Experimental determination of the two-photon absorption cross sections of Silicon and Tin^{IV} compounds

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We have experimentally determined the two-photon absorption cross sections (δ) of two silicon phthalocyanines and a series of seven tin^{IV} derivatives with substituted salicylidene-2-aminophenols by the two-photon excitation fluorescence technique. The determination of δ for the phthalocyanines (Pcs) was found to be limited by one-photon absorption at wavelengths near the first electronic transition. δ values for tin^{IV} compounds were below 20×10^{-50} cm^4 s photon^{-1}, one to two orders of magnitude lower than those found for Pcs. The differences on δ due to the nature and position of the substituents were noticeable enough to establish an initial relationship between the molecular structure and the non-linear optical properties for these Tin^{IV} compounds.

Keywords: Two-photon excitation fluorescence; two-photon absorption cross section; two-photon absorption.

Mediante la técnica de detección de fluorescencia por excitación de dos fotones, se determinaron experimentalmente los valores de la sección eficaz de absorción de dos fotones (δ) para dos ftalocianinas de silicio y siete derivados de estaño^{IV} con saliciliden-2-aminofenoles sustituidos. Se encontró que a longitudes de onda cercanas a la primera transición electrónica, la determinación de δ para las ftalocianinas (Pcs) está limitada por la existencia de procesos de absorción monofotónica. Todos los valores de δ para los compuestos de estaño^{IV} están por debajo de los 20×10^{-50} cm^4 s fotón^{-1}, de uno a dos órdenes de magnitud menores que los encontrados para las Pcs. Gracias a las diferencias en los valores de δ originados por la posición y naturaleza de los sustituyentes incluidos en los compuestos de estaño^{IV}, fue posible establecer una correspondencia inicial entre sus propiedades ópticas no lineales y su estructura.

Descriptores: Fluorescencia por excitación de dos fotones; sección eficaz de absorción de dos fotones; absorción de dos fotones.

1. Introduction

Since it was first predicted by Marie Göppert-Mayer [1], the absorption of two photons in the same quantum event has become a sustained issue of interest at both atomic and molecular levels. Molecules that can be excited by the simultaneous absorption of two photons have attracted considerable attention because of their numerous applications [2-5]. Due to the fact that most organic molecules have small two-photon absorption (TPA) capacities, reflected on low two-photon absorption cross sections (δ) of the order of 10^{-50} cm^4 s photon^{-1}, there has been a continuous effort directed to understand the features that can drive a molecule to have large δ values. It has been proposed that some of the major contributors to this are the extension of the conjugation in the molecule and an increase in the transition dipole moments involved in the TPA transitions ($S_{dark} \leftarrow S_0$ and $S_n \leftarrow S_{dark}$), which is in turn related to a substantial intramolecular charge transfer upon excitation... [2,3]. The common approaches to achieve such goals are based on the use of extended π systems and the inclusion of several charge donating and withdrawing groups in the same molecule [2-4].

For this study we have measured δ for two silicon phthalocyanines (compounds **1** and **2**) and a series of seven

Tin^{IV} derivatives with doubly hydroxylated Schiff bases (compounds **3-9**; see Scheme 1) in the 760-820 nm range. We have taken advantage of the fluorescent character of these metallated compounds to determine their δ by the two-photon excitation fluorescence (TPEF) technique [5-7] that is based on the integration of the fluorescence coming from a rapidly populated first single excited state (S_1) after the TPA process drives the molecule to a symmetry allowed upper singlet excite state (S_n) lying above S_1. The different molecular systems presented herein were chosen on account of several important properties:

(i) phthalocyanines (Pcs) are π delocalized macrocycles that are well known for their optical non-linearity response[2,8];

(ii) in addition of having higher thermal stability, metallated Pcs allow the inclusion of axial ligands that improve their solubility by reducing the $\pi - \pi$ staking, which is also responsible for a fast depletion of the excited states [8-10]; and

(iii) the Tin^{IV} derivatives with doubly hydroxylated Schiff bases offer a contrasting picture when compared with their parent Schiff base salicylidene-2-aminophenol

(**10**) since this last shows a low fluorescent nature due to its fast excited state decays.

