



Enhanced nonlinear optical response of benzothiazole substituted ball-type phthalocyanines in the presence of metallic nanoparticles



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ABSTRACT

The synthesis of zinc-zinc, gallium-gallium and indium-indium ball-type phthalocyanines (complexes **4**, **5** and **6**) and the surface assembly of the complexes onto metallic gold and silver nanoparticles are reported in this work. Furthermore, their photophysical and nonlinear optical dynamics were investigated. Decreases in the fluorescence quantum yields with a corresponding increase in the triplet quantum yields of the nanoconjugates in comparison to complexes **4**, **5** and **6** alone were observed. The mechanism of strong reverse saturable absorption observed was found to be predominantly dependent on excited state absorption. The optical limiting thresholds range from 0.09 to 0.19 J/cm². Enhanced triplet parameters and nonlinear optical responses were found when the complexes were conjugated to metallic nanoparticles.

1. Introduction

The increasing applications of high-power laser devices in many and varied areas of human activity has lead to a rising research interest toward designing materials that can protect optical sensors including the human eye from laser-induced damage [1,2]. The design of nonlinear optical (NLO) materials that can limit the intensity of light resulting from interaction of radiation with matter is urgent. Although there is a wealth of information on NLO materials operating with different mechanisms, the demand for material with ideal optical response against intense laser radiation has not been met. One interesting property of a good optical limiting material is the possession of high π -conjugated system as well as high photo-stability [3,4].

A considerable research attention has been given to the nonlinear optical performance of phthalocyanines among the many and diverse materials for NLO applications due to their thermal stability and extensive delocalized π -electron systems [1,4–6]. Ball-type phthalocyanines (Pcs) and their derivatives are a relatively new class of highly π -conjugated Pcs, in which two Pc monomer rings are cofacially arranged, with bridged four substituents on the peripheral positions of the benzene rings [7,8]. Thus, this class of macrocycle possess the structural requirements of good NLO materials.

On the other hand, research focus toward formulating new classes of versatile, robust and multi-functional nanomaterials using organic-inorganic hybrid such as gold (AuNPs) and silver (AgNPs) nanoparticles blended with Pcs has been on the rise [9–12]. The enhancement of photophysical properties of Pcs in the presence of metallic nanoparticles has been reported [9,10].

In this study, we report on the synthesis, photophysical and enhanced nonlinear optical response of benzothiazole derivatized ball-type Pcs when linked to AuNPs and AgNPs. The choice of benzothiazole stems from the fact that inclusion of a sulphur heteroatom in the π -conjugated system of a chromophore such as a phthalocyanine, favors the enhancement in nonlinear optical response [13]. Apart from this, thiazole units have been shown to be attractive building blocks for the synthesis of dyes with two-photon absorption (2PA) [13]. This work is the first report of a benzothiazole bridged ball-type Pc. We have reported on the NLO behaviour of benzothiazole substituted mononuclear phthalocyanines alone [14] or when linked to Au nanoparticles (AuNPs) [15]. We have also reported on the linking of ball-type phthalocyanines to AuNPs and AgNPs but using an amide bond [16]. This work reports for the first time on the synthesis of a ball type phthalocyanines bridged by sulphur/nitrogen containing groups, which allows for ease of assembly onto AuNPs and AgNPs, rather than the more involved amide bond reported in literature [16]. AgNPs and AuNPs will increase intersystem crossing to the triplet state through the heavy atom, hence improving NLO parameters, hence are employed in this work. In addition, AgNPs and AuNPs are known [17,18] NLO materials. Thus, this study was designed to integrate three optical limiting materials (ball-type Pc, benzothiazole and NPs) into one with enhanced nonlinear optical potentials.

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2. Experimental

2.1. Materials

3,4-Dihydroxybenzaldehyde, 2-aminothiophenol, cetyltrimethyl ammonium bromide (CTAB), zinc acetate, gallium(III) chloride and indium(III) chloride, 4-nitrophthalonitrile (**2**) were obtained from Sigma Aldrich. 1-Pentanol, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), dimethylformamide (DMF), methanol and dimethyl sulphoxide (DMSO), tetrahydrofuran (THF) were obtained from Merck. The purification processes were carried out on silica gel 60 (0.063–0.200 mm) for column chromatography.

2.2. Equipment

Fourier transformed Infrared (FTIR) spectra were obtained using Bruker ALPHA FT-IR spectrometer with universal attenuated total reflectance (ATR) sampling accessory. ^1H NMR spectra were recorded on Bruker AVANCE II 600 MHz NMR spectrometer with tetramethylsilane (TMS) as an internal reference standard. Elemental analyses were performed 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. The electronic absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Fluorescence measurement was obtained using a Varian Eclipse spectrofluorimeter with appropriate filters. Fluorescence lifetimes were measured using a time-correlated single photon counting setup (TCSPC) (FluoTime 300, Picoquant GmbH) as described before [9]. X-ray diffraction (XRD) patterns were measured on a Bruker[®] D8 Discover diffractometer, equipped with a Lynx Eye detector, under Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$) [9]. The triplet quantum yields were obtained using a laser flash photolysis system described before [10].

