



Enhanced optical limiting performance in phthalocyanine-quantum dot nanocomposites by free-carrier absorption mechanism



Kayode Sanusi, Samson Khene, Tebello Nyokong*

Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

ARTICLE INFO

Article history:

Received 15 April 2014

Received in revised form 13 July 2014

Accepted 21 July 2014

Available online 20 August 2014

Keywords:

Free-carrier absorption

Two photon absorption

Nonlinear optical absorption

Indium phthalocyanine

ABSTRACT

Enhanced nonlinear optical properties (in dimethyl sulphoxide) is observed for 2(3),9(10),16(17),23(24)-tetrakis-(4-aminophenoxy)phthalocyaninato indium(III) chloride (InPc) when covalently linked to CdSe/ZnS or CdSe quantum dots (QDs). The experimental nonlinear optical parameters were obtained from Z-Scan measurements. Contributions from two-photon absorption (2PA) due to the InPc, and free-carrier absorption (FCA) by QDs have been identified as the main factors responsible for the enhanced optical limiting. The effective nonlinear absorption coefficient for InPc-CdSe/ZnS was found to be 700.0 cm/GW. The FCA cross-sections for InPc-CdSe/ZnS and InPc-CdSe composites were found to be 1.52×10^{-19} and 6.00×10^{-20} cm² respectively. A much lower limiting threshold of 92 mJ cm⁻² was observed for InPc-CdSe/ZnS nanocomposite, hence, making it suitable for use as optical limiting material. Density Functional Theory (DFT) calculations on similar phthalocyanine-quantum dots system was modeled in order to explain the enhancement in the observed nonlinear optical properties of the Pc in the presence of the QDs. The experimentally determined nonlinear optical properties are well within the range of the DFT calculated properties.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

An ideal optical limiter is a device that exhibits a linear transmittance below a threshold, and clamps the output to a constant above it; thus providing protection to sensors and the eyes [1]. A wide range of materials with strong nonlinear optical (NLO) properties contributing to optical limiting (OL) have been investigated [2,3]. Most of the materials reported were shown to perform their OL functions via a two-photon (2PA) or multiphoton (nPA) reverse saturable absorption (RSA), excited state absorption (ESA), nonlinear light scattering (NLS), nonlinear refraction (NLR) or free-carrier absorption (FCA) mechanisms [2–5]. Usually, the investigated materials have displayed more than one of these NLO processes [2,5]. Researchers over the years have devised means of blending two or more materials with the intent of developing an efficient optical limiter. However, previous attempts in this regard, have focused mostly on the functionalization of carbon nanostructures with either porphyrins, phthalocyanines (Pcs) or other highly aromatic organic chromophores [6–8].

In recent years, the optical limiting behavior of various types of semiconductor quantum dots (QDs) has become a subject of interest [9]. Phthalocyanines on the other hand are known to exhibit

good OL behavior with large nonlinear absorption coefficients (β_{eff}) [10–13]. In spite of the advantages abound in these two materials, it is surprising to know that research on the use of phthalocyanine-quantum dot nanocomposites for OL applications is still relatively scarce. Britton et al. reported on the OL behavior of some selected metallophthalocyanines (MPcs) in the presence of CdTe QDs without covalent linkage [14]. It should be mentioned that Pc-QDs composites obtained via a covalent interaction are known [15]. However to the best of our knowledge, such nanocomposite materials have not been studied before for OL applications. It is thus expected that the combination of these two materials: Pcs and QDs, will yield materials with enhanced NLO properties.

Among the underlining mechanisms for NLO processes, 2PA, FCA and NLS have been particularly identified as the major processes contributing to the OL behavior of semiconductor nanoparticles [1,16,17]. Since QDs fluoresce upon excitation by one-photon absorption in the visible spectral range, and two-photon absorption in the IR spectral range [17], it is expected that at 532 nm, the contribution of QDs to OL via a 2PA would be negligible. However for Pcs, the wavelengths for 2PA include 532 nm, the region with negligible linear absorption and reasonably strong triplet-triplet absorption [18,19]. FCA on the other hand is usually produced when excitation takes place at the wavelengths where there is linear absorption [16]. FCA may be attributed to the excited-state absorption of electrons in the conduction band, and holes in the

* Corresponding author. Tel.: +27 46 603 8801; fax: +27 46 622 5109.

