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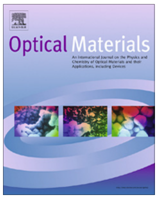

Nonlinear optical behavior of alkyne terminated phthalocyanines in solution and when embedded in polysulfone as thin films: Effects of aggregation

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ABSTRACT

We report here for the first time, on the comparative studies of the photophysical and optical limiting behavior of our two novel phthalocyanines namely 2(3), 9(10), 16(17), 23(24)-tetrakis-(4-(5-methylhex-1-yn-3-yloxy)) phthalocyanines **2**, and 2(3), 9(10), 16(17), 23(24)-tetrakis-(4-(5-methylhex-1-yn-3-yloxy)) phthalocyaninato zinc (II) (**3**) in solution and thin films. Nonlinear optical (NLO) properties of the samples in solution and contained in polysulfone (PSU) thin films were evaluated using Z-scan technique at 532 nm and 10 ns pulsed duration. Effects of aggregation and disaggregation on the NLO performance of metal-free phthalocyanine are reported in detail. Our findings showed that the prepared Pcs show larger nonlinear absorption coefficient and lower limiting thresholds when embedded in polysulfone films compared to in solutions. The values of nonlinear susceptibility and hyperpolarizability recorded for **3-PSU** in this work are respectively, $\sim 2.09 \times 10^{-8}$ esu and $\sim 1.02 \times 10^{-26}$ esu. These values are among the largest values reported for phthalocyanines and other macrocycles doped on polymer matrices.

1. Introduction

Metallophthalocyanines (MPcs) and their derivatives are promising and extensively studied macrocycle for photo-driven processes, especially in the development of nonlinear optical devices [1–3], due to their long wavelength absorption, photoelectric property, chemical and thermal stability [4].

Optical limiting devices are used to protect light-sensitive materials such as sensors, human eyes, and optical components from laser radiation, by effectively limiting the energy output of an incident light [5,6]. Phthalocyanines (Pcs) are good optical limiters as a result of their ease of processability to optical components [7], low dielectric constant, large third-order nonlinear susceptibility and polarizability [1,2]. Previous studies on phthalocyanines have shown that improving the solubility of MPcs in common organic solvents by placing substituents on the Pc ring [8,9], and variation of central metals of Pcs [10,11] can lead to enhanced photophysical and nonlinear optical (NLO) properties of phthalocyanines.

Insertion of heavy metal atoms in the Pcs rings helps to populate the excited states of the molecule via intersystem crossing (ISC), such that a molecule already in an electronically excited state absorbs more photons to possess large absorption cross-section ratio ($k > 1$). This phenomenon is referred to as reverse saturable absorption (RSA), which is the dominant mechanism responsible for NLA in metallophthalocyanines [3].

In the present paper, we report on the synthesis, photophysical and nonlinear optical characterizations of novel zinc and metal-free phthalocyanines functionalized with branched alkyne substituents at the peripheral positions (complexes **2** and **3**, Scheme 1). It has been reported that groups containing triple bonds enhance the intersystem crossing rate [12], hence we employed these groups in this work. Aggregation of phthalocyanines in solution is known to adversely affect photophysical parameters [13]. This is because excited-state lifetimes of phthalocyanine aggregates are short and there is enhancement of internal conversion rates [13]. However it has been reported that aggregation of Pcs in thin films improves NLO behavior of phthalocyanines [14]. We show in this work that even though aggregation in solution is known to negatively affect photophysical parameters, it improves NLO behavior of phthalocyanines. Also as stated above, heavy metals are known to enhance intersystem crossing to the triplet state, which is expected to improve the reverse saturable absorption of Pcs. However, we show in this work that a metal free Pc shows good NLO behavior. Thus, this works shows that the factors which