Transmission electron microscope (TEM) images were determined using a Zeiss 1210 TEM operated at 100 kV accelerating voltage. Energy dispersive X-ray spectroscopy (EDX) was done on an INCA PENTA FET coupled to the VAGA TESCAM using 20 kV accelerating voltage. Magnetic circular dichroism (MCD) spectra were obtained using a Chirascan plus spectrodichrometer equipped with a 1 T (tesla) permanent magnet by using both the parallel and antiparallel fields. The conventions of Piepho and Schatz are used to describe the sign of the MCD signal and the Faraday terms [19].

All Z-scan measurements 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) and 10 Hz repetition rate was used to avoid thermal contribution.

2.3. Synthesis

2.3.1. Synthesis of 3, 4-Dihydroxybenzothiazole (**1**)

3, 4-Dihydroxybenzothiazole (**1**) was synthesized following similar literature method for synthesis of benzothiazole from aldehyde [20] as follows: a mixture of 3, 4-dihydroxybenzaldehyde (1 g, 7.2 mmol) and 0.14 g (0.38 mmol) of CTAB was stirred in 50 mL of water at 80 °C for 30 min, followed with addition of 2-aminothiophenol (1.08 g, 8.69 mmol). The reaction mixture was allowed to reflux at 150 °C for 5 h. On cooling, the reaction mixture was diluted with ethyl acetate (EtOAc) (200 mL) and was transferred to a separating funnel. The organic layer was isolated and washed with NaHCO₃ (100 mL), and the aqueous layer further extracted with fresh EtOAc (3 × 100 mL). The combined organic extracts were washed with water (3 × 100 mL), isolated, dried using Na₂SO₄ and concentrated under reduced pressure. The crude product was purified using silica gel column chromatography with petroleum ether/ethyl acetate (9:1) as eluent to give bright yellow solid. Yield: 1.6 g (82%), IR (ATR) (cm^{-1}) ν_{max} 2973.17 (C-H from Ar-

H stretch), 2934.37, 1519.56 (C=N stretch), 756.34 (C-S stretch), ^1H NMR (600 MHz, DMSO) δ (ppm) 8.05–7.58 (dd, $J = 8.2, 7.6 \text{ Hz}$, 2H, Ar-H), 7.54–7.07 (m, 4H, Ar-H), 7.0–6.58 (d, $J = 7.5 \text{ Hz}$, 1H, Ar-H), 3.55–3.50 (s, 2H, H-hydroxyl group). Anal. Calc. For C₁₃H₉NO₂S: C, 64.18; H, 3.73; N, 5.76; S, 13.18, Found: C, 64.22; H, 3.70; N, 5.78; S, 13.22.

2.3.2. Synthesis of 4,4'-((4-(benzo[d]thiazol-2-yl)-1,2-bis(phenoxy))diphthalonitrile (**3**)

A mixture of 3,4-dihydroxybenzylbenzothiazole (**1**) (1.00 g, 4.11 mmol) and 4-nitrophthalonitrile (**2**) (1.42 g, 8.22 mmol) in dry DMF (25 mL) was stirred in a 100 mL round-bottomed flask at 50 °C under an inert atmosphere for 1 h. Dry K₂CO₃ (3 g, 21 mmol) was added in six equal portions at 1 h intervals and the mixture was allowed to stir undisturbed at ambient temperature for 7 days. The mixture was poured into ice water and the precipitated product was filtered under reduced pressure. The light yellow precipitate was purified by column chromatography using hexane/ethyl acetate (8:2) as eluent to give a crystalline yellow solid (**3**). Yield: 1.03 g, (42%), IR (ATR) (cm^{-1}): 3034 (Ar-CH stretch), 2230 (C=N stretch), 1676 (C=O stretch), 748 (C-S stretch). ^1H NMR (600 MHz, DMSO) δ (ppm) 8.21 (d, $J = 8.7 \text{ Hz}$, 5H, Ar-H), 8.16 (dd, $J = 8.3, 4.8 \text{ Hz}$, 1H, Ar-H), 8.08 (d, $J = 8.0 \text{ Hz}$, 1H, Ar-H), 7.96 (d, $J = 2.5 \text{ Hz}$, 1H, Ar-H), 7.59–7.54 (m, 3H, Ar-H), 7.50–7.46 (m, 1H, Ar-H), 7.38 (d, $J = 8.7 \text{ Hz}$, 1H, Ar-H). ^{13}C NMR (600 MHz, CDCl₃) δ 165.82, 160.52, 160.07, 153.84, 147.75, 145.57, 136.67, 132.47, 127.58, 127.15, 127.10, 126.30, 122.81, 122.64, 122.97, 122.80, 122.77, 122.75, 122.35, 122.28, 117.93, 116.25, 116.20, 115.67, 115.57, 109.86, 109.59, 109.33, 109.25. Anal. Calc. For C₂₉H₁₃N₅O₂S: C, 70.29; H, 2.64; N, 14.13; S, 6.47, Found: C, 69.08; H, 2.72; N, 14.09; S, 6.25.

