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

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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 nm 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.

Keywords: Diorganotin complexes, NonLinear Optics, Two-Photon Absorption, DFT

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] microfabrication,[18] 2D[19] or 3D[20] data storage and in biophotonics. Recently two-photon microscopy (TPM) has become an important tool in biomedical research[21–23], because it offers high spatial resolution and deep tissue penetration using laser radiation at wavelength within biomedical window (700 – 950 nm).[24,25] Kim and Cho[26] suggested that a suitable chromophore for TPM should have a two-photon brightness larger than 50 GM in order to avoid photodamage of the sample at laser powers commonly used in this technique, for which brightness[27] is defined as the product ($\sigma'_{\text{TPA}} = \sigma_{\text{TPA}} \times \phi$) where ϕ is the fluorescent quantum yield.

Few examples of organotin complexes with TPA properties have been explored in the literature.[9–12] They exhibit nonlinear absorption at the infrared wavelength of 750 – 800 nm with σ_{TPA} values ranging from 10 to 2500 GM (Figure 1)

In continuation of our study of the third-order NLO properties in organotin complexes, and in a continuous effort aimed at extending their range of applications, herein we report the multicomponent synthesis and characterization of four novel pentacoordinated diorganotin complexes starting from 4-([9H-fluorene-2-yl]ethynyl)-2-hydroxybenzaldehyde, 2-amino-5-nitrophenol and diphenyl or dibutyl-tin oxides. Complexes were designed using Schiff-bases functionalized with ethynylfluorene in *para* position to the C=N group as ligands to increase the TPA response, fluorene was introduced because it is well known that it provides a better TPA response and favor efficient luminescence properties.[28–36]

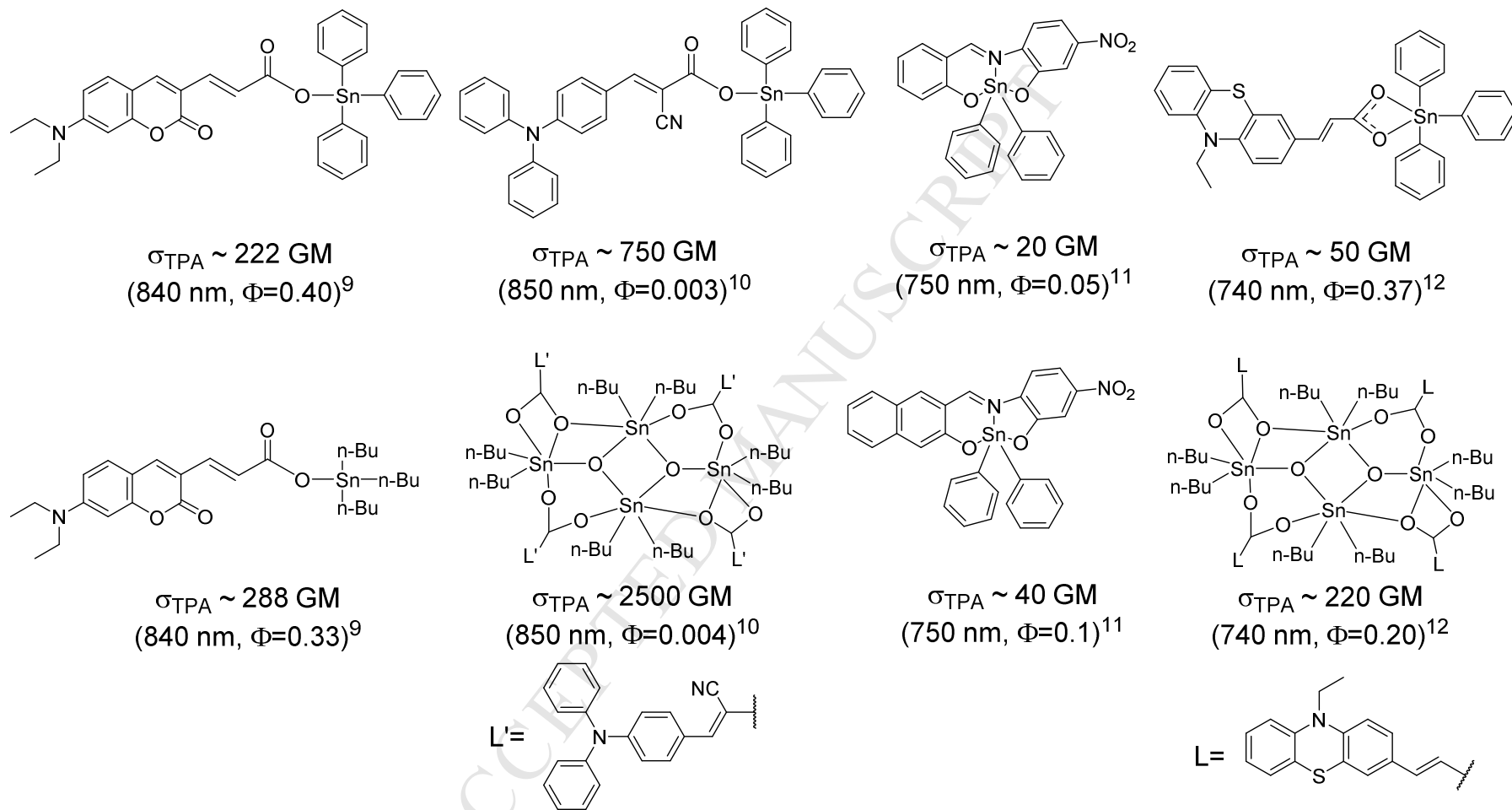


Figure 1.- Organotin complexes with TPA properties reported in the literature. The wavelength of the incident laser to measure σ_{TPA} is written in parentheses.

