Contents lists available at ScienceDirect

# Optical Materials

# Synthesis of ytterbium bisphthalocyanines: Photophysicochemical properties and nonlinear absorption behavior

Kutloano E. Sekhosana, Tebello Nyokong *

Department of Chemistry, Rhodes University, PO Box 94, Grahamstown 6140, South Africa

ABSTRACT

Herein we report on the syntheses, photophysico-chemical properties and nonlinear absorption parameters of bis-{1(4), 8(11), 15(18), 22(25)-(tetrapyridin-2-yloxy phthalocyaninato)} ytterbium (III) (**3**) and bis-{1(4), 8(11), 15(18), 22(25)-(tetrapyridin-4-yloxy phthalocyaninato)} ytterbium (III) (**4**). The fluorescence and singlet oxygen quantum yields obtained for complexes **3** and **4** are low. The triplet quantum yield obtained for complex **3** is high at $\Phi_T$ = 0.89 whereas for complex **4** $\Phi_T$ = 0.48. The third order optical susceptibility values are of the order: $10^{-11}$ esu (for complex **3**), and $10^{-13}$ esu (for complex **4**) while the hyperpolarizability values are of the order: $10^{-28}$ esu (for complex **3**) and $10^{-31}$ esu (for complex **4**). Complexes **3** and **4** show two-photon absorption coefficients of the order of $10^{-46}$ cm⁴ s/photon and $10^{-48}$ cm⁴ s/photon, and threshold intensities as low as 0.3 J cm⁻² and 0.0045 J cm⁻², respectively.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

In lanthanide bisphthalocyanines (LnPc₂) two Pc rings are coordinated to the lanthanide ion to create a very stable π-electronic bonding system [1,2]. The applications of LnPc₂ include as electronic materials [3], in sensors [4] and in electronic displays [5,6]. Monomeric phthalocyanines have attracted considerable attention as nonlinear optical (NLO) materials [7]. The presence of the extensive π electron conjugated system plays an important role in the optical nonlinearities of phthalocyanines. The NLO properties of Pcs can be modified by changing the central metal atoms or by altering the axial and peripheral functionalities [7]. The NLO limiting properties of Pcs have been shown to be based on reverse saturable absorption (RSA) mechanisms [8–11]. LnPc₂ complexes also show NLO behavior [12–18]. However the reported NLO behavior of LnPc₂ complexes has concentrated on unsubstituted or peripherally substituted derivatives [12–18]. This work presents YbPc₂ derivatives substituted at non-peripheral positions, which will results in reduced aggregation. The bulky pyridine substituents will also reduce aggregation. NLO parameters such as third order optical susceptibility and hyperpolarizability have been extensively reported for monomeric phthalocyanines, but are still limited for LnPc₂ and are thus reported in this work. The photophysical properties of the YbPc₂ complexes are also reported and

related to NLO properties. The complexes studied in this work are: bis-{1(4), 8(11), 15(18), 22(25)-(tetrapyridin-2-yloxy phthalocyaninato)} ytterbium (III) (**3**) and bis-{1(4), 8(11), 15(18), 22(25)-(tetrapyridin-4-yloxy phthalocyaninato)} ytterbium (III) (**4**).

## 2. Experimental

### 2.1. Materials

1-Pentanol, 1,3-diphenylisobenzofuran (DPBF) and ytterbium (III) chloride hexahydrate were purchased from Sigma–Aldrich, while dimethyl sulphoxide (DMSO), dimethyl formamide (DMF) and acetone were purchased from Merck. Tetrahydrofuran (THF) was purchased from MINEMA. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was purchased from Fluka. The syntheses of 3-(pyridine-2-yloxy)-phthalonitrile (1) [19] and 3-(pyridine-4-yloxy)-phthalonitrile (2) [20,21], have been reported before.

