

Long-lifetime reverse saturable absorption in a bipyridyl platinum(II) complex bearing naphthalimidylethynyl-substituted fluorenylacetylide ligands



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ABSTRACT

By fitting femtosecond transient difference absorption time series at multiple wavelengths, the singlet excited-state lifetime of a particular platinum(II) 2,2'-bipyridyl complex bearing naphthalimidylethynyl-substituted fluorenyl-acetylide ligands was determined to be 83.5 ± 39 ps in toluene solution. A triplet quantum yield of 0.06 was measured using relative actinometry. Excited-state absorption cross sections of 5.6×10^{-17} cm² (singlet) and 7.8×10^{-16} cm² (triplet) at 532 nm were obtained by using a five-level dynamic model to fit open-aperture Z scans at picosecond and nanosecond pulse widths and a variety of pulse energies. Most significantly, fits of nanosecond transient difference absorption decay data yield a value of 16.3 μ s for the triplet excited-state lifetime of the complex in deoxygenated toluene solution, longer by a factor of almost 20 than the lifetime of the analogous complex with benzothiazolyl-substituted ligands.

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1. Introduction

The recent scientific literature contains reports of all-optical switching in a variety of material systems: in photonic crystals [1], in gases [2], and in solutions and thin films of conjugated organic molecules exhibiting two-photon absorption and/or reverse saturable absorption [3,4]. Reverse saturable absorption (RSA) arises when a material's ground-state absorption cross section at a given wavelength, $\sigma_G(\lambda)$, is less than its excited-state absorption cross section(s) at that wavelength. The effect of this nonlinearity is evidently enhanced when the excited state in question is long-lived, allowing the build-up of a population of strongly absorbing excited molecules. For this reason, the ratio $\sigma_T(\lambda)/\sigma_G(\lambda)$, where $\sigma_T(\lambda)$ is the triplet excited-state cross section at wavelength λ , has long been used as a figure of merit for RSA materials [5]. Large values of the ratio $\sigma_T(\lambda)/\sigma_G(\lambda)$ have been reported in both in platinum(II) diimine [6–11] and terpyridine complexes [11–13], and the observation of phosphorescence in room temperature solutions of both classes of complexes [14,15] evidences rapid

intersystem crossing, necessary to insure the accessibility of the highly absorbing, long-lived triplet state.

In order to optimally exploit RSA for an optical switching application, the lifetime of the excited state should be of the same order of magnitude or greater than the switching time scale. Now, the molecule whose photophysical parameters were reported in [16,9] a 4,4'-di-*tert*-butyl-2,2'-bipyridyl platinum(II) complex bearing a pair of 2-(benzothiazol-2'-yl)-7-ethynyl-9,9-diethylfluorenyl ligands, exhibits one of the largest values of the cross-section ratio $\sigma_T(532 \text{ nm})/\sigma_G(532 \text{ nm})$ ever reported, but it has a triplet excited-state lifetime τ_T of only ~ 800 ns in deoxygenated toluene solution. In an effort to increase this molecule's τ_T by an order of magnitude, so as to permit effective optical switching on time scales of tens of microseconds [17] and, at the same time, to investigate how the excited-state absorption properties of the complex are influenced by the character of the ligand, we replaced the benzothiazolyl (BTZ) group at the 2-position of the fluorene in the ligand with an *N*-butylnaphthalimid-4-yl-ethynyl group, here abbreviated C \equiv C–NI. (In addition, the ethyl groups at the 9-position of the fluorenes and the *tert*-butyl groups at the 4- and 4'-positions of the bipyridine were replaced by longer, branched alkyl chains, but this substitution should not affect the nonlinear properties of the molecule.) The structure of the resulting molecule, which we will

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represent here as $\text{bpyPt}(\text{C}\equiv\text{C}-\text{F}-\text{C}\equiv\text{C}-\text{NI})_2$, is shown in Fig. 1. Our choice of the $\text{C}\equiv\text{C}-\text{NI}$ group to replace the BTZ group was motivated by reports of an extremely long-lived naphthalimide-based triplet excited state in a platinum diimine complex with $\text{C}\equiv\text{C}-\text{NI}$ ligands [18].

