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multi-photon absorption spectra

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14. ABSTRACT

This report presents the progress we have made on the project Determination of multi-photon absorption spectra: a comparison between transmittance change and fluorescence methods, and refers to the period from November/2013 to February/2015. Initially we present new results on the two-photon absorption cross-section of a specific platinum acetylide complex. Then a summary of the 2PA studies in the whole family of platinum acetylide complexes, investigate during this period of three years is presented, as well as a comparison between Z-scan and fluorescent methods to obtain the 2PA spectra. Finally, the three-photon absorption spectrum of the platinum acetylide complexs is presented and discussed.

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Determination of multi-photon absorption spectra: a comparison between transmittance change and fluorescence methods

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Objectives

The goal of this project is to determine the multi-photon absorption spectrum of organic compounds, in order to establish its correlation with the molecular structure, to develop strategies to improve the nonlinear optical response of materials, with implications in photonic devices. Such task will be carried out using transmission measurements, such as the Z-scan, as well as fluorescence methods. The results interpretation we will be performed by using the sum-over-essential-states approach, combined with quantum-chemical calculations within the DFT framework.

Status of effort

This report presents the progress we have made on the project *Determination of multi-photon absorption spectra: a comparison between transmittance change and fluorescence methods*, and refers to the period from November/2013 to February/2015. Initially we present new results on the two-photon absorption cross-section of a specific platinum acetylide complex. Then a summary of the 2PA studies in the whole family of platinum acetylide complexes, investigate during this period of three years is presented, as well as a comparison between Z-scan and fluorescent methods to obtain the 2PA spectra. Finally, the three-photon absorption spectrum of the platinum acetylide complexs is presented and discussed.

Accomplishments

The platinum acetylide complexes (PE's) are materials with remarkable optical properties as such as high singlet and triplet absorption (from 10^4 to 10^5 $M^{-1}cm^{-1}$) [1-4], efficient generation of singlet oxygen [5], intense two (thousands of GM units) [3, 6] and three-photon absorption (~10^{-78} $cm^6.s^2.photon^{-2}$) [7], ultrafast intersystem crossing (from fs to ps) and long phosphorescence time (μs). [8] These characteristics are directly associated with the acetylide group that allows high electron mobility and the metallic center (platinum) with weak bound electrons, which provides a metal-to-ligand or ligand-to-metal charge transfer, ideal to nonlinear optical applications. [9, 10] Among the possible applications of these materials, we can cite ones related with chemosensing [11], photodynamics therapy [8, 12], optical switching [13] to name a few.

One of the first PEs to have their nonlinear optical properties investigated was the *trans*-Pt(PBu_3)$_2$ (C≡C-C_6H_4-C≡C-C_6H_5)$_2$, named **PE2**, by Staromlynska et. al. [14]. According to their results, there is a direct transition from the ground state (S_0) to the T_0 state at 520 nm, indicating that the triplet state absorption dominates the nonlinear optical effect for pulse lengths from picoseconds to hundreds of nanoseconds.

To avoid the mixing between the single and triplet states absorptions and to obtain the "pure" 2PA spectrum for the **PE2**, we have used 160-fs laser pulses operating at low repetition rate (1 kHz). The short pulse duration allows one to obtain pure 2PA because only negligible absorption from the population generated in the excited states happens, while the low repetition rate (1 KHz) helps to avoid cumulative effects between consecutive pulses, coming from possible triplet-triplet absorption. In this context, herein we report the two-photon spectrum of **PE2** platinum acetylide complex from the visible to the near-infrared. The 2PA absorption spectrum was measured using the Z-scan technique with femtosecond pulses. As shown in Fig. 1, the **PE2** present high conjugation length, composed by alternate single and double (or triple) bonds, which, in principle, should increase the nonlinear optical properties.

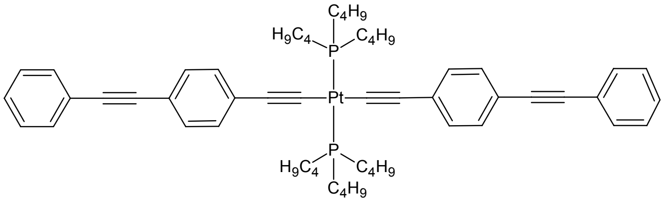


Figure 1 - Molecular structure of platinum acetylide complexes *trans*-Pt(PBu_3)$_2$ (C≡C-C_6H_4-C≡C-C_6H_5)$_2$.

Figure 2 presents the experimental molar absorptivity (squares), experimental 2PA spectra (diamonds) and theoretical 2PA spectra (solid line), in which the last one was obtained by Nguyen et. al. [9] for the **PE2** platinum acetylide complex. The **PE2** absorption spectrum presents the lowest energy band centered at 357 nm with maximum molar absorptivity of 8.95 x 10^4 $M^{-1}cm^{-1}$ in dichloromethane. This band is related to the $S_0 \rightarrow S_1$ ($\pi\pi^*$) transitions with strong metal-to-ligand charge transfer character.

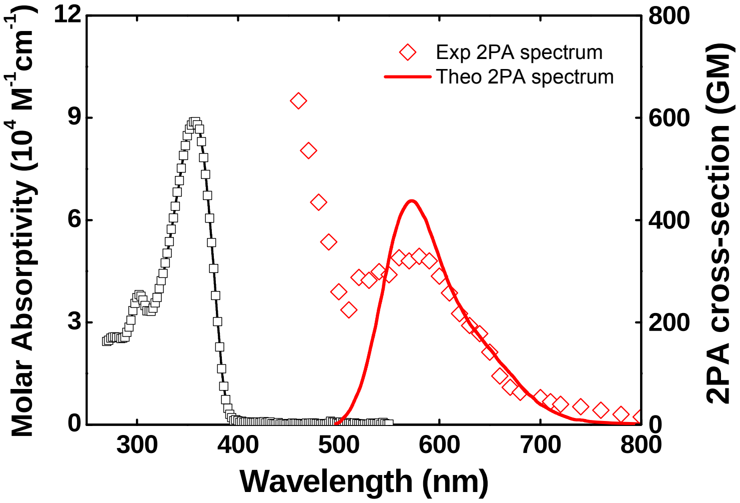


Figure 2 – Ground-state molar absorptivity (squares – left axes), experimental 2PA spectra (diamonds – right axes) and theoretical 2PA spectra (solid line) of **PE2**, in which the latter was reported in Ref. [9]. The standard deviation in the experimental 2PA cross-section was determined to be 20 %.

