

# Interpreting Strong Two-Photon Absorption of PE3 Platinum Acetylide Complex: Double Resonance and Excited State Absorption

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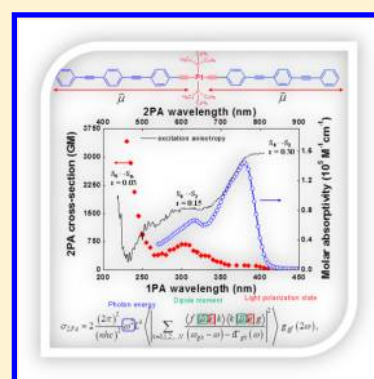
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**ABSTRACT:** This paper reports on the strong two-photon absorption (2PA) of the *trans*-Pt(PBu<sub>3</sub>)<sub>2</sub>(C≡C-C<sub>6</sub>H<sub>4</sub>-C≡C-C<sub>6</sub>H<sub>4</sub>-C≡C-C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (PE3) platinum acetylide complex dissolved in dichloromethane in the visible and near-infrared region. The 2PA spectrum was measured through the open-aperture Z-scan technique using an amplified femtosecond laser system (150 fs) operating at low repetition rate (1 kHz). Since PEs present short intersystem crossing time (ps) and long phosphorescence time (μs), the 2PA cross-section obtained from the Z-scan technique may have contribution from the triplet states. However, we show by a rate equations model and pump-probe experiments that the rate of population transferred to the triplet state via 2PA, employing a 150 fs laser, and low repetition is negligible (<1%). Consequently, 2PA cross-section from tens to thousands of GM units, observed along the nonlinear spectrum, is due to pure singlet-singlet transitions. Our results also reveal that the 2PA spectrum of PE3 in dichloromethane exhibits two 2PA allowed bands centered at 760 nm (120 GM) and 610 nm (680 GM) and is very intense for wavelengths below of 500 nm (>1000 GM). The first 2PA band was attributed to the S<sub>0</sub> → S<sub>1</sub> (1<sup>1</sup>Ag-like → 1<sup>1</sup>Bu-like) transition, which is made possible because of a relaxation of the selection rules for PE3 that, in solution, present centrosymmetric and noncentrosymmetric conformers. The second 2PA band was ascribed to the S<sub>0</sub> → S<sub>2</sub> (1<sup>1</sup>Ag-like → 3<sup>1</sup>Ag-like) transition strongly 2PA allowed characteristic in PE's chromophores. On the other hand, the sizable 2PA cross-section observed for the region 460–500 nm was ascribed to a double resonance effect and high singlet excited state absorption (S<sub>0</sub> → S<sub>n</sub>).

**KEYWORDS:** Z-scan, femtosecond pulses, PE3, platinum acetylide complex, sum-over-essential states approach



Multiphoton absorbing materials have been extensively studied in the last decades because of their applicability in optical-based technologies, including 3D data storage,<sup>1,2</sup> fluorescence imaging,<sup>3,4</sup> all-optical switching,<sup>5,6</sup> photodynamic therapy,<sup>7,8</sup> frequency upconverted lasing,<sup>9</sup> microfabrication via photopolymerization,<sup>10,11</sup> micromachining,<sup>12,13</sup> and so on. In this direction, platinum acetylide complexes have recently emerged as excellent candidates to develop novel optical devices because of their extraordinary excited state absorption (ESA) properties, such as high singlet and triplet absorption (from 10<sup>4</sup> to 10<sup>5</sup> M<sup>-1</sup> cm<sup>-1</sup>),<sup>14–16</sup> intense two (thousands of GM units<sup>16,17</sup>) and three-photon absorption (~10<sup>-78</sup> cm<sup>6</sup>·s<sup>2</sup>·photon<sup>-2</sup>),<sup>18</sup> ultrafast intersystem crossing (from fs to ps), and long phosphorescence time (μs).<sup>14,19</sup> 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.<sup>16,20,21</sup>

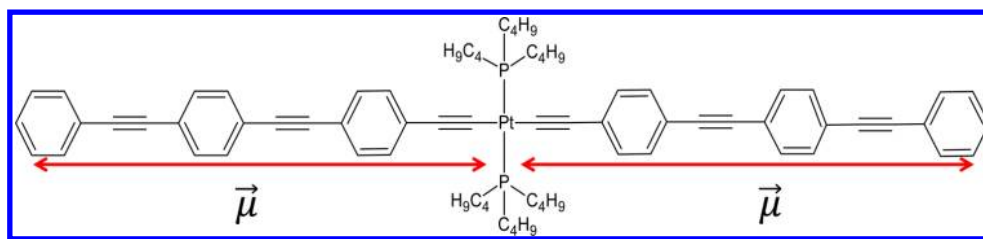
Although some information about the linear and nonlinear optical properties of distinct platinum acetylide complexes is available in the literature,<sup>15,16,20–23</sup> to the best of our

knowledge, there is no experimental or theoretical data about the spectral behavior and magnitude of the 2PA cross-section for the *trans*-Pt(PBu<sub>3</sub>)<sub>2</sub>(C≡C-C<sub>6</sub>H<sub>4</sub>-C≡C-C<sub>6</sub>H<sub>4</sub>-C≡C-C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (PE3). PE3, whose molecular structure is shown in Figure 1, can be visualized as two branches containing three phenylacetylene units, each one linked by a platinum center, completely transparent in the visible region.