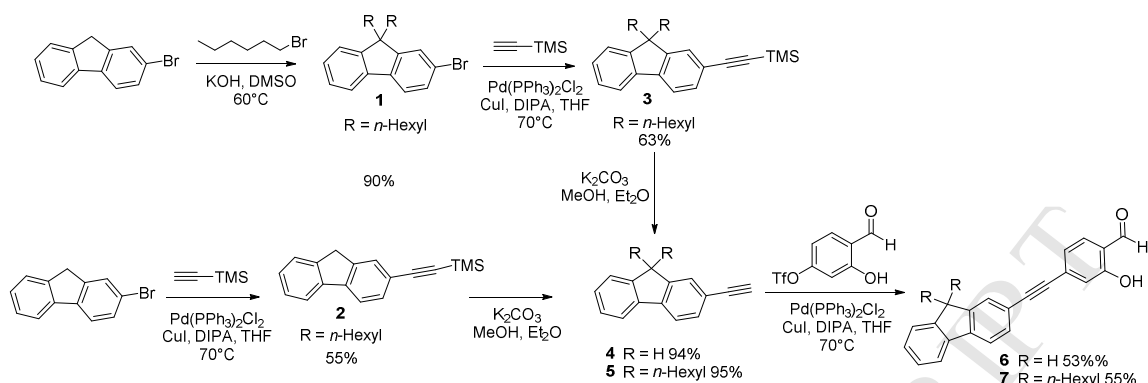
2. EXPERIMENTAL SECTION

2.1 General Considerations

Melting points were measured in a Barnstead Electrothermal 9300 apparatus and are uncorrected. ATR-FTIR experiments were registered in a PerkinElmer Spectrum 400 spectrometer. Absorption spectra were obtained with a Perkin Elmer spectrofluorometer Lambda 900 UV/Vis/NIR. Emission spectra were obtained with an Edinburgh Instruments spectrofluorometer FS5, with an excitation source of 405 nm; the fluorescence quantum yields were measured also with FS5 using an integrating sphere. The values of σ_{TPA} were obtained through the two-photon excited fluorescence technique (TPEF) using a femtosecond laser Chameleon UltraTM tunable in the wavelength 700-1050 nm. ¹H-NMR spectra were recorded using a Varian MR-400 operating at 400 MHz; ¹³C-NMR spectra were recorded at 100.58 MHz; ¹¹⁹Sn spectra were recorded using a Jeol 270 instrument operating at 100.74 MHz; chemical shifts are relative to the residual non deuterated solvent signals, fixed on $\delta = 7.26$ ppm for ¹H and $\delta = 77.00$ ppm for ¹³C. HRMS data was acquired in an Agilent Technologies MS TOF spectrometer. The elemental analyses were obtained in a Perkin Elmer 2400 for CHNS. Starting materials were purchased from commercial sources and used without further purification.

2.2. Syntheses

In order to obtain the four Schiff bases, it was necessary to prepare the two different fluorene aldehyde derivatives shown in Scheme 1. In turn, 4-formyl-3-hydroxyphenyl trifluoromethanesulfonate,[37] 2-bromo-9,9-dihexyl-9H-fluorene (**1**),[38] 2-ethynyl-9H-fluorene (**4**) and 2-ethynyl-9,9-dihexyl-9H-fluorene (**5**)[39] were prepared as described in the literature.

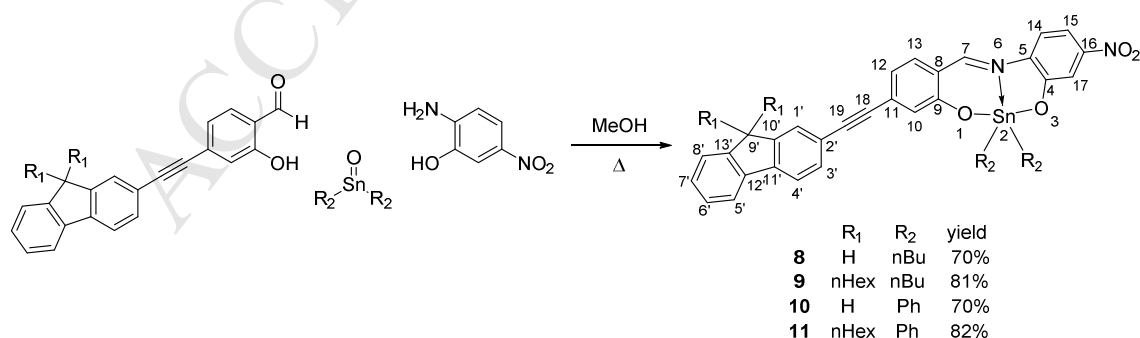


Scheme 1. Synthesis of the starting materials **6** and **7**.

2.2.1 General procedure for the synthesis of diorganotin complexes

Diorganotin complexes **8-11** were synthesized as shown in Scheme 2, using the following general procedure; in a round-bottom flask were placed the aldehyde **6** or **7**, 2-amino-5-nitrophenol and dibutyltin or diphenyltin oxide in an equimolar ratio. The reaction mixture was heated to reflux and vigorously stirred. After 4 h the solution was cooled to room temperature and the mixture was decanted. Finally, the precipitated solid was filtered under high vacuum and washed with cold methanol to yield the pure complexes in high yields.

The features of the multicomponent methodology provide not only high yield but a simplified purification and the ability to synthesize diverse molecules with several degrees of structural variety.



Scheme 2. Synthesis of diorganotin complexes **8-11**, with the corresponding atom numbering.

4-([9H-fluorene-2-yl]ethynyl)-2-hydroxybenzaldehyde (6)

In a round-bottom flask were placed 168 mg (0.88 mmol) of **4**, 200 mg (0.74 mmol) of the aldehyde, 38 mg (0.055 mmol) of Pd(PPh₃)₂Cl₂, 7 mg (0.037 mmol) of CuI under nitrogen atmosphere followed by addition of 15 ml of anhydrous THF and 0.62 ml (4.44 mmol) of anhydrous DIPA and the solution was refluxed for 4 hrs. The reaction was allowed to reach room temperature and quenched with a saturated solution of NH₄Cl. The organic phase was extracted with ethyl acetate, dried using Na₂SO₄ and evaporated under vacuum followed by purification over silica gel to yield 144 mg (53%) of the desired product. ¹H-NMR (300 MHz, CDCl₃) δ11.08 (s, OH), 9.89 (s, CHO), 7.85 – 7.72 (m, 3H), 7.63 – 7.52 (m, 3H), 7.47 – 7.29 (m, 2H), 7.21 – 7.13 (m, 2H), 3.94 (s, 2H). HRMS (ESI⁺-TOF) for C₂₂H₁₅O₂ (calcd. 311.1067): m/z (%) = 311.1067 (M+H)⁺, error 0.01 ppm. Anal. calcd. for C₂₂H₁₄O₂: C 85.14, H 4.55; found: C 82.73, H 4.78.