The linear spectrum (molar absorptivity) reveals that the absorption is entirely located in the near-UV region, shorter than 400 nm, which indicates to be completely transparent in the visible range, ideal to applications in photonic. In addition, as previously described by Staromlynska et. al. [14], **PE2** presents a very small absorption peak at 520 nm with molar absorptivity extremely low (1.3 $M^{-1}cm^{-1}$) assigned the direct $S_0 \rightarrow T_1$ transition.

In Fig. 2, the diamonds illustrate the 2PA spectrum obtained for the **PE2** in dichloromethane solution using 160-fs laser pulses and low repetition rate (1 kHz). As it can be noted, the experimental 2PA spectrum for the **PE2** exhibits two bands located at 570 and 710 nm with cross-section of approximately 320 and 45 GM, respectively, as well as the resonant enhancement effect observed for wavelengths shorter than 500 nm. In Fig. 3, we show a few of our Z-scan curves corresponding to the three spectral regions previously described as well as the irradiance employed during the experiments. The decrease observed in the normalized transmittance as a function of the z position indicates a 2PA process, since excitation took place in nonresonant conditions.

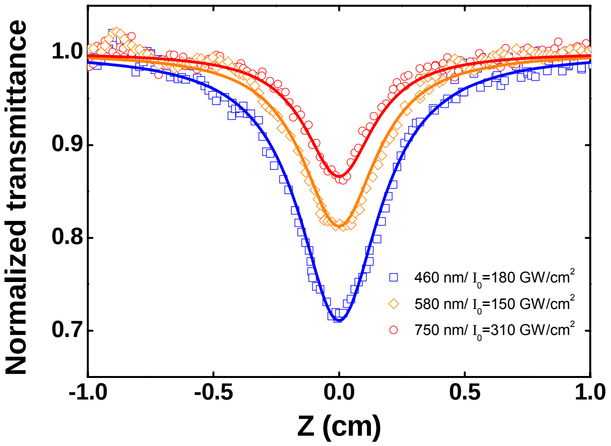


Figure 3 – Open-aperture Z-scan curves for the three different regions described along the nonlinear spectrum as well as the irradiance employed during the experiments. The solid lines represent the fitting employing the Eq. (1).

It is worth mentioning that at 595 nm, we found 2PA cross-section value around 290 GM for the **PE2**, which is approximately 1.23 times higher than one obtained by Staromlynska et. al. [14] by means of picosecond laser pulses. This value is within of our experimental error estimated at 20 %. Moreover, the authors from Ref. [14] used a 10 mm cuvette for the nonlinear absorption measurements, which is much higher than the Rayleigh length of the laser beam ($z_0 \sim 2.0$ *mm*) [20]. Moreover the authors used a concentration ten times higher than ones used in our Z-scan measurements, which may interfere considerably in suitable determination of the 2PA cross-section. Other point that can be considered to explain the difference in the 2PA cross-section is the population on the excited singlet and triplet states [15-19]. In this case, for longer pulse widths (ps and ns), excited state absorption are not anymore negligible. Consequently, for longer pulses, the total absorption cross-section has contribution from a 2PA transition and 1PA excited state transitions that, at the present case, could decrease the effective absorption cross-section due to a lower excited state absorption cross-section at the excitation wavelength.

It is important to mention here that at last few years, in nonlinear optical measurements, the resonant enhancement have been widely explored because it is possible to obtain nonlinear optical effects extremely high only tuning the excitation wavelength close to the first one-photon allowed excited state [21-23]. Alternatively, it is also possible to tune the optical bandgap of material through the molecular engineer to obtain in determined spectral range as the telecommunications region (1300-1550 nm) extraordinary nonlinear optical effects [24]. Based on these points, we can observe that **PE2** presents a monotonic increase on the 2PA cross-section in the enhancement effect region given an increase of about 14 times of magnitude (635 GM at 460nm) if compared with the lowest energy 2PA band peak at 710 nm.

In order to verify if the maximum peak intensity used in Z-scan experiments could cause photodegradation or interfere in determination of the 2PA cross-section, we display the normalized transmittance as a function of the irradiance at 570 nm in Fig. 4, corresponding to the peak of the higher energy 2PA band. As can be seen, in the irradiance range used, the **PE2** molecule does not present any spurious effect that could contribute to an inappropriate determination of the 2PA cross-section. The value obtained through of this experiment correspond exactly to one found by means of Z-scan technique at 570 nm. Alternatively, to verify if any photodecomposition was taking place during the Z-scan, we measured the linear absorption spectra after the experiment and we did not observe any degradation for the intensity range used.

Recently, Nguyen et. al. [9] theoretical investigated the one- and two-photon absorption spectra of platinum acetylide chromophores using time-dependent density functional theory (TDDFT). In that paper, they studied the influence of different conformations on the ground state geometry of the chromophores on the linear and 2PA spectra.

