



Synthesis and third-order nonlinear optical properties of a sandwich-type mixed (phthalocyaninato)(schiff-base) triple-decker complexes



Zhongguo Li ^a, Feng Gao ^b, Zhengguo Xiao ^a, Guanghong Ao ^a, Xingzhi Wu ^a, Yu Fang ^c,
Zhongquan Nie ^a, Tai-Huei Wei ^a, Junyi Yang ^c, Yuxiao Wang ^a, Xueru Zhang ^a,
Jinglin Zuo ^{b,*}, Yinglin Song ^{a,c,**}

^a Department of Physics, Harbin Institute of Technology, Harbin 150001, PR China

^b State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, PR China

^c College of Physics, Optoelectronics and Energy, Soochow University, Suzhou 215006, PR China

ARTICLE INFO

Article history:

Received 8 November 2014

Received in revised form

21 March 2015

Accepted 24 March 2015

Available online 1 April 2015

Keywords:

Phthalocyanine

Sandwich complex

Third-order optical nonlinearity

Z-scan

Lanthanide

Optical material

ABSTRACT

A novel sandwich-type erbium triple-decker complexes with mixed phthalocyanine and Schiff-base ligands was synthesized and characterized by optical absorption spectroscopy. The third-order nonlinear optical properties of the sandwich-type complexes in dichloromethane were investigated using Z-scan measurement at 532 nm with 20 ps pulses. The Z-scan results reveal that the sandwich-type complexes exhibit strong reverse saturable absorption and self-focusing effect. The third-order nonlinear susceptibility and second-order hyperpolarizability of the complexes are estimated to be 7.31×10^{-13} esu and 0.94×10^{-30} esu, respectively. Our results indicate that the sandwich-type mixed (phthalocyaninato)(Schiff-base) complexes are promising candidate materials for future nonlinear optical applications such as wavelength conversion and optical switching.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Phthalocyanines (Pcs) have been attracting great attention of chemists in past few decades due to their potential applications in solar cells, photodynamic therapy, gas sensor, organic film transistor, etc [1,2]. Because of its large delocalized π -electron system, excellent structure flexibility and chemical stability, phthalocyanine is recognized as a promising nonlinear optical (NLO) material. And considerable research efforts have been devoted to study the third-order nonlinear optical properties of phthalocyanine and its derivatives [3–13]. It is known that rare earth metal ions can bring these tetrapyrrole derivatives together to form an interesting series of sandwich-type double- and/or triple-decker complexes [14]. Due to the strong intra-molecular π - π interactions and the presence of the heavy lanthanide metal ion, these sandwich-type complexes can display characteristic features that cannot be found in their

monolayer counterparts, enabling them to be used in various areas such as single molecular magnets, field effect transistors, etc [14,15]. Similar to their monomeric counterpart, the third-order NLO properties of sandwich-type lanthanide multiple-decker complexes have also been widely explored [16–27]. Previous experimental results demonstrate that the cubic hyperpolarizability (γ) of sandwich-type complexes is larger than those of the typical monomeric phthalocyanines, which is related to their expanded π -electron system and the heavy metal effect [17–19,21,26]. Despite these efforts, however, most of previous research in this area has been limited to tetrapyrrole-based multiple-deckers which composed of monomeric phthalocyanine and/or porphyrin ligands. As a result, the vast potential of organometallic complexes still remains largely unexplored. It is of great importance to design and characterize novel sandwich-type multiple-decker complexes with new macrocyclic ligands for future NLO devices.

Recently, a new kind of sandwich-type complexes with mixed phthalocyanine and schiff base ligands has been reported [28–30]. Due to the strong magnetic coupling between the two lanthanide ions in these mixed (phthalocyaninato)(schiff-base) complexes, these multiple-decker complexes are found to be excellent single-

* Corresponding author.

** Corresponding author. Department of Physics, Harbin Institute of Technology, Harbin 150001, PR China.

E-mail addresses: zuojl@nju.edu.cn (J. Zuo), ylsong@hit.edu.cn (Y. Song).

molecule magnets (SMMs) [29]. However, the photo-physical properties of these sandwich-type mixed (phthalocyaninato)(-schiff-base) complexes have not been well studied. As a result, it is essential to study the NLO properties of these newly obtained sandwich-type complexes not only for exploring their functionalities but also for deeper understanding the structure-property relationship of sandwich-type rare-earth multiple-decker complexes.

In this paper, the third-order NLO properties of a sandwich-type mixed (phthalocyaninato)(Schiff-base) triple-decker complexes were investigated using Z-scan technique at 532 nm. The sandwich-type complexes exhibited strong reverse saturable absorption and self-focusing effect, and the third-order nonlinear susceptibility ($\chi^{(3)}$) was evaluated to be on the order of 10^{-13} esu. To the best of our knowledge, this paper represents the first report on the third-order NLO properties of the sandwich-type mixed (phthalocyaninato)(Schiff-base) rare-earth triple-decker complexes. Our results indicate that this new sandwich-type triple-decker complex is a promising material for NLO applications on picosecond time regime.

2. Experiment

2.1. Materials

All the reagents were commercially available and used without further purification. The solvent CH_2Cl_2 was obtained from Alfa Aesar Company and used as received without further purification. The half-sandwich lanthanide complex $[\text{Er}(\text{Pc})(\text{acac})]$ (Pc = phthalocyaninate, acac = acetylacetonate) and chiral Schiff base ligand H_2L were prepared according to the published procedure [31,32]. The sandwich-type mixed (phthalocyaninato)(Schiff-base) triple-decker complexes was synthesized according to the procedures reported in our pervious literature, [30] as shown in Fig. 1.