E-mail address: t.nyokong@ru.ac.za (T. Nyokong).

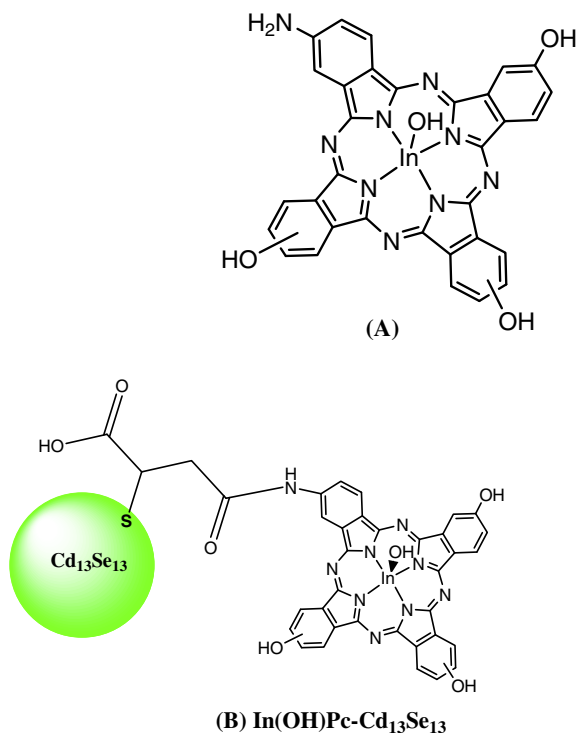


Fig. 1. The structure of (A) hypothetical phthalocyanine (In(OH)Pc) investigated by DFT method using Gaussian 03 and (B) of the hypothetical nanocomposite.

valence band. These free carriers (electrons and holes) are generated by interband transitions due to linear absorption [2]. Since the investigated QDs exhibit linear absorption in the wavelength domain encompassing the excitation wavelength (532 nm), it is expected that FCA will play a major role in the composites' optical limiting behavior. The effects of Förster resonance energy transfer (FRET) process which is expected to occur between the QDs and the Pc are in addition examined using fluorescence studies and DFT calculations. Processes such as nonlinear scattering due to the QDs [1], and 2PA of the Pc moiety [18,20] are also important aspects for consideration.

In the present paper, enhanced NLO properties of the covalently linked phthalocyanine-QD nanocomposites are described. The QDs employed are CdSe core and CdSe/ZnS coreshell capped with 2-mercaptosuccinic acid (MSA). Employing a core and a coreshell allows us to compare the effects of the properties of the core and the coreshell on the OL behavior of the nanocomposites. MSA was chosen to aid water solubility of the QDs, and also to allow for coupling between the $-\text{COOH}$ group of the QDs and the amino group of the InPc. Indium was chosen as a central metal because of its ability to enhance intersystem crossing to the triplet state due to heavy atom effect [4,10,13,19]. We also performed DFT calculations to understand the underlying mechanisms of the nonlinear optical processes in these nanocomposites using a simpler indium(III) aminotrihydroxy phthalocyanine (Fig. 1A), which would be referred to here as In(OH)Pc and CdSe cluster ($\text{Cd}_{13}\text{Se}_{13}$), as a model for the semiconductor quantum dots.