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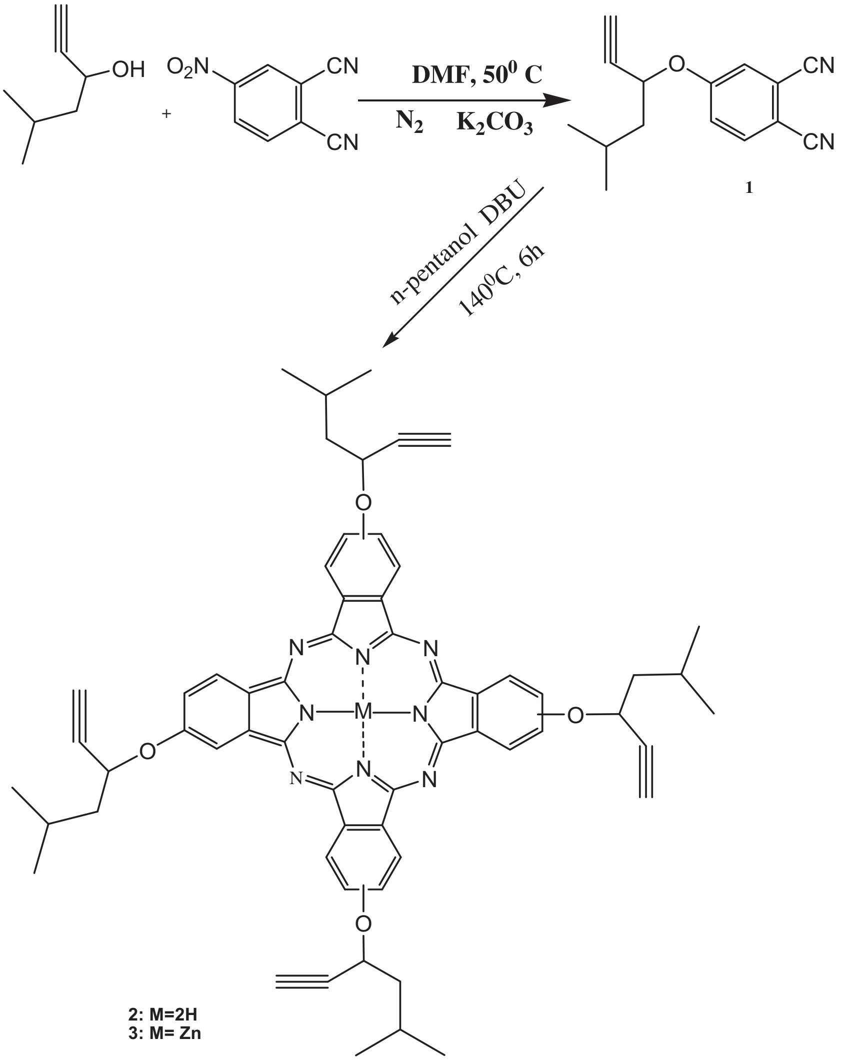

Scheme 1. Synthetic route for 2(3),9(10),16(17),23(24)-tetrakis-(4-(5-methylhex-1-yn-3-yloxy))phthalocyanine (**2**), and 2(3), 9(10), 16(17), 23(24)-tetrakis-(4-(5-methylhex-1-yn-3-yloxy))phthalocyaninato zinc (II) (**3**).

decrease triplet state parameters such as aggregation and the lack of the heavy central metal, do not adversely affect NLO parameters.

The optical limiting behavior of Pcs is enhanced on solid supports [2,15,16], than in solution [2,17]. Poly (methyl methacrylate) (PMMA) has been the preferred polymer for embedding Pcs for NLO [18,19], with poly(bisphenol A carbonate) (PBC) also having been employed [15,20]. Lor et al. [21], reported that polysulfone (PSU) was preferred over PMMA as host material due to its good optical clarity, easy thin film formation, and relatively high glass transition temperature (140–190 °C) [21]. We report here on the formation of thin films complexes **2** and **3** when embedded in polysulfone. Our aim, therefore, is to investigate the effect of aggregation on photophysical and NLO properties of complexes **2** and **3** in solution and when embedded in PSU thin films.

2. Experimental

2.1. Materials

5-Methylhex-1-yn-3-ol, 4-nitrophthalonitrile, polysulfone (Mw ~35,000 g/mol) Zn (II) acetate, *n*-pentanol, and anhydrous potassium carbonate were obtained from Sigma Aldrich. Deuterated chloroform ($CDCl_3$), tetrahydrofuran (THF), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), dimethyl formamide (DMF), dichloromethane (DCM), methanol and dimethyl sulphoxide (DMSO) were purchased from Merck. All solvents were of reagent grade and were freshly distilled before use. The purification processes was carried out on silica gel 60 (0.063–0.200 mm) for column chromatography.

2.2. Equipment and methods

Infrared spectra were measured on a Perkin-Elmer Spectrum One FTIR spectrophotometer equipped with an ATR sampling accessory. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE II 400 MHz NMR spectrometers using tetramethylsilane (TMS) as an internal reference. Elemental analyses were done using a Vario-Elementar Microcube ELIII, while mass spectra data were collected on a Bruker AutoFLEX III Smart-beam TOF/TOF mass spectrometer using α-cyano-4-hydrocinnamic acid as the matrix in the positive ion mode. Ground state electronic absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer.

Fluorescence excitation and emission spectra were measured on a Varian Eclipse® spectrofluorimeter using a 360–1100 nm filter. Fluorescence lifetimes were measured using a time correlated single photon counting setup (TCSPC) (FluoTime 300, Picoquant® GmbH) with a diode laser (LDH-P-670, Picoquant® GmbH,