### 2.2. Synthesis of bisphthalocyanines

#### 2.2.1. Synthesis of bis-{1(4), 8(11), 15(18), 22(25)-(tetrapyridin-2-yloxy phthalocyaninato)} ytterbium (III) (3) (Scheme 1)

Complex **3** was synthesized according to methods employed for other LnPc₂ complexes [22]. Briefly, compound (**1**) (400 mg, 1.95 mmol) and ytterbium (III) chloride hexahydrate (94.4 mg, 0.244 mmol) were added into a round bottom flask and heated

* Corresponding author. Tel.: +27 46 603 8260; fax: +27 46 622 5109.
E-mail address: t.nyokong@ru.ac.za (T. Nyokong).

for three minutes. DBU (2 mL) and 1-pentanol (15 mL) were added to the reaction mixture, followed by heating under reflux for 21 h to obtain a green product of **3**. The product obtained was transferred into a centrifuge tube, followed by addition of THF. After centrifugation at 3500 rpm for several minutes, the supernatant obtained was evaporated under reduced pressure. The product was further purified with column chromatography packed with silica and C18 reverse phase column using DMF and THF ($v/v$; 1:2) solvent mixture as an eluent, yielding complex **3**. Yield: 23%. IR: [KBr, $v$, cm$^{-1}$] 809, 825, 840, 825, 892, 1006 (Pc skeleton), 1046, 1072, 1111, 1136, 1158, 1225, 1244, 1286, 1316, 1496, 1530 (C–O–C), 1574, 1658, 1728 (–C=N–), 2856, 2924, 3068 (C–H, aromatic), 3291, 3397 (OH). UV–Vis (DMSO): $\lambda_{max}$ nm (log$\varepsilon$), 395 (4.23), 612 (4.03), 675 (4.73). Anal. Calc. for $C_{104}H_{56}N_{24}O_8Yb$: C, 64.30; H, 2.91; N, 17.30. Found: C, 63.28; H, 3.96; N, 16.53%. $^1$H NMR (DMSO-d$_6$): $\delta$, ppm 9.94 (1H, s, Pc-H), 8.16–7.53 (13H, m, Pc-H), 7.07–6.82 (10H, m, Pyr-H), 6.48 (1H, s, Pyr-H), 6.33 (1H, s, Pyr-H), 5.35 (1H, s, Pyr-H), 3.75–3.22 (29H, m, Pyr-H). MS (MALDI-TOF): ($m/z$): Calc. 1942 amu. Found: 1949 amu [M + 7H$^+$].

### 2.2.2. Synthesis of bis-{1(4), 8(11), 15(18), 22(25)-(tetrapyridin-4-yloxy phthalocyaninato)} ytterbium (III) (4)

Complex **4** was prepared as described for complex **3** except that complex **2** (200 mg, 0.975 mmol) and ytterbium (III) chloride hexahydrate (47.2 mg, 0.112 mmol) were employed. Once obtained, the complex was subjected to centrifugation in acetone and DCM (dichloromethane, 1:1). After drying the supernatant, the Soxhlet method was employed to further purify the complex, using acetone as a solvent. The product was then centrifuged in a mixture of ethanol and THF (2:3), with the supernatant giving a green product on drying in open air. The product was further purified with column chromatography as described for **3** above to give complex **4**.

Yield: 57%. IR: [KBr, $v$, cm$^{-1}$] 663, 680, 750, 811, 847, 892, 974 (Pc skeleton), 1044, 1080, 1127, 1189, 1264, 1322, 1403, 1482, (C–O–C), 1562, 1633 (–C=N–), 2924, 3058 (C–H, aromatic), 3230 (OH). UV–Vis (DMSO): $\lambda_{max}$ nm (log$\varepsilon$), 655 (3.98), 694 (4.21). Anal. Calc. for $C_{104}H_{56}N_{24}O_8Yb$: C, 64.30; H, 2.91; N, 17.30. Found: C, 63.78; H, 4.04; N, 16.91%. $^1$H NMR (DMSO-d6): $\delta$, ppm 8.23–8.22 (4H, s, Pyr), 7.92 (12H, s, Pyr), 7.81–7.71 (3H, m, Pc), 7.63–7.56 (11H, m, Pc), 7.52–7.49 (6H, m, Pc), 7.39–7.38 (4H, d, Pc), 6.45–6.38 (8H, m, Pyr), 6.28–6.18 (8H, m, Pyr). MS (MALDI-TOF): (m/z): Calc. 1942 amu. Found: 1945 amu [M + 3H$^+$].