4-([9,9-dihexyl-9H-fluorene-2-yl]ethynyl)-2-hydroxybenzaldehyde (7)

The procedure is the same as described above for **6** using compound **5** as a starting material. ¹H-NMR (300 MHz, CDCl₃) δ11.08 (s, OH), 9.89 (s, CHO), 7.76 – 7.64 (m, 2H), 7.58 – 7.50 (m, 3H), 7.42 – 7.29 (m, 3H), 7.22 – 7.16 (m, 2H), 1.98 (t, J = 8.1 Hz, 4H), 1.20 – 0.95 (m, 13H), 0.76 (t, J = 6.9 Hz, 5H), 0.69 – 0.52 (m, 4H). HRMS (ESI⁺-TOF) for C₃₄H₃₉O₂ (calcd. 479.2945): m/z (%) = 479.2945 (M+H)⁺, error 0.04 ppm. Anal. calcd. for C₃₄H₃₈O₂: C 85.31, H 8.0; found: C 85.05, H 8.05.

2,2-Dibutyl-6-aza-1,3-dioxo-11-([9H-fluorene-2-yl]ethynyl)-16-nitro-2-stanna-[d,h]dibenzocyclononene (8)

Aldehyde **6** (76 mg, 0.244 mmol), 2-amino-5-nitrophenol (37 mg, 0.244 mmol) and dibutyltin oxide (61 mg, 0.244 mmol) were used following the general procedure. Compound **8** was obtained as a red solid (116 mg, 70 %). M.p.: decomposes at 186 °C. FTIR-ATR (ν , cm^{-1}): 2956, 2921, 2200, 1598 (C=N), 1586 (C=N), 1560, 1495, 1334(NO_2), 1285(NO_2). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 8.67 (s, $^3J(\text{Sn-H}) = 41.7$ Hz, 1H), 7.84 – 7.75 (m, 2H), 7.73 (s, 1H), 7.65 (d, $J = 2.5$ Hz, 1H), 7.61 – 7.53 (m, 3H), 7.41 (td, $J = 7.4, 1.2$ Hz, 1H), 7.39 (d, $J = 9.0$ Hz, 1H), 7.35 (td, $J = 7.4, 1.2$ Hz, 1H), 7.25 (d, $J = 8.2$ Hz, 1H), 6.99 (d, $J = 1.5$ Hz, 1H), 6.90 (dd, $J = 8.2, 1.5$ Hz, 1H), 3.93 (s, 2H), 1.72 – 1.58 (m, 4H), 1.60 – 1.49 (m, 4H), 1.35 (hex, $J = 7.3$ Hz, 4H), 0.87 (t, $J = 7.3$ Hz, 6H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 170.3, 163.3, 159.9, 148.6, 143.8, 143.4, 142.9, 141.0, 137.5, 135.7, 133.5, 131.1, 128.6, 127.6, 127.2, 125.5, 125.3, 120.7, 120.6, 120.5, 120.1, 117.7, 115.0, 113.4, 111.5, 96.0, 89.4, 36.9, 27.1, 26.8, 22.7, 13.7. $^{119}\text{Sn-NMR}$ (100 MHz, CDCl_3) δ -176.0. HRMS (ESI⁺-TOF) for $\text{C}_{36}\text{H}_{35}\text{N}_2\text{O}_4\text{Sn}$ (calcd. 679.1613): m/z (%) = 679.1609 (M+H)⁺, error -0.59 ppm. Anal. calcd. for $\text{C}_{36}\text{H}_{34}\text{N}_2\text{O}_4\text{Sn}$: C 63.83, H 5.06, N 4.14; found: C 63.32, H 4.81, N 4.34.

2,2-Dibutyl-6-aza-1,3-dioxo-11-([9,9-dihexyl-9H-fluorene-2-yl]ethynyl)-16-nitro-2-stanna-[d,h]dibenzocyclononene (9)

Aldehyde **7** (250 mg, 0.522 mmol), 2-amino-5-nitrophenol (81 mg, 0.522 mmol) and dibutyltin oxide (130 mg, 0.522 mmol) were used following the general procedure. Compound **9** was obtained as a red solid (370 mg yield 81%). M.p.: 143-144 °C FTIR-ATR (ν , cm^{-1}): 2954, 2924, 2199, 1587 (C=N), 1561, 1496, 1335 (NO_2), 1285 (NO_2). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 8.69 (s, $^3J(\text{Sn-H}) = 41.6$ Hz, 1H), 7.74 – 7.66 (m, 2H), 7.65 (d,

