Triplet-Triplet Annihilation in Platinum Poly-ynes. Implications for Application to Optical Pulse Limiting

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Abstract

Platinum(II) poly-ynes, [-*trans*-Pt(PBu_3)$_2$-CC-Ph-CC-]$_n$ (**Poly-Pt-n**, n = 13, 57 and 183), display 10-fold lower transient absorption (TA) due to the triplet excited state compared to a molecular complex (**Pt-2**) with the same structure as the polymer repeat unit. Power-dependent transient absorption and phosphorescence studies carried out with dilute solutions of **Poly-Pt-n** and **Pt-2** reveal that the diminished transient absorption in the polymers is due to intrachain triplet-triplet annihilation (t-tA) on polymer chains that feature two or more triplet excitons. Monte Carlo dynamics simulations suggest that the t-tA occurs as a result of rapid exciton migration along the Pt poly-yne chains.

Keywords: platinum polyyne, non-linear absorption, triplet state, optical limiting

TEXT

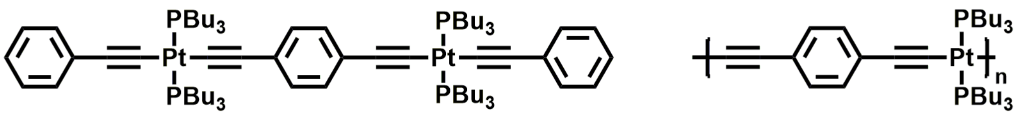
Platinum poly-ynes have garnered considerable interest over the past several decades owing to their fascinating fundamental properties as well as their potential for application in non-linear optics and organic electronics.[1-8] These polymers are conveniently synthesized according to an approach that was first reported by Hagihara, involving the polymerization of Pt(PR_3)Cl_2 with a bis-terminal acetylene in the presence of amine base and Cu(I) catalyst.[9-10] Platinum poly-ynes are thermally and air-stable, soluble in organic solvents, and they display optical properties characteristic of π-conjugated polymers: namely strong near-UV and visible absorption and photoluminescence.[11]

One particularly interesting aspect of platinum poly-ynes is that, because of the heavy atom Pt, there is a significant spin-orbit coupling that makes population of the triplet excited state very efficient, and the polymers often feature room-temperature phosphorescence.[11] In addition, the triplet state usually has a relatively long lifetime (1 – 20 μs) and it gives rise to a characteristic triplet-triplet absorption (triplet TA) in the mid-visible region.[2-3,11] The combination of extended π-conjugation and triplet TA makes platinum poly-ynes attractive chromophores for optical pulse limiting via non-linear absorption.[12-16] Optical pulse limiting involves the non-linear absorption of light in intense laser pulses due to several mechanisms, including but not limited to instantaneous multiphoton absorption, absorption by excited or charged states produced by photoexcitation (reverse saturable absorption), optical lensing due to changes in refractive index, and scattering processes.[17-18] Optical pulse limiting finds practical application in optical sensor and eye protection materials and devices.[19-20] The general concept of optical limiting is to reduce or limit the effective energy in an optical pulse, thereby protecting an optical element or system that is exposed to an intense pulse.[18] Platinum poly-yne materials give rise to optical limiting by a combination of non-linear absorption processes, including instantaneous 2-photon absorption and multiphoton absorption due to the strong, long-lifetime triplet TA. The instantaneous 2-photon absorption is useful for the optical limiting of ultrashort pulses (< 1 ps); however, long pulse (10 ns or longer) limiting requires a strong and long-lived triplet TA.[12,21] Many molecular platinum acetylides have been carefully assessed for their ability to limit ultrashort and nanosecond pulses and some have displayed outstanding limiting properties.[16,22 23]

In previous work, we noted an unusual feature characteristic of platinum poly-ynes, namely that their triplet TA is attenuated relative to that of molecular platinum acetylides with a similar structure.[5,24] We hypothesized that this effect might be due to a process of triplet-triplet annihilation (t-tA) that occurs on individual platinum poly-yne chains, which limits the triplet population that can be obtained under saturating laser-pulse excitation. This effect, although fundamentally interesting, could also affect the optical pulse limiting performance of platinum poly-ynes, since their ability to limit long laser pulses is directly proportional to the triplet population that can be produced in a saturating optical pulse.

