U.S. Air Force Research

U.S. Department of Defense

2015

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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} cm^2 (singlet) and 7.8×10^{-16} cm^2 (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 μs 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.

Published by Elsevier B.V.

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≡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

represent here as bpyPt(C≡C—F—C≡C—NI)$_2$, is shown in Fig. 1. Our choice of the C≡C—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 C≡C—NI ligands [18].

2. Experimental measurements

The bpyPt(C≡C—F—C≡C—NI)$_2$ complex was synthesized as described in [19] and fully characterized by UV–vis, ^{1}H 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 (ε_{590} = 70,000 M^{-1} cm^{-1}, Φ = 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 bpyPt(C≡C—F—C≡C—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 bpyPt(C≡C—F—C≡C—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 bpyPt(C≡C—F—C≡C—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 bpyPt(C≡C—F—C≡C—NI)$_2$ in toluene. The nanosecond Z scans employed a spatially Gaussian beam with a 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 π (f/#)^2 λ, 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 bpyPt(C≡C—F—C≡C—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 bpyPt(C≡C—F—C≡C—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 bpyPt(C≡C—F—C≡C—NI)$_2$ in solution at room temperature can
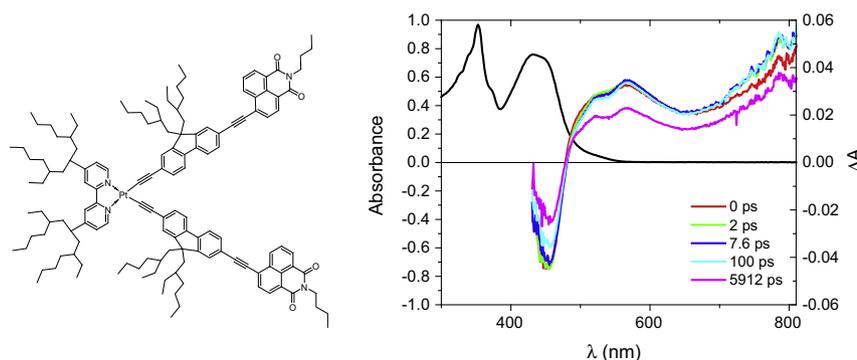
Fig. 1. Structure (left) and spectra in toluene (right) of bpyPt(C≡C—F—C≡C—NI)$_2$: absorption spectrum (black curve) and femtosecond transient difference absorption spectra (colored curves). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
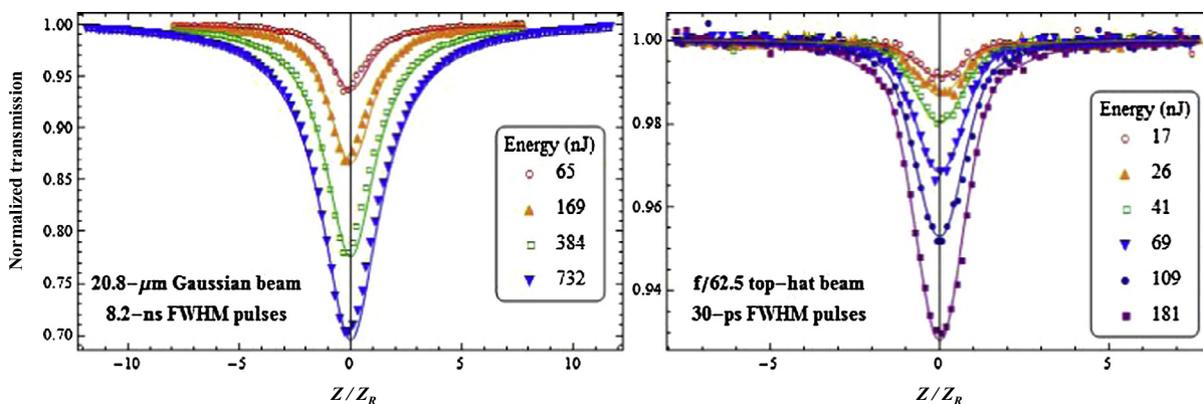
Fig. 2. Z scans of bpyPt(C≡C—F—C≡C—NI)₂ in toluene obtained using nanosecