

# Photophysical and nonlinear optical studies of tetraalkynyl zincphthalocyanine and its “clicked” analogue



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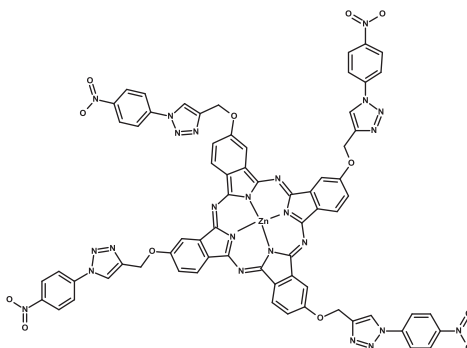
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## HIGHLIGHTS

- Tetra-substituted alkynyl zinc phthalocyanine and its “clicked” analogue are synthesized.
- Two-photon absorption and reverse saturable absorption are the dominant nonlinear absorption mechanisms.
- The presence of electron acceptor groups fused with triazole linkers enhanced photophysical and nonlinear optical behavior.

## GRAPHICAL ABSTRACT

Tetra-substituted alkynyl zinc phthalocyanine and its “clicked” analogue exhibit strong triplet absorption with high triplet yields. Both two-photon absorption and reverse saturable absorption are the dominant mechanisms for nonlinear absorption.



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## ABSTRACT

We report here for the first time on the photophysical and nonlinear optical behavior of tetra-substituted alkynyl zinc phthalocyanine and its “clicked” analogue (**4** and **5**). The compounds exhibited high triplet quantum yields in dimethylsulphoxide (DMSO). Nonlinear optical (NLO) properties were also evaluated for the two compounds at 532 nm and 10 ns in DMSO. We observed two-photon absorption (2PA) and strong reverse saturable absorption (RSA) as the dominant mechanisms at nanosecond laser excitation. The presence of electron acceptor groups fused with triazole linkers in the peripheral positions of **4** provide excellent coexistent features, such as enhanced triplet quantum yields and lifetimes compared to **5**. Large third-order susceptibility ( $2.09 \times 10^{-11}$  and  $3.53 \times 10^{-9}$  esu) and hyperpolarizability ( $1.09 \times 10^{-30}$  and  $9.13 \times 10^{-29}$  esu) were estimated for complexes **4** and **5**, respectively.

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## Introduction

Phthalocyanines (Pcs) and their derivatives have been widely used for many applications such as photosensitizers in photodynamic therapy (PDT) [1,2], chemical sensors, semiconductors,

electrochromic devices, electrocatalysis [3–5] and nonlinear optical devices [6,7]. In recent years, research efforts have been intensified to develop nonlinear optical materials which can effectively shield human eyes and optical sensors [8] from potentially dangerous radiation.

The photophysical and nonlinear optical (NLO) properties of phthalocyanine macrocycles can be improved by the presence of substituents containing  $\pi$  electrons [9–11]. In addition, studies

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have shown that the presence of 1,2,3-triazole groups improves NLO properties [12]. However, the studies of photophysical and NLO properties of 1,2,3-triazole functionalized phthalocyanines molecules have been limited in the literature.

This present work describes the nonlinear optical materials of two complexes. The first, is a ZnPc functionalized with four acetylene units at the peripheral positions (2,9,16,23-Tetra-(propynyloxy)-phthalocyanine zinc(II), **5**), whose synthesis has been reported before [13,14]. The second molecule contains electron withdrawing frame work of 1,2,3 triazole-fused nitrophenyl ZnPc (**4**). The synthesis of complex **3** (a precursor of **4**) has been reported but without the nitro group [14]. In this work we show the importance of the nitro groups in nonlinear optical behavior of the phthalocyanine complexes.

Photophysical and nonlinear studies of series of  $\alpha$  and  $\beta$  tetranitro-substituted phthalocyanines of tin (IV) and germanium (IV) have been reported [15]. Electron withdrawing nitro groups were used to generate large excited dipole moments that are primarily responsible for reverse saturable absorption (RSA) mechanisms upon which NLO limiting properties are based. Improved photophysical properties and enhanced NLO behavior are expected for **4** due to the synergistic effect of NO<sub>2</sub> and triazole linkers on the peripheral positions. Our aim, therefore, is to investigate the photophysical and nonlinear optical properties of these phthalocyanine derivatives and compare the results with those previously reported in the literature.

The nonlinear optical behavior of the synthesized complexes was measured using the Z-scan technique [16]. Open-aperture Z-scan experiments which measure the total transmittance through the sample as a function of intensity of incident laser, are used to determine the optical limiting behavior of the synthesized molecules.

## Experimental

### Materials

Dichloromethane (DCM), copper sulfate pentahydrate, sodium ascorbate (NaAsc), potassium carbonate and Zn(CH<sub>3</sub>COO)<sub>2</sub> were obtained from Sigma Aldrich. Deuterated dimethyl sulphoxide (DMSO-*d*<sub>6</sub>), methanol, ethanol, hexane, 2-dimethylaminoethanol (DMAE), dimethyl formamide (DMF), tetrahydrofuran (THF) and dimethyl sulphoxide (DMSO) were purchased from Merck. All solvents were of reagent grade and were freshly distilled before use. The progress of the syntheses was monitored using thin layer chromatography (TLC, SiO<sub>2</sub>).

### Equipment and methods

Infra-red spectra were collected on a Perkin-Elmer Universal ATR Sampling accessory spectrum 100 FT-IR spectrometer. <sup>1</sup>H NMR spectra were obtained using a Bruker AVANCE 600 MHz NMR spectrometer in DMSO-*d*<sub>6</sub>. 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  $\alpha$ -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).

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 0.1–0.1 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).

The laser flash photolysis set-up used to investigate the triplet state behaviors comprised of coupled laser systems, a Nd-YAG laser (already described above) pumping Lambda-Physik FL3002 dye (Pyridin 1 dye in methanol) laser was employed. The analyzing beam source was a Thermo Oriel 66902 xenon arc lamp. A Kratos Lis Projekte MLIS-X3 photomultiplier coupled with a monochromator allows for selective excitation at wavelengths between 400 and 800 nm when required. Signals were recorded with a two-channel, 300 MHz digital real time oscilloscope (Tektronix TDS 3032C).

### Synthesis

The synthesis of complex **5** (2,9,16,23-tetra-(propynyloxy)-phthalocyanine zinc(II)) has been reported before [13,14].

#### 4-nitro-1-Benzyl-4-(3,4-dicyanophenoxymethyl)-1H-1,2,3-triazole (**3**)

4-Nitrophenyl azide (**1**) was synthesized following a procedure reported by Pagoti et al. [17]. The synthesis of 4-(2-propynyloxy)-phthalonitrile (**2**) has been reported before [14]. The dinitrile (**3**) was synthesized following the methods reported for a similar compound without the nitro group [14] as follows: A mixture of 4-(2-propynyloxy)-phthalonitrile (**2**, 131.6 mg, 0.72 mmol), 4-nitrophenyl azide (**1**, 130.0 mg, 0.792 mmol), CuSO<sub>4</sub>·5H<sub>2</sub>O (14.3 mg, 0.072 mmol, 0.1 eq) and sodium ascorbate (8.9 mg, 0.036 mmol, 0.05 eq) was dissolved in 10 mL of THF/H<sub>2</sub>O (1:1). The mixture was stirred at room temperature for 48 h under Ar. Then the reaction mixture was poured into 100 mL of cold water. The precipitate was filtered off and washed with water, until the filtrate was neutral. The crude residue was crystallized from THF-methanol (1:1) to give the desired product, 4-nitro-1-benzyl-4-(3,4-dicyanophenoxymethyl)-1H-1,2,3-triazole (**3**) as brown powder. Yield: 79%. IR (KBr)  $\nu_{\max}$ /cm<sup>-1</sup>: 3156 (triazole N<sub>3</sub>); 2232 (CN); 1526 (As-NO<sub>2</sub>); 1593, 1504 (C=C phenyl); 1341 (Sym-NO<sub>2</sub>); 1316 (Ar-O-C); 1306, 1256, 1011, 829, 670. Anal. Calcd for C<sub>17</sub>H<sub>10</sub>N<sub>6</sub>O<sub>3</sub>: C 58.96, H 2.91, N 24.27%; found: C 58.77, H 3.61, N 24.13%. MS. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>):  $\delta$ , ppm: 9.21 (s, 1H, H<sub>triazole</sub>), 8.25 (Ar-H, d, 2H), 8.25 (Ar-H, d, 2H), 8.12 (Ar-H, d, 1H), 7.95 (Ar-H, d, 1H), 7.62 (Ar-H, dd, 1H), 5.50 (CH<sub>2</sub>-O-, t, 2H).

#### Synthesis of 2,9(10),16(17),23(24)-tetrakis 4-nitro-1-benzyl-4-(3,4-dicyanophenoxymethyl)-1H-1,2,3-triazole (**4**)

A mixture of dinitrile (**3**) (0.065 g, 0.187 mmol, 4 eq) and Zn(CH<sub>3</sub>COO)<sub>2</sub> (0.011 g, 0.052 mmol, 1.1 eq) in dimethylaminoethanol (5 mL) was heated to 180 °C for 18 h under nitrogen. The dark green colored product was cooled to room temperature and washed with methanol and ethanol. The residue was further purified by Soxhlet extraction using methanol-water (1:1) for 72 h. The blue-green zinc phthalocyanine obtained was thereafter concentrated, dried and ground. Yield: (75%). UV-Vis (DMSO):  $\lambda_{\max}$ /nm (log  $\epsilon$ ): 683 (4.92), 615 (4.32), 353 (4.70).

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