Here we report a study of the triplet-triplet absorption of a series of platinum poly-ynes of varying degrees of polymerization (**Poly-Pt-n**) and compare it with a molecular platinum acetylide complex (**Pt-2**) that features the same molecular structure as the repeat units in **Poly-Pt-n** (Scheme 1). The results show that the triplet TA intensity of the polymers is dramatically lower compared to that of the molecular complex **Pt-2** under identical ground state chromophore concentration and pulse excitation conditions. The results are consistent with the occurrence of rapid t-tA that occurs on individual **Poly-Pt-n** chains. Excitation power dependence studies reveal that at saturation the triplet TA of **Poly-Pt-n** is consistent with ~1 triplet exciton per 10 repeat units. Monte Carlo dynamics simulations are consistent with t-tA occurring on a timescale of 100 ps – 30 ns. The implications of these findings on the application of platinum poly-ynes in optical pulse limiting is considered.

Scheme 1



Pt-2

Poly-Pt-n
n= 13, 57 and 183

Poly-Pt-n polymers and **Pt-2** were prepared as previously described and the detailed characterization is provided in the supporting information (SI). The molecular weight of **Poly-Pt-n** was controlled by the addition of ethynylbenzene as an end-capping reagent and/or control of reaction conditions.[25-28] The molecular weights of **Poly-Pt-n** were determined by solution gel permeation chromatography (Fig. S13). Three samples of **Poly-Pt-n** with M_n values of 9,300 Da, 41,600 Da, and 132,700 Da were obtained with polydispersity Đ = ~2, as expected for step-growth polymerization. By using the molecular weight of the [-Pt(PBu$_3$)$_2$-CC-C$_6$H$_4$-CC-] repeat units, the number-average degree of polymerization (DP) for the three samples was estimated as DP = 13, 57, and 183. All of the photophysical and laser measurements described herein were carried out with relatively dilute solutions in tetrahydrofuran (THF), with monomer or repeat unit concentrations ~10 μM range. THF is a good solvent for the polymers, thus in dilute solution the polymers exist as unaggregated, molecularly dissolved chains.

Poly-Pt-n polymers and **Pt-2** display strong absorption in the near-UV region, with the polymers' absorption red-shifted by approximately 20 nm relative to **Pt-2** (Fig. 1a). As reported previously,[29-30] these materials display moderately efficient phosphorescence with λ_{max} = ~520 nm (Fig. 1a, see Table S1 for phosphorescence yields and lifetimes). The absorption and phosphorescence arise from π,π* transitions localized on the phenylene ethynylene units. The phosphorescence energy is approximately the same for the molecular and polymer chromophores; this has been previously attributed to the fact that the π,π* triplet exciton is spatially localized on one or two repeat units in the polymers, so there is little stabilization that occurs due to the increased π−conjugation in the polymers.[30]

Nanosecond-microsecond transient absorption spectroscopy was carried out on the materials using a 355 nm excitation. As reported previously, **Pt-2** exhibits a moderately strong transient absorption with λ_{max} = ~650 nm (Fig. 1b).[31] The transient absorption is due to absorption of the triplet excited state (triplet TA); consistent with this assignment, the triplet TA decays with a lifetime of ~20 μs. Interestingly, when the transient absorption is measured for any of the **Poly-**

Pt-n samples with the same conditions (same laser pulse energy, same ground state absorption), the triplet TA is similar in shape and wavelength, but it is considerably weaker. For example, as shown in Fig. 1c, the triplet TA of **Poly-Pt-13** is approximately 10-fold weaker in absolute intensity compared to the triplet TA of **Pt-2** obtained under the exact same conditions (355 nm excitation, 35.7 mJ/cm^{-2} fluence, matched O.D. samples at 355 nm). Similar results were obtained for the **Poly-Pt-n** samples with longer chain lengths (see Fig. S14).