Because of the large delocalization of π-electrons allied to the strong intramolecular interaction between the branches, due to its platinum center, it is expected that PE3 presents high optical nonlinearities. In this context, this paper reports a study on the relationship between the molecular properties and the strong 2PA capability of PE3. For that, we performed ground-state absorption, fs pump-probe spectroscopy, Stoke shift solvatochromic measurements, excitation fluorescence anisotropy, and wavelength-tunable fs Z-scan measurements. From the data obtained with such techniques and employing the sum-over-essential states approach, we explain the three distinct regions observed on the 2PA spectrum of PE3 that present cross-

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**Figure 1.** Molecular structure of PE3. According to ref 14, the singlet state is delocalized along the whole molecule.

section with reasonable (120 GM at 760 nm), high (680 GM at 610 nm), and sizable (>1000 GM between 460 and 500 nm) magnitudes.

## ■ EXPERIMENTAL SECTION

**A. Linear Optical Measurements.** For the ground-state, Stoke shift, and excitation anisotropy measurements, PE3 was dissolved in dichloromethane in a concentration of  $6 \times 10^{14}$  molecules/cm<sup>3</sup> ( $\sim 1.0 \times 10^{-6}$  Mol/L). In these experiments, the samples were placed in 1 cm thick quartz cuvette. The steady-state absorption and photoluminescence spectra were recorded using a Shimadzu UV-1800 spectrophotometer and a Perkin-Elmer LS55 fluorimeter, respectively.

**B. Femtosecond Pump-Probe Measurements.** Femto-second time-resolved ESA spectra were recorded using 150 fs pulses (775 nm) from a Ti:sapphire chirped pulse amplified system operating at 1 kHz repetition rate. This beam was divided in two using a beam splitter (90–10%). The stronger beam was doubled (387.5 nm) using a BBO crystal and employed as the pump pulse. A small portion of the weaker beam was used to generate the white-light continuum (WLC) probe, using a sapphire window (2 mm of thickness). The time delay between pump and probe pulses was carefully varied by a computer controlled translation stage, providing a resolution of 187.5 fs. The intensity of the relative spectral components of WLC probe pulse, at each specific time, that characterize the time-resolved transient absorption ( $\Delta A$ ), was monitored by means of a fast spectrometer. The chirp of WLC probe pulse was measured to be <1 ps in the 400–700 nm spectral regions. Pump and probe pulses with energy smaller than 1  $\mu$ J and 1 nJ, respectively, were used.

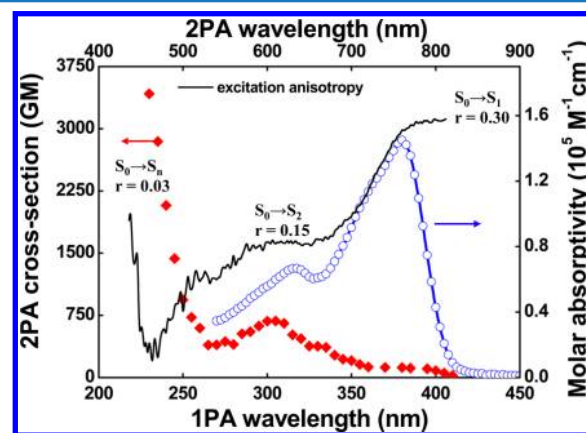
**C. 2PA Experiments.** For the 2PA measurements, PE3 was dissolved in dichloromethane in a concentration of  $1 \times 10^{18}$  molecules/cm<sup>3</sup> ( $1.65 \times 10^{-3}$  Mol/L) and placed in 2 mm thick quartz cuvette. To obtain the 2PA cross-section we employed the open aperture Z-scan technique, using 120–160 fs laser pulses from an optical parametric amplifier pumped by 150 fs pulses (775 nm) from a Ti:sapphire chirped pulse amplified system. The Z-scan measurements were carried out with intensities ranging from 20 to 300 GW/cm<sup>2</sup> (15–150 nJ/pulse) and with beam waist size at the focus varying from 16 to 22  $\mu$ m. To ensure a Gaussian profile for the laser beam used in the experiments, spatial filtering is performed before the Z-scan setup. A silicon detector was used to monitor the laser beam intensity in the far-field. To improve the signal-to-noise ratio, we employed the oscillatory Z-scan method, in which the sample is continuously scanned, repeating the experiment several times. Moreover, we used a lock-in amplifier to integrate 1000 shots for each point of the Z-scan signature. In order 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.

In the open aperture Z-scan technique, 2PA cross-section is determined by translating the sample through the focal plane of a focused Gaussian beam, while transmittance changes in the far field intensity are monitored. For a 2PA process, the light field creates an intensity dependent absorption,  $\alpha = \alpha_0 + \beta I$ , in which  $I$  is the laser beam intensity,  $\alpha_0$  is the linear absorption coefficient, and  $\beta$  is the 2PA coefficient. The nonlinear coefficient  $\beta$  is obtained by fitting the Z-scan data. The 2PA cross-section,  $\sigma_{2PA}$ , is determined from  $\sigma_{2PA} = \hbar\omega\beta/N$ , where  $\hbar\omega$  is the excitation photon energy and  $N$  is the number of chromophores per cm<sup>3</sup>. The 2PA cross-section is expressed in Göppert-Mayer units (GM), in which  $1 \text{ GM} = 1 \times 10^{-50} \text{ cm}^4 \cdot \text{s} \cdot \text{photon}^{-1}$ .

## ■ RESULTS AND DISCUSSION

Figure 2 shows the ground-state absorption (circles, right axis), 2PA (diamonds, left axis) and excitation anisotropy spectra of PE3.



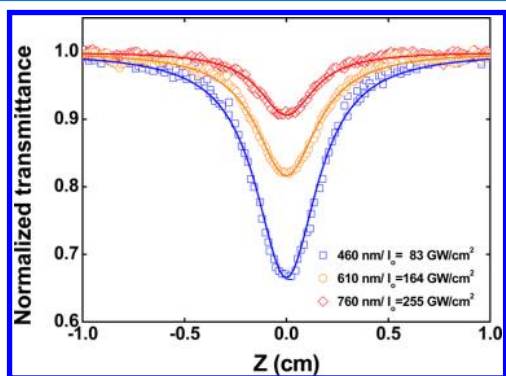
**Figure 2.** (a) Ground-state (circles, right axes), two-photon absorption (squares, right axes) and excitation fluorescence anisotropy (solid line) spectra of PE3. The standard deviation in the 2PA cross-section was determined to be 20%.