2.3.3. Synthesis of tetrakis-[4,4'-((4-(benzo[d]thiazol-2-yl)-1,2-bis(phenoxy))]diphthalocyaninato zinc (II) (**4**)

A mixture of zinc acetate (0.2 g, 1.4 mmol), 4,4'-((4-(benzo[d]thiazol-2-yl)-1, 2-bis(phenoxy))diphthalonitrile (**3**) (0.3 g, 0.61 mmol), DBU (0.3 mL) and 1-pentanol (10 mL) was refluxed under argon atmosphere at 180 °C for 24 h. The reaction mixture upon cooling was precipitated using methanol and the precipitate was collected by centrifugation. The green product was subsequently washed with methanol, ethanol and diethyl ether and purified by column chromatography using THF and methanol (9:1) as eluent. The product was dried under fume hood. Yield: 0.12 g, (24%), IR (ATR): (cm^{-1}): 3047 (Ar-C-H stretch), 1477 - 1655 cm^{-1} (C=C stretch), 1496–1560 cm^{-1} (C=N stretch), 748 (C-S stretch). ^1H NMR (600 MHz, DMSO) δ (ppm) 8.15–8.05 (dd, $J = 8.5, 5.7 \text{ Hz}$, 11H, Ar-H), 8.00–7.98 (d, $J = 7.6 \text{ Hz}$, 5H, Ar-H), 7.96–7.94 (m, 5H, Ar-H), 7.90–7.88 (m, 4H, Ar-H), 7.80 (m, 4H, Ar-H), 7.55–7.50 (t, $J = 6.8 \text{ Hz}$, 6H, Ar-H), 7.45–7.40 (t, $J = 7.2 \text{ Hz}$, 6H, Ar-H), 7.35 (m, 5H, Ar-H), 7.20 (d, $J = 7.2 \text{ Hz}$, 6H, Ar-H). Anal. Calc. for C₁₁₆H₅₂N₂₀O₈S₄Zn₂: C, 65.94; H, 2.48; N, 13.26, S, 6.07. Found: C, 64.89; H, 3.05; N, 13.93, S, 5.85. UV-vis, $\lambda_{\text{max}}/\text{nm}$ (log ϵ): (DMSO), 681(5.44), 612 (4.77), 341 (5.36). MALDI TOF-MS: Calculated: 2112.86; Found: 2113.92 [M + 1]⁺.

2.3.4. Synthesis of tetrakis-[4,4'-((4-(benzo[d]thiazol-2-yl)-1,2-bis(phenoxy))]diphthalocyaninato gallium (III) chloride (**5**)

Complex **5** was synthesized as described for **4** using gallium (III) chloride salt (0.28 g, 1.6 mmol) instead of Zn acetate. Yield: 0.15 g (26%), IR (ATR): (cm^{-1}): 3052 (Ar-C-H stretch), 1451–1636 cm^{-1} (C=C stretch), 1487–1560 cm^{-1} (C=N stretch), 754 (C-S stretch). ^1H NMR (600 MHz, DMSO) δ (ppm) 8.05–7.97 (dd, $J = 8.5, 5.7 \text{ Hz}$, 11H, Ar-H), 7.95–7.84 (d, $J = 7.6 \text{ Hz}$, 5H, Ar-H), 7.82–7.77 (m, 5H, Ar-H), 7.75–7.68 (m, 4H, Ar-H), 7.65 (m, 4H, Ar-H), 7.56–7.51 (t, $J = 6.8 \text{ Hz}$, 6H, Ar-H), 7.47–7.41 (t, $J = 7.2 \text{ Hz}$, 6H, Ar-H), 7.28 (m, 5H, Ar-H), 7.23 (d, $J = 7.25 \text{ Hz}$, 6H, Ar-H). Anal. Calc. for C₁₁₆H₅₂N₂₀O₈S₄Ga₂Cl₂: C, 63.55; H, 2.39; N, 12.78, S, 5.85. Found: C, 64.81; H, 2.97; N, 13.22, S, 6.09. UV-vis, $\lambda_{\text{max}}/\text{nm}$ (log ϵ): (DMSO), 698(5.59), 624 (5.07), 370 (5.52). MALDI TOF-MS: Calculated: 2192.43; Found: 2193.17 [M + 1]⁺.

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