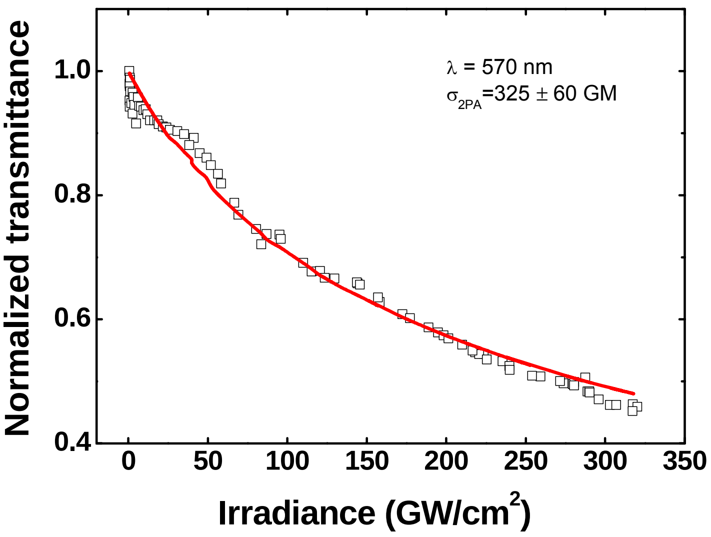


Figure 4 – Normalized transmittance as a function of irradiance at 570 nm for **PE2** in dichloromethane solution (optical length of cuvette used 2 mm). The solid lines represent the fit obtained using a model based only in 2PA.

Because of the facile rotations of the trimethylphosphinyl and phenylene groups, PEs may exhibit several conformations. In this sense, Nguyen et. al. [9] apply a Boltzmann-weighted average over thermally accessible conformations to obtain the final 2PA spectrum (solid line in Fig. 2). As it can be seen, the theoretical spectrum reproduces well the higher energy 2PA-allowed band for both spectral position and 2PA cross-section magnitude. This band has been assigned preferentially to the 1^1Ag-like→4^1A_g-like transition that is related to the strong intramolecular interaction between the branches due to the presence of platinum atom. Contrariwise, the experimental 2PA spectrum presents a band around at 710 nm with 45 GM (hv = 355 nm), which does not appear in the theoretical spectrum. It is observed that this band has a spectral correspondence with the lowest-energy band of the linear absorption spectrum (~ 357.5 nm).

Recently it has been shown that PEs in solution exhibit a mixing of centrosymmetric and noncentrosymmetric conformations [1]. It is well known that for centrosymmetric molecules, one-photon allowed transitions are two-photon forbidden[25]. However, as PEs exhibit this mixing of conformations, it is expected that the selection rules are relaxed since it is not possible to define precisely the excited state parity [9, 10, 26]. Consequently, transitions are allowed by one and two-photon absorption. As a result, the nature of the lowest-energy 2PA band for the PEs is associated with the breaking of symmetry of these chromospheres in solution. Such behavior generates a permanent dipole moment change ($\Delta\vec{\mu}$) that can be visualized as if the charge density is localized on only one ligand [1].

In the context of the sum-over essential states approach, the value of the permanent dipole moment change is proportional to the 2PA cross-section at the peak in the same transition and can be written as [27, 28]:

$$\left|\Delta\vec{\mu}_{01}\right| = \left(\frac{5}{2(2\pi)^3} \frac{N_A hc}{3\times10^3 \ln(10)} \frac{n}{L^2} \frac{\omega_{01}}{\varepsilon_{\max}(\omega_{01})} \sigma_{01}^{(2PA-\max)}(\omega_{01}) \right)^{1/2} \quad (1),$$

in which *h* is Planck's constant, *c* is the speed of light, $\vec{\mu}_{01}$ is the transition dipole moment, $\Delta\vec{\mu}_{01}$ is the difference between the permanent dipole moment vectors of the excited ($\vec{\mu}_{11}$) and ground ($\vec{\mu}_{00}$) states. $L = 3n^2/\left(2n^2+1\right)$ is the Onsager local field factor introduced to take into account the medium effect with *n=1.424* for dichloromethane at 20°C. $\varepsilon_{\max}(\omega_{01})$ is the molar absorptivity in the frequency (ω_{01}) of the peak of the lowest energy 1PA band, and N_A is the Avogadro's number.

Substituting the 2PA cross-section value obtained through the femtosecond Z-scan technique (~45 GM at 710 nm), we found $\left|\Delta\vec{\mu}_{01}\right| = 3.0 Debye$. Such a value is feasible if the Franck-Condon excitation is localized on only one ligand as has been reported for the PEs family [3, 6, 29, 30]. From the quantum chemical calculations point of view, still remains a challenge to describe correctly the molecular symmetry breaking of PEs in solution and, consequently, the lowest-energy 2PA allowed band observed experimentally.

In order to corroborate that the 2PA spectrum do not have significant contributions coming from the triplet state absorption, we estimate the fraction of the population excited by 2PA that is transferred to the triplet state through intersystem-crossing (~300 ps intersystem-crossing time) and direct transition

($S_0 \rightarrow T_1$) using the rate equation model [30]. Considering the 160-fs duration of our pulse and including the $S_0 \rightarrow T_1$ transition in the methodology reported in Ref. [30], the population transferred to the triplet state at 595 nm, after the 160-fs and 27-ps pulse interaction, is showed in Fig. 5. It is important to mention that the 2PA cross-section and irradiance values used in Fig. 5 corresponds those employed here to fs pulses (290 GM, 260 GW/cm^2) and reported in Ref. [14] to ps pulses (235 GM, 10 GW/cm^2). As it can be noted, the population transferred to the triplet state after fs-pulses irradiation calculated is less than 1% of the population excited to singlet states while to ps-pulses the percentage is of approximately 30 %. Therefore, the influence of the triplet state population in the total nonlinear absorption excited via fs pulses is negligible within our experimental error.