$J = 2.5$ Hz, 1H), 7.58 (dd, $J = 8.8, 2.5$ Hz, 1H), 7.55 – 7.50 (m, 2H), 7.40 (d, $J = 8.8$ Hz, 1H), 7.37 – 7.32 (m, 3H), 7.27 (d, $J = 8.2$ Hz, 2H), 7.02 (s, 1H), 6.93 (d, $J = 8.2$ Hz, 1H), 1.98 (t, $J = 8.2$ Hz, 4H), 1.71 – 1.59 (m, 4H), 1.59 – 1.50 (m, 4H), 1.35 (h, $J = 7.3$ Hz, 4H), 1.19 – 0.97 (m, 12H), 0.87 (t, $J = 7.3$ Hz, 6H), 0.77 (t, $J = 7.1$ Hz, 6H), 0.68 – 0.55 (m, 4H). ^{13}C -NMR (100 MHz, CDCl_3) δ 170.4, 163.3, 159.9, 151.3, 151.1, 148.6, 142.5, 140.3, 137.5, 135.7, 133.5, 131.2, 128.0, 127.1, 126.4, 125.5, 123.1, 120.7, 120.6, 120.3, 119.9, 117.7, 115.0, 113.4, 111.5, 96.4, 89.3, 55.3, 40.5, 31.7, 29.8, 27.1, 26.8, 23.9, 22.7, 22.7, 14.1, 13.7. ^{119}Sn -NMR (100 MHz, CDCl_3) δ -176.1. HRMS (ESI⁺-TOF) for $\text{C}_{48}\text{H}_{59}\text{N}_2\text{O}_4\text{Sn}$ (calcd. 847.3491): m/z (%) = 847.3482 (M+H)⁺, error -1.09 ppm Anal. calcd for $\text{C}_{48}\text{H}_{58}\text{N}_2\text{O}_4\text{Sn}$: C 68.17, H 6.91, N 3.31; found: C 68.43, H 7.17, N 3.69

2,2-Diphenyl-6-aza-1,3-dioxo-11-([9H-fluorene-2-yl]ethynyl)-16-nitro-2-stanna-[d,h]dibenzocyclononene (10)

Aldehyde **6** (50 mg, 0.161 mmol), 2-amino-5-nitrophenol (25 mg, 0.161 mmol) and diphenyltin oxide (47 mg, 0.161 mmol) were used following the general procedure. Compound **10** was obtained as a red solid (81 mg yield 70%). M.p.: 194-196 °C. FTIR-ATR (ν , cm^{-1}): 3049, 2197, 1596 (C=N), 1588 (C=N), 1564, 1500, 1340 (NO_2), 1281 (NO_2). ^1H -NMR (400 MHz, CDCl_3) δ 8.71 (s, $^3J(\text{Sn-H}) = 52.2\text{Hz}$, 1H), 7.97 – 7.87 (m, 5H), 7.85 – 7.76 (m, 3H), 7.65 – 7.55 (m, 3H), 7.47 – 7.41 (m, 8H), 7.39 – 7.31 (m, 2H), 7.26 (m, 1H), 6.97 (dd, $J = 8.2, 1.5$ Hz, 1H), 3.96 (s, 2H). ^{13}C -NMR (100 MHz, CDCl_3) δ 170.2, 163.3, 159.2, 148.6, 143.9, 143.5, 143.1, 141.0, 138.9, 136.9, 136.6, 136.0, 133.9, 131.1, 130.9, 129.1, 128.7, 127.7, 127.2, 125.7, 125.3, 121.3, 120.6, 120.4, 120.1, 117.7, 115.0, 114.0, 112.1, 96.6, 89.4, 36.9. ^{119}Sn -NMR (100 MHz, CDCl_3) δ -320.6. HRMS

(ESI⁺-TOF) for C₄₀H₂₇N₂O₄Sn (calcd. 719.0987): m/z (%) = 719.0992 (M+H)⁺, error 0.64ppm).

2,2-Diphenyl-6-aza-1,3-dioxo-11-([9,9-dihexyl-9H-fluorene-2-yl]ethynyl)-16-nitro-2-stanna-[d,h]dibenzocyclononene (11)

Aldehyde **7** (250 mg, 0.522 mmol), 2-amino-5-nitrophenol (81 mg, 0.522 mmol) and diphenyl oxide (151 mg, 0.522 mmol) were used following the general procedure. Compound **11** was obtained as a red solid (393 mg yield 82%). M.p.: 211-212 °C. FTIR-ATR (ν, cm⁻¹): 2952, 2926, 2854, 2198, 1589 (C=N), 1563, 1497, 1337 (NO₂), 1283 (NO₂). ¹H-NMR (400 MHz, CDCl₃) δ 8.68 (s, ³J(Sn-H) = 52.1Hz, 1H), 7.94 – 7.89 (m, 4H), 7.75 – 7.69 (m, 2H), 7.59 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.48 – 7.33 (m, 12H), 7.26 (d, *J* = 8.1 Hz, 1H), 6.97 (dd, *J* = 8.1, 1.5 Hz, 1H), 2.00 (t, *J* = 8.2 Hz, 4H), 1.23 – 0.95 (m, 12H), 0.77 (t, *J* = 7.0 Hz, 6H), 0.71 – 0.54 (m, 4H). ¹³C-NMR (101 MHz, CDCl₃)δ 170.2, 163.2, 159.2, 151.3, 151.1, 148.7, 142.6, 140.3, 139.0, 136.9, 136.6, 136.0, 134.0, 131.2, 130.9, 129.1, 128.0, 127.1, 126.5, 125.6, 123.1, 121.3, 120.6, 120.3, 119.9, 117.7, 115.0, 114.0, 112.1, 97.0, 89.3, 55.4, 40.5, 31.7, 29.9, 23.9, 22.7, 14.2. ¹¹⁹Sn-NMR (100 MHz, CDCl₃) δ -320.6. HRMS (ESI⁺-TOF) for C₅₂H₅₁N₂O₄Sn (calcd. 887.2865): m/z (%) = 887.2870 (M+H)⁺, error 0.53 ppm) Anal. calcd for C₅₂H₅₀N₂O₄Sn: C 70.52, H 5.69, N 3.16; found: C 70.13, H 5.26, N 3.39

