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Photophysics and NLO properties of Ga(III) and In(III) phthalocyaninates bearing diethyleneglycol chains

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Dedicated to Professor Kazuchiko Ohta on the occassion of his retirement

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ABSTRACT: This work reports on synthesis and characterizations of Ga(III) and In(III) complexes, formed by 2,3-bis[2′-(2″-hydroxyethoxy)ethoxy]-9,10,16,17,23,24-hexa-*n*-butoxy phthalocyanine (**1H$_2$**) coordinating acetatoindium(III) (**1InOAc**) and hydroxogallium(III) (**1GaOH**). Photophysical properties of hydroxogallium(III) phthalocyaninate **1GaOH** and acetatoindium(III) phthalocyaninate **1InOAc** were studied by UV-vis, fluorescence spectroscopy and time-resolved methods. The nonlinear absorption of the complexes was studied using the Z-scan technique at 532 nm and 10 ns pulse in DMSO and in thin films formed by composite with poly(bisphenol A carbonate) — PBC. The magnitude of absorption coefficients and other nonlinear optical parameters estimated in this work showed that complex **1InOAc** exhibited the strongest nonlinear optical behavior in comparison with **1GaOH** in solution and a reverse tendency when embedded in PBC thin films. DFT calculations were used to rationalize these results.

KEYWORDS: phthalocyanine, indium, gallium, optical limiting, thin films, hyperpolirizabilty.

INTRODUCTION

Optical limiting (OL) materials have become of interest to research because of the need to protect sensitive optical devices, such as human eyes, against high intensity light sources such as lasers [1]. When OL materials are exposed to very intense light, they have the ability to limit the output energy of the emerging beam. The optical limiting process is a result of a highly populated excited triplet state with respect to the ground state. This phenomenon is known as reverse saturable absorption (RSA), as opposed to saturable absorption (SA) that is seen in most molecules [2–4].

Phthalocyanines (Pcs) have shown potential applications as optical limiters, optical switches and optical signal-processing devices due to their highly delocalized π-electron systems [5–8]. Advantages of Pcs include architectural flexibility, ease of processing into thin films/optical devices, ultrafast response time, high triplet state yields, and stability [9–13]. Metallophthalocyanines (MPcs) having heavy central metals such as indium exhibit better optical limiting due to the heavy metal effect, which enhances the intersystem crossing through spin orbit coupling, leading to a higher triplet state population [14–16]. Asymmetric MPcs are desired due to the presence of permanent dipole moment which encourages nonlinear optical (NLO) response [17–20]. Incorporation of Pcs into nanomaterials is also known to have profound effect on their NLO properties [21, 22]. For practical purposes in NLO applications, Pc complexes can be embedded in thin films of polymers

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