(solid line) of the platinum acetylide complex PE3. According to recent results,<sup>14,15,20,24,25</sup> the ground-state absorption spectrum of platinum acetylide complex, such as PE3, is related to  $\pi\pi^*$  transitions with metal-to-ligand charge transfer character. These results show that the HOMO (highest occupied molecular orbital) of platinum acetylide complexes consists of a  $\pi$  orbital from acetylene and aromatic groups, with contribution from the  $5d_{xy}$  orbital of platinum, while the LUMO (lowest unoccupied molecular orbital) consists only of a  $\pi^*$  orbital, with no contribution from the platinum.<sup>21,26</sup> Both HOMO and LUMO are delocalized across the platinum atom.<sup>14</sup>

The lowest energy linear absorption band of PE3 dissolved in dichloromethane exhibits molar absorptivity of about  $1.45 \pm 0.10 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ . It is important to mention that such molar absorptivity magnitude (in dichloromethane) is 1.7 times higher than when dissolved in benzene.<sup>14</sup> Moreover, it has also been shown elsewhere that PE3 presents vibronic progressions separated by  $\sim 215 \text{ meV}$ , which are associated with the C–C/C=C (in benzene ring  $-148 \text{ meV}$ ) and C $\equiv$ C stretch modes ( $260 \text{ meV}$ ).<sup>14,15,27</sup>

Recently, Nguyen et al.<sup>20</sup> investigated the theoretical 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 PE's chromophores on 1PA and 2PA spectra. According to such a study, the lowest energy 1PA allowed band of PE3 ( $S_0 \rightarrow S_1$ ), with  $C_{2h}$  symmetry, is assigned to the  $1^1\text{Ag-like} \rightarrow 1^1\text{Bu-like}$  transition, while the peak at  $315 \text{ nm}$  ( $S_0 \rightarrow S_2$ ) is attributed to the  $1^1\text{Ag-like} \rightarrow 2^1\text{Bu-like}$  transition. These transitions are corroborated by the outcome of the excitation anisotropy shown in Figure 2 (solid lines). As it can be seen, the constant value of 0.3 on the excitation anisotropy ( $r$ ) between  $410$  and  $380 \text{ nm}$  can be attributed to a transition from the ground-state to the first singlet excited state ( $1^1\text{Ag-like} \rightarrow 1^1\text{Bu-like}$ ). A change in the excitation anisotropy value from  $r = 0.30$  ( $385 \text{ nm}$ ) to  $r = 0.15$  ( $335 \text{ nm}$ ) indicates that the second excited state is being reached ( $1^1\text{Ag-like} \rightarrow 2^1\text{Bu-like}$ ). The value practically constant of  $r$  between  $335$  to  $290 \text{ nm}$  and the peak observed in the ground-state spectrum at  $315 \text{ nm}$  supports this result. Finally, the spectral region at  $230 \text{ nm}$  ( $r = 0.03$ ) is ascribed to a  $S_0 \rightarrow S_n$  transition.

In Figure 2, the diamonds show the 2PA cross-section, from  $460 \text{ nm}$  up to  $820 \text{ nm}$ , obtained for the PE3 employing the wavelength-tunable femtosecond Z-scan. As it can be noted, the nonlinear spectrum has two 2PA allowed bands centered at  $760$  and  $610 \text{ nm}$  and a very intense 2PA absorption for wavelengths shorter than  $500 \text{ nm}$ . In Figure 3 we show Z-scan curves



**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 line represents the fitting employing the theory described in ref 38.

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.

For centrosymmetric molecules, the selection rules for two-photon allowed transitions are very strict.<sup>28</sup> However, according

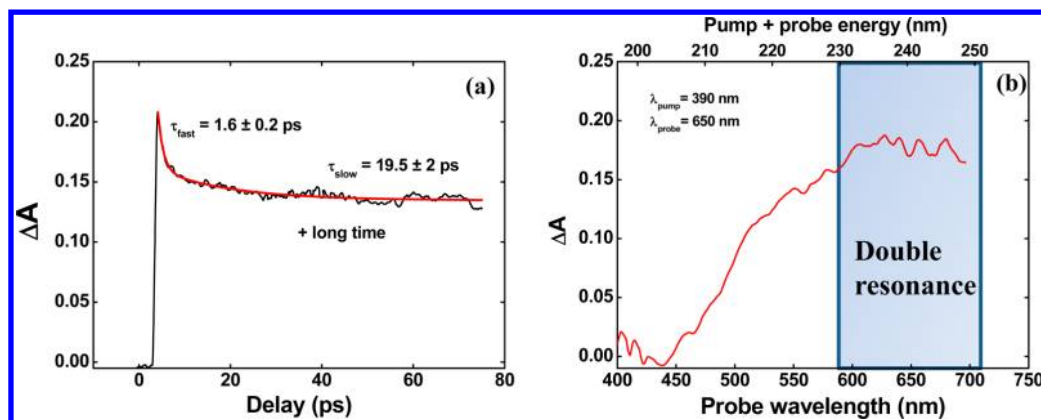
to Nguyen et al.,<sup>20</sup> PEs may exist as an equilibrium of at least two conformations, with at least one of them being centrosymmetric and the others noncentrosymmetric. Therefore, in this configuration it is expected that transition selection rules are relaxed. Consequently, transitions are allowed by one and two photons simultaneously, as shown by the correspondence between the first peak in the 2PA ( $\sim 760 \text{ nm}$ ) and 1PA ( $\sim 380 \text{ nm}$ ) spectra. Moreover, the violation of selection rules<sup>29</sup> reported here has been observed in other platinum acetylide complexes<sup>16</sup> and, more recently, in centrosymmetric phenylene vinylene platinum derivatives.<sup>17</sup>