2.3 Computational details

The four compounds (**8-11**) were fully optimized without any constraints and symmetry requirement using the Gaussian-09 program package[40] within the framework of the Density Functional Theory (DFT).The hybrid functional B3PW91[41,42] was selected for

the computations of the molecular geometries, in relation to its previous use in related tin derivatives with Schiff base ligands.[43–46] The LANL2DZ pseudo-potential was used to account for relativistic effects on the tin atom.[47] In order to provide a reliable comparison with the experimental data, solvent effects were included by using the polarizable continuum model (PCM) implemented in Gaussian09 for chloroform ($\epsilon = 4.7113$). Owing to the difficulties encountered to get geometry convergence in the case of molecules containing long alkyl chains, the two hexyl chains present on the fluorenyl fragment of compounds **9** and **11** were replaced by two ethyl chains in the actual geometries used for the computations. However, as the dominant contribution to the transitions of interest is restricted to the π -delocalized electronic core only (*vide infra*), the properties of these slightly modified species can readily account for those of **9** and **11**. After each computation, vibrational analysis was performed at the same level in order to establish the presence of a minimum on the potential energy surfaces. The UV-visible spectra were computed with the CAM-B3LYP[48] functional, which is usually efficient for computations involving long range electronic effect, and which was found to reproduce the spectra with a better accuracy than related B3LYP, B3PW91, and PBE0. Within this computational method, the difference between experiment and computation is about 0.35 eV and 0.40 eV for the first and second transition, respectively (Table **S11**). These values are a little large compared to the average discrepancy around 0.25 - 0.30 eV encountered in medium size organic molecules,[49] but fully acceptable in molecules of large size, with heavy metal atoms (*e.g.* Sn) and long range charge transfer capabilities. Molecular orbitals were plotted with GABEDIT 2.4.8.[50]

3. RESULTS AND DISCUSSION

3.1. Chemical characterization

The synthesis of diorganotin complexes **8-11** was corroborated through solution NMR, ^1H , ^{13}C , HSQC, HMBC and COSY experiments. The ^1H -NMR spectra show that the chemical shifts for H7 (HC=N) lie in the range between $\delta=8.67$ - 8.71 ppm; the $^3\text{J}(^{119/117}\text{Sn}-^1\text{H})$ coupling constants for H7 are between 41.7 Hz and 41.6 Hz for the dibutyl tin, and 52.4 Hz and 52.1 Hz for the diphenyl tin derivatives, which are in agreement with previous reports.[43][51] The ^{13}C -NMR spectra show that the chemical shifts for C7 appear between 163.2 and 163.5 ppm; this indicates an enhanced π -bridging between the *ortho*-aminophenol and the salicylidene moiety. The C=N fragment shows a characteristic intense band in the IR spectra around 1590 cm^{-1} for the four complexes (see Table 1 and Table S5-6 for the complete NMR data).

Table 1.- Selected spectroscopic data.

Compound	NMR (ppm)			IR (cm^{-1})		
	H-7 ($J(^{119/117}\text{Sn})^a$)	C-7	Sn	C=N	NO _(asym)	NO _(sym)
8	8.67 (41.7)	163.3	-176.0	1586	1334	1285
9	8.68 (41.6)	163.5	-176.1	1587	1335	1285
10	8.71 (52.4)	163.3	-320.6	1588	1340	1281
11	8.68 (52.1)	163.2	-320.6	1589	1337	1283

^a $J(^{119/117}\text{Sn})$ in Hz

3.2. One-photon absorption and photoluminescence properties

The electronic absorption spectra of the four diorganotin complexes show two bands with peaks at *ca* 380 and 490 nm (Figure 2) that correspond to π - π^* transitions; while the emission spectra have a peak located around 605 nm although with a red shifting effect in complexes **8** and **9** compared with **10** and **11**.

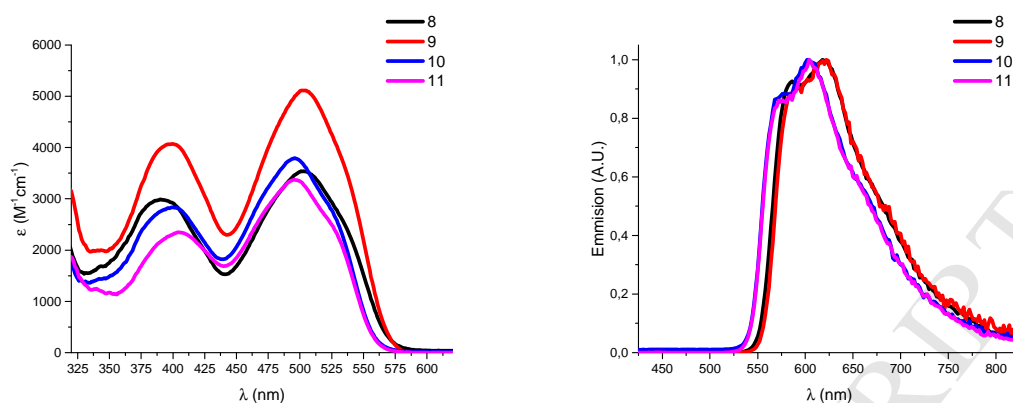


Figure 2.- Absorption (left) and emission (right) spectra of 0.1mM **8-11** in CHCl_3 .

It is well known that the optical spectra of π -conjugated chromophores substituted by donor/acceptor groups are dominated by intense low-lying transitions having charge transfer character within the π -organic linkage. Along this line, the nature of the alkyl substituent in the fluorene moiety ($\text{R}_1 = \text{H}$ in **8** and **10**, and $\text{R}_1 = \text{C}_6\text{H}_{13}$ in **9** and **11**, as shown in Scheme 2) is not expected to affect significantly the UV-Visible spectra of the investigated species.

The presence of a metal within the conjugation pathway of a π -conjugated chromophore has occasionally been reported to strongly affect the NLO properties of the Schiff-base complexes, by virtue of a specific contribution of the d-orbitals along the conjugation pathway.[52][53] On the other hand, the possibility for charge transfer from a π -conjugated substituent (e.g. phenyl) towards a withdrawing fragment through the tin atom has not been evidenced in previous investigations of “push-pull” organotin derivatives.[43]

The dominant low-lying transitions computed by DFT are shown in Table S10 and are compared to the experimental data using chloroform as a solvent. The agreement between computation and experiment appears satisfactory, with blue shifted transitions observed in the DFT data. In particular, both approaches indicate that the electronic transitions are

roughly the same for the four different species, with a general trend for a more intense transition at longer wavelength.

