

Excited state absorption and optical limiting of platinum(II) 4'-arylterpyridyl acetylide complexes

Wenfang Sun and Fengqi Guo

Department of Chemistry, Biochemistry and Molecular Biology, North Dakota State University, Fargo, ND 58105-5516, USA

The excited state absorption and optical limiting of a series of platinum(II) 4'-arylterpyridyl acetylide complexes have been investigated. These complexes possess relatively long triplet excited state lifetime that varies from tens of nanoseconds to several microseconds; and exhibit broad triplet excited state absorption in most of the visible to near infrared spectral region. Nonlinear transmission experiments demonstrate that all of the complexes show pronounced optical limiting for ns laser pulses at 532 nm. The photophysical properties and optical limiting characteristics are influenced significantly by the nature of 4'-aryl substituent and the acetylide ligand.

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Organic materials with strong and broadband reverse saturable absorption (RSA) are desired for optical limiting applications. Pt:Poly-nyl complexes are particularly attractive candidates for this application due to their broadband spectral (450–1100 nm) and temporal (picoseconds to hundreds of nanoseconds) nonlinear responses^[1–4]. However, the instability upon exposure to laser irradiation prevents their application as practical optical limiting materials.

Square-planar platinum(II) terpyridyl complexes have attracted special interest in recent years because of their unique spectroscopic properties, such as room temperature phosphorescence in fluid^[5–8]. However, little work has been reported on the excited state absorption and optical limiting properties of these complexes^[9]. To remedy this deficiency, a series of platinum(II) 4'-arylterpyridyl acetylide complexes (shown in Fig. 1) that contain different acetylide ligands and 4'-aryl substituents have been synthesized and investigated. According to the reported work on the platinum(II) terpyridyl complexes, the lowest excited state for most of the complexes is metal-to-ligand charge transfer (MLCT) in character^[5–8]. Variation of the 4'-substituents could change the energy of the terpyridyl based LUMO, while the energy of the metal based HOMO could be affected by the acetylide ligand. As a result, the characteristics of the MLCT excited state could be altered. In some cases, the variation of the 4'-substituent on the terpyridyl ligand can even change the orbital parentage of the lowest excited state, as reported by McMillin and co-workers for the 4'-pyrenylterpyridyl chloride complex, in which the lowest excited state is intraligand charge transfer in character^[8]. Therefore, it is

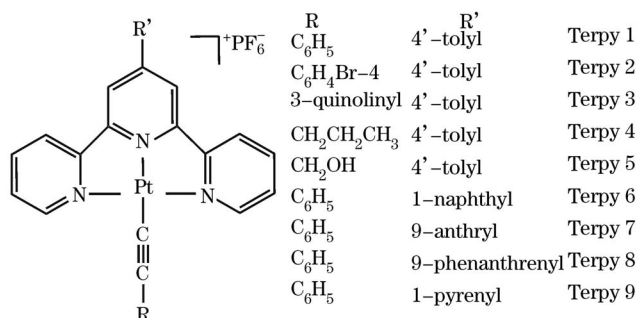


Fig. 1. Chemical structures of platinum(II) 4'-arylterpyridyl acetylide complexes.

expected that these structural alternations could have a significant influence on the excited state absorption and optical limiting characteristics of the complexes, which has been investigated in our group and the preliminary results are presented in this letter.

The complexes used for this study were synthesized by modification of literature procedures^[7], and were characterized by UV-Vis, IR, ¹H-NMR, HRMS, and elemental analyses to ensure the purity. The synthetic work has been (will be) reported elsewhere^[10,11].

It is well known that in order for reverse saturable absorption to occur, the excited state absorption cross-section must exceed the ground state absorption cross-section. The higher the ratio of the excited state