2. Experimental measurements

The $\text{bpyPt}(\text{C}\equiv\text{C}-\text{F}-\text{C}\equiv\text{C}-\text{NI})_2$ complex was synthesized as described in [19] and fully characterized by UV-vis, ^1H NMR, high-resolution mass spectroscopy, and elemental analysis. The linear absorption spectrum, indicated by the black line in the right-hand panel of Fig. 1, was measured using a Perkin Elmer Lambda 20 UV-vis spectrometer. The triplet excited-state lifetime τ_T of the complex in deoxygenated toluene solution was obtained by fitting nanosecond transient difference absorption (ns TA) decay data to a single exponential: the ns TA measurement was repeated three times and the lifetimes obtained by fitting the three resulting time series at the peak of the triplet-triplet absorption spectrum, 575 nm, were averaged, giving a value of 16.3 μs . The triplet quantum yield Φ was measured by relative actinometry [20] with SiNc in benzene ($\epsilon_{590} = 70,000 \text{ M}^{-1} \text{ cm}^{-1}$, $\Phi = 0.20$) as a reference [21], yielding a value of 0.06. These results compare to the values 29.6 μs for τ_T and 0.09 for Φ reported in [19] for $\text{bpyPt}(\text{C}\equiv\text{C}-\text{F}-\text{C}\equiv\text{C}-\text{NI})_2$ in acetonitrile, a significantly more polar solvent.

2.1. Femtosecond transient difference absorption spectra

As in other platinum complexes, the heavy-atom effect of platinum in $\text{bpyPt}(\text{C}\equiv\text{C}-\text{F}-\text{C}\equiv\text{C}-\text{NI})_2$ quenches fluorescence from the singlet excited state, making a direct measurement of the singlet excited-state lifetime from the fluorescence decay data impossible. For this reason, a femtosecond time-resolved transient difference absorption (fs TA) measurement was performed to determine the singlet excited-state lifetime of the complex. The fs TA measurements were performed using a femtosecond pump-probe UV-vis spectrometer (HELIOS) manufactured by Ultrafast Systems LLC. The sample solution in a 2-mm cuvette was excited at 400 nm using a 105-fs Ti:Sapphire laser (Spectra Physics Hurricane, 1 kHz repetition rate, 1 mJ/pulse at 800 nm) and the absorption was probed from 425 to 800 nm with sapphire-generated white-light continuum. The measurement results for $\text{bpyPt}(\text{C}\equiv\text{C}-\text{F}-\text{C}\equiv\text{C}-\text{NI})_2$ in air-saturated toluene solution are shown on the right in Fig. 1, along with the ground-state absorption spectrum. The fs TA spectrum measured at long time delay is consistent with the ns TA data reported in [19]. Fitting the fs TA decay data at a number of randomly selected wavelengths and averaging the results yields a value of 83.5 ± 39 ps for the singlet-state lifetime τ_S ; the relatively large uncertainty reflects the large variation in the fitting results at different

wavelengths. The time scale for intersystem crossing, given by τ_S/Φ , is 1.4 ns.

2.2. Open-aperture Z-scan measurements

Two series of open-aperture Z scans [22], one using nanosecond pulses and the other, picosecond pulses, were performed at a wavelength of 532 nm on a 1-mm sample of 0.408-mM $\text{bpyPt}(\text{C}\equiv\text{C}-\text{F}-\text{C}\equiv\text{C}-\text{NI})_2$ in toluene. The nanosecond Z scans employed a spatially Gaussian beam with a $\text{HW}(e^{-2})M$ of 20.8 μm , corresponding to a Rayleigh range Z_R of 2.55 mm. These Z scans utilized 8.2-ns FWHM pulses at 10 Hz generated by an EKSPLA NL 101-SH diode-pumped, frequency-doubled Nd:YAG laser. A total of four nanosecond Z scans were performed using energies of 64.7, 168.8, 384.1, and 732.3 nJ/pulse.