### 2.3. Equipment

Infrared spectra were recorded on a Perkin Elmer 100 ART FT-IR spectrometer. Ultraviolet–visible spectra (UV–Vis) were recorded on a Shimadzu UV–Vis 2550 spectrophotometer. The emission spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. Luminescence lifetimes were measured using time correlated single photon counting setup (TCSPC) (PicoQuant Fluo-Time 200). The excitation source was a diode laser LDH-P-670 with PDL 800-B, 670 nm and 20 MHz repetition rate Picoquant GmbH. Details have been provided before [23]. $^1$H NMR nuclear magnetic resonance signals were recorded on a Bruker AMX 600 NMR spectrometer. Raman spectra were obtained using a Bruker Vertex 70-Ram II spectrometer equipped with a Nd:YAG laser that emit at 1064 nm and liquid nitrogen cooled germanium detector. Mass spectral data were collected with a Bruker AutoFLEX III Smart beam TOF/TOF Mass spectrometer. The spectra were acquired using 2,5-dihydroxy benzoic acid as the MALDI matrix, and a 355 nm Nd:YAG laser as the ionizing source. Elemental analyses were carried out on a Vario EL III MicroCube CHNS instrument Analyzer.

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 (full width at half maximum) 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 μJ – 0.1 mJ, 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 × 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).

Laser flash photolysis experiments were performed with light pulses produced by a Quanta-Ray Nd:YAG laser providing 400 mJ, 9 ns pulses of laser light at 10 Hz, pumping a Lambda-Physik FL3002 dye laser (Pyridin 1 dye in methanol). Details have been provided before [23].

Photo-irradiations for singlet oxygen quantum yields were done using a General Electric Quartz line lamp (300 W). A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations respectively. An interference filter (Intor, 670 nm with a band width of 40 nm) was additionally placed in the light path before the sample. Light intensities were measured with a POWER MAX 5100 (Molelectron Detector Inc.) power meter.

Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker EPR 300E X-band (10 GHz) spectrometer equipped with a TM probe with a flat quartz cell. The spin Hamiltonian parameters were obtained by simulation of the spectra. The static field (3462–3465 G), center field (3488–3495 G), the modulation amplitude (6.25–6.38 G), the time constant (10.24 ms), the conversion time (5.12 ms), the resolution (1024 pts), power (2.00 mW) and the modulation frequency (100 kHz) were used as the experimental parameters at 298 K with one scan.

### 2.4. Photophysical parameters

Fluorescence ($\Phi_F$), triplet ($\Phi_T$) and singlet oxygen ($\Phi_\Delta$) quantum yields were determined using relative methods described before [24–27] using ZnPc as a standard in DMSO. $\Phi_F$ = 0.2 [25], $\Phi_T$ = 0.65 [26] and $\Phi_\Delta$ = 0.67 [27] for ZnPc standard in DMSO. DPBF was employed as a quencher for singlet oxygen studies.

### 2.5. Nonlinear optical process and parameters

Devices such as optical limiters or saturable filters exhibit optical limiting effects when the intensity of light beam is strongly attenuated, once the input intensity exceeds a threshold value ($I_{lim}$). The latter is determined by the characteristics of the system interacting with the beam, and represents critical parameters for the evaluation of the optical limiting (OL) properties of the device. Using nonlinear regression technique, all aperture Z-scan data were fitted with the Eq. (1), in which the normalized transmittance ($T_{Norm}(z)$) is defined as a function of position $z$ [28]:

$$T_{Norm}(z) = \frac{1}{1 + \beta_2 L_{eff}\left(\frac{I_0}{1+(z/z_0)^2}\right)} \quad (1)$$

where $\beta_2$ and $I_0$ are the effective intensity dependent nonlinear absorption coefficient and the intensity of the beam at focus respectively. $L_{eff}$ is the effective thickness of the sample and is given by Eq. (2) [29]. $z$ and $z_0$ are sample position with respect to the input intensity and Rayleigh length, respectively.

$$L_{eff} = \frac{1 - e^{-(\alpha L)}}{\alpha} \quad (2)$$