



Two-photon absorption properties of four new pentacoordinated diorganotin complexes derived from Schiff bases with fluorene

Alejandro Enríquez-Cabrera^a, Alberto Vega-Peñaloza^a, Violeta Álvarez-Venicio^{a, b, 1}, Margarita Romero-Ávila^a, Pascal G. Lacroix^c, Gabriel Ramos-Ortiz^b, Rosa Santillan^d, Norberto Farfán^{a, *}

^a Facultad de Química, Departamento de Química Orgánica, Universidad Nacional Autónoma de México, Cd. Universitaria, Ciudad de México No. 04510, Mexico

^b Centro de Investigaciones en Optica, CIO, Apdo., Postal 1-948, 37000 Leon Gto, Mexico

^c Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, F-31077 Toulouse, France

^d Departamento de Química, Centro de Investigación y de Estudios Avanzados del IPN, CINVESTAV, Apdo., Postal 14-740, Ciudad de México 07000, Mexico

ARTICLE INFO

Article history:

Received 4 October 2017

Received in revised form

8 December 2017

Accepted 9 December 2017

Available online 11 December 2017

Keywords:

Diorganotin complexes

NonLinear optics

Two-photon absorption

DFT

ABSTRACT

In this paper we report the synthesis and characterization of four novel pentacoordinated diorganotin complexes, obtained through a methodology that involves a multicomponent reaction of 4-([9H-fluorene-2-yl]ethynyl)-2-hydroxybenzaldehyde, 2-amino-5-nitrophenol and diphenyl or dibutyl-tin oxides. Diorganotin complexes **8–11** were obtained in high yields (70–80%) and were fully characterized by solution NMR (¹H, ¹³C and ¹¹⁹Sn), high resolution mass spectrometry (ESI-TOF) and ATR-FTIR. The optical properties were investigated by UV/Vis spectroscopy and Two-Photon Excitation Fluorescence (TPEF). The One-Photon Absorption (OPA) spectra shows two bands located around 400 and 500 nm, additionally, in the Two-Photon Absorption (TPA) spectra there is one main band located around 750 nm characterized by maximum values of TPA cross section (σ_{TPA}) in the range 450–500 GM with a secondary band located at 1000 nm with maximum σ_{TPA} values of 70 GM; the maximum brightness was observed for 2,2-Dibutyl-6-aza-1,3-dioxo-11-([9,9-dihexyl-9H-fluorene-2-yl]ethynyl)-16-nitro-2-stanna-[d,h]dibenzocyclononene with a value of 150 GM. A theoretical approach within the framework of DFT was applied to study the electronic transitions, showing that the 500 nm band is mainly associated to a HOMO → LUMO transition, and the band at 400 nm to a HOMO-1 → LUMO transition. As main highlights the quantum efficiency of fluorescence of these excited states is as large as 0.43 due to the presence of the tin atom which favors molecular rigidity, these compounds possess TPA responses which are significantly enhanced with respect to related organotin chromophores previously reported.

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1. Introduction

The development of new materials for nonlinear optics (NLO) has increased during the last decades due to their potential applications in optoelectronics. In particular, materials based on organic compounds with extended conjugated π -systems between electron-donor and electron-withdrawing groups result of high interest due to their high molecular hyperpolarizability, efficient

and tunable electronic response, chemical versatility and accessibility at low cost. Until the mid-90's, most of the efficient NLO candidates were based on the benchmark stilbazole skeleton [1],[2], nevertheless various heteroatoms and metals have gradually been incorporated into organic chromophores to develop molecules of greater electronic complexity, and enhanced capabilities [3]. Within this field, organotin complexes are well-known scaffolds that can be used to construct NLO compounds [4]. In addition to the well known biological activities [5–8], the π -conjugated structure of organotin complexes have proved to be suitable for NLO properties [9–15], and optoelectronic applications such as OLEDs [16] (Organic Light Emitting Diodes).

The TPA phenomenon has become one of the most promising NLO properties, due to their applications in photolithography [17],

* Corresponding author.

E-mail address: norberto.farfán@gmail.com (N. Farfán).

¹ From February 01, 2013 to January 31, 2015 V.A.-V. had a postdoctoral fellowship at UNAM and from February 01, 2015 to July 31, 2016 at CIO.