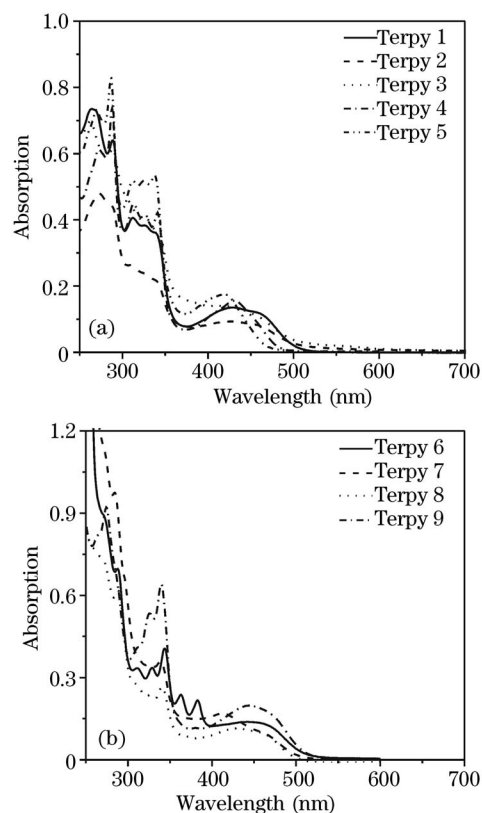


Fig. 2. Linear absorption spectra of platinum(II) 4'-arylterpyridyl acetylide complexes in acetonitrile in a 1-cm cell. $c = 1.0 \times 10^{-5}$ mol/L.

absorption to ground state absorption is, the stronger the reverse saturable absorption will be. To increase this ratio, one can either decrease the ground state absorption or increase the excited state absorption. Therefore, it is important to study the ground state absorption characteristics. The linear absorption spectra of the platinum(II) 4'-arylterpyridyl acetylide complexes were measured using a Varian 500 UV-VIS-NIR spectrophotometer and the results are shown in Fig. 2. All of the spectra feature intense absorption in the 260–350 nm regions and a broad band above 400 nm. According to the reported work on similar platinum(II) terpyridyl acetylide complexes, the intense UV absorption bands arise from π, π^* intraligand (IL) transitions of the terpyridyl ligands and the acetylide ligands, as well as the charge transfer transition involved in the Pt–C \equiv CR moieties; while the broad band above 400 nm can be attributed to the $d\pi(\text{Pt}) \rightarrow \pi^*(\text{terpy})$ metal-to-ligand charge transfer transition (MLCT)^[5,8,12]. Although both the substituents on the 4'-position of the terpyridyl ligand and the substituents on the acetylide ligand influence the UV absorption bands, the substituents on the acetylide ligand influence the MLCT transition more significantly. Arylacetylide ligands cause a red shift of the MLCT transition, which can be attributed to the increase of the metal-based HOMO orbital energy of the MLCT transition. Stronger π -electron donating groups, such as aryl substituents increase the energy of the $d\pi(\text{Pt})$ orbital, while the energy of the terpyridyl based π^* orbital remains constant^[12]. This decreases the energy gap between the $d\pi(\text{Pt})$ orbital and the $\pi^*(\text{terpy})$ orbital, resulting in the red shift of the MLCT band. Nevertheless, the absorption spectra of these complexes are essentially transparent above 550 nm, indicating that nonlinear absorption (reverse saturable absorption or two-photon absorption) could occur in most of the visible and near infrared region.

The reverse saturable absorption of nanosecond laser pulses are generally dominated by the triplet excited state absorption when the intersystem crossing time is shorter than the laser pulsewidth. It has been reported that the intersystem crossing time for a platinum ethynyl complex is ~ 330 ps^[2]. It is reasonable to assume that the intersystem crossing rate is also rapid for the platinum(II) terpyridyl complexes due to the heavy-metal enhanced spin-orbital coupling. Thus, the reverse saturable absorption of nanosecond laser pulses by the platinum(II) terpyridyl complexes should be dominated by the triplet excited state absorption. In this case, if the triplet excited state possesses long lifetime, high quantum yield and large absorption cross-section, the reverse saturable absorption would be enhanced.

To determine the lifetime of the triplet excited state and the spectral range for reverse saturable absorption, the kinetic transient difference absorption spectra of the platinum(II) 4'-arylterpyridyl acetylide complexes were measured using an Edinburgh LP920 laser flash photolysis spectrometer. As shown in Fig. 3, all of the complexes exhibit a broad transient absorption band from 480 to 800 nm, indicating that the triplet excited state absorption of these complexes is stronger than that of the ground state absorption in the visible to near-IR spectral region. Therefore, reverse saturable absorption could occur in this spectral range. Meanwhile, the triplet

excited state lifetime (see Table 1) are measured to be in the order of tens of nanoseconds to several microseconds, which is sufficiently long to allow for optical limiting of nanosecond laser pulses to occur. In addition, the quantum yields of the triplet excited state are found to be $88\% \pm 7\%$ for Terpy 1, $77\% \pm 8\%$ for Terpy 2 and $60\% \pm 5\%$ for Terpy 3 due to the heavy-metal enhanced spin-orbital coupling effect^[10]. The quantum yields of the rest of the complexes have not been determined, but presumably comparable to these three complexes. The relatively long lifetime, high quantum yield, and the broad and strong triplet excited absorption of these complexes provide the necessary conditions for reverse saturable absorption to occur. Therefore, these complexes are promising candidates for broadband optical limiting applications.

