



# The nonlinear absorption in new lanthanide double decker pyridine-based phthalocyanines in solution and thin films



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## ARTICLE INFO

### Article history:

Received 5 March 2015

Received in revised form 18 April 2015

Accepted 5 May 2015

Available online 3 June 2015

### Keywords:

Optical behavior

Susceptibility

Hyperpolarization

Threshold

Nonlinear

Transmission

## ABSTRACT

The optical behavior of bis-{2(3), 9(10), 16(17), 23(24)-(tetrapyrroline-4-yloxy phthalocyaninato)} lanthanum (III) (**2**) and its ytterbium (**3**) counterpart in dimethyl sulfoxide are presented and compared to bis-{1(4), 8(11), 15(18), 22(25)-(tetrapyrroline-4-yloxy phthalocyaninato)} ytterbium (III) (**4**). We report on the third-order susceptibility, second-order hyperpolarizability and the limiting threshold values. The nonlinear optical limiting threshold values of complexes **2**, **3** and **4** showed improvement in the solid state (thin films), with complex **4** giving the best value at  $0.033 \text{ J cm}^{-2}$ .

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## 1. Introduction

Bis(phthalocyaninato) lanthanide ( $\text{LnPc}_2$ ) complexes are interesting due to their unique physical, spectroscopic and electrochemical properties [1].  $\text{LnPc}_2$  complexes have applications in many areas such as in nonlinear optics (NLO) [2–4], effect transistors, molecular magnets, molecular-based multibit information storage materials, receptors for metal ions and saccharides, and molecular solar cells [5–11].  $\text{LnPc}_2$  complexes exhibit high reverse saturable absorption (RSA) [12,13] due to extensive  $\pi$ -electron system caused by  $\pi$ - $\pi$  interaction of two Pc macrocyclic rings coordinated to a lanthanide ion. However, the NLO studies of  $\text{LnPc}_2$  complexes are still limited [2–4,14,15]. We have recently reported on the NLO behavior of bis-{1(4), 8(11), 15(18), 22(25)-(tetrapyrroline-4-yloxy phthalocyaninato)} ytterbium (III) (complex **4** in Scheme 1) which is substituted with pyridin-4-yloxy groups at the non-peripheral positions [16]. Substitution at non-peripheral positions is expected to reduce aggregation and improve photophysical parameters. Liu et al. [17] examined indium phthalocyanine, both in solution and in a polymer film, and observed a significant increase in optical limiting ability along with observations of phthalocyanine aggregation in the polymer film. In this work we compare the NLO behavior of non-peripherally substituted complex **4**, with that of the

peripherally substituted bis-{2(3), 9(10), 16(17), 23(24)-(tetrapyrroline-4-yloxy phthalocyaninato)} ytterbium (III) (complex **3** in Scheme 1). The NLO behaviors of **3** and **4** are compared to that of La derivative (bis-{2(3), 9(10), 16(17), 23(24)-(tetrapyrroline-4-yloxy phthalocyaninato)} lanthanum (III) (complex **2** in Scheme 1). The latter was highly aggregated in solution, but showed reasonable NLO behavior. The bulky pyridine substituents are expected to reduce aggregation, but this is not always the case as will be shown in this work.

This work presents the nonlinear optical properties of complexes **2**, **3** and **4** in solution and when embedded in poly (methyl methacrylate) (PMMA).

## 2. Experimental

### 2.1. Materials

1-Pentanol, lutetium (III) chloride and ytterbium (III) chloride hexahydrate were purchased from Sigma–Aldrich. Dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) and poly (methyl methacrylate) (PMMA) were purchased from Merck. Tetrahydrofuran (THF) was purchased from MINEMA. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was purchased from Fluka. The synthesis of 4-(pyridin-4-yloxy)-phthalonitrile (**1**) was according to literature methods [18].

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