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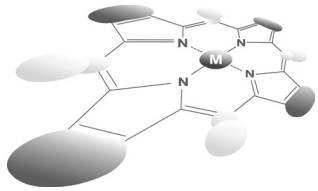

Improvement of nonlinear optical properties of phthalocyanine bearing diethyleneglycole chains: Influence of symmetry lowering *vs.* heavy atom effect

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Dedicated to Professor Tomás Torres on the occasion of his 65th birthday

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ABSTRACT: This paper reports the successful synthesis of the low symmetry phthalocyanines: metal-free 2,3-bis[2′-(2″-hydroxyethoxy)ethoxy]-9,10,16,17,23,24-hexa-*n*-butoxyphthalocyanine **1H$_2$** and its zinc complex **1Zn** along with their nonlinear optical (NLO) behavior in solution and in thin films. ^{1}H NMR investigations evidenced of higher dissymmetry of electronic density in **1H$_2$** in comparison with **1Zn.** This dissymmetry is responsible for unusually higher values of Im[$\chi^{(3)}$]/α, β_{eff}, and γ for **1H$_2$** in contrast to **1Zn**, where the notable effect of heavy-metal enhancement of ISC was expected. Both compounds showed Im[$\chi^{(3)}$]/α values of the order of 10^{-11} in chloroform which are higher in comparison to the symmetrical octabutoxyphthalocyanine $H_2[(BuO)_8Pc]$. NLO properties of **1H$_2$** were improved *via* its incorporation into polycarbonate polymeric matrix together with CdSe@CdS-TOPO quantum dots. In such composite the value of Im[$\chi^{(3)}$]/α was almost three times higher in comparison with **1H$_2$** solution in chloroform. The obtained composites are expected to be perspective components of optical materials, capable of protection against strong light irradiation.

KEYWORDS: low symmetry phthalocyanines, nonlinear optics, hyperpolirizabilty, third order optical susceptibility, quantum dots.

INTRODUCTION

Since the discovery of phthalocyanines, the main efforts are geared towards the synthetic strategies in order to increase the range of possible molecules [1–3]. Phthalocyanines are currently the most promising class of complexes with applications including as sensors [4–7], in nonlinear optics (NLO) [8, 9], in dye sensitized solar cells [10–12], semiconductor materials [13], among others. Phthalocyanines (Pcs) are one of the most widely investigated molecules for optical limiting (OL) applications [8, 9, 14–20]. One of the reasons Pcs have attracted so much attention is the versatility of their synthetic methods to allow for structural variation in order to achieve effective optical limiting. Optical limiting materials are of interest due to the need to protect sensitive optical devices, especially human eyes from high intensity light sources such as lasers. When exposed to very intense light, OL materials limit the output energy of the emerging beam.

Previous reports have shown the influence of asymmetry on the photophysical, photochemical and optical limiting (OL) properties of phthalocyanines [21, 22]. Thus, this work

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