We have compared the excited state dynamics of the tin^{IV} compound **3** with those of the free Schiff base **10** by time-resolved fluorescence up-conversion experiments, and found a dramatic fluorescence lifetime increase for **3**. The enhanced fluorescent character of the easy-to-synthesize Tin^{IV} compounds allowed their characterization by fluorescence-based techniques and the study of the effects that different substituents have on their TPA properties.
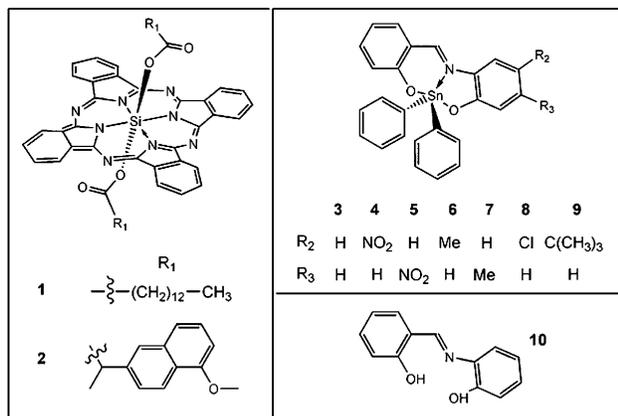
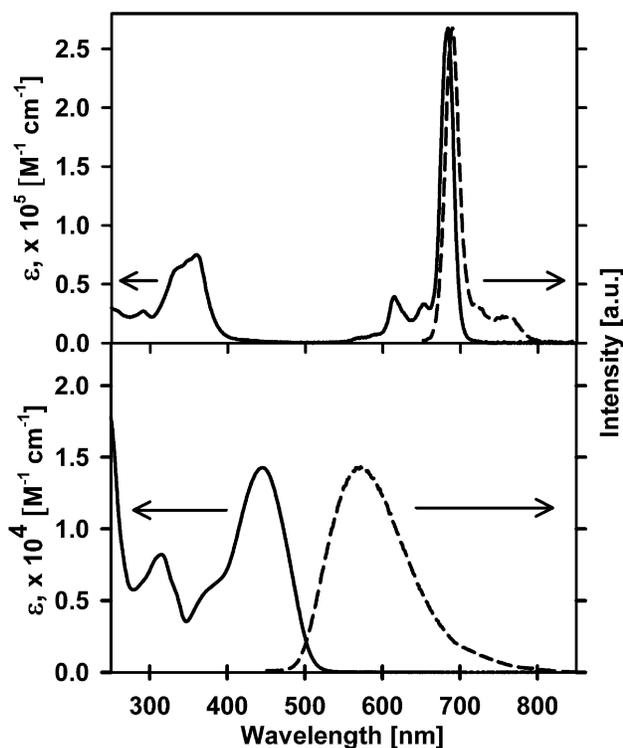SCHEME 1. Molecular structures of the compounds of this study.

FIGURE 1. Steady-state absorption (solid line) and normalized fluorescence (dashed line) spectra of compounds **1** (top) and **3** (bottom).
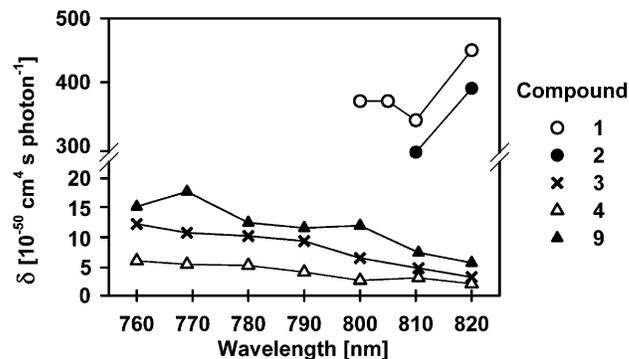

FIGURE 2. Two-photon absorption cross sections (δ) of **1** and **2** in dichloromethane solution, and **3**, **4**, and **9** in ethanol solution. Standard deviations from three independent measurements are of approximately 15%.

2. Experimental methods

Starting materials were purchased from Aldrich and used without further purification. Compounds **1** and **2** were obtained from a 2.5 hrs DMF reflux of silicon phthalocyanine dichloride and the corresponding sodium salt of the specific carboxylic acid (sodium myristate for **1**, and sodium (S)-(+)-naproxenate for **2**). Compounds **3**-**9** and **10** were obtained as indicated in Refs. 11 and 12, respectively. Characterization data for all compounds matches with that previously reported [9-12].

