



# Nanosecond nonlinear optical limiting properties of new trinuclear lanthanide phthalocyanines in solution and as thin films



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## ABSTRACT

2,4,6-Tris[3-thio-9,10,16,17,23,24-hexa(4-tertbutylphenoxy) phthalocyaninato ytterbium (III) chloride]-s-triazin (**3**) and its lutetium counterpart (**4**) were synthesized. The nonlinear optical behavior of **3** and **4** were characterized in solution and when embedded in polymer as thin films. Thin films of complexes **3** and **4** in poly(bisphenol A carbonate) showed improved nonlinear optical properties when compared to solution. Complex **3** showed a lower threshold for optical limiting intensity ( $I_{lim}$ ) than complex **4**, and for phthalocyanines in general.  $I_{lim}$  values were even lower in films compared to solutions.

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## 1. Introduction

The current and potential applications of phthalocyanines (Pcs) are as a result of their overall stability and exceptional electronic properties [1]. These applications include as molecular conductors and semiconductors [2], non-linear optical (NLO) materials [3], dyes and pigments [4], light-emitting diodes [5], photoconductors in laser printers [6], photosensitizers in photodynamic therapy [7], electrochromic materials [8,9] and components of organic photovoltaic cells [10]. Lanthanide phthalocyanines in particular have been found to exhibit NLO behavior [11,12]. It has been suggested that lanthanide bisphthalocyanines show improved optical nonlinearities due to their expanded  $\pi$  electron system and the presence of the heavy lanthanide central metal [13–16] which enhances the rate of intersystem crossing (ISC) to the triplet state. Hence in this work we study the NLO and photophysical behavior of trimeric tri-lanthanide phthalocyanines. Previous reports have shown the importance of asymmetry on the photophysical, photochemical and optical limiting (OL) properties of phthalocyanines [17–19]. This work explores photophysical and NLO behavior of new trimeric tri-lanthanide phthalocyanines, which are expected to show improved NLO properties due to their low symmetry.

S-triazine oxygen (or nitrogen, ethynyl and ethenyl) bridged trinuclear phthalocyanines have been reported for Zn, Co, Lu and Cu as central metals and containing long chain ring substituents

[20–23]. S-triazine sulfur bridged lutetium phthalocyanine containing long chain substituents has recently been reported [24]. This work reports for the first time on a S-triazine sulfur bridged Yb phthalocyanine (Scheme 1) and also reports on the Lu counterpart, both substituted with tert-butyl substituents for improved solubility. The NLO behavior of S-triazine phthalocyanines has not received much attention [23,25]. The asymmetric nature of these complexes is expected to enhance NLO behavior.

Practical optical limiting devices require the casting of the phthalocyanines in the solid state. Poly (methyl methacrylate) (PMMA) has been the preferred polymer for embedding Pcs for NLO [26,27]. In this work poly(bisphenol A carbonate) (PBC) is employed. PBC has been used as a material for making safety visors in the past and has great affinity for modification [28], hence it is employed in this work instead of PMMA.

## 2. Experimental

### 2.1. Materials

1-Pentanol, lutetium (III) chloride and ytterbium (III) chloride hexahydrate were purchased from Sigma–Aldrich, dichloromethane (DCM), dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) were purchased from Merck. Tetrahydrofuran (THF) was purchased from MINEMA. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and poly(bisphenol A carbonate) were purchased from Fluka. 3-Nitrophthalonitrile [29] and 4,5-bis-(4-tertbutyl phenoxy)-phthalonitrile (**1**) [30] were synthesized according to literature methods.

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