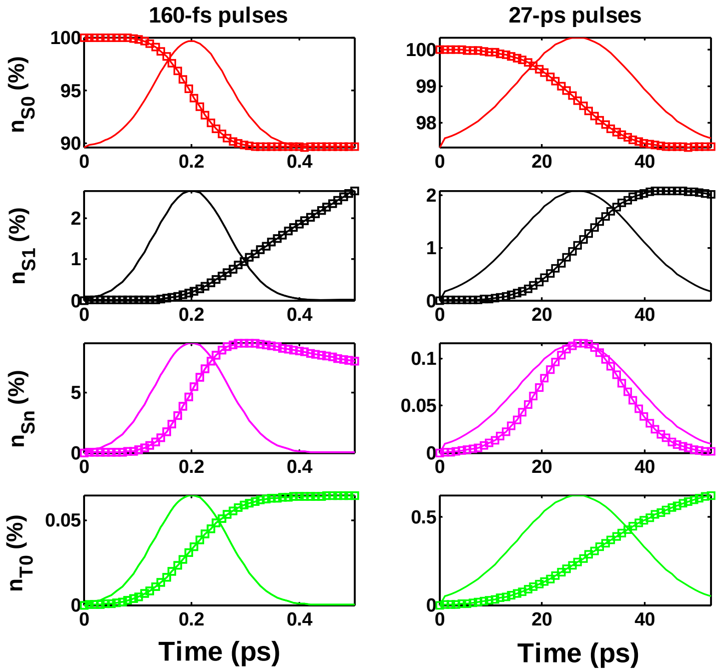
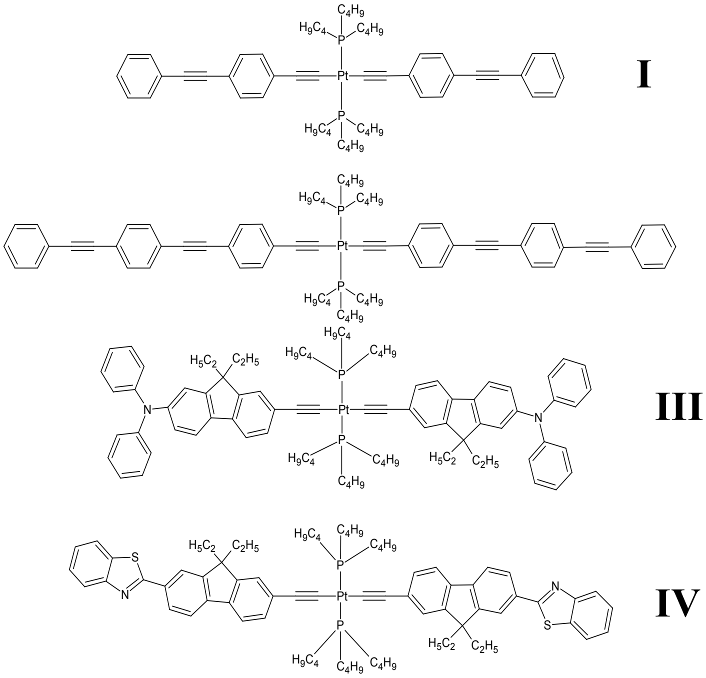


Figure 5 – Calculation of the population dynamics induced by 2PA described by the rate equations at 595 nm (see Ref. [30]). The left side shows the population dynamics after fs-pulses irradiation while the right side shows the ps-pulses irradiation. The solid lines show the normalized laser pulse, while the squares describe the distribution of populations excited by 2PA.

2- Brief summary of 2PA studies in Platinum Acetylide Complexes

The results shown up to this point are the latest ones obtained in this period. Since this is the final report regarding this project, I would like to present a very brief summary of the results obtained in the whole period of 3-years, related to the study of two-photon absorption in the Platinum Acetylide Complex (PAC) studies, displayed in Fig. 6.



I

II

III

IV

Figure 6 - Molecular structures of platinum acetylide complexes studied in the project.

In Fig. 7 we show the 2PA spectra (red squares) for all PACs (presented in Fig. 6), plotted along the linear absorption for each sample. As it can be seen, from the 2PA spectra, there are three main features that appear for all compounds; (1) the resonant enhancement region, (2) a 2PA band around 300 nm and (3) a 2PA band (less intense) around 350 – 400 nm.This 2PA band is typical of both centrosymmetric and noncentrosymmetric platinum acetylide complexes, and can achieve cross-section values from few hundreds up to five thousands GMs, and are ascribed to the transistios displayed in the shaded area of Fig. 7.

As it can be seen from Fig. 7, our results indicate a 2PA for the same transition where there is a 1PA. As we know, a state that is 1PA allowed should be forbidden by 2PA. Therefore, such transition is made possible due to relaxation of the selection rules.

The first 2PA band was attributed to the $S_0 \rightarrow S_1$ (1^1Ag-like→1^1Bu-like) transition, which is made possible because of a relaxation of the selection rules for PAC's that, in solution, present centrosymmetric and noncentrosymmetric conformers.