The small blue-shift ( $10 \text{ nm}$  or  $\sim 130 \text{ meV}$ ) observed for the second peak of the 2PA spectrum in respect to the second peak of 1PA spectrum ( $1^1\text{Ag-like} \rightarrow 2^1\text{Bu-like}$ ) is an indication that the 2PA transition does not correspond necessarily to the same 1PA allowed transition. Once again, according to Nguyen et al.,<sup>20</sup> the PE's chromophores present an excited state labeled as  $3^1\text{Ag-like}$  strongly 2PA allowed located a little above (in energy) the  $2^1\text{Bu-like}$  1PA allowed state, which explains the blue-shift observed for the 2PA band ( $305 \text{ nm}$ ) as compared with the 1PA band (at  $315 \text{ nm}$ ). Consequently, these results reveal that the 2PA band located at  $610 \text{ nm}$  should be primarily ascribed to the  $1^1\text{Ag-like} \rightarrow 3^1\text{Ag-like}$  transition. Furthermore, it is important to mention that, in general (not as a rule), the transitions strongly 1PA allowed are weakly 2PA allowed and vice versa.<sup>28</sup>

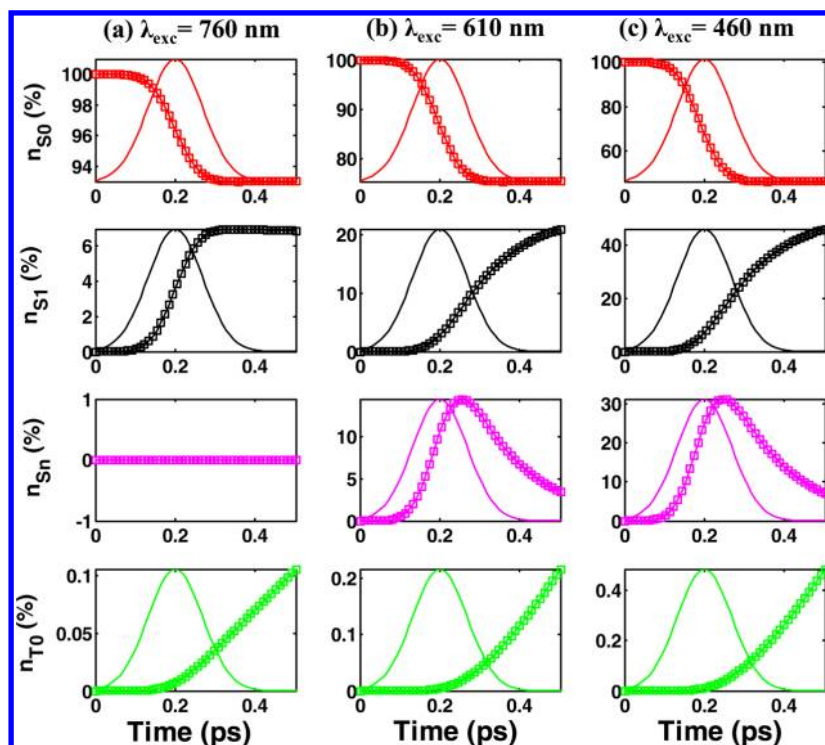
The cross-section values in the peaks of the 2PA bands were determined to be about  $120 \pm 25 \text{ GM}$  at  $760 \text{ nm}$ ,  $680 \pm 120 \text{ GM}$  at  $610 \text{ nm}$  and higher than  $1000 \text{ GM}$  for the resonance enhancement region (below  $500 \text{ nm}$ ). The 2PA cross sections obtained for compounds based on platinum acetylide complex have shown values in the order of tens to thousands of  $\text{GM}$ ,<sup>16,30,31</sup> close to the ones reported here. As it is well-known for platinum acetylide derivatives, the short intersystem crossing time (ps)<sup>32</sup> and long phosphorescence lifetime ( $\mu\text{s}$ )<sup>15</sup> allow accumulation of molecules in the triplet state, which may influence a proper determination of the 2PA cross-section. To avoid a considerable triplet state absorption, the nonlinear effect was measured using femtosecond laser pulses and a repetition rate of  $1 \text{ kHz}$ . The short pulse duration allows obtaining pure 2PA because only negligible absorption comes from the population generated in the excited states,<sup>33</sup> while the low repetition rate ( $1 \text{ kHz}$ ) helps to avoid cumulative effects between consecutive pulses, coming from possible triplet–triplet absorption.

To corroborate the magnitude of the 2PA cross-section reported here, we estimate the fraction of the population excited by 2PA that is transferred to the triplet state by intersystem crossing. For that, we considered three situations that reflect the three distinct regions observed in the 2PA spectrum. In the first situation, corresponding to the lowest energy 2PA allowed band (excitation at  $760 \text{ nm}$ ), electrons are promoted from ground-state ( $S_0$ ) to the first excited state ( $S_1$ ) via 2PA. Intersystem crossing converts population from  $S_1$  to  $T_1$  with a characteristic time ( $\tau_{\text{isc}}$ ), after which relaxation to the ground-state, characterized by the time constant  $\tau_{\text{phos}}$  takes place. We have also taken into consideration the direct relaxation from  $S_1$  to  $S_0$  ( $\tau_{\text{S1}}$ ). In the second situation, for the 2PA allowed band at  $610 \text{ nm}$ , electrons are promoted from the ground-state ( $S_0$ ) to the second excited state ( $S_2$ ) via two-photon transition. Quickly, electrons in  $S_2$  relax to  $S_1$  ( $\tau_{\text{S2} \rightarrow \text{S1}}$ ) followed by intersystem crossing to  $T_1$  ( $\tau_{\text{isc}}$ ), and, after  $\tau_{\text{phos}}$  decay to the ground-state. The direct relaxation from  $S_1$  to  $S_0$





**Figure 4.** (a) Decay curve obtained employing fs pump–probe technique (390 nm, and probe component at 600 nm from the WLC). (b) Singlet excited state absorption spectrum for the PE3 in dichloromethane after 7.5 ps.



**Figure 5.** Calculation of the population dynamics induced by 2PA described by the rate equations (eqs 1–4). The solid lines show the normalized laser pulse, while the squares describe the distribution of populations excited by 2PA.

( $\tau_{S1}$ ) also has been taken into consideration. In the last situation, corresponding to the resonance enhancement region (460–500 nm), electrons are promoted from the ground-state ( $S_0$ ) to the  $n$ th excited state ( $S_n$ ) via 2PA. Rapidly, electrons in  $S_n$  relax to  $S_1$  ( $\tau_{S_n \rightarrow S_1}$ ) followed by intersystem crossing to  $T_1$  ( $\tau_{isc}$ ), with a subsequent relaxation to the ground-state ( $\tau_{phos}$ ). Analogous to the previous cases, we have taken into account the direct relaxation from  $S_1$  to  $S_0$  ( $\tau_{S1}$ ). Such population dynamics, induced by ultrashort laser pulses, can be calculated through the following rate equations:<sup>34</sup>

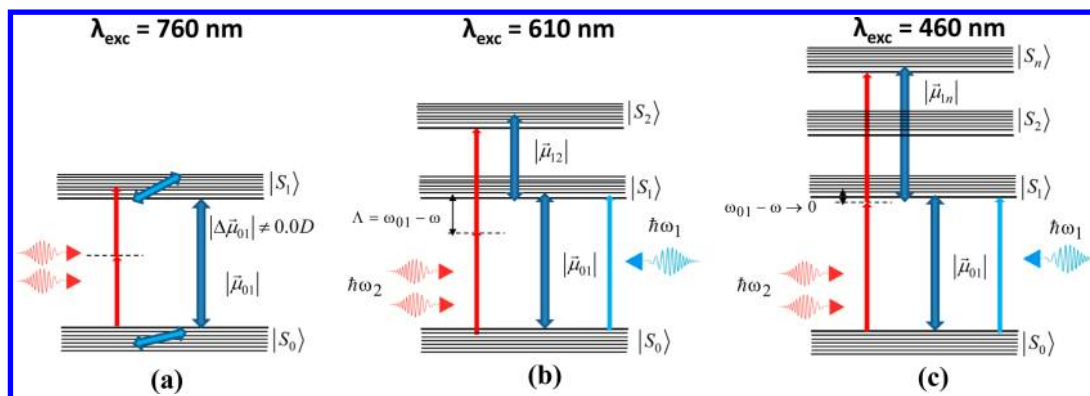
$$\frac{dn_{S_0}(t)}{dt} = -n_{S_0}(t)W_{of}^{2PA} + \frac{n_{S_1}(t)}{\tau_{S_1}} + \frac{n_{T_0}(t)}{\tau_{phos}} \quad (1)$$

$$\frac{dn_{S_n}(t)}{dt} = +n_{S_0}(t)W_{of}^{2PA} - \frac{n_{S_n}(t)}{\tau_{S_n \rightarrow S_1}} \quad (2)$$

$$\frac{dn_{S_1}(t)}{dt} = +\frac{n_{S_n}(t)}{\tau_{S_n \rightarrow S_1}} - \frac{n_{S_1}(t)}{\tau_{isc}} - \frac{n_{S_1}(t)}{\tau_{S_1}} \quad (3)$$

$$\frac{dn_{T_0}(t)}{dt} = +\frac{n_{S_1}(t)}{\tau_{isc}} - \frac{n_{T_0}(t)}{\tau_{phos}} \quad (4)$$

in which the 2PA transition rate is given by  $W_{of}^{2PA} = \sigma_{of}^{2PA} I^2 / (\hbar\omega)^2$ . Here,  $\sigma_{of}^{2PA}$  is the 2PA cross-section obtained through the Z-scan data.  $I$  is the irradiance,  $\hbar$  is the Planck constant, and  $\nu$  is the photon frequency.  $\tau_{isc}$  and  $\tau_{phos}$  are the intersystem crossing and phosphorescence times, respectively. The lifetime of the first singlet excited-state ( $\tau_{S_1}$ ), measured through fluorescence, is defined as  $\tau_{S_1}^{-1} = \tau_{S_{10}}^{-1} + \tau_{isc}^{-1}$ , where  $\tau_{S_{10}}^{-1}$  contains the contribution of internal conversion ( $\tau_{ic}$ ) and radiative lifetime ( $\tau_r$ ) of the  $S_1 \rightarrow S_0$  transition ( $\tau_{S_{10}}^{-1} = \tau_r^{-1} + \tau_{ic}^{-1}$ ). However, as



**Figure 6.** (a) 2PA transition in a two-level system with a permanent dipole moment difference between ground and final excited state ( $\Delta\vec{\mu}_{01} \neq 0$ ). (b) 2PA transition in a three-energy level system with one real intermediate energy level. (c) 2PA transition in a three-energy level system in condition of double-resonance.

the triplet quantum yield for **PEs** is around 0.9 to 1.0,<sup>14,35</sup> we have considered  $\tau_{S_1}^{-1} \approx \tau_{isc}^{-1}$ . To find both times ( $\tau_{S_1}$  and  $\tau_{isc}$ ) for **PE3** in dichloromethane, we performed femtosecond pump–probe measurements, as described in the Experimental Section. Figure 4a depicts the absorbance change as a function of the delay between the pump (390 nm) and the probe (component at 600 nm from the WLC), while Figure 4b illustrates the singlet ESA spectrum for **PE3** after 7.5 ps. It is observed that the peak of the ESA spectrum is between 230 and 250 nm that correspond, in energy, exactly to the resonance enhancement region observed in the 2PA spectrum.

