Optical Materials 37 (2014) 139–146

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

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

ARTICLE INFO

Article history:
Received 29 October 2013
Received in revised form 23 April 2014
Accepted 7 May 2014
Available online 15 June 2014

Keywords:
Bisphthalocyanines
Photophysico-chemical
Nonlinear absorption
Quantum yields
Third order optical susceptibility
Hyperpolarizability

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^{-12} 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} cm^4 s/photon and 10^{-48} cm^4 s/photon, and threshold intensities as low as 0.3 J cm^{-2} and 0.0045 J cm^{-2}, respectively.

1. Introduction

In lanthanide bisphthalocyanines ($LnPc_2$) two Pc rings are coordinated to the lanthanide ion to create a very stable π-electronic bonding system [1,2]. The applications of $LnPc_2$ 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]. $LnPc_2$ complexes also show NLO behavior [12–18]. However the reported NLO behavior of $LnPc_2$ complexes has concentrated on unsubstituted or peripherally substituted derivatives [12–18]. This work presents $YbPc_2$ 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 $LnPc_2$ and are thus reported in this work. The photophysical properties of the $YbPc_2$ 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 $LnPc_2$ 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).

http://dx.doi.org/10.1016/j.optmat.2014.05.013
0925-3467/