In order to demonstrate the feasibility of these complexes for optical limiting application, nonlinear transmission measurements were conducted at 532 nm. A frequency-doubled (532 nm), Q-switched Quantel Brilliant Nd:YAG laser with 4.1 ns (FWHM) pulsewidth and 10-Hz repetition rate was used as the light source. The energy of the incident laser beam was attenuated by a combination of a half-wave plate and a polarizable cubic beamsplitter. Then the beam was split by a wedged beamsplitter. One of the reflected beams was used to monitor the incident energy, and the transmitted beam was reduced to half of the original size by a telescope and was focused by a 25-cm plano-convex lens ($f/65.6$) to the center of a 2-mm sample cell. The radius of the beam waist was approximate $22.2 \mu\text{m}$. The incident energy and the output energy were monitored by two molelectron

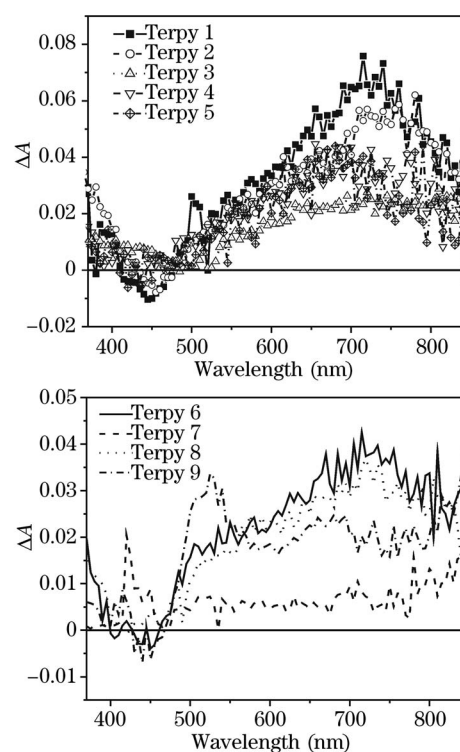


Fig. 3. Triplet excited state transient difference absorption spectra of platinum(II) 4'-arylterpyridyl acetylide complexes in acetonitrile in a 1-cm cell. The spectra are monitored right after the laser excitation at 355 nm.

Table 1. Photophysical and Optical Limiting Parameters for the Platinum(II) 4'-arylterpyridyl Acetylde Complexes in Acetonitrile

Complex	τ_T^a (ns)	σ_0^b ($\times 10^{-19}$ cm 2)	F_{th}^c (at $T/T_0 = 0.9$) (mJ/cm 2)	T_{lim}^d	σ_{eff}/σ_g
Terpy 1	766	2.43	48	0.28 ^e , 0.25 ^f	>3.57 ^e , >3.89 ^f
Terpy 2	659	7.18	144	0.34 ^e	>3.02 ^e
Terpy 3	672	11.2	1090	0.44 ^e	>2.30 ^e
Terpy 4	62	5.31	62	0.19 ^e	>4.66 ^e
Terpy 5	51	2.40	900	0.45 ^e	>2.24 ^e
Terpy 6	338	18.1	250	0.27 ^f	>3.67 ^f
Terpy 7	479	17.6	490	0.32 ^f	>3.19 ^f
Terpy 8	420	4.30	370	0.27 ^f	>3.67 ^f
Terpy 9	2540	13.4	52	0.18 ^f	>4.81 ^f

^aTriplet excited state lifetime measured by the decay of the transient absorption at 700 nm, ^bground state absorption cross-section at 532 nm, ^cRSA threshold when the transmittance drops to 90% of the linear transmittance, ^dnonlinear transmittance at high incident fluence, ^eat incident fluence of 2.5 J/cm 2 , and ^fat incident fluence of 3.0 J/cm 2

J4-09 pyroelectric joule meters. The nonlinear transmission results are shown in Fig. 4.