According to ref 16, the fast component at  $1.6 \pm 0.2$  ps is due to internal conversion from higher singlet states, vibrational relaxation, and solvent reorganization around the molecule. The slower decay ( $19.5 \pm 2$  ps) is assigned to intersystem crossing of the relaxed singlet state to the triplet state.<sup>16</sup> Thus, using  $\tau_{S_1} = \tau_{isc} = 19.5 \pm 2$  ps,  $\tau_{phos} = 500$  ns (obtained from the ref 30), and considering the duration of our pulse (150 fs), the population transferred to the triplet state for the three excitation regions (760, 610, and 460 nm) was obtained, whose results are displayed in Figure 5a–c, respectively.

In Figure 5, the solid lines correspond to the laser pulse with full width at half-maximum (FWHM) of 150 fs, while the squares represent the distribution of population excited by 2PA. It is clear that during the fs-pulse interaction, the population transferred to the triplet state is less than 1% of the population promoted to excited states via 2PA. Therefore, the influence of the triplet state population for the total 2PA cross-section is, within our experimental error, completely negligible.

Organometallic compounds might present spin forbidden transitions from the singlet to triplet ground-state ( $S_0 \rightarrow T_1$ ) due to spin–orbit coupling from a heavy atom.<sup>29</sup> In this context, some years ago, Staromlynska et al.<sup>36</sup> showed that **PE2** present a small absorption peak at 520 nm that was assigned as a spin-forbidden radiative transition from  $S_0 \rightarrow T_1$ . After some years, Rogers et al.<sup>15</sup> investigated this same phenomenon using a long cell (10 cm) and concentrations around at 1 mM to avoid aggregation and the same time to be able to observe this effect. In that experiment, a little shoulder with molar absorptivity around at  $1 \text{ M}^{-1} \text{ cm}^{-1}$  was observed for the **PE2**; however, for the **PE3**, the authors does not observe any band or shoulder in the ground-state absorption spectrum due to an  $S_0 \rightarrow T_1$  transition. Therefore, once again the 2PA cross-section from tens to thousands of GM units, observed along the nonlinear spectrum, is due to pure singlet–singlet transitions.

To shed more light on the 2PA cross sections spectrum of **PE3** and associate them to its molecular properties, we used the sum-over-essential states approach. For the lowest energy 2PA band located at 760 nm ( $S_0 \rightarrow S_1$ ), we assumed a two-energy level system (see Figure 6a). Taking into account the average overall possible molecular orientations in an isotropic medium and considering excitation with linearly polarized light, the 2PA cross-section can be written as<sup>20,35</sup>

$$\sigma_{01}^{(2PA)}(\omega) = 2 \frac{(2\pi)^5}{(nhc)^2} \left( \frac{2 \cos^2(\theta) + 1}{15} \right) L^4 |\vec{\mu}_{01}|^2 |\Delta\vec{\mu}_{01}|^2 g_{01}(2\omega) \quad (5)$$

in which  $c$  is the speed of light, and  $L = 3n^2/(2n^2 + 1)$  is the Onsager local field factor introduced to take into account the medium effect<sup>37</sup> with the refractive index  $n = 1.424$  for dichloromethane at 20 °C.  $\vec{\mu}_{01}$  is the transition dipole moment,  $\Delta\vec{\mu}_{01}$  is the difference between the permanent dipole moments vectors of the excited ( $\vec{\mu}_{11}$ ) and ground ( $\vec{\mu}_{00}$ ) states, and  $\theta$  is the angle between the dipole moments  $\vec{\mu}_{01}$  and  $\Delta\vec{\mu}_{01}$ . By measuring the 2PA with linearly and circularly polarized light,<sup>31,38</sup> we determined that  $\theta \approx 0^\circ$ .  $g(2\omega)$  represents the normalized line-shape function of the excited state that we assumed as a Gaussian function:<sup>20</sup>

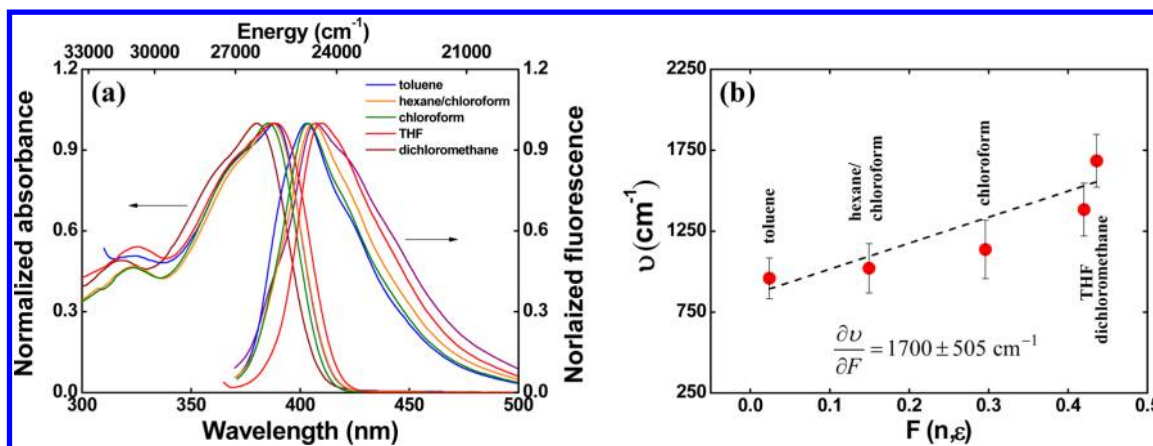
$$g_{g \rightarrow f}(2\omega) = \sqrt{\frac{4 \ln(2)}{\pi \Gamma_{gf}^2}} \exp \left[ -\frac{4 \ln(2)}{\Gamma_{gf}^2} (2\omega - \omega_{gf})^2 \right] \quad (6)$$

in which,  $\omega_{gf}$  is the transition frequency,  $\Gamma_{gf}$  is the damping constant, describing FWHM of the final state line width.

