



Research paper

The optical limiting of blue and green ytterbium double-decker phthalocyanines in solution and in poly(acrylic acid) as thin films



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ABSTRACT

Bis{1(4), 8(11), 15(18), 22(25)-tetra(4-*tert*-butylphenoxy)phthalocyaninato} ytterbium(III) (**2a**) (the green form) was synthesized and reduced to form **2b** (the blue form). Nonlinear optical parameters for complex **2** in green and blue forms were determined using the Z-scan technique and the values of third-order imaginary susceptibility ($\text{Im}[\chi^{(3)}]$) and second-order hyperpolarizability (γ) of the order of 10^{-9} (for **2b**) and 10^{-27} esu, respectively, were obtained in solution. In poly(acrylic acid) as a thin film, complex **2a** showed extremely high $\text{Im}[\chi^{(3)}]$ and γ values of the order 10^{-8} and 10^{-25} respectively. A low optical limiting threshold value of 0.075 J cm^{-2} was obtained for the thin film **2a**.

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1. Introduction

Double- or triple-decker phthalocyanines exhibiting characteristic optical and electronic properties can be employed in fields that include as electronic materials [1], sensors [2], electronic displays [3,4], organic field-effect transistors [5,6], single molecule magnets [8–11], self-assembly [12] and nonlinear optics [13]. Lanthanide bisphthalocyanine (LnPc_2) complexes exist as green (neutral) or blue (reduced) forms. Neutral LnPc_2 complexes exist as stable radicals with an unpaired electron on an orbital delocalized over two phthalocyanine (Pc) rings [14]. This is usually referred to as the “green” form, $\text{Pc}^1-\text{Ln}^{3+}\text{Pc}^{2-}$. One-electron reduction leads to the formation of the so called blue form, $[\text{Pc}^{2-}\text{Ln}^{3+}\text{Pc}^{2-}]^-$. There has been extensive studies on the extent of hole delocalization in green (neutral) forms in order to understand the nature and extent of interactions in these molecules [15–18]. LnPc_2 complexes show improved optical nonlinearities due to their expanded electron π system and the presence of the heavy lanthanide central metal [19–21] which enhances the rate of intersystem crossing (ISC) to the triplet state. We have recently reported on the improved nonlinear optical (NLO) behavior of the blue (reduced) form of bis{2,3,9,10,16,17,23,24-octa(4-*tert*-butylphenoxy)phthalocyaninato}lutetium(III) complex compared to the green form [22]. While the reported complex contains the diamagnetic lutetium(III) central metal cation, the complex studied in the current work contains Yb(III) ion which is paramagnetic. This means that the reduced

form of a Pc ring will still contain a paramagnetic central metal which may affect the NLO behavior. Thus, we continue our studies on the effect of reduction on NLO of LnPc_2 , this time using a paramagnetic central metal. The NLO properties of Pcs have been shown to be based on reverse saturable absorption (RSA) mechanisms [23]. RSA depends on the differences in the excited state absorption (ESA) of the singlet and triplet states, where ESA in the triplet state has to be larger. Paramagnetism shortens triplet state lifetimes hence reducing ESA. This work explores the effect of the paramagnetic central metal on the NLO behavior of a LnPc_2 derivative.

This manuscript presents the synthesis of bis{1(4), 8(11), 15(18), 22(25)-tetra(4-*tert*-butylphenoxy)phthalocyaninato} ytterbium(III) (**2a**) (Scheme 1) and its NLO properties in comparison with those of its blue form. Complex **2b** was obtained by reduction of **2a** using hydrazine. Only the ring is expected to be reduced from $\text{Pc}^1-\text{Ln}^{3+}\text{Pc}^{2-}$ (for **2a**) to $[\text{Pc}^{2-}\text{Ln}^{3+}\text{Pc}^{2-}]^-$ (for **2b**). The central ytterbium will remain paramagnetic. The tetrasubstituted derivatives are employed in this work since they show improved solubility compared to the symmetrically octasubstituted derivatives (employed in the previous work [22]) due to the presence of four positional isomers in the former [24]. For practical purposes in NLO applications, Pc complexes are embedded in thin films of polymers such as poly(methyl methacrylate) (PMMA) [25] or poly(bisphenol A carbonate) (PBC) [26] resulting in improved optical limiting behavior compared to when in solution. Recently, poly(acrylic acid) (PAA) [27] was shown to result in improved optical limiting behavior when compared to PMMA, hence the employment of the former in this work.

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