Absorption and emission properties of complexes **8-11** were studied with different solvents (hexane, dioxane, toluene, chloroform, tetrahydrofuran, acetone, methanol, acetonitrile and dimethylsulfoxide (for detailed information see the supporting information). The results show that the complexes can be grouped according to the tin substituent (R_2 in Scheme 2), as observed in Table S9, the absorption bands located around 490 nm for **8** and **9** are bathochromically shifted about 10 nm compared to **10** and **11**, and the band located around 380 nm is hypsochromically shifted around 10nm (except when using DMSO as solvent); for the emission band there is also a bathochromic shift of about 10 nm when comparing **8** and **9** with **10** and **11** (except when using acetone and DMSO as solvent). In nonpolar solvents, the quantum yield ϕ of fluorescence for the four complexes was in the range 0.23-0.43. In these solvents (except hexane) the value of ϕ for **10** and **11** is approximately 20% larger compared with **8** and **9**. Such improvement in the photoluminescence can be partly associated to the higher molecular rigidity introduced by phenyl substitution in the tin atom. In polar solvents, the values of ϕ tend to decrease (with the exception of DMSO).

The pentacoordinated diorganotin complexes were envisioned with a *push-pull* structure; in order to detect possible charge-transfer properties, solvatochromism effects were analyzed using the Lippert-Mataga theory[54] and the Catalán[55] scale to perform a more detailed analysis (see supporting information), resulting in a lack of response towards the polarity of the solvent.

To further analyze the origin of the optical properties of **8-11**, the description of their low-lying transitions at the orbital level is also provided (see Table S11). The data indicate the

same origin for the low energy transitions ($1 \rightarrow 2$ and $1 \rightarrow 3$), arising from a dominant combination of HOMO-1 \rightarrow LUMO and HOMO \rightarrow LUMO excitations, in all cases.

The orbitals involved in the transitions are depicted in Figure 3. They appear to be very similar for the four (**8-11**) derivatives. In any case, the electron density is delocalized on the entire extent of the π -conjugated structure in the occupied HOMO-1 and HOMO levels; and located on the metal organic rigid skeleton without any contribution of the fluorene moieties in the LUMO level. Interestingly, there is no contribution of either the alkyl chains (R_1 in Scheme 2) of the fluorene or the butyl and phenyl ligands (R_2 in Scheme 2) of the tin atom, in either HOMO-1, HOMO, and LUMO levels, which strongly supports the idea of closely related electron transitions, arising from the same π -electronic structures along the **8-11** series. This overall description brings a sizeable charge transfer character to the electron transitions with the expectation of associated solvatochromic and NLO properties.

3.3 Two-photon absorption studies

We are currently interested in developing metal coordination compounds with high TPA properties.[56–59] Thus the σ_{TPA} of the pentacoordinated diorganotin complexes were measured by the TPEF technique in DMSO, THF and $CHCl_3$. The σ_{TPA} values were calculated through TPEF technique as follows:

$$\sigma_{TPA} = \sigma_R \frac{F_S C_R \phi_R \eta_R}{F_R C_S \phi_S \eta_S}$$

Where F is the integrated area of the emission band, C is the molar concentration (mol L^{-1}), ϕ is the fluorescence quantum yield and η is the refraction index, the subscript S or R stands for the sample or the dye used as reference (Rhodamine B).

Figure 4 shows the values of σ_{TPA} as a function of wavelength for three different solvents. As we can see, the solvent influences the optical nonlinearities exhibited by the organotin

complexes. In the polar solvents such as THF and DMSO the maximum σ_{TPA} values are between 200 and 240 GM at 750 nm, while in chloroform (nonpolar solvent) the maximum values of σ_{TPA} increase almost by a factor of two. The enhancement of TPA response in chloroform allows to observe a secondary peak at 1000 nm with a maximum $\sigma_{\text{TPA}} \sim 70$ GM. Considering the *push-pull* structure of the diorganotin complexes, the electronic transitions corresponding to the absorption bands shown in Figure 2 are allowed through optical excitation of one or two photons. Thus the TPA peaks at *ca* 750 and 1000 nm correspond to OPA bands at 380 and 490 nm, respectively

3.4 Discussion

From the DFT results, the orbitals involved in the low-lying transitions of the UV-Vis spectra are very similar for the four molecules (HOMO-1 \rightarrow LUMO; HOMO \rightarrow LUMO), in all cases the tin atom and its substituents (butyl or phenyl) are not involved in these transitions, although they increase the structural rigidity, promoting a greater π -delocalization; the structural rigidity seems to be somewhat increased when phenyl is employed as substituent in the tin atom favoring an increase in the fluorescence quantum yield in agreement with the experimental results. In all complexes the transitions arise from a very similar π -electronic structure, which is confirmed experimentally through the UV-Vis due to the small change in the bands when switching from **8** or **9** (butyl) to **10** or **11** (phenyl) in the same solvent.