In eq 5, the product between the damping constants  $\Gamma_{01}$  and the transition dipole moment  $|\vec{\mu}_{01}|^2$  can be obtained from the ground-state spectrum using

$$|\vec{\mu}_{gf}|^2 g_{gf}^{\max} = \frac{3 \times 10^3 \ln(10) hc}{(2\pi)^2 N_A} \frac{n \epsilon_{gf}^{\max}}{L^2 \omega_{gf}} \quad (7)$$

in which,  $\epsilon_{gf}^{\max}$  is the maximum molar absorptivity,  $N_A$  is the Avogadro's number, and  $\epsilon_{gf}^{\max} = (4 \ln(2)/\pi \Gamma_{gf}^2)^{1/2}$  represents the maximum value of the normalized line width function (Gaussian line-shape), in which  $\Gamma_{gf}$  is the damping constant describing FWHM of the final state line width. Moreover, the permanent dipole moment change,  $|\Delta\vec{\mu}_{01}|$ , can be obtained in the dipole–dipole interaction from solvatochromic shift measurements as follow:



**Figure 7.** Normalized absorption and fluorescence spectra for **PE3** in five different solvents (toluene, hexane/chloroform (50–50%), chloroform, THF, and dichloromethane). (b) Solvatochromic Stokes shift ( $\nu$ ) measurements obtained as a function of the Onsager polarity function ( $F(n, \epsilon)$ ).

$$|\Delta\vec{\mu}_{01}|^2 = \frac{3}{4\pi} hc \frac{\partial \nu}{\partial F} \text{vol} \quad (8)$$

in which,  $\nu = \nu_{\text{abs}} - \nu_{\text{em}}$  is the difference between the peak of fluorescence and absorption in  $\text{cm}^{-1}$ .  $F(n, \epsilon) = 2 [(\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)]$  is the Onsager polarity function, in which,  $\epsilon$  is the dielectric constant of the solvent, and vol is the volume of the molecular cavity. To find the molecular cavity volume, we assume that it is equal to the hydrodynamic volume of the molecule under study. The latter is calculated using the Smolukhovsky-Einstein theory of rotational diffusion, which relates the hydrodynamic volume to the fluorescence anisotropy ( $r$ ):<sup>39</sup>

$$\text{vol} = \frac{\tau_f k T}{\eta \left( \frac{0.4}{r} - 1 \right)} \quad (9)$$

in which  $\eta$  is the solvent viscosity,  $\tau_f$  is the fluorescence lifetime,  $k$  is the Boltzmann constant, and  $T$  is the temperature. With such an approach, we determined a hydrodynamics volume for **PE3** of approximately  $560 \text{ \AA}^3$ .

Figure 7a shows the steady-state absorption and fluorescence spectra of **PE3** in five different solvents (toluene, hexane/chloroform (50–50%), chloroform, THF, and dichloromethane), while Figure 7b illustrates the result of the Stokes shift ( $\nu$ ) as a function of the Onsager polarity parameter ( $F(n, \epsilon)$ ). We calculated a positive linear slope  $\partial \nu / \partial F = 1700 \pm 505 \text{ cm}^{-1}$ , indicating that the permanent dipole moment from first excited state is higher than the ground-state one ( $\vec{\mu}_{11} > \vec{\mu}_{00}$ ).<sup>40</sup> Using this result and the hydrodynamic volume calculated through the Smolukhovsky-Einstein theory, we obtained the dipole moment change as being  $|\Delta\vec{\mu}_{01}| = 6.5 \text{ D}$ . Such value is in good agreement with values (5–10 D) reported in refs 16 and 22 for similar molecules. For noncentrosymmetric conformers, such considerable change of permanent dipole moment is probably related to the breaking of symmetry, such that a Franck–Condon excitation is localized on only one ligand.<sup>16</sup>

Substituting  $|\vec{\mu}_{01}| = 13 \text{ D}$  (obtained from the ground-state absorption spectrum),  $|\Delta\vec{\mu}_{01}| = 6.5 \text{ D}$ , and eq 7 in eq 5, we found  $\sigma_{01}^{(2\text{PA-SS})} = 110 \text{ GM}$ , that is in good agreement with the one obtained from the Z-scan data ( $120 \pm 25 \text{ GM}$ ).

To model the higher energy 2PA allowed band, attributed to  $S_0 \rightarrow S_2$  transition, we considered a three-level energy system consisting of the ground-state ( $S_0$ ), one intermediate 1PA allowed excited state ( $S_1$ ) and the 2PA allowed final excited

state ( $S_2$ ). For this system, the 2PA cross-section can be written as (assuming linearly polarized light and that the dipole moments are parallel):<sup>35</sup>

$$\sigma_{0 \rightarrow 2}^{(2\text{PA})}(\omega) = \frac{2}{5} \frac{(2\pi)^5}{(nhc)^2} L^4 R(\omega) |\vec{\mu}_{01}|^2 |\vec{\mu}_{12}|^2 g_{0 \rightarrow 2}(2\omega) \quad (10)$$