To probe the origin of the difference in triplet TA intensity for the molecular and polymer chromophores, we carried out a laser power (fluence) dependence study. Figure 2 shows how the triplet TA (ΔO.D. at 100 ns after laser excitation, $\lambda = 355$ nm) varies with laser fluence for **Pt-2** and the three **Poly-Pt-n** samples. For these samples, the ground state absorption at the excitation wavelength (355 nm) was identical. For **Pt-2**, the triplet TA increases nearly linearly to 20 mJ-cm^{-2} and then it increases less with increasing power until it saturates at ca. $\Delta A = 0.09$ above 40 mJ-cm^{-2} fluence. By contrast, the triplet TA of **Poly-Pt-n** is non-linear at very low fluence (< 1 mJ-cm^{-2}) and the signal is saturated for energy > 15 mJ-cm^{-2}. At saturation, the ΔO.D. signals for **Poly-Pt-n** are more than 10-fold weaker compared to **Pt-2**. The different behavior of **Poly-Pt-n** compared to **Pt-2** indicates that at saturation the concentration of triplet excitons is at least 10-fold less for the polymer samples. We conclude that for the polymer samples, the triplet exciton concentration is limited due to rapid intrachain t-tA.

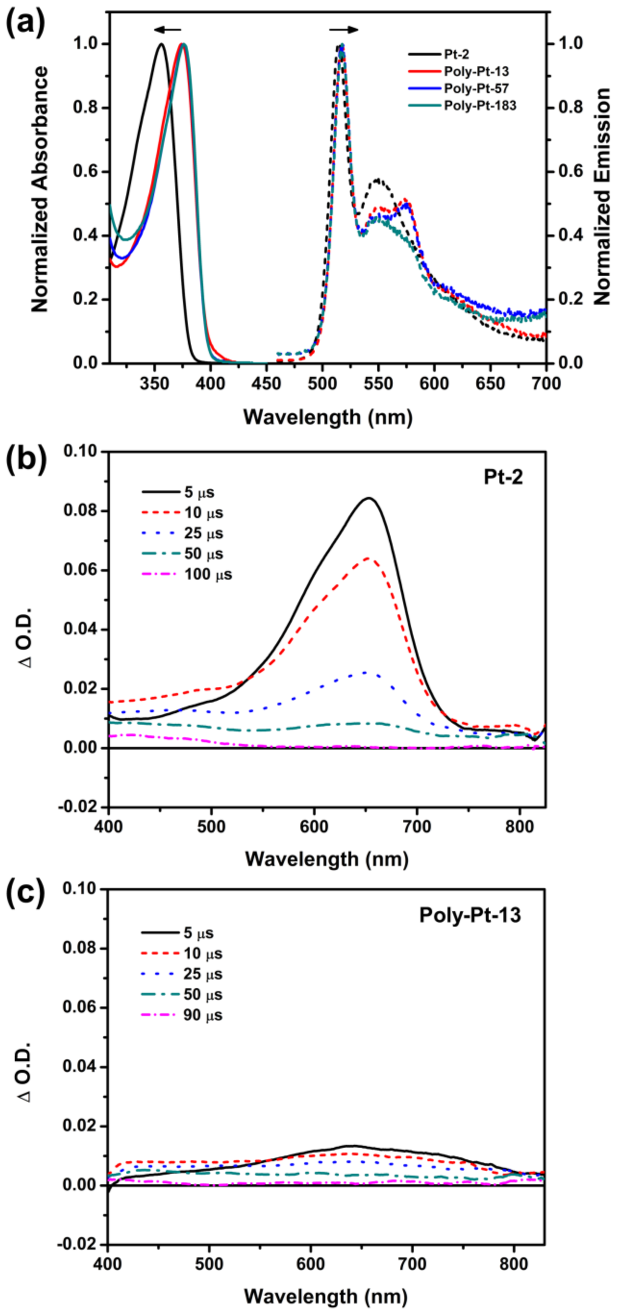


Figure 1. (a) Absorption and phosphorescence spectra of **Pt-2** and **Poly-Pt-n** in THF solution. Transient absorption spectra of (b) **Pt-2** and (c) **Poly-Pt-13** on microsecond timescale in THF solution. Sample concentrations: **Pt-2** = 8.2 μM; **Poly-Pt-13** = 14 μM in terms of repeat unit. Excitation at 355 nm (5 ns pulse, 35.7 mJ-cm^{-2} fluence), samples had matched O.D. of 0.58 at 355 nm at 355 nm.

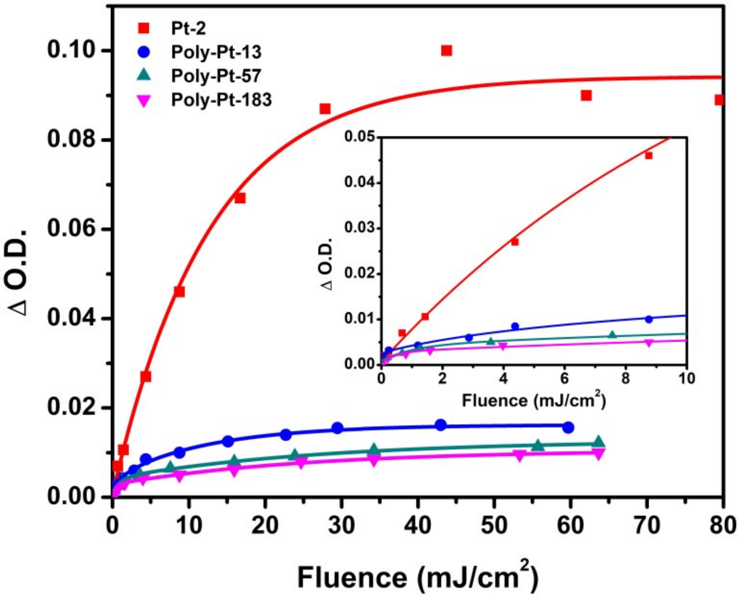


