



# Synthesis and nonlinear optical examination of 3(4),15(16)-Bis-(4-*tert*-butyl-phenoxy)-10,22-diaminohemiporphyrizinato chloroindium



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## HIGHLIGHTS

- Chloroindium hemiporphyrazine was synthesized.
- Nonlinear optical parameters were determined using the Z scan.
- The complex showed improved nonlinear behavior compared to phthalocyanines.

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## ABSTRACT

3(4),15(16)-Bis-(4-*tert*-butyl-phenoxy)-10,22-diaminohemiporphyrizinato chloroindium hemiporphyrazine was synthesized from 1,3,5-triaminobenzene and 4-*tert*-butyl-phenoxyisindoline. The structure of the complex was confirmed using mass, nuclear magnetic resonance and infrared spectroscopies. The nonlinear parameters of the compound was also analyzed in dimethylformamide and found to be significantly greater than previously analyzed phthalocyanines.

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## 1. Introduction

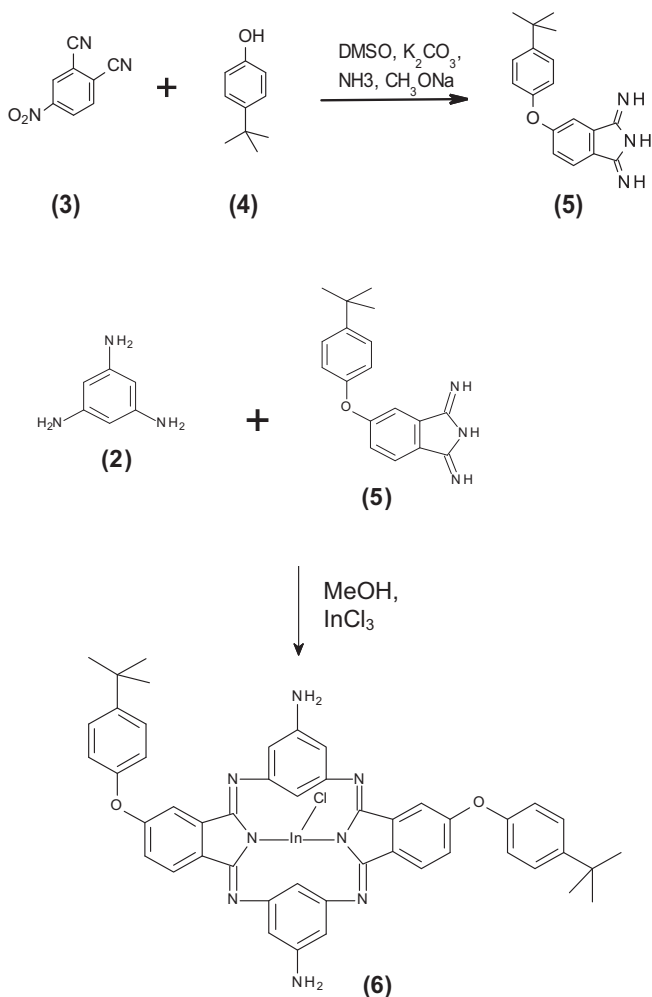
A hemiporphyrazine (Hp) is a phthalocyanine analogue where two opposite facing isoindoles are replaced by either benzene or pyridine ring systems, thus giving it  $C_{2v}$  symmetry. There have also been reports of Hps being able to accommodate a large variety of central metals into their cavities, similarly to phthalocyanines (Pcs). Interestingly, despite their similarity in structure to Pcs, Hps have an absorbance spectrum without any bands in the visible and near-infrared [1]. In fact their absorption maxima can be found near the UV region. Hps can also exist in polymers, in what is termed a ladder configuration [2]. This concept is realized by the synthesis of monomeric macrocycles capable of Diels–Alder reactions, such as the hemiporphyrazines, and their reactions with dienes and dienophiles.

Hps with heavy metal centers have also shown great promise as optical limiters due to the presence of a large nonlinear absorption

[1]. As an added benefit over Pcs, Hps have little to no visible absorption present (which is an advantage for nonlinear optical applications), meaning that no visible light obstruction will occur whereas Pcs absorb red light and cause the transmitted light to appear green [3–5]. This work reports on an chloroindium hemiporphyrazine (Scheme 1, ClInHp, **6**) containing two *tert*-butyl phenoxy substituents since phthalocyanines containing this group were found to give the best third order nonlinear optical (NLO) behavior [6]. The two amino groups have a possibility of linking to carboxylic acid containing polymers such as poly (methyl acrylic acid) (PMAA), and forming a polymer for future NLO studies. Hps containing *tert*-butyl phenoxy have been reported [1,7], and those containing secondary amine groups are also known [2,8]. This work reports for the first time on an Hp containing both a *tert*-butyl phenoxy and primary amine groups.

It has also been observed that zinc tetraamino phthalocyanine showed saturable absorption (SA) rather than reverse saturable absorption (RSA) [9], hence the need to examine the effects of amino groups on NLO behavior of phthalocyanine type complexes. Indium was chosen as a central metal due to its size since it can

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Scheme 1. Synthetic route for ClInHp (6).

enhance intersystem crossing to the triplet state and hence improve NLO parameters. The NLO studies in this work were conducted in DMF solutions.

## 2. Experimental

### 2.1. Materials

3,5-Dinitroaniline (**1**), 4-nitrophthalonitrile (**3**), 4-tert-butylphenol (**4**), methanol (MeOH), ethanol (EtOH), palladium on activated carbon, celite, dimethylsulphoxide (DMSO), dimethylformamide (DMF), potassium carbonate, sodium methoxide, ammonia gas, indium chloride and tetrahydrofuran (THF) were obtained from Sigma–Aldrich. 1,3,5-Triaminobenzene (**2**) was synthesized from complex 1, according to literature reports [10].

