

# Photophysical and non-linear optical behavior of novel tetra alkynyl terminated indium phthalocyanines: Effects of the carbon chain length



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## ABSTRACT

We report on the synthesis, photophysical and nonlinear optical behavior of tetra-substituted alkynyl indium phthalocyanine complexes (**3a** and **3b**). Both complexes showed large triplet quantum yields. Nonlinear optical properties were also evaluated for the two complexes at a wavelength of 532 nm using nanosecond Z-scan technique in dimethylsulfoxide. We observed two-photon absorption (2PA) and strong reverse saturable absorption (RSA) as the dominant mechanisms at nanosecond laser excitation. The underlying 2PA and observed RSA were subjected to further scrutiny by comparing the analytical absorption model to the transmittance optical absorption theory. The theoretical results were in good agreement to the observed RSA and the 2PA mechanism. Large two-photon absorption cross-section ( $1.29 \times 10^{-42}$  and  $1.15 \times 10^{-42}$  cm<sup>4</sup> s/photon), third-order susceptibility ( $2.10 \times 10^{-14}$  and  $2.15 \times 10^{-14}$  esu) and hyperpolarizability ( $2.70 \times 10^{-32}$  and  $3.19 \times 10^{-32}$  esu) were estimated for complex **3a** and **3b**, respectively.

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## 1. Introduction

Phthalocyanines (Pcs) have been used for a diverse range of applications including in liquid crystals, photodynamic therapy (PDT), Langmuir–Blodgett films, chemical sensors, semiconductors, electrochromic devices, ink-jet printing, electrophotography and electrocatalysis [1–8]. The aforementioned applications rely on the Pcs' degree of aromaticity, unique electronic properties, high thermal- and photo-stability and the architectural flexibility [9].

One of the emerging applications of these molecules as discussed in this work is their use as potential nonlinear optical limiters [10–13]. The application of phthalocyanines as potential nonlinear optical (NLO) materials is partly based on the mechanism known as reverse saturable absorption (RSA) [14–18]. The other mechanism responsible is two-photon absorption. NLO materials protect sensors and human eyes from laser radiation by effectively limiting the energy output of an incident light [19,20]. Modifications of phthalocyanine structures for improved optical limiting purposes include the use of a variety of central metal atoms, axial ligands and/or peripheral substituents [21].

Intense investigation into photophysical behavior of indium, gallium and lead phthalocyanine derivatives as potential nonlinear optical materials, have been carried out [22–24]. This paper describes for the first time, the synthesis, photophysical studies

and nonlinear properties of indium phthalocyanines functionalized with alkynyl-containing moieties at the peripheral positions of the phthalocyanine ring. The rationale behind this novel idea as contained in this research is based on: (1) the use of heavy metal atom at the centre of the phthalocyanines and (2) presence of chromophore containing an acetylene unit.

Indium is used as the central metal to increase the rate of inter-system crossing via spin–orbit coupling and also to increase the hyperpolarizability of the phthalocyanines [25]. The axial ligation (Cl used in this case) minimizes intermolecular interactions which cause aggregation of phthalocyanines in solution [26]. It has been reported that the Introduction of groups containing triple bonds enhances the intersystem crossing rate [27], hence we employed these groups in this work.

To the best of our knowledge, placing terminal alkynyl moieties on the peripheral positions of indium phthalocyanines has not been reported before. Thus, we report for the first time the synthesis, characterization and nonlinear optical properties of In-phthalocyanine tetra-substituted 5-hexyl-1-ol and 2-propyl-1-ol on the peripheral positions, Scheme 1. The effect of the chain length is assessed. NLO behavior of alkynyl substituted phthalocyanines have been reported for complexes containing Zn and Co [28] and with no spacer between the terminal group and the Pc ring. Low values of hyperpolarizability were obtained [28]. In this work, spacers are placed between the Pc ring and the terminal alkynyl group, with improved hyperpolarizability. The presence of the alkynyl group allows for future modification of the molecules using click chemistry.

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The optical limiting behavior of phthalocyanines molecules have been assessed by using different techniques including transient absorption and Z-scan methods [29] and third harmonic generation (THG) [30]. The nonlinear behavior of the synthesized complexes are measured using the Z-scan in this work.

## 2. Experimental

### 2.1. Materials

5-Hexy-1-ol, propargyl alcohol, dichloromethane (DCM), 4-nitrophthalonitrile, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), zinc phthalocyanine (ZnPc), *n*-pentanol, diethylether, potassium carbonate and indium (III) chloride were obtained from Sigma Aldrich. Deuterated dimethyl sulfoxide (DMSO- $d_6$ ), *n*-hexane, methanol, dimethyl formamide (DMF) and dimethyl sulfoxide (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 SiO<sub>2</sub> thin layer chromatography (TLC).

### 2.2. 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 400 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  $\alpha$ -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  $\mu$ J–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 ( $l \times w \times h$ ) used was 600 mm  $\times$  300 mm  $\times$  350 mm (excluding the computer, energy meter, translation stage driver and laser sys-

tem). The liquid samples were placed in a cuvette (internal dimensions: 2 mm  $\times$  10 mm  $\times$  55 mm, 0.7 mL) and a path length of 2 mm (Starna 21-G-2).

