



Electrochemical and non-linear optical behavior of a new neodymium double-decker phthalocyanine



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ABSTRACT

This manuscript presents the non-linear optical parameters obtained specifically at 532 nm using the new bis-{1(4),8(11),15(18),22(25)-(tetrapyrroline-3-yl)oxy} phthalocyaninato} neodymium(III) complex in green (**2a**) and blue (**2b**) forms as well thin films prepared from the green form in the presence of poly(bisphenol A) carbonate. It is interesting to note a huge improvement of the reduction efficiency of transmission of the green form by 34% in poly(bisphenol A) carbonate as a thin film. The same observation is noted for the blue form at 25%. The same trend was observed for the excited state cross sections in which the blue form of the bis-{1(4),8(11),15(18),22(25)-(tetrapyrroline-3-yl)oxy} phthalocyaninato} neodymium(III) complex as well as the thin film exhibited values that were about three and six times greater than those of the green form, respectively. The electrochemical properties were also studied, with complex **2a** exhibiting six redox processes in DCM, by employing tetrabutylammonium tetrafluoroborate as an electrolyte.

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1. Introduction

The first double-decker lanthanide phthalocyanines were currently reported by the two independent Russian research groups of Plyushev and Kirin in the 1960s [1,2]. Since then, lanthanide diphthalocyanines (LnPc_2) have attracted huge research interest [3–7], particularly lutetium derivatives [8,9] which exhibit electrochromic [9,10] and non-linear optical (NLO) properties [11–17]. Other interesting properties of LnPc_2 include tunable spectroscopic, electronic and redox characteristics [18], allowing them to be used as ambipolar organic field-effect transistors [19], self-assembled nanostructures [20,21], single molecule magnets [22,23], supramolecular spin valves [24] and in electrochemistry [25]. The presence of the extensive π -electron conjugated system in phthalocyanines (Pcs) enhances optical non-linearities [13]. The improved NLO behavior of LnPc_2 complexes is due to the presence of two Pc macrocyclic rings coordinated to a lanthanide ion. The structural flexibility of Pcs, which allows for changes in the central metal as well as the number and location of peripheral (and non-peripheral) substituents, has opened a way to design new materials with desirable NLO properties [26]. Materials exhibiting strong NLO properties result in an optical limiting (OL) effect which is characterized by a decrease in optical transmittance under strong

illumination [13]. Non-linear absorption (NLA), non-linear refraction, non-linear scattering [26,27] and reverse saturable absorption (RSA) [28,29] are some of the known mechanisms by which the OL effect takes place in Pc complexes. Neutral LnPc_2 complexes exist as stable radicals with an unpaired electron on an orbital delocalized over the two phthalocyanine (Pc) rings. This is usually referred to as the “green” form, $\text{Pc}^1\text{-Ln}^{3+}\text{Pc}^{2-}$, represented as **2a** in this work. One-electron reduction leads to the formation of the so called “blue” form, $[\text{Pc}^{2-}\text{-Ln}^{3+}\text{Pc}^{2-}]^-$, represented as **2b**. Our previous studies indicated that reduced LnPc_2 complexes exhibit stronger NLO properties than the neutral derivatives [30,31]. This manuscript discusses the synthesis of a new neodymium diphthalocyanine complex and explores its electrochemical properties and NLO behavior in solution and when grafted on poly(bisphenol A) carbonate as a thin film. For practical purposes in NLO applications, Pc complexes are embedded in thin films of polymers with improved NLO behaviour [32], hence the Pc is embedded in thin films in this work. The size of the lanthanide ion is known to affect the interaction of the two Pc macrocyclic rings, hence there is more interaction across the lanthanide series from left to right [18]. While the electrochemical properties of LnPc_2 compounds have been investigated from the viewpoint of electrochromic displays, electrochemical properties and other applications [33–36], neodymium diphthalocyanines containing pyridine substituents have not been explored. For this reason, we explore the effects of the flexibility and coordinating nature of the pyridine ring in the α -position on the

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