Figure 2. Laser power dependence study in THF solution. ΔO.D. (100 ns delay) at 650 nm vs laser fluence for **Pt-2** and **Poly-Pt-n**, the inset shows the zoomed-in 0-10 mJ/cm^2 region. Sample concentrations: **Pt-2** = 8.2 μM; **Poly-Pt-n** = 14 μM in terms of repeat unit. Excitation at 355 nm, samples have matched O.D. of 0.58 at 355 nm.

In order to gain insight into the mechanism and dynamics of the intrachain t-tA process, Monte Carlo simulations were carried out to compute the time evolution of the triplet population on individual chains that feature 2 or more triplet excitons. The details of the simulations are provided in the SI. Briefly, polymer chains with different lengths (10 – 120 repeat units) were prepared with N_t triplets where $N_t = m\rho_t$ where m = polymer chain length and ρ_t is the triplet density. The triplets migrate along the chains in a 1D random walk (steps), and when 2 triplets occupy the same repeat unit they annihilate. Technically, t-tA produces a singlet exciton, but since singlet to triplet intersystem crossing is very rapid in platinum poly-ynes,[32] annihilation is approximated to produce one triplet exciton. Figure 3 summarizes the results of the simulations. In these plots, the x-axis (bottom) represents the number of exciton hopping steps and the y-axis represents the triplet population, which is proportional to the experimental triplet TA intensity. The top x-axis is scaled in time, which is based on a 27.2 ps step time increment which was experimentally determined in previous work.[33] The simulation results reveal several important features: 1) Under all conditions examined, the triplet population decays to < 10% of the initial value within 1000 steps, which corresponds to ~30 ns; 2) For a fixed initial exciton density, the triplet decay due to t-tA is faster for shorter polymer chains; 3) The exciton decay accelerates with increasing density ρ_t, which corresponds experimentally to increasing laser pulse energy.