The nanosecond flash photolysis set-up to investigate the triplet state behavior comprised of coupled laser systems, a Nd-YAG laser (already described above) pumping Lambda-Physik FL3002 dye (Pyridin 1 dye in methanol) laser. The analyzing beam source was a Thermo Oriol 66902 xenon arc lamp. Details have been provided before [22].

### 2.3. Synthesis

#### 2.3.1. 4-Hexy-5-ynyloxy-phthalonitrile (**2a**) (Scheme 1)

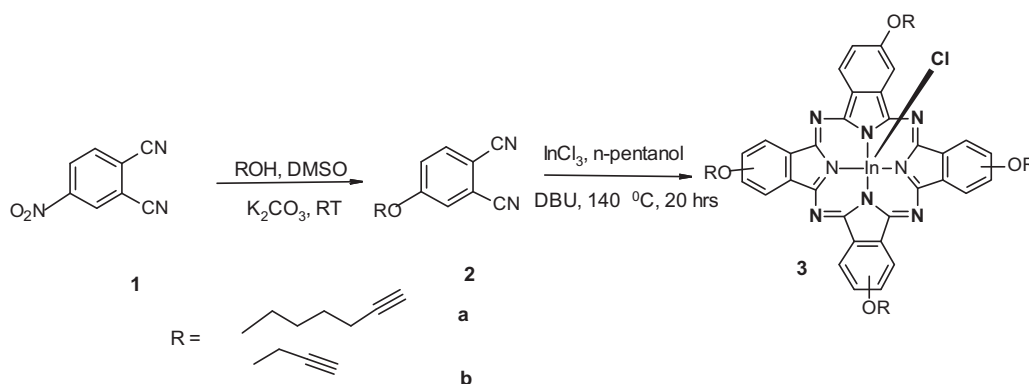
4-Nitrophthalonitrile (**1**) (2 g, 11.5 mmol) was dissolved in dry DMSO (20 mL) and 5-hexyn-1-ol (1.69 g, 11.5 mmol) added under a nitrogen atmosphere. After stirring for 10 min, finely ground anhydrous K<sub>2</sub>CO<sub>3</sub> (2.16 g, 15.6 mmol) was added in portions over 2 h, with stirring. The reaction mixture was stirred at 40 °C for 48 h under nitrogen. Then the mixture was poured into 400 mL of cold water. The precipitate was filtered off and washed with water, until the filtrate was neutral. Recrystallization from hexane and methanol gives the desired compound as a yellow crystalline powder. Yield: 1.74 g (60%). IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 3282 ( $\equiv\text{C-H}$ ); 2228 (CN); 2222 ( $\text{C}\equiv\text{C}$ ); 1557, 1488 (C=C phenyl); 1287 (Ar-O-C); 1308 1251, 1003, 840, 660. *Anal. Calc.* for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O: C, 74.98; H, 5.39; N, 12.49. *Found:* C, 74.56; H, 5.23; N, 12.36%. <sup>1</sup>H NMR (600 MHz, DMSO- $d_6$ ):  $\delta$ , ppm: 8.02 (Ar-H, s, 1H), 7.75 (Ar-H, d, 1H), 7.43 (Ar-H, d, 1H), 4.15 (CH<sub>2</sub>-O-, t, 2H), 2.77 (C $\equiv$ CH, s, 1H), 2.22 (CH<sub>2</sub>, t, 2H), 1.81 (CH<sub>2</sub>, m, 2H), 1.58 (CH<sub>2</sub>, m, 2H).

#### 2.3.2. 4-Propy-2-ynyloxy-phthalonitrile (**2b**) (Scheme 1)

Compound **2b**, Scheme 1, was synthesized following the method described above for compound **2a**, using propargyl alcohol (**b**) (0.64 g, 11.5 mmol) in place of 5-hexyn-1-ol. Yield: 1.42 g (75%). IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 3286 ( $\equiv\text{C-H}$ ); 2229 (CN); 2222 ( $\text{C}\equiv\text{C}$ ); 1557, 1488 (C=C phenyl); 1288 (Ar-O-C); 1306, 1256, 1011, 829, 670. *Anal. Calc.* for C<sub>11</sub>H<sub>6</sub>N<sub>2</sub>O: C, 72.52; H, 3.32; N, 15.38. *Found:* C, 71.77; H, 3.14; N, 15.19%. <sup>1</sup>H NMR (600 MHz, DMSO- $d_6$ ):  $\delta$ , ppm: 8.09 (Ar-H, d, 1H), 7.80 (Ar-H, d, 1H), 7.49 (Ar-H, dd, 1H), 5.00 (CH<sub>2</sub>-O-, t, 2H), 3.70 (C $\equiv$ CH, s, 1H).

#### 2.3.3. 2,9(10),16(17),23(24)-Tetrakis(hex-5-ynoxy)phthalocyanatoindium(III) chloride (**3a**) (Scheme 1)

A mixture of 4-hexy-5-ynyloxy-phthalonitrile (**2a**) (0.25 g, 1.11 mmol), indium (III) chloride (0.25 g, 1.11 mmol) and few drops of catalytic DBU in *n*-pentanol (1.5 mL) was stirred under reflux at 140 °C for 20 h. The reaction was carried out under argon. The crude dark blue product was cooled to room temperature and washed with methanol, ethanol, 1 M HCl and acetone in succes-



Scheme 1. Synthetic pathway for complexes **3a** and **3b**.

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