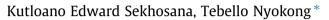
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# The nonlinear absorption in new lanthanide double decker pyridinebased phthalocyanines in solution and thin films



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# ABSTRACT

The optical behavior of bis-{2(3), 9(10), 16(17), 23(249) tetrapyridin-4-yloxy phthalocyaninato)} lanthanum (III) (2) and its ytterbium (3) counterpart in a methyl sulfoxide are presented and compared to bis-{1(4), 8(11), 15(18), 22(25)-(tetrapyridin-4-viewy 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 or complexes 2, 3 and 4 showed improvement in the solid state (thin films), with complex **4** giving **best** value at 0.033 J cm<sup>-2</sup>.

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### 1. Introduction

Bis(phthalocyaninato) lanthanide (LnPc<sub>2</sub>) complexes are interesting due to their unique physical, spectromodel and electrochemical properties [1]. LnPc<sub>2</sub> complexes have applications in many areas such as in nonlinear optics (NO) [2-4], effect transistors, molecular magnets, molecular-based multibit information storage materials, receptors for mean ions and saccharides, and molecular solar cells [5–11]. LnPc<sub>2</sub> 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 LnPc<sub>2</sub> complexes are still limited [2-4,14,15]. We have recently reported of bis-{1(4), on the NLO behavior 8(11), 15(18), 22(25)-(tetrapyridin-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

THE FULTERT, VISIT peripherally substituted bis-{2(3), 9(10), 16(17), 23(24)-(tetrapyridin-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)-(tetrapyridin-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-Diazabi cyclo[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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