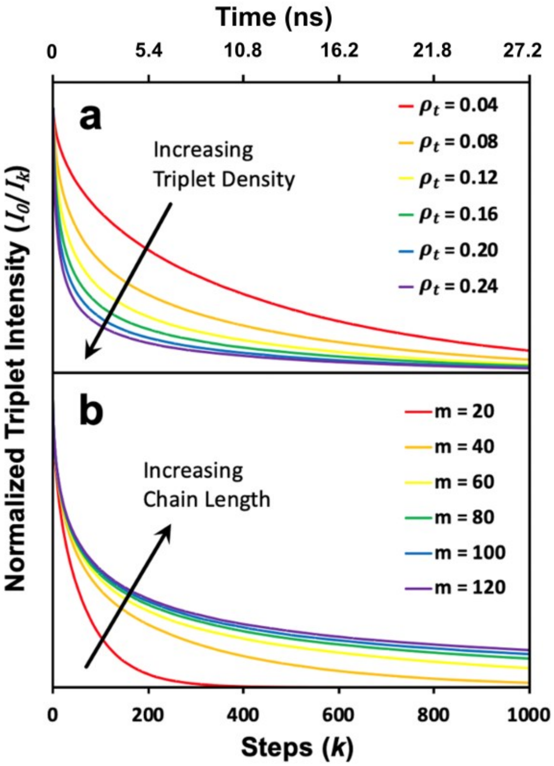


Figure 3. Simulated triplet intensity versus the number of hopping events (steps). Simulations were done by maintaining a fixed polymer chain length of m = 50 and varying the initial triplet exciton density (a), or by maintaining a fixed initial triplet density of $\rho_t = 0.10$ and varying the polymer chain length (b).