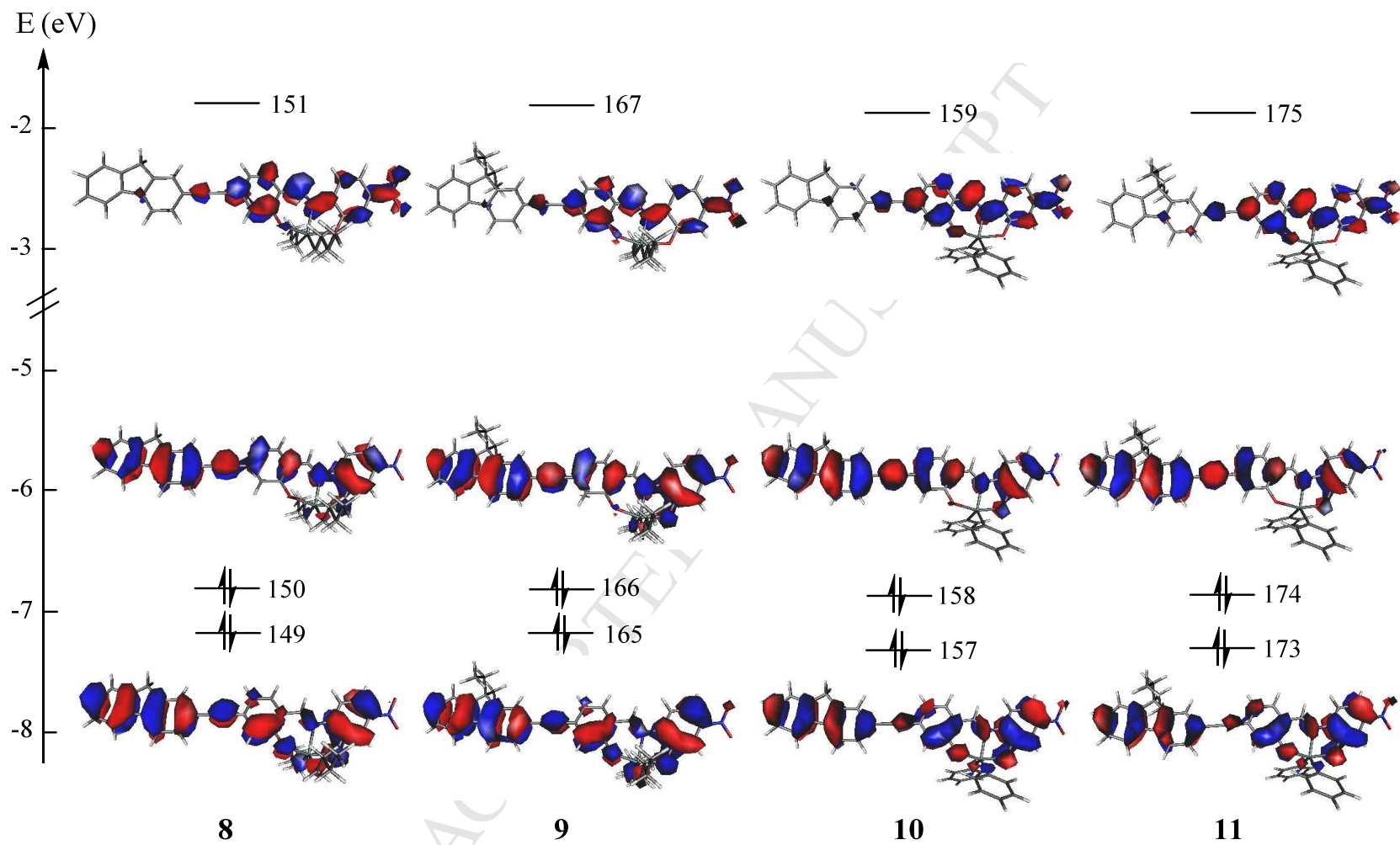


Figure 3.- Frontier orbitals involved in the low-lying transitions of 8-11, with relative energies.

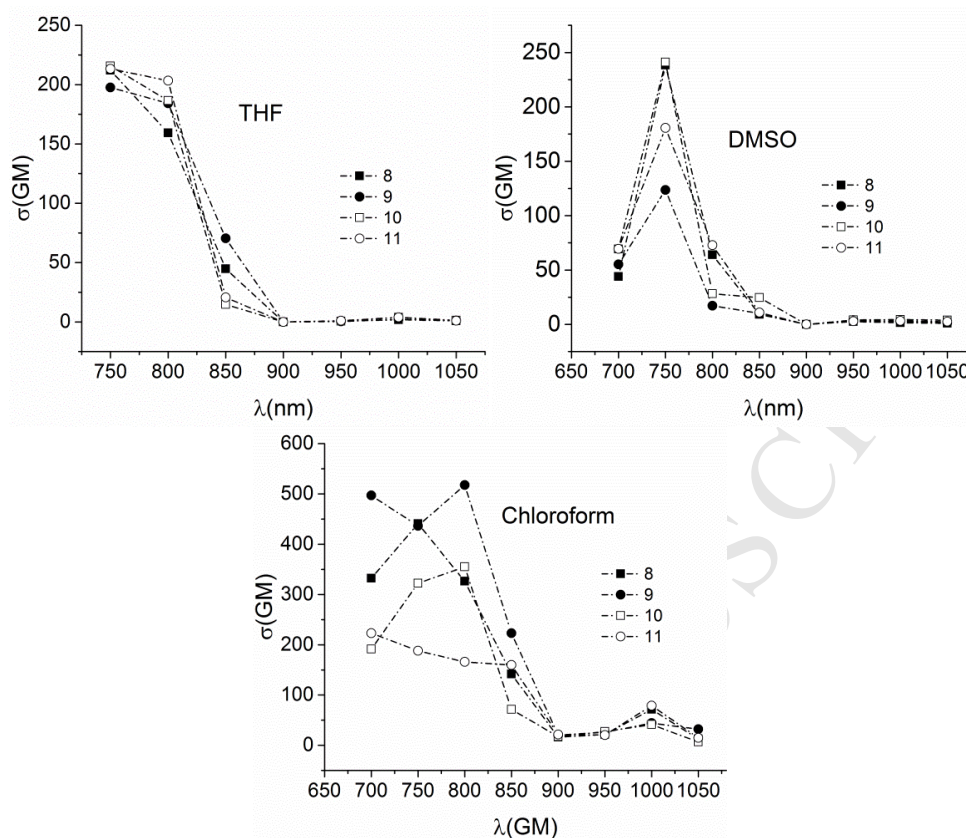


Figure 4. σ_{TPA} at different wavelength in THF (upper left panel), DMSO(upper right panel) and CHCl_3 (lower panel)

The nonlinear absorption spectra show that the excited states corresponding to OPA band at 400 nm can be also produced by TPA activity, providing a maximum σ_{TPA} around 750 nm when DMSO or THF are used as solvents. The OPA band at 490 nm has a weak TPA response at 1000 nm (roughly observed in TPA spectra). In contrast, in chloroform, the excited states corresponding to the band at 490 nm exhibits clearly enhanced TPA response at 1000 nm, in addition to the band at 800 nm (400 nm of OPA). From the examination of Figure 4, the role of the substituents (butyl and phenyl) on the σ_{TPA} it seems to have a significant effect in chloroform in the range from 700 to 800 nm with σ_{TPA} values of **8** and **9** being larger than **10** and **11**, however in THF or DMSO there is not a substantial difference between dibutyl and diphenyl substituent.