All solvents used for optical measurements were HPLC quality (Aldrich). Steady-state absorption and fluorescence spectra were taken with Cary-50 and Cary-Eclipse spectrophotometers (Varian), respectively. To determine δ we followed the TPEF technique [5-7], using a mode-locked Ti:Sapphire laser pumped by a 5 W Verdi V5 laser (Coherent Inc.) to obtain a 100 MHz femtosecond pulsed train tunable in the 750-890 nm range that was passed through a fused silica compressor and a half wave plate followed by a calcite Glan-Taylor polarizer before it was focused into the center of a 1 cm length quartz cell containing the continuously stirred liquid samples. The two-photon excitation fluorescence emission was focused and detected by a UV-vis portable spectrophotometer (Ocean Optics) with variable integration time. δ values were calculated as indicated elsewhere [5-7], using Rhodamine B (Aldrich) in methanol as a standard. Fluorescence quantum yields, necessary to calculate δ here also calculated with reference to Rhodamine B in methanol, as pointed out in Ref. [6]. The time duration of the pulses was measured to be 100 fs (FWHM) through second-harmonic generation auto-correlation measurements.

Our fluorescence up-conversion experiments were carried out as previously reported [13], with the polarization of the pump beam set to the magic angle. The instrument response function was determined by Raman dispersion of the solvent, and found to be 190 ± 5 fs. The obtained data were modeled as exponential decays analytically convoluted with the instrument response function.
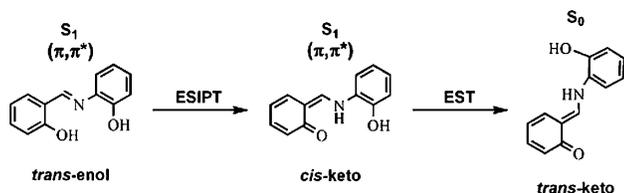
SCHEME 2. Resumed photoinduced pathway of the free Schiff base **10** showing the excited state intramolecular proton transfer (ESIPT) and excited state tautomerization (EST). Besides the tautomerization towards the *trans*-keto form, depletion of the *cis*-keto isomer is also due to other radiationless processes [13-15].

3. Results and discussion

Figure 1 shows typical steady-state absorption and fluorescence spectra of a representative case for each series of compounds. From Fig. 2 (top), it can be seen that δ values of **1** and **2** in dichloromethane are in the 300-450 10^{-50} cm^4 s photon^{-1} range, in agreement with the interval of earlier reported data for somewhat similar systems [2]. The relatively small wavelength range at which we report δ for Pcs is due to the non-negligible contribution of monophotonic excitation occurring together with the TPA process. That is, for **1** and **2** there is also a contribution of one-photon absorption below 800 and 810 nm, respectively. The characterization of the excitation as an exclusive TPA event was carefully done by testing and assuring a square dependence of the obtained fluorescence signal with beam intensity. Although at a first glance the two-photon excitation wavelength may appear to be far from the first allowed optical transition, the broad spectral distribution of the Gaussian-shaped excitation pulses can be enough to slightly overlap with the red edge of the absorption $S_1 \leftarrow S_0$ band centered around 690 nm, allowing one-photon processes to occur. This appears to restrict the experimental measurement of the highest δ values expected for Pcs since the sum-over-states procedure followed for δ calculations [2,3] suggests that TPA would become significant where the excitation energy is near the $S_{dark} \leftarrow S_0$ transition, being S_1 a likely intermediate state (S_{dark}) in Pcs systems [2].

Figure 2 also shows representative data for the tin^{IV} series compounds in ethanol solutions. For all of them, the δ values are below 20 10^{-50} cm^4 s photon^{-1}. Such considerably lower values than those measured for Pcs may be explained by the lower π conjugation on the tin^{IV} compounds. The δ differences on **3-9** arising from the included substituents are noticeable enough to establish an initial structure-properties relationship: The electron donor groups at R$_2$ position and electron withdrawing groups at R$_3$ position (see Scheme 1 for position numbering) are responsible for an increase in δ due to the apparent inferred enlargement of the aromaticity in the overall system. The fluorescent character which made possible the determination of δ for all tin^{IV} compounds by the TPEF technique is far from the very low fluorescent character of their basic framework free Schiff base **10**. Similarly to other related Schiff bases, the excited state dynamics of **10** comprises two fast processes that are