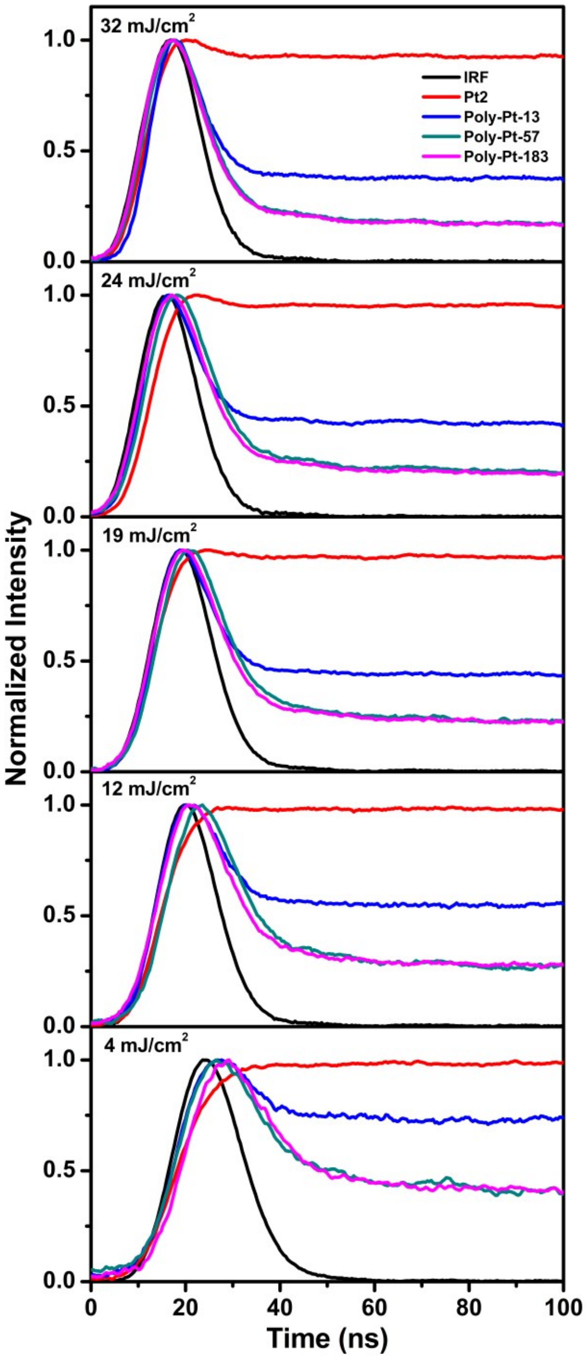


Figure 4. Phosphorescence dynamics of **Pt-2** and **Poly-Pt-n** in THF solution. Sample concentrations: **Pt-2** = 9.3 μM; **Poly-Pt-n** = 16 μM in terms of repeat unit. Excitation at 355 nm, samples have matched O.D. at 355 nm of 0.66, laser fluence: 4 mJ/cm^2 to 32 mJ/cm^2. In each panel, the black plot represents the instrument response function (IRF).

Since phosphorescence intensity is a sensitive probe of the triplet exciton population, we used time resolved emission to experimentally monitor the triplet dynamics. Figure 4 compares the emission dynamics for **Pt-2** and the **Poly-Pt-n** samples monitored in time following 355 nm pulsed excitation (10 ns FWHM) with varying laser fluence. Here it is seen that for all laser fluence values, the emission of the molecule **Pt-2** rises during the laser pulse and remains relatively constant for times > 100 ns, consistent with the 20 μs lifetime. By contrast, the emission transients for the **Poly-Pt-n** samples show a pronounced fast decay that occurs during the excitation pulse and continues for some time following the pulse, ultimately settling into a signal that persists for > 100 ns. Inspection of the data in Fig. 4 reveals the following trends: 1) The amplitude of the fast decay phase relative to the long-lived component increases with increasing laser pulse fluence; 2) The amplitude of the fast phase relative to the long-lived component is greater for the higher MW samples (**Poly-Pt-n**, n = 57, 183) compared to the shortest polymer **Poly-Pt-13**; 3) The overall decay dynamics for all the polymers become faster at higher laser fluence. These trends in the emission dynamics, although qualitative, are fully consistent with the simulations which indicate that the annihilation will lead to a more rapid triplet population decay at higher triplet density (higher laser fluence). Experiments were performed with femtosecond TA spectroscopy in an attempt to better resolve the triplet population dynamics. However, unfortunately these experiments failed to detect the t-tA process since the accessible pulse fluences are ~10,000-fold lower compared to those accessible under the nanosecond excitation (see SI for comparison).

Interestingly, the data in Fig. 2 show that at saturation the triplet exciton population is ~10 times lower for **Poly-Pt-13** compared to **Pt-2**. Assuming that the absorptivity of the triplet exciton is comparable for the polymer and molecular triplet states, this suggests that at saturation the polymers support a triplet exciton density of ~ 0.1 triplets per repeat unit. For optical limiting applications, this difference means that the platinum poly-ynes would be ~10-fold less effective at long-pulse limiting, other factors being equal.

The current study provides very clear evidence that t-tA occurs on a relatively rapid time scale in platinum poly-ynes. This result is not surprising in view of previous experiments which reveal that intrachain triplet diffusion in platinum poly-ynes is relatively rapid.[33-34] The findings are also consistent with previous studies demonstrating that singlet and triplet exciton annihilation are important processes in conjugated polymers and must be accounted for when modeling their performance under conditions of high optical pulse excitation.[35-38]

Associated Content

Supporting Information

The Supporting Information is available free of charge on the ACS Publication website at http://pubs.acs.org/. Experimental details, NMR spectra, GPC data, photophysical properties measurements, simulations details and photon concentration calculations.

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Notes

The authors declare no competing financial interest.

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