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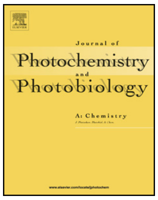

Nonlinear optical response of a low symmetry phthalocyanine in the presence of gold nanoparticles when in solution or embedded in poly acrylic acid polymer thin films

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ABSTRACT

In this article, we explored the photophysical and nonlinear optical (NLO) characterizations of low symmetry phthalocyanine (ZnPc-NH_2) covalently linked to MPA-capped AuNPs (ZnPc-NH_2-AuNPs) and poly acrylic acid (ZnPc-NH_2-PAA). Nonlinear optical (NLO) properties of the samples were evaluated using Z-scan technique at 532 nm and 10 ns pulsed duration. We observed enhanced photophysical and nonlinear optical behaviour for the ZnPc-NH_2 in presence of AuNPs. By virtue of the magnitude of absorption coefficients and other NLO optical parameters estimated in this work, ZnPc-NH_2-AuNPs was found to exhibit improved nonlinear optical response compared to the ZnPc-NH_2 and ZnPc-NH_2-PAA. Both ZnPc-NH_2-AuNPs and ZnPc-NH_2 doped in PAA possess strong nonlinear absorption coefficients and very low limiting thresholds than when measured in solution.

1. Introduction

Metallophthalocyanines (MPcs) and their derivatives are extensively studied macrocycles as passive optical limiters due to their ease of proccessability into optical components [1], low dielectric constant, large third-order nonlinear susceptibility and polarizability [2,3]. In spite of the numerous advantages of MPcs over other macrocyles as optical limiters, there is still room for improvement on their optical limiting (OL) performance. Recently, research efforts have been intensified to further improve nonlinear optical (NLO) properties of MPcs by incorporating them into other potential optical limiters such as quantum dots [4,5], and polymeric materials [6,7]. However, NLO behaviour of MPc in presence of metallic nanoparticles such as gold nanoparticles (AuNPs) has not received enough attention.

Previous reports have shown that conjugation of AuNPs to MPcs resulted in enhanced triplet state parameters [8–12] due to increased intersystem crossing as a result of the heavy atom effect of the AuNPs. The triplet state parameters improve as the size of the AuNPs increase [12]. Improved triplet–triplet absorption efficiency results in enhanced reverse saturable absorption (RSA), which is the predominant mechanism primarily responsible for observed nonlinearity in MPcs. Thus the increase in triplet state quantum yield in the presence of AuNPs is expected to enhance RSA. AuNPs have been reported to possess fascinating optical limiting properties which are size and shape dependent [13,14]. Several mechanisms such as free carrier absorption (FCA) [15,16], multiphoton absorption (mPA) [17], nonlinear scattering [18,19] or reverse saturable absorption [20], have been proposed as the dominant mechanisms responsible for the observed nonlinearity in AuNPs. Francois et al [18,19]. attributed nonlinear light scattering as the dominant mechanism responsible for the observed nonlinearity for AuNPs with core diameter >9; while free-carrier absorption mechanism has been reported for AuNPs with core size of ca. 3 nm [15,16].

In this work, we aim to further enhance the photophysical and NLO properties of phthalocyanines through covalent linking to AuNPs and poly acrylic acid. This is the first time that AuNPs are linked to MPcs complexes for NLO studies. The low symmetry phthalocyanine (ZnPc-NH_2, Scheme 1) is linked to AuNPs or poly acrylic acid (PAA) via an amide bond using the COOH groups of the AuNPs (or PAA) and the NH_2 group of ZnPc-NH_2. The conjugates are represented as ZnPc-NH_2-AuNPs and ZnPc-NH_2-PAA, respectively. The NLO properties of symmetrically substituted tetraamino-zinc phthalocyanine covalently linked to poly acrylic acid has been reported before [21]. This is the first time an asymmetrical Pc is linked to a polymer. Previous reports have shown the importance of asymmetry on the photophysical, photochemical and OL properties of phthalocyanines [22]. Thus, we expect ZnPc-NH_2-AuNPs and ZnPc-NH_2-PAA composites to exhibit enhanced photophysical and

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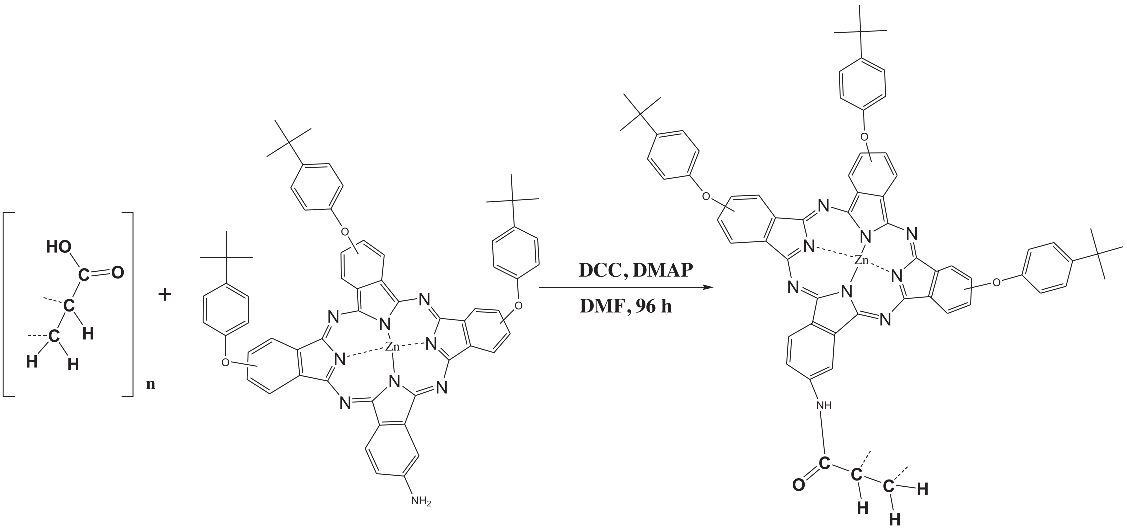

Scheme 1. Covalent linking between ZnPc-NH_2 and PAA.