essential to explain its low fluorescence: an excited state intramolecular proton transfer and an excited state tautomerization [13-15]. Scheme 2 resumes these two processes on the photoinduced pathway of **10** that takes place once the *trans*-enol S_0 state has been excited. We have resolved the emission component coming from the $^1(\pi - \pi^*)$ *cis*-keto excited isomer of **10** in ethanol solution by ultrafast fluorescence up-conversion experiments and found its depletion time to be 39 ± 1 ps ($\lambda_{exs} = 422$ nm, $\lambda_{ems} = 517$ nm). Numbers in parentheses indicate the excitation (λ_{exc}) and the emission detection (λ_{ems}) wavelengths. In contrast to **10**, compound **3** has an overall 'long' decay time of 1.70 ± 0.1 ns ($\lambda_{exs} = 422$ nm, $\lambda_{ems} = 580$ nm) also in ethanol solution. From the noticeable increase of more than 40 times in the fluorescence lifetimes when going from **10** to **3**, and from the fluorescent character of other related compounds [16], the tin^{IV} center can be seen as a molecular feature that holds the Schiff base skeleton impeding excited state tautomerization processes that otherwise would rapidly deactivate the fluorescent excited states.

4. Conclusions

We have determined δ for 9 different silicon and tin^{IV} compounds in the 760-820 nm range. The experimental determination of δ for **1** and **2** near the first optical transition is limited by the existence of one-photon absorption processes. By verifying the excitation as an exclusive TPA event at wavelengths above 790 nm, we were able to get as close as possible to the first electronic transition, which is likely to correspond to the S_{dark} state [2]. Besides the fact that the studied Pcs are important models towards the design of molecules with optical non-linearity response and improved solubility, our results can be seen as reliable data to be compared with further theoretical investigations.

Compounds **3-9** have an increased fluorescent character when they are compared with the basic framework **10**. This improved emissive quality allows their characterization by fluorescence-based procedures, such as the TPEF technique to estimate their TPA properties. On behalf of the differences found in δ due to the position and nature of the substituents included, we were able to establish an initial relationship between their structure and properties. In this respect, compounds **3-9** can be proposed as parent molecules to be used for the design of related compounds with convenient δ values, tuned by the inclusion of different substituents and π-bonded groups.

1. M. Göppert-Mayer, *Ann. Phys.* **401** (1931) 273.

2. X. Zhou, A.M. Ren, J.K. Feng, and X.J. Liu, *Can. J. Chem.* **82** (2004) 19.

3. M. Albota *et al.*, *Science* **281** (1998) 1653.

4. Ó. Rubio-Pons, Y. Luo, and H. Agren, *J. Chem. Phys.* **124** (2006).

5. D.A. Oulianov, I.V. Tomov, A.S. Dvornikov, and P.M. Rentzepis, *Opt. Commun.* **191** (2001) 235.

6. A. Fischer, C. Cremer, and E.H.K. Stelzer, *Appl. Opt.* **34** (1995) 1989.

7. C. Xu and W.W. Webb, *J. Opt. Soc. Am. B: Opt. Phys.* **13** (1996) 481.

8. Q. Zhong, Z. Wang, Y. Liu, Q. Zhu, and F. Kong, *J. Chem. Phys.* **105** (1996) 5377.

9. J.L. Sosa-Sánchez *et al.*, *J. Porphyrins Phthalocyanines* **6** (2002) 198.

10. J.L. Sosa-Sánchez *et al.*, *Chem. Eur. J.* **11** (2005) 4263.

11. H.I. Beltrán, C. Damian-Zea, S. Hernández-Ortega, A. Nieto-Camacho, and M.T. Ramírez-Apan, *J. Inorg. Biochem.* **101** (2007) 1070.

12. V. Barba, D. Cuahutle, R. Santillan, and N. Farfán, *Can. J. Chem.* **79** (2001) 1229.

13. W. Rodríguez-Córdoba, J.S. Zugazagoitia, E. Collado-Fregoso, and J. Peon, *J. Phys. Chem. A* 111 (2007) 6241.

14. P.F. Barbara, L.E. Brus, and P.M. Rentzepis, *J. Am. Chem. Soc.* **102** (1980) 5631.

15. P.F. Barbara, P.M. Rentzepis, and L.E. Brus, *J. Am. Chem. Soc.* **102** (1980) 2786.

16. K. Morisige, *J. Inorg. Nucl. Chem.* **40** (1978) 843.