### 2.2. Synthesis of In hemiporphyrine (Hp)

#### 2.2.1. Synthesis of 4-tert-butyl-phenoxyisoindoline (**5**), Scheme 1

4-Nitrophthalonitrile (**3**) (0.50 g, 2.89 mmol) and 4-tert-butylphenol (**4**) (0.43 g, 2.89 mmol) were stirred overnight in DMSO in the presence of excess potassium carbonate. The resulting compound was purified using a silica gel column, the solvent removed and then rinsed with water to remove any remaining potassium carbonate and allowed to dry. The compound (0.56 g, 2.02 mmol) was then placed in methanol, along with sodium methoxide

(0.11 g, 2.02 mmol) and ammonia gas was bubbled through the solution under stirring at room temperature for several hours until the solution took on a pale green color. After removing the solvent, the residue was dissolved in toluene and washed several times with water.

Yield 0.47 g (80%)  $^1\text{H}$  NMR (THF- $d_6$ ):  $\delta$  = 8.62 (3H, s, NH), 7.99 (2H, d, Ar–H), 7.33 (2H, d, Ar–H), 7.14 (1H, s, Ar–H), 7.06 (1H, d, Ar–H), 6.80 (1H, d, Ar–H). IR spectrum: 2949  $\text{cm}^{-1}$  (C–H stretch), 1598  $\text{cm}^{-1}$  (C=C aromatic), 1533  $\text{cm}^{-1}$  (C=C aromatic), 1506  $\text{cm}^{-1}$  (C=C aromatic), 1435  $\text{cm}^{-1}$  ( $\text{CH}_3$  bending), 1269  $\text{cm}^{-1}$  (C–O–C stretch), 1229  $\text{cm}^{-1}$  (C–O–C stretch), 1144  $\text{cm}^{-1}$  (C–O–C stretch), 1053  $\text{cm}^{-1}$  (C–O–C stretch).

#### 2.2.2. Synthesis of indium hemiporphyrine (ClInHp, **6**), Scheme 1

ClInHp was synthesized by combining 4-tert-butyl-phenoxyisoindoline (**5**) (0.18 g, 0.63 mmol),  $\text{InCl}_3$  (0.14 g, 0.63 mmol) and 1, 3, 5-triaminobenzene (**2**) (0.077 g, 0.63 mmol) in methanol and stirring under reflux overnight. The product was then purified using a silica column and THF, followed by THF:water 40:60 mixture and finally EtOH as eluents, so as to separate all the components. The final product in EtOH fraction was the compound of interest.

ClInHp: Yield: 0.16 g, 28%. UV–visible (DMF):  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 392.5 (3.29), 424.5 (3.18), 454 (2.99). NMR data listed in Table 1. IR spectrum: 3300  $\text{cm}^{-1}$  (N–H stretch), 1711  $\text{cm}^{-1}$  (C=N groups), 1625  $\text{cm}^{-1}$  (N–H bending), 1357  $\text{cm}^{-1}$  (C–N aryl stretch), 1313  $\text{cm}^{-1}$  (C–N aryl stretch), 1222  $\text{cm}^{-1}$  (aromatic ether), 1021  $\text{cm}^{-1}$  (aliphatic amine). Mass Spectrum Calculated: 912.2 amu. Found: 913.1 amu  $[\text{M}+1]^+$ .

#### 2.2.3. Equipment

A convenient and fast experimental method to assess materials for NLO (including optical limiting) is the open aperture Z-scan experiment. This measures the total transmittance through the sample as a function of incident laser intensity while the sample is gradually moved through the focus of a lens (along the z-axis). The Z-scan equipment employed in this work was fabricated at the University of Stellenbosch in South Africa. All experiments described in this study were performed using a tunable laser system consisting of an Nd:YAG laser (355 nm, 135 mJ/4–6 ns, repetition rate = 20 Hz) pumping an optical parametric oscillator (OPO, 30 mJ/3–5 ns) with a wavelength range of 420–2300 nm (NT-342B, Ekspla).

UV–visible spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Mass spectrometer used was a Bruker MALDI-TOF/TOF Mass Spectrometer (Autoflex III), with the compound placed in an  $\alpha$ -cyano-4-hydroxycinnamic acid matrix.  $^1\text{H}$ ,  $^{13}\text{C}$ , DEPT135 (DEPT = distortionless enhancement by polarization transfer) and 2D NMR spectra (Heteronuclear Single Quantum Coherence (HSQC), Heteronuclear Multiple Bond Correlation (HMBC) and Nuclear Overhauser Enhancement Spectroscopy (NOESY)) were obtained on a Bruker Avance AMX 600 MHz spectrometer using THF- $d_6$  as a solvent. Fluorescence measurements were taken on a Varian Eclipse spectrofluorimeter. Infra-red spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR Spectrometer.

#### 2.2.4. Third order parameters

Once the open aperture data was collected with the Z scan, it was analyzed by using the procedure described by Sheik-Bahae et al. [11], using the following equation:

$$T(z) = \frac{1}{\sqrt{\pi}q_0(z)} \int_{-\infty}^{\infty} \ln[1 + q_0(z)e^{-t^2}] dt \quad (1)$$

where  $T(z)$  is the normalized transmittance of the sample and  $q_0(z)$  is given by the following equation:

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