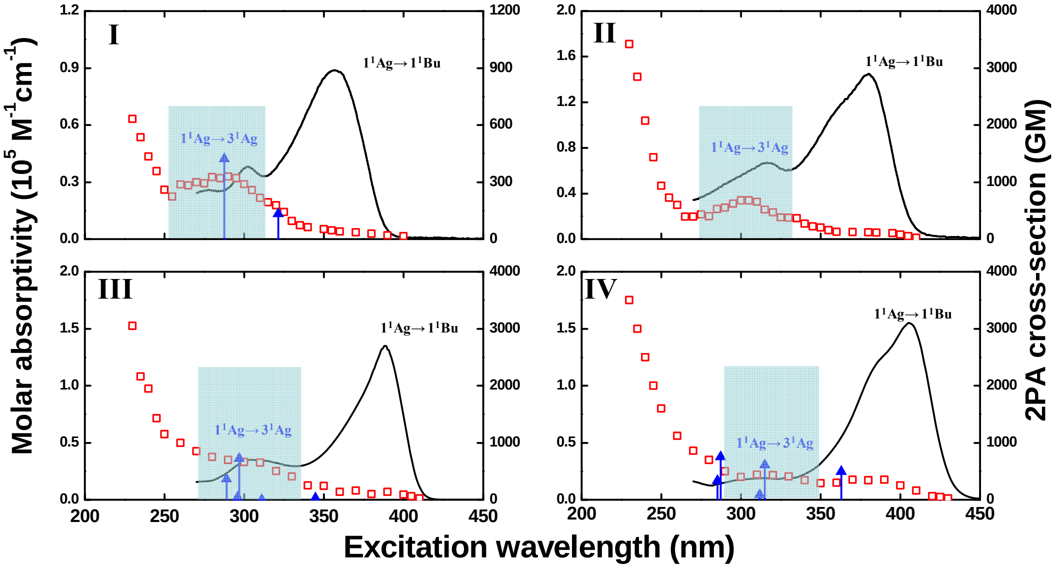


Figure 7 - Experimental 2PA spectra (red squares – right axes) and 1PA spectra (solid line - black) for PACs displayed in Fig. 6.

Therefore, these molecules should present a difference between dipole moment (static or permanent) of the ground state and excited state, since the dipolar contribution term is the one responsible for 2PA in molecules that are noncentrosymmetric. From the 2PA spectra (Fig. 7) we are able to determine the dipole moment change ($\Delta\mu$). Such results as presented in Fig. 8.

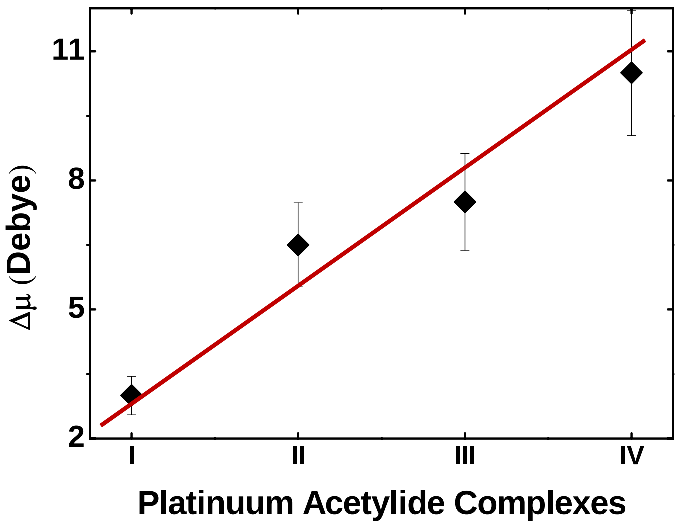


Figure 8 - Dipole moment change (Δμ) obtained from the 2PA spectra for all PACs studied

The results of Fig. 8 reveal that molecule **IV** present the higher value for Δμ, which should indicate that for this molecule a higher charge delocalization is occurring in the excited state. Such break of symmetry, that actually relax the transition selection rules, can be explained due to a large twisting angle of the ligand's phenyl rings relative to the Pt core, which generate a permanent dipole moment difference between the excited and ground state non-null.

Finally, in Fig. 9 we present illustrative results on the comparison between 2PA spectra obtained using the Z-scan approaches (transmissive), performed in our laboratory, with the ones obtained by fluorescence techniques (from literature). As it can be seen, this comparison clearly shows that there is significant differences from results obtained using both methods.

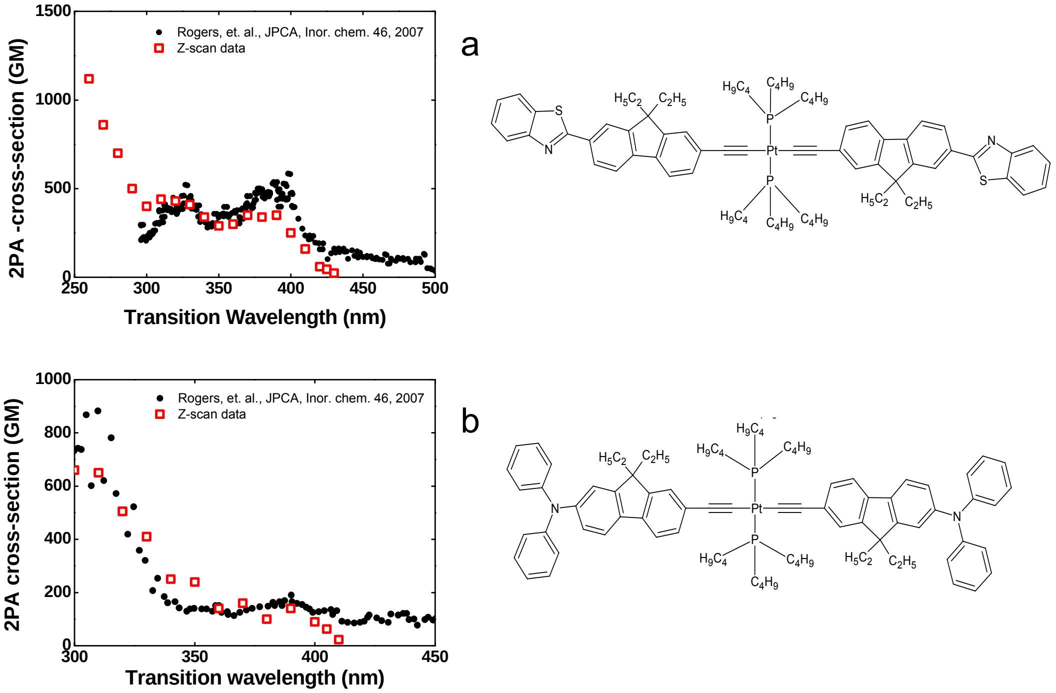


Figure 9 – Comparison between 2PA spectra we measured by using Z-scan technique (square – red) with the ones obtained via fluorescent methods (black circles). Such spectra correspond to the molecules illustrate in the left hand side of the figure.

