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Synthesis and optical limiting properties of new lanthanide bis- and tris-phthalocyanines

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ABSTRACT

This manuscript reports on syntheses of new multi-decker phthalocyanines, namely: *bis-{2,3,9,10,16,10,16,17,23,24-octa(4-tertbutylphenoxy) phthalocyaninato} cerium(III)* (**2**), *tris-{2,3,9,10,16,10,16,17,23,24-octa(4-tertbutylphenoxy) phthalocyaninato} dicerium(III)* (**4**) and *bis-{2,3,9,10,16,10,16,17,23,24-octa(4-tertbutylphenoxy) phthalocyaninato} gadolinium(III)* (**5**). Complex **4** which is a tris phthalocyanine showed better nonlinear optical behavior in solution than **2** which is a bis phthalocyanine, both containing the same central metal, Ce. All the three molecules possess good optical limiting properties judged by the limiting threshold values which ranged from 0.04 to 0.09 J cm^{-2} with complex **5** embedded in thin films showing the lowest value of 0.04 J cm^{-2}. Furthermore, nonlinear optical processes responsible for reverse saturable absorption data are investigated.

1. Introduction

Phthalocyanines (Pcs) are well known nonlinear optical (NLO) materials [1,2]. Pcs exhibiting one photon (1PA) [3,4], two photon (2PA) [5–8] and three photon (3PA) [9–11] absorptions have been reported. Reverse saturable absorption (RSA) mechanisms are the main processes on which the NLO properties of Pcs are based [12–14]. Sandwich-Pc complexes containing La [15], Sm and Gd [16], Sm and Cd [17,18] and Eu [19] have been investigated for their third-order NLO properties with potential practical applications in optical limiting devices. It has been suggested that lanthanide bis phthalocyanine ($LnPc_2$) complexes can present improved optical nonlinearities owing to their large π electron system and the presence of the heavy lanthanide ions which encourages inter-system crossing to the triplet state [20,21].

In this manuscript, we present photophysics and nonlinear optical data of newly designed multi-decker complexes, namely: bis-{2,3,9,10,16,10,16,17,23,24-octa(4-tertbutylphenoxy) phthalocyaninato} cerium(III) (**2**), tris-{2,3,9,10,16,10,16,17,23,24-octa(4-tertbutylphenoxy) phthalocyaninato} dicerium(III), (**4**) and bis-{2,3,9,10,16,10,16,17,23,24-octa(4-tertbutylphenoxy) phthalocyaninato} gadolinium(III) (**5**) in dichloromethane as well as when embedded in poly acrylic acid (PAA) as thin films. Apart from our recent work [22], the NLO behavior of Ln_2Pc_3 (Ln = lanthanide) complexes has been un-explored. Unlike the neutral double decker ($Pc^{-1}LnPc^{-2}$) counterparts which are paramagnetic, the positive charge on the two Ln (III) in Ln_2Pc_3 balances the negative charge in the three Pc ligands, hence Ln_2Pc_3 complexes are neutral. We have recently shown that Nd_2Pc_3 complex shows good NLO behavior [22]. Also even though there have been some reports on the NLO behavior of a Gd phthalocyanine derivatives [23], studies for the Ce derivatives are nonexistent, hence are subject of this work. Also this work presents the first study of Ln_2Pc_3 when embedded in thin films. Recently [24], poly acrylic acid (PAA) was shown to result in improved optical limiting behavior when compared to other polymers such as poly (methyl methacrylate), hence the former is employed in this work.

2. Experimental

2.1. Materials

Dimethyl sulfoxide (DMSO) was purchased from SAARCHEM. Cerium (III) chloride, gadolinium (III) chloride, deuterated chloroform ($CDCl_3$-d_1), 1-pentanol and poly acrylic acid (PAA) were purchased from Sigma-Aldrich. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was purchased from Fluka. The synthesis of 4,5-bis-{4-*tert*-butylphenoxy}-phthalonitrile (**1**), which was used as a precursor

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