use the n of chloroform at 20 °C ($n = 1.446$) as the refractive index of the solution. The values of $f(\alpha)$ are calculated to be 1.05 and 1.02 at 830 nm for the solutions of $Sm_2(Pc)_2(TPP)$ and $Sm_2(Pc)(TPP)_2$ at 5.0×10^{-5} and 4.6×10^{-5} M, respectively.

The typical OKE responses of $Sm_2(Pc)(TPP)_2$ in chloroform are demonstrated in Fig. 3. The contribution from the solvent was measured to be very small and will be subtracted while calculating. And the signals for CS_2 under identical conditions have been obtained for calculation. According to Eqs. (1) and (2), the third-order NLO susceptibilities for the solutions of $Sm_2(Pc)_2(TPP)$ at 5.0×10^{-5} M and $Sm_2(Pc)(TPP)_2$ at 4.6×10^{-5} M are deduced to be 2.6×10^{-13} and 2.1×10^{-13} esu, respectively. We notice that their NLO responses are in the same time scale as the pulse duration and no decay process is observed. Such instantaneous response in femtosecond time scale proves that the delocalization of electrons contributes to the measured NLO response predominantly [33].

Meanwhile, the OKE signals of a sample at different concentrations have been measured. A linear dependence of the measured $\chi^{(3)}$ on the solute concentration is proved and shown in Fig. 4 with $Sm_2(Pc)(TPP)_2$ as a representative. The linear fit of the three values of $\chi^{(3)}$ (2.1×10^{-13}, 1.4×10^{-13} and 0.95×10^{-13} esu) on the concentrations (4.6×10^{-5}, 3.1×10^{-5} and 2.0×10^{-5} M) is excellent, and the fitted line is very close to origin. It concludes that our experimental measurement is reliable and the following equation:

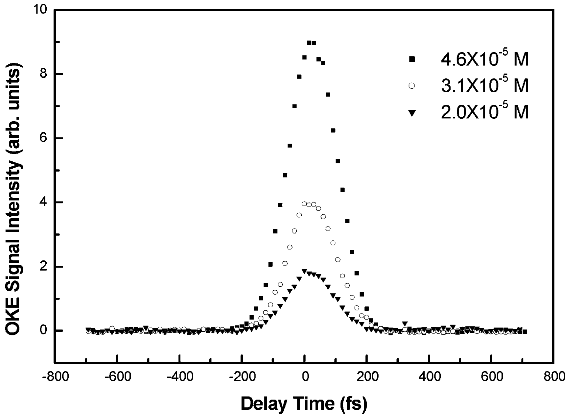

Fig. 3. The optical Kerr effect response of the solution of $Sm_2(Pc)(TPP)_2$ dissolved in chloroform at concentrations of 4.6×10^{-5}, 3.1×10^{-5} and 2.0×10^{-5} M.

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

can be introduced to estimate the second-order hyperpolarizability of the sample molecule. N is the number density of the sample molecule and L is the local field correction factor given by $[(n^2 + 2)/3]^4$. For $Sm_2(Pc)(TPP)_2$ the calculated γ

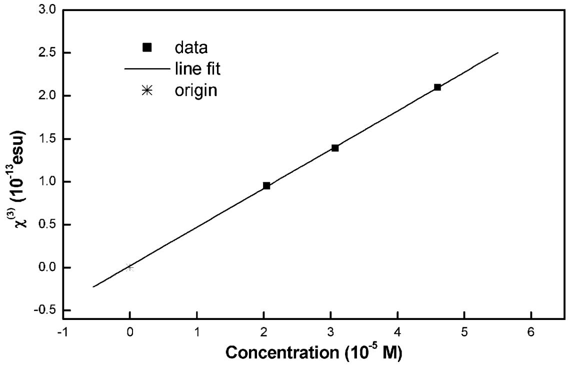

Fig. 4. Linear fit of the third-order NLO susceptibility $\chi^{(3)}$ of $Sm_2(Pc)(TPP)_2$ in chloroform dependence on the concentration.

is 2.2×10^{-30} esu. And the γ of $Sm_2(Pc)_2(TPP)$ is deduced to be 2.6×10^{-30} esu.