3- Three-photon absorption in Platinum Acetylide Complexes

We have also studied the three-photon absorption (3PA) spectrum of the PAC´s complexes displayed in Fig. 6, using the Z-scan methods. In Fig. 10 we present typical 3PA Z-scan curves, obtained at 900 nm for the investigated compounds.

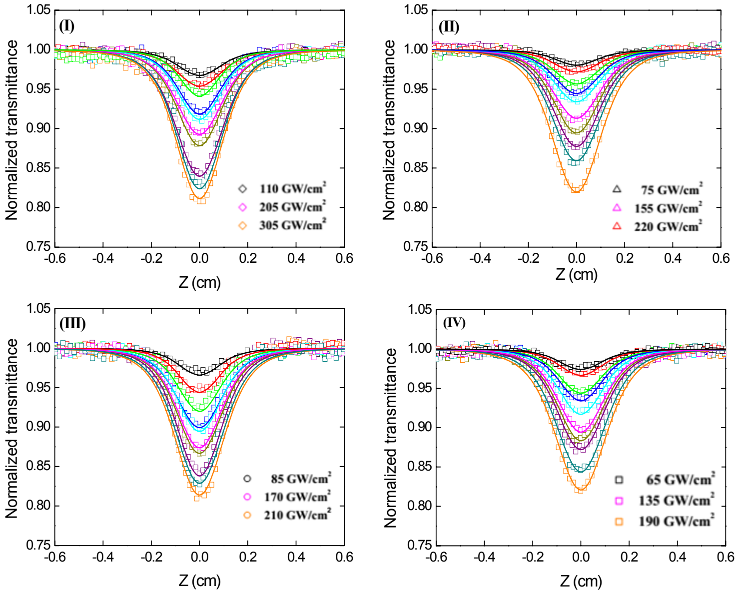


Figure 10 – Z-scan curves of PAC compounds obtained at 900 nm, corresponding to a 3PA process.

To confirm the actual three-photon absorption nature of the observed results, we measured the dependence of the Z-scan normalized transmittance change (ΔT) as a function of the excitation irradiance (Fig. 11). The slope derived from a linear fit (log-log scale) of ΔT as a function of excitation intensity indicates the mechanism of absorption. Therefore, a slope of 1.0 indicates a 2PA, while a slope of 2.0 reveals a 3PA. Slopes whose values are intermediate indicate a mixture of processes. As shown in Fig. 11 (right) for 900 nm, a slope of approximately 2.0 was observed for all compounds, signifying a 3PA mechanisms. Another evidence of the three-photon nature of the observed nonlinear absorption is given in Fig. 11 (left). The dotted line represents the best fitting obtained considering a 2PA process. As it can be seen, the fitting does not describe properly the experimental results. On the other hand, the fitting obtained when the 3PA is considered (solid line) agrees very well with the experimental data.

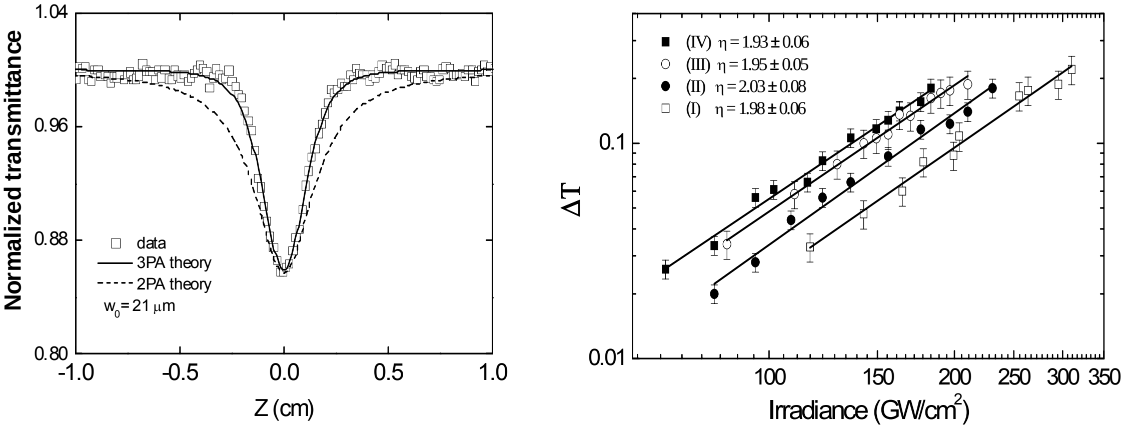


Figure 11 – Experimental **o**pen aperture Z-scan signature for compound **III** at 900 nm. The dotted and solid line represents the best fitting obtained considering a 2PA and 3PA process (left). Normalized transmittance change (ΔT) as a function of the excitation irradiance at 900 nm for the four acetylide platinum complexes. The inset shows the slope for each molecule.

Figure 12 displays the 3PA cross-section spectra of platinum acetylides from approximately 850 nm to 1200 nm (circles). As it can be seen, the 3PA cross-section increases as the excitation wavelength approaches the visible region, reaching values of approximately 3×10^{-78} cm^6 s^2 $photon^{-2}$ for compounds **II**, **III** and **IV;** and 1.6×10^{-78} cm^6 s^2 $photon^{-2}$ for compound **I**. Such behavior, observed for all compounds, is associated to the resonant enhancement of the nonlinearity that takes place when two photons of the excitation wavelength approach the lower two-photon allowed states of the molecules, which are located in visible. The 2PA spectra of this family of compounds cover the entire visible region, with peaks from 600 nm to 750 nm, depending on the compound. It is worth mentioning that the 2PA spectrum of the compounds studied here are negligible in the near infrared (around 850 nm). Additionally, the 3PA spectra for compounds **II**, **III** and **IV** present a band around 1180 nm that correspond to an one-photon allowed state located between 380 - 400 nm. Such transitions are allowed because the electric-dipole selection rules are the same to both types of process (1PA and 3PA).