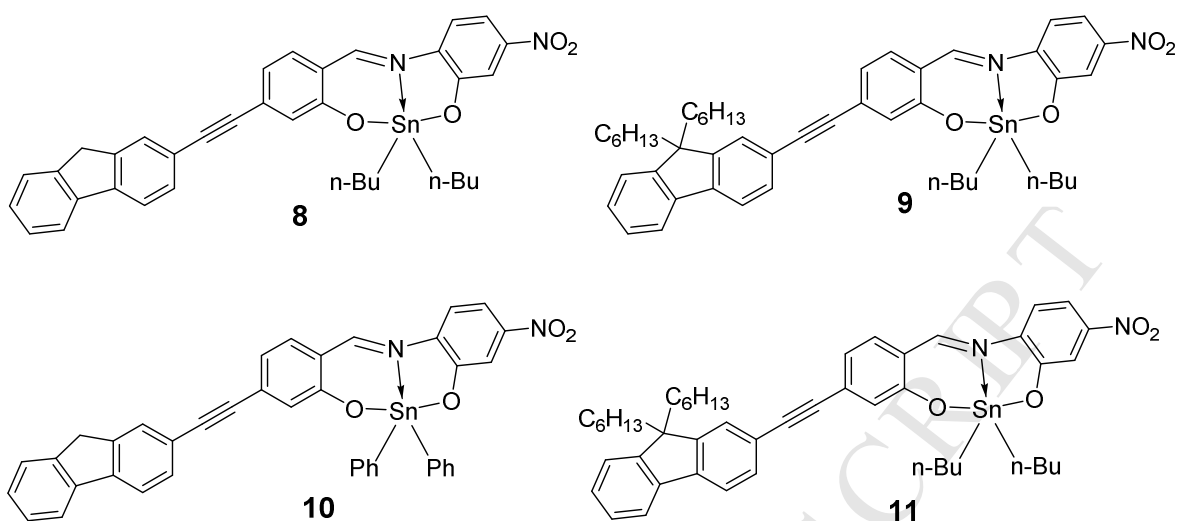


Figure 5.- Organotin compounds synthesized in this work.

The need to develop chromophores that are highly soluble in organic solvents is achieved by the introduction of the hexyl chains on the fluorene, with the expectation that this shall not interfere significantly in the optical properties, however as can be seen in the Figure 4 this is not the case for σ_{TPA} , in DMSO when the hexyl chains are present (**9** or **11**) the TPA is higher than without it (**8** or **10**), in chloroform it seems to be the opposite, and in THF there is not a substantial difference

Comparison of the values obtained for **10** and **11** with those of a similar molecule, shows that the σ_{TPA} for the molecules described in this work is approximately 10 times larger than the value in a previous report (see Figure 6).[11] This enhancement of the TPA can be attributed to an increased π conjugation as a result of the introduction of the fluorene moiety and the triple bond.

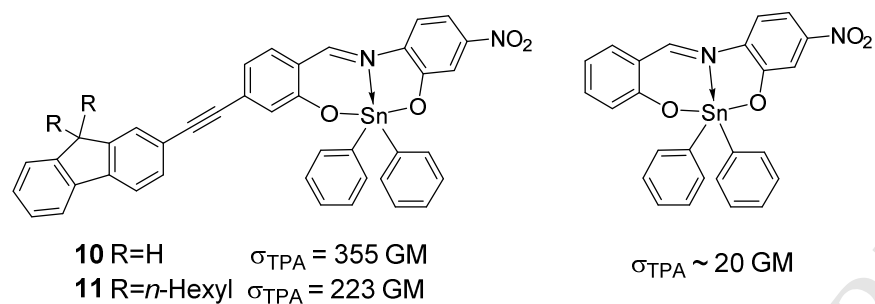


Figure 6.- Comparison of σ_{TPA} for **10** and **11** (left), a previously reported molecule (right).

4.- CONCLUSIONS

We synthesized four novel pentacoordinated diorganotin compounds which were fully characterized. A solvatochromic study showed no dependence on solvent polarity pointing out to the existence of specific interactions and a small change in the dipole moment. These complexes can be grouped depending on the substituent of the tin atom, either diphenyl or dibutyl, due to the small changes in their optical properties attributed only to the rigidity of the framework provided by the tin center, which is better for the phenyl substituent than the butyl. The TPA spectra were evaluated in three different solvents, in all cases, the band located around 400 nm in the OPA spectra was TPA active with a σ_{TPA} up to 517 GM for **9** when using chloroform as solvent, the band located around 500 nm in the OPA spectra was also active for the four complexes. Furthermore the maximum brightness observed in our complexes was 150 GM that corresponds to **9** in chloroform, which is ten times larger than the one measured by Peon et al[11] and almost twice as large than the one measured by Tian et al[9] (95 GM in DMF). These results suggest that these complexes can be used for Two-Photon Microscopy, due to their better brightness.

The new tin complexes show an enhancement in the TPA property probably related to an increase in the π conjugation pathway due to the presence of the fluorene (donor) and the

nitro (acceptor) group. Both, the TPA and fluorescence properties were then improved compared with other organotin compounds, also with the introduction of a dialkylated fluorene the solubility of this type of compounds is greatly enhanced allowing for further applications in solution.

5.- SUPPORTING INFORMATION

UV-vis/fluorescence spectra and solvatochromic analysis, ^1H NMR, ^{13}C NMR, ^{119}Sn NMR and infrared spectra for the compounds **8-11**, molecular geometries and orbitals energies obtained by DFT calculations.

6.- ACKNOWLEDGEMENTS

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ACCEPTED MANUSCRIPT

Four novel pentacoordinated diorganotin compounds were synthesized and fully characterized.

The Two-Photon absorption spectra was recorded in three different solvents resulting in a maximum of 517GM and a brightness of 150GM.

An enhancement of the two-photon absorption properties are achieved thanks to the introduction of a fluorene moiety.