NLO behaviour compared to symmetrically substituted Pcs. The *tert*-butyl substituents in ZnPc-NH_2 were chosen in order to enhance solubility. Zn central will enhance triplet state quantum yield due to the heavy atom effect and NH_2 substituent was chosen to allow for linking to carboxy substituents on MPA-AuNPs or PAA. Studies were also done where ZnPc-NH_2 or ZnPc-NH_2-AuNPs were also embedded into PAA as thin films (TF), without linking to PAA for the former, to form ZnPc-NH_2/PAA-TF or ZnPc-NH_2-AuNPs/PAA-TF. The NLO behaviour of ZnPc-NH_2 when linked to graphene oxide has been reported [23]. We show in this work that linking this complex to AuNPs improves the NLO behaviour considerably.

As stated above, FCA (due to AuNPs) and/or RSA (due to ZnPc-NH_2) are expected as the combined predominant mechanisms for NLO properties of ZnPc-NH_2-AuNPs [20] composite. Negligible contribution from mPA for NLO for MPc-quantum dots at 532 nm as a result of FCA has been reported [4]. The nonlinear absorption for ZnPc-NH_2-PAA composite can be either mPA, where there is simultaneous absorption of photons by already excited molecules, or reverse saturable absorption (RSA), where there is sequential absorption of photons.

Open-aperture Z-scan experiments [24], which measures the total transmittance through the sample as a function of intensity of incident laser, are used to determine the nonlinear optical behavior of the molecules.

2. Experimental

2.1. Materials

Poly acrylic acid (PAA), *N*,*N*'-dicyclohexylcarbodiimide (DCC) and mercaptopropionic acid (MPA) were purchased from Sigma–Aldrich; while 4-dimethylaminopyridine (DMAP) and ammonium molybdate were obtained from SAAR Chem. Tetrahydrofuran (THF), dimethylformamide (DMF) and dimethyl sulphoxide (DMSO) were purchased from Merck. *N*-hydroxysuccinimide (NHS) and *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride (EDC) were from Fluka. All solvents were of reagent grade and were freshly distilled before use. The synthesis of ZnPc-NH_2 has been reported [23].

2.2. Equipment and methods

Infra-red spectra were collected on a PerkinElmer Universal ATR Sampling accessory spectrum 100 FT-IR spectrometer. ^1H NMR spectra were obtained using a Bruker AVANCE 600 MHz NMR spectrometer in DMSO-d_6. 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 emission spectra were recorded on a Varian Eclipse spectrofluorimeter. Time Correlated Single Photon Counting (TCSPC) setup (FluoTime 200, Picoquant GmbH) was used for the fluorescence decay studies. The excitation source was a diode laser (LDH-P-670 driven by PDL 800-B, 670 nm, 20 MHz repetition rate, 44 ps pulse width, Picoquant GmbH).

Transmission electron microscope (TEM) images were obtained using a JEOL TEM 1210 transmission electron microscope at 100 kV accelerating voltage. TEM samples were prepared by placing a drop of conjugates or nanoparticle solution on the sample grid and allowing it to dry before measurements. X-ray powder diffraction patterns were recorded on a Bruker D8 Discover equipped with a LynxEye detector, using CuKα radiation (λ = 1.5405 Å, nickel filter). Data were collected in the range from $2\theta = 5^\circ$ to 100°, scanning at $1^\circ\ min^{-1}$ with a filter time-constant of 2.5 s per step and a slit width of 6.0 mm. Samples were placed on a zero background silicon wafer slide. The X-ray diffraction data were treated using Eva (evaluation curve fitting) software. Baseline correction was performed on each diffraction pattern.

All Z-scan analyses were performed using a frequency-doubled Nd:YAG laser (Quanta-Ray, 1.5 J/10 ns fwhm pulse duration) as the excitation source. The laser was operated in a near Gaussian transverse mode at 532 nm (second harmonic), with a pulse repetition rate of 10 Hz and energy range of 0.1 μJ–0.1 mJ, as limited by the energy detectors (Coherent J5-09). The low repetition rate of the laser prevents cumulative thermal nonlinearities. The beam was spatially filtered to remove the higher order modes and tightly focused with a 15 cm focal length lens. The Z-scan system size (l × w × h) used was 600 mm × 300 mm × 350 mm (excluding the computer, energy meter, translation stage driver and laser system). The liquid samples were placed in a cuvette (internal dimensions: 2 mm × 10 mm × 55 mm, 0.7 mL) and a path length of 2 mm (Starna 21-G-2). No damage of the film was detected between runs since the sample was moved or replaced.