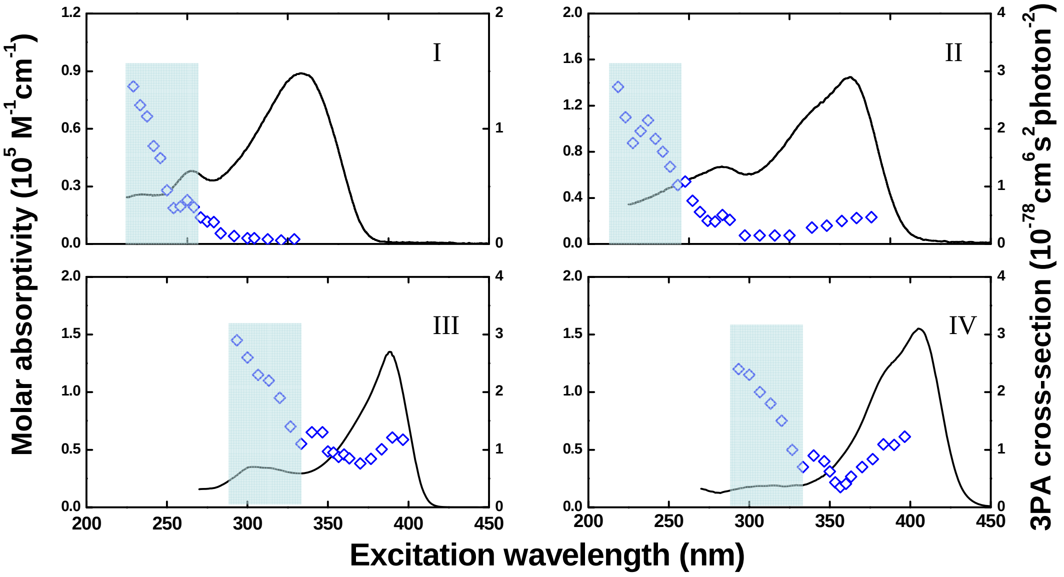


Figure 12 – Normalized absorbance (solid line – left axes) and three-photon absorption (solid circles – right axes) spectra of platinum acetylide complexes.

Personnel Supported

List of personnel involved with the research:

Dr. Cleber R Mendonca

Dr. Leonardo De Boni

Dr. Marcelo G. Vivas

New discoveries, inventions, or patent disclosures

None

Publications discoveries, inventions, or patent disclosures

Paper published in the period from Nov/2013 to Feb/2015 directly related to this project. Considering the whole period (3 years), we have published 11 papers directed related to this project.

1. D. L. SILVA, R. D. FONSECA, M. G. VIVAS, E. ISHOW, S. CANUTO, C. R. MENDONCA, L. DE BONI

Experimental and theoretical investigation of the first-order hyperpolarizability of a class of triarylamine derivatives
J. Chem. Phys. 142, 064312 (2015)

2. J. C. L. SOUSA, M. G. VIVAS, J. L. FERRARI, C. R. MENDONCA AND M. A. SCHIAVON
Determination of particle size distribution of water-soluble CdTe quantum dots by optical spectroscopy
RSC Advances, 4, 36024–36030 (2014)

3. M. G. VIVAS, L. DE BONI, T. M. COOPER AND C. R. MENDONCA
Understanding the Two-Photon Absorption Spectrum of PE2 Platinum Acetylide Complex
J. Phys. Chem. A, 118, 5608−5613 (2014)

4. LEONARDO DE BONI, RUBEN D. FONSECA, KLEBER R. A. CARDOSO, ISABEL GROVA, LENI AKCELRUD, DANIEL S. CORREA, CLEBER R. MENDONÇA
Characterization of Two- and Three-Photon Absorption of Polyfluorene Derivatives
J. Poly. Science B: Polymer Physics, 52, 747-754

5. M. G. VIVAS, D. L. SILVA, J. MALINGE, M. BOUJTITA , R. ZALESNY, W. BARTKOWIAK, H. AGREN, S. CANUTO, L. DE BONI , E. ISHOW, C. R. MENDONCA
Molecular Structure – Optical Property Relationships for a Series of Non-Centrosymmetric Two-photon Absorbing Push-Pull Triarylamine Molecules
Scientific Reports (Nature), 4, 4447, 2014

6. M. G. VIVAS, L. DE BONI,T. M. COOPER, C. R. MENDONCA
Interpreting Strong Two-Photon Absorption of PE3 Platinum Acetylide Complex: Double Resonance and Excited State Absorption
ACS Photonics, 1, 106–113 (2014)

7. M. G. VIVAS, L. DE BONI, L. GAFFO, C. R. MENDONÇA
Investigation of ground and excited state photophysical properties of gadolinium phthalocyanine
Dyes and Pigments, 338–343 (2014)