2.2. Instruments

Elemental analysis was carried out with a Elementar Vario MICRO analyzer. IR spectra were recorded on a Vector22 Bruker spectrophotometer with KBr pellets. Melting points were determined with X – 4 digital micro melting point apparatus. UV–vis spectra were obtained with a UV – 3600 spectrophotometer.

The third-order NLO properties of the sandwich-type triple-decker complexes were characterized by Z-scan technique [33]. The experimental configuration has been described in details elsewhere [34]. In the present work, the light source was a mode-locked

Nd:YAG laser (PL2143B, EKSPILA) providing 20 ps laser pulses at 532 nm. The repetition rate was set to 10 Hz to avoid thermal effect. The sample solution was contained in a 2-mm quartz cuvette. The incident laser beam was focused by a 400 mm focal length lens into the quartz cuvette. The beam waist at the focal plane was $\sim 27 \mu\text{m}$, giving a Raleigh length of ~ 3 mm. The relation between the normalized transmittance $T(z)$ and z position was obtained by moving the quartz cuvette along the axis of the incident beam (z -direction) with respect to the focal point. The incident and transmitted energies were detected simultaneously by an energy meter (Laser Probe Corporation, Rj-7620). The experiments were performed with sample dissolved in neat CH_2Cl_2 with concentrations of 3×10^{-4} M. The Z-scan system was calibrated using the benchmark Kerr liquid CS_2 .

2.3. Preparation of the sandwich-type triple-decker complexes

The half-sandwich complex $[\text{Er}(\text{Pc})(\text{acac})]$ (46.45 mg, 0.06 mmol) and chiral Schiff base ligand H_2L (14.68 mg, 0.03 mmol) were mixed in 15 mL $\text{CHCl}_3/\text{CH}_3\text{OH}$ ($v/v = 2:1$). The resulted mixture was stirred for about 2 h at room temperature, sealed in 25 mL Teflon-lined stainless steel autoclave, and heated at 80°C for 24 h. Blue block-shaped crystals were collected by filtration after slow evaporation of the resulting solution for several days. The synthesized crystals are well soluble in common organic solvents and air stable in both solution and solid state. M. p. $> 300^\circ\text{C}$. Anal. Calcd for $\text{C}_{92}\text{H}_{52}\text{Cl}_2\text{Er}_2\text{N}_{18}\text{O}_3$ (%): C, 59.31; H, 2.81; N, 13.53. Found: C, 59.60; H, 3.13; N, 13.77. IR (KBr, cm^{-1}): 3394(m), 2969(s), 1613(m), 1480(m), 1404(m), 1327(m), 1161(s), 1065(m), 883(s), 824(s), 731(m), 636(s). UV–vis (CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$): 340, 618, 673, 684.

3. Results and discussion

3.1. UV–vis absorption spectra

The UV–vis absorption spectrum of sandwich-type erbium triple-decker complexes in CH_2Cl_2 is illustrated in Fig. 2. It is found that the spectrum of the sandwich-type complexes displays typical features of the monomeric metal phthalocyanine with a strong Q band at around 670–685 nm and a medium Soret band at about 341 nm. This result indicates that the two Pc rings in the triple-decker complexes show an almost independent behavior [35]. The erbium ion was found to have little effect on the absorption spectra expect for a small split component of the Q-band. The absence of new absorption band indicates the weak intra-

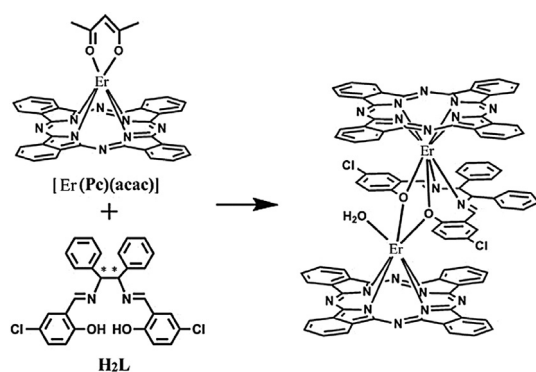


Fig. 1. Synthetic procedure of sandwich-type erbium triple-decker complexes with mixed phthalocyanine and Schiff-base ligands.

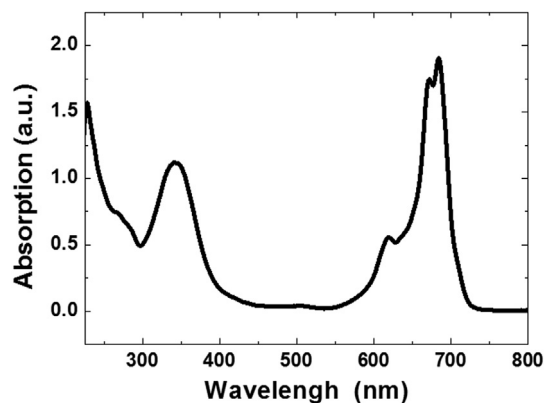


Fig. 2. UV–Vis absorption spectra of the sandwich-type erbium triple-decker complexes in CH_2Cl_2 at a concentration of 1×10^{-5} M.

Download English Version:

<https://daneshyari.com/en/article/175844>

Download Persian Version:

<https://daneshyari.com/article/175844>

[Daneshyari.com](https://daneshyari.com)