It is quite obvious that the absorption curves for all of the complexes deviate significantly from the linear absorption curve, suggesting the occurrence of optical limiting. The limiting threshold at $T/T_0 = 0.9$, and the nonlinear transmittance at incident fluence of 2.5 J/cm 2 (or 3.0 J/cm 2) are listed in Table 1. The optical limiting characteristics of these complexes are influenced dramatically by the nature of the chemical structures. Terpy 4 and Terpy 9 show the strongest reverse saturable absorption with the transmittance drop

to 19% at the incident fluence of 2.5 J/cm 2 for Terpy 4, and 18% at 3.0 J/cm 2 for Terpy 9. The strength of the optical limiting appears to be Terpy 4 > Terpy 9 > Terpy 1 > Terpy 6 \approx Terpy 8 > Terpy 2 > Terpy 7 > Terpy 3 \approx Terpy 5. The strong optical limiting of Terpy 9 could be related to its long triplet excited state lifetime and the large excited state absorption cross-section at 532 nm; while the factors that contribute to the strong optical limiting of Terpy 4 is not clear at this time. One possible explanation could be due to the high quantum yield of the triplet excited state, which needs to be verified later. However, the relative weak optical limiting of complexes Terpy 3, 5, and 7 should be related to their low triplet excited state absorption and/or the short lifetime of the triplet excited state. Except for Terpy 4 and 9, the optical limiting appears to be related to the electron-donating ability of the acetylde ligand and the 4'-aryl substituents. The stronger the electron donor, the better the optical limiting.

To quantitatively compare the strength of optical limiting of the complexes, a figure of merit σ_{eff}/σ_g is used, where σ_{eff} is the effective excited state absorption cross-section and σ_g is the ground state absorption cross-section. At the incident fluence of 2.5 J/cm 2 , which is much higher than the saturable fluence $F_{sat} = h\nu/\sigma_g\Phi_t^{[13]}$, the ground state is greatly bleached, and the excited state population is mainly distributed at the triplet excited state. In this case, σ_{eff}/σ_g can be defined as $\sigma_{eff}/\sigma_g = \ln T_{sat}/\ln T_{lin}^{[13]}$, where T_{sat} is the transmittance at the saturable fluence, T_{lin} is the linear transmittance. However, the damage threshold of the quartz cell (5 J/cm 2) limited the maximum incident fluence that could be used in our experiments; therefore, we were unable to reach the saturable transmittance. Nevertheless, we can use the lowest transmittance at the highest incident fluence to calculate the lowest bound of σ_{eff}/σ_g for these complexes. The results are shown in Table 1. It is very clear that this ratio is much higher for Terpy 4 and 9, which is another factor that accounts for the strong optical limiting of these two complexes.

In summary, the platinum(II) 4'-arylterpyridyl acetylde complexes possess a high quantum yield of

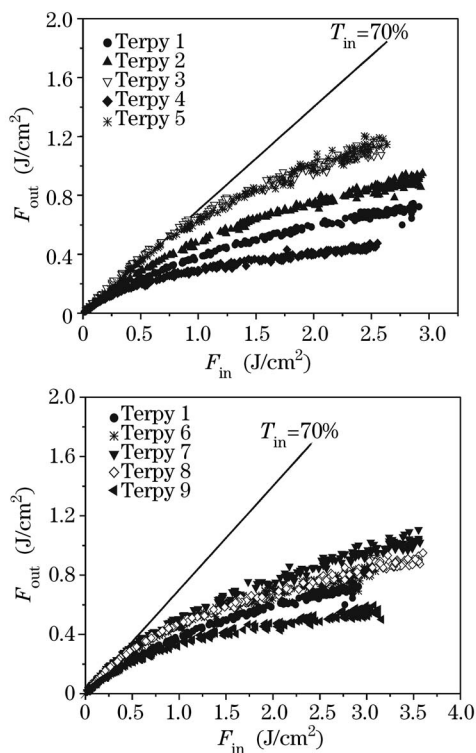


Fig. 4. Optical limiting curves of platinum(II) 4'-arylterpyridyl acetylde complexes in acetonitrile in a 2-mm cell. The linear transmission for all of the solutions is 70%.

the triplet excited state, relatively long triplet excited state lifetime, and strong and broad triplet excited state absorption, which result in the significant optical limiting of nanosecond laser pulses. The optical limiting performances are influenced drastically by the nature of the 4'-aryl substituents and the acetylide ligands. These complexes are promising candidates for broadband optical limiting applications.

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