References

1. Cooper, T.M., et al., *Spectroscopic characterization of a series of platinum acetylide complexes having a localized triplet exciton.* Journal of Physical Chemistry A, 2006. **110**(13): p. 4369-4375.
2. Rogers, J.E., et al., *Photophysical characterization of a series of platinum(II)-containing phenyl-ethynyl oligomers.* Journal of Physical Chemistry A, 2002. **106**(43): p. 10108-10115.
3. Rogers, J.E., et al., *Platinum acetylide two-photon chromophores.* Inorganic Chemistry, 2007. **46**(16): p. 6483-6494.
4. He, G.S., et al., *Multiphoton absorbing materials: Molecular designs, characterizations, and applications.* Chemical Reviews, 2008. **108**(4): p. 1245-1330.
5. Glimsdal, E., et al., *Luminescence, Singlet Oxygen Production, and Optical Power Limiting of Some Diacetylide Platinum(II) Diphosphine Complexes.* Journal of Physical Chemistry A, 2010. **114**(10): p. 3431-3442.
6. Dubinina, G.G., et al., *Phenylene Vinylene Platinum(II) Acetylides with Prodigious Two-Photon Absorption.* Journal of the American Chemical Society, 2012. **134**(47): p. 19346-19349.
7. Vivas, M.G., et al., *Broadband three-photon absorption spectra of platinum acetylide complexes.* Optical Materials Express, 2011. **1**(4): p. 700-710.
8. Ramakrishna, G., et al., *Ultrafast Intersystem Crossing: Excited State Dynamics of Platinum Acetylide Complexes.* Journal of Physical Chemistry C, 2009. **113**(3): p. 1060-1066.
9. Nguyen, K.A., P.N. Day, and R. Pachter, *One- and Two-Photon Spectra of Platinum Acetylide Chromophores: A TDDFT Study.* Journal of Physical Chemistry A, 2009. **113**(50): p. 13943-13952.
10. Yang, Z.D., J.K. Feng, and A.M. Ren, *Theoretical Investigation of One- and Two-Photon Absorption Properties of Platinum Acetylide Chromophores.* Inorganic Chemistry, 2008. **47**(23): p. 10841-10850.
11. Fillaut, J.-L., et al. *Engineering of cyclometallated platinum(II) complexes incorporating acetylide ligands for chemosensing*. in *ICTON Mediterranean Winter Conference*. 2009. Angers: ICTON Mediterranean Winter Conference.
12. Koehler, A. and H. Baessler, *Triplet states in organic semiconductors.* Materials Science & Engineering R-Reports, 2009. **66**(4-6): p. 71-109.
13. Vacher, A., et al., *Cis and trans-bis(tetrathiafulvalene-acetylide) platinum(II) complexes: syntheses, crystal structures, and influence of the ancillary ligands on their electronic properties.* Dalton Transactions, 2013. **42**(2): p. 383-394.
14. Staromlynska, J., et al., *Evidence for broadband optical limiting in a Pt : ethynyl compound.* Journal of the Optical Society of America B-Optical Physics, 1998. **15**(6): p. 1731-1736.
15. Turro, N.J., *Modern Molecular Photochemistry* 1991, University Science Books: Sausalito: University Science Books: Sausalito.
16. McKay, T.J., et al., *Linear and nonlinear optical properties of platinum-ethynyl.* Journal of Chemical Physics, 1998. **108**(13): p. 5537-5541.

17. Rogers, J.E., et al., *Effect of platinum on the photophysical properties of a series of phenyl-ethynyl oligomers.* Journal of Chemical Physics, 2005. **122**(21).
18. Belfield, K.D., et al., *Two-photon absorption cross section determination for fluorene derivatives: Analysis of the methodology and elucidation of the origin of the absorption processes.* Journal of Physical Chemistry B, 2007. **111**(44): p. 12723-12729.
19. Glimsdal, E., et al., *Excited states and two-photon absorption of some novel thiophenyl Pt(II)-ethynyl derivatives.* Journal of Physical Chemistry A, 2007. **111**(2): p. 244-250.
20. Sheikbahae, M., et al., *Sensitive Measurement of Optical Nonlinearities Using a Single Beam.* Ieee Journal of Quantum Electronics, 1990. **26**(4): p. 760-769.
21. Drobizhev, M., et al., *Resonance enhancement of two-photon absorption in fluorescent proteins.* Journal of Physical Chemistry B, 2007. **111**(50): p. 14051-14054.
22. Cirloganu, C.M., et al., *Extremely nondegenerate two-photon absorption in direct-gap semiconductors Invited.* Optics Express, 2011. **19**(23): p. 22951-22960.
23. Hales, J.M., et al., *Design of Polymethine Dyes with Large Third-Order Optical Nonlinearities and Loss Figures of Merit.* Science, 2010. **327**(5972): p. 1485-1488.
24. Mukhopadhyay, S., et al., *Polymethine dyes for all-optical switching applications: a quantum-chemical characterization of counter-ion and aggregation effects on the third-order nonlinear optical response.* Chemical Science, 2012. **3**(10): p. 3103-3112.
25. Lim, E.C., *Excited states*. Vol. 3. 1977, New York: Academic press. 347.
26. Emmert, L.A., et al., *The excited-state symmetry characteristics of platinum phenylacetylene compounds.* Journal of Physical Chemistry A, 2003. **107**(51): p. 11340-11346.
27. Vivas, M.G., et al., *Revealing the Electronic and Molecular Structure of Randomly Oriented Molecules by Polarized Two-Photon Spectroscopy.* Journal of Physical Chemistry Letters, 2013. **4**(10): p. 1753-1759.
28. Vivas, M.G., et al., *Experimental and Theoretical Study on the One- and Two-Photon Absorption Properties of Novel Organic Molecules Based on Phenylacetylene and Azoaromatic Moieties.* Journal of Physical Chemistry B, 2012. **116**(50): p. 14677-14688.
29. Kim, K.Y., et al., *Optimizing Simultaneous Two-Photon Absorption and Transient Triplet-Triplet Absorption in Platinum Acetylide Chromophores.* Journal of Physical Chemistry A, 2010. **114**(26): p. 7003-7013.
30. Vivas, M.G., et al., *Interpreting Strong Two-Photon Absorption of PE3 Platinum Acetylide Complex: Double Resonance and Excited State Absorption.* ACS photonics, 2014.

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Abstract

This report presents the progress we have made on the project Determination of multi-photon absorption spectra: a comparison between transmittance change and fluorescence methods, and refers to the period from November/2013 to February/2015. Initially we present new results on the two-photon absorption cross-section of a specific platinum acetylide complex. Then a summary of the 2PA studies in the whole family of platinum acetylide complexes, investigate during this period of three years is presented, as well as a comparison between Z-scan and fluorescent methods to obtain the 2PA spectra. Finally, the three-photon absorption spectrum of the platinum acetylide complexs is presented and discussed.

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