Several reviews have manifestly summarized the research of the third-order NLO property of metallophthalocyanines and metalloporphyrins [10–15]. The nonresonant γ of metal-free Pc has been measured as 2×10^{-33} esu at 1064 nm by DFWM [11]. While, the nonresonant γ of metal-free porphyrin is scarce. The reported values of metalloporphyrins deviated in five orders due to the different effects of resonance [11]. We suggest the acceptable nonresonant γ for metal-free tetraphenylporphyrin is about 10^{-33} esu because most of the metalloporphyrins' nonresonant second-order hyperpolarizabilities are in this scale. Even the differences of measurement technologies 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 two triple-decker mixed phthalocyaninato and porphyrinato Sm complexes is strongly enhanced with about three orders relative to the mono-layer metal-free Pc and TPP.

We consider that there are three factors that lead to such enhancement. The first mechanism is the introducing of Lanthanide metal atom Sm. It is well-known that the γ of metallophthalocyanines are about one-order larger than that of the metal-free Pc [11]. It is concluded that the metal substitution introduces new electronic states into the Pc's electronic manifold, and the charge transfer between metal and ligand can enhances the third-order optical nonlinearity strongly. Especially, when incorporating the transition metals such as Co, Pt and Ni that can provide incomplete d-shell, they should introduce more low-lying electronic states than a main group metal and have exhibited much larger γ [10–12]. Bearing an analogy with these transition metals, the Sm substitution should enhance the nonlinearity by charge transfer and may have stronger effect than a main group metal for its incomplete f-shell. The second mechanism is the intermacrocycle interactions. Using SiPcO oligomers as models, this mechanism has been theoretically analyzed by Manas et al. [22]. They divided the sum over states expression for γ to two parts with opposite signs that were well balanced to exhibit a small value in all at first. But by weak intermacrocycle interactions, such balance can be disrupted and the value of γ will be strongly enhanced. They have suggested that this mechanism is responsible for the 25-fold enhancement of the γ of $(SiPcO)_2$ dimer to SiPcO monomer. The third mechanism is the two-photon resonance at 415 nm. The B band of TTP locates exactly about 415 nm, the double-frequency wavelength of 830 nm in our experiment. Manas et al. [22] have also considered the influence of two-photon resonance and suggested that it attributes to the 4-fold enhancement of the γ of $(SiPcO)_3$ trimer to $(SiPcO)_2$ dimer. However, we cannot acquire the double-decker Sm compounds. The γ of $Sm(Pc)_2$ has been measured by DFWM at 532 nm as 43.6×10^{-32} esu [17]. And the γ of similar compounds including different Lanthanide metals has also been reported as 15–41×10^{-32} esu using DFWM at 1064 nm under picosecond excitation [16]. The 5- to 6-fold enhancement on γ for our samples to $Sm(Pc)_2$ might be attributed to the two-photon resonance. Considering all the three mechanisms, the enhancement of γ for our samples to metal-free Pc and TTP can be deduced to be about $(\sim 10) \times (\sim 25) \times (\sim 5) \approx 1250$ folds. It agrees excellently with the measured results.

4. Conclusions

In summary, the third-order optical nonlinearity of two triple-decker mixed porphyrinato–phthalocyaninato Sm compounds, $Sm_2(Pc)_2(TPP)$ and $Sm_2(Pc)(TPP)_2$, is explored by femtosecond optical Kerr gate method. The instantaneous second-order hyperpolarizabilities of $Sm_2(Pc)_2(TPP)$ and $Sm_2(Pc)(TPP)_2$ are estimated to be as great as 2.6×10^{-30} and 2.2×10^{-30} esu, respectively. In comparing with metal-free Pc and TPP, about three orders enhancement on γ is explained by the incorporation of Lanthanide metal atom, intermacrocycle interactions and two-photon resonance.

Acknowledgements

The authors are grateful to Prof. Chunling Liu for her assistance in the absorption spectroscopy measurement. The work was supported by the National Key Basic Research Special Foundation, China, under Grant No. TG1999075209, National Natural Science Foundation of China under Grant Nos. 90206003, 10104003 and 90101027.

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