2. Experimental section

2.1. Materials

The synthesis of 2(3),9(10),16(17),23(24)-Tetrakis-(4-amino-phenoxy)-phthalocyaninato indium (III) chloride (InPc) has been reported [21]. Acetone, methanol (MeOH) and absolute ethanol (abs. EtOH) were obtained from SAARCHEM. 1-Ethyl-3-(3-dimethyl-

ylaminopropyl)-carbodiimide (EDC), N-hydroxysuccinimide (NHS), 2-mercaptosuccinic acid (MSA), spectroscopic grade dimethyl sulphoxide (DMSO), selenium powder, potassium hydroxide pellets, trioctyl phosphine oxide (TOPO), 1-octadecene (ODE), oleic acid, zinc powder, sulfur powder, cadmium oxide and chloroform were obtained from Sigma Aldrich. All materials were used as received without any further purification. All aqueous solutions were prepared with ultrapure water obtained from a Milli-Q Water System (Millipore Corp. Bedford, MA, USA).

2.2. Instrumentation

Infra-red spectra were collected on a Perkin-Elmer Universal ATR Sampling accessory on Spectrum 100 FT-IR spectrometer. Raman spectra were obtained using a Bruker RAM II spectrometer equipped with a 1064 nm Nd:YAG laser and a liquid nitrogen cooled germanium detector.

All Z-scan experiments described in this study were performed using a frequency-doubled Nd:YAG laser (Quanta-Ray, 1.5 J/10 ns fwhm pulse duration) as the excitation source. Details are as described before [18]. Transmission electron microscope (TEM) images were obtained using a Zeiss Libra TEM, 120 model and operated at 90 kV accelerating voltage. QDs and composite samples for TEM were prepared separately by ultrasonication in abs. EtOH. X-ray powder diffraction patterns were recorded on a Bruker D8 Discover, equipped with a LynxEye detector, using Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$, nickel filter). Other details of the XRD instrumentation are as previously described [22].

Ground state electronic absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Fluorescence emission spectra were recorded on a Varian Eclipse spectrofluorimeter. Fluorescence lifetime measurements were carried out using a time correlated single photon counting (TCSPC) setup (FluoTime 200, Picoquant GmbH). The excitation source was a diode laser (LDH-P-C-485 with 10 MHz repetition rate, 88 ps pulse width). Further details on TCSPC are available in a previous publication [23].

DFT calculations were performed on Gaussian 03 program [24] running on an Intel/Linux cluster. Geometry optimization calculations on $\text{Cd}_{13}\text{Se}_{13}$ and In(OH)Pc were done separately at B3LYP/LanL2DZ level. The optimized $\text{Cd}_{13}\text{Se}_{13}$ was linked to the fully optimized In(OH)Pc structure using MSA as a spacer. A second optimization calculation was then performed on the nanocomposite, represented in Fig. 1B at UB3LYP/LanL2DZ level. Single-point energy calculations to determine the NLO response (β_{ijk}) using UB3LYP/LanL2DZ formalism were performed following the methods described in the literature [25]. Gausview 4.1 program was used for all visualization [24].

2.3. Preparation of MSA-capped CdSe and MSA-capped CdSe/ZnS QDs and their purifications

MSA capped CdSe and CdSe/ZnS were synthesized using a modified version of the methods described in the literature [26–29]. Firstly, TOPO-capped CdSe core and CdSe/ZnS core-shell were synthesized as follows: A mixture of CdO (1.30 g 10.10 mmol), oleic acid (30 mL), and ODE (50 mL) was heated in a three-necked flask under N_2 to 300 °C to get a clear solution. The temperature of the solution was lowered to $\sim 230 \text{ }^\circ\text{C}$, followed by addition of a slurry prepared by stirring a mixture of 0.30 g (3.80 mmol) Se powder and 1.93 g (4.99 mmol) TOPO in 25 mL ODE at room temperature for 24 h under a N_2 atmosphere. The size of the core CdSe QDs was controlled by lowering the temperature of the solution and recording the emission and the absorption spectra of the aliquots at different time intervals. Once the desired CdSe core size was obtained, a portion of it was collected, precipitated with excess

Download English Version:

<https://daneshyari.com/en/article/1494211>

Download Persian Version:

<https://daneshyari.com/article/1494211>

[Daneshyari.com](https://daneshyari.com)