The picosecond Z scans employed a top-hat beam: After expansion using a telescope, the beam from an EKSPLA PG401 Optical Parametric Generator (OPG) was clipped to a diameter of 4 mm by an iris and brought to a focus using a lens of focal length 250 mm in an $f/62.5$ focusing geometry. Following the convention of Refs. [23] and [24], in which the Rayleigh range Z_R of a top-hat beam is defined in terms of the f -number of the system and the wavelength λ by $\pi (f/\#)^2 \lambda$, the Rayleigh range of the $f/62.5$ system operating at 532-nm wavelength is 6.53 mm. The laser/OPG system delivered 30-ps FWHM pulses at a repetition rate of 10 Hz. Each data point represents an average of ten shots within a 2% energy window. A total of six 532-nm, picosecond Z scans were performed at energies of 17, 26, 41, 69, 109, and 181 nJ/pulse. The data obtained in the nanosecond and picosecond Z-scan measurements at 532-nm wavelength are displayed as symbols in Fig. 2.

In addition to the 532-nm picosecond Z scans just described, open-aperture, picosecond top-hat Z scans were also performed at twelve other visible wavelengths using the identical 1-mm sample of 0.408-mM $\text{bpyPt}(\text{C}\equiv\text{C}-\text{F}-\text{C}\equiv\text{C}-\text{NI})_2$ in toluene employed for the 532-nm scans. These measurements employed the same $f/62.5$ focusing geometry as the 532-nm top-hat Z-scans described above. The quality of the beam delivered by the OPG varied only slightly with wavelength, as evidenced by the measured M^2 values, which ranged from 1.38 to 1.45 across the tuning range of 450 to 650 nm. Fig. 3 shows Z scans at two representative wavelengths: 475 nm, where the ground-state absorption is sufficiently strong that $\text{bpyPt}(\text{C}\equiv\text{C}-\text{F}-\text{C}\equiv\text{C}-\text{NI})_2$ exhibits saturable absorption, and 550 nm, where the material displays RSA.

3. Integrated analysis of Z-scan and femtosecond transient difference absorption data

Nonlinear absorption by organometallic complexes such as $\text{bpyPt}(\text{C}\equiv\text{C}-\text{F}-\text{C}\equiv\text{C}-\text{NI})_2$ in solution at room temperature can

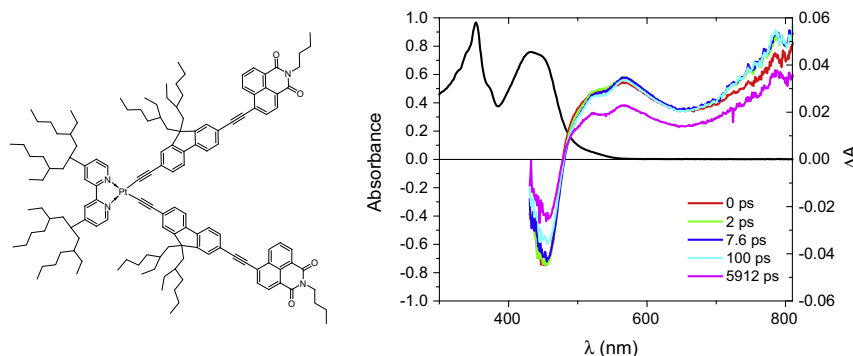


Fig. 1. Structure (left) and spectra in toluene (right) of $\text{bpyPt}(\text{C}\equiv\text{C}-\text{F}-\text{C}\equiv\text{C}-\text{NI})_2$: absorption spectrum (black curve) and femtosecond transient difference absorption spectra (colored curves). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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