in which,  $\omega$  is the excitation laser,  $\vec{\mu}_{12}$  is the transition dipole moment between the excited states  $|S_1\rangle \rightarrow |S_2\rangle$ , and  $R(\omega) = \omega^2 / [(\omega_{01} - \omega)^2 + \Gamma_{01}^2(\omega)]$  is the resonance enhancement factor. In general, for noncentrosymmetric molecules, eq 10 presents additional terms related with the permanent dipole moment change and the interference term between the two distinct excitation channels.<sup>35</sup> However, in molecular system with weak push–pull character like **PE3**, the factor  $R(\omega) |\vec{\mu}_{01}|^2 |\vec{\mu}_{12}|^2$  dominates the 2PA allowed transition. Considering the experimental data obtained from the Z-scan measurements,  $\sigma_{0 \rightarrow 2}^{(2\text{PA-max})} = 680 \text{ GM}$ , we found  $|\vec{\mu}_{12}| = 13.5 \text{ D}$ , that corresponds to a pronounced value to the transition dipole moments between excited states. Such value is related, most probably, to the strong intramolecular interaction between the branches due to the presence of platinum atom and because the singlet state is delocalized along the entire molecule.<sup>14</sup> Therefore, **PE3** behaves as an acceptor–donor–acceptor type quadrupole molecule. This band is characteristic of both centrosymmetric and noncentrosymmetric platinum acetylide complexes and can achieve cross-section values from a few hundreds<sup>16,22</sup> up to five thousand GM, for instance, in phenylene vinylene platinum.<sup>17</sup> Another important feature of **PE3** is the spectral coincidence between the 2PA at 610 nm and the triplet absorption (at 630 nm).<sup>19</sup>

For the resonance enhancement region (shorter than 500 nm), the  $S_0 \rightarrow S_1$  transition is almost exactly half the way to  $S_0 \rightarrow S_n$ , which characterizes the double-resonance effect (see Figure 6c), and therefore, the degenerate 2PA into this band would be highly enhanced by an intermediate state resonance. Moreover, it is important to mention that the degenerate 2PA excitation region between 460 and 500 nm corresponds exactly, in energy (230–250 nm), to the peak of the singlet ESA spectrum, according to our pump–probe data (see Figure 4b). Therefore, this is a perfect picture to observe exceptional 2PA cross sections. On this configuration, eq 9 can be rewritten as<sup>41</sup>



$$\sigma_{0 \rightarrow n}^{(2PA-\max)}(\omega) = \frac{2}{5} \frac{(2\pi)^5}{(nhc)^2} L^4 [4 \ln(2)]^{1/2} \frac{|\vec{\mu}_{01}|^2 |\vec{\mu}_{1n}|^2 \omega^2}{\pi^{1/2} \Gamma_{0n}^3} \quad (10)$$

Proceeding in this way, we found  $|\vec{\mu}_{1n}| = 12.5$  D. Such value corresponds to a molar absorptivity of approximately  $1.0 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ , which is in good agreement with results published for similar platinum acetylide complexes.<sup>22</sup> Therefore, the sizable 2PA cross-section observed in this region can be ascribed by both double-resonance condition and high singlet ESA. Table 1 shows the photophysical parameters found for the PE3 in dichloromethane solution in the present work.

**Table 1. Photophysical Parameters Obtained for the PE3 in Dichloromethane Solution**

PE3	$\nu_{gf}$ (nm)	$\epsilon_{\max}$ ( $10^5 \text{ M}^{-1} \text{ cm}^{-1}$ )	$\vec{\mu}_{gf}$ (D)	$\Delta\vec{\mu}_{gf}$ (D)	$\Gamma_{gf}$ (eV)	$\sigma_{2PA}^{\max}$ (GM)
$S_0 \rightarrow S_1$	380 (3.26 eV)	1.45	13.0	6.5	0.40	120
$S_0 \rightarrow S_2$	315 (3.94 eV)	0.75	10.5	NA	0.50	680
$S_0 \rightarrow S_n$	230 (5.39 eV)	NA	NA	NA	0.60	3450
$S_1 \rightarrow S_2$	1825 (0.68 eV)	1.0	13.5	NA	NA	NA
$S_1 \rightarrow S_n$	650 (1.90 eV)	NA	12.5	NA	NA	NA

## FINAL REMARKS

In this report we have studied the strong 2PA cross-section observed for a platinum acetylide complex, named PE3, dissolved in dichloromethane using a series of linear and nonlinear optical techniques. To explain the three distinct regions observed along the 2PA spectrum we have used the sum-over-essential states approach. The first region, with reasonable 2PA cross-section (120 GM) around 760 nm, was attributed to present of the noncentrosymmetric conformer of PE3. The presence of this conformer allows the relaxation of the selection rules since the Franck–Condon excitation is localized on one specific ligand, and, in this case, the transition strongly allowed by 1PA ( $1^1\text{Ag-like} \rightarrow 1^1\text{Bu-like}$ ) becomes allowed by 2PA. The second spectral region, with high 2PA cross-section (680 GM), located around 610 nm was ascribed to the  $1^1\text{Ag-like} \rightarrow 3^1\text{Ag-like}$  transition, which is associated with the strong intramolecular interaction between the branches due to the presence of platinum atom. This band is typical of both centrosymmetric and noncentrosymmetric platinum acetylide complexes and can achieve cross-section values from few hundreds<sup>16,22</sup> up to five thousand GMs. Additionally, it is known that this 2PA band, in several platinum acetylide complexes, exhibits spectral coincidence with the triplet absorption band<sup>35</sup> and, therefore, these chromophores are considered noteworthy materials for applications in photonics. Finally, the strong 2PA cross-section observed between 460 and 500 nm (>1000 GM) was assign to the double resonance effect and spectral coincidence of the final state in the transition induced by 2PA with the intense peak singlet ESA, which contribute to an effective intermediate state resonance.

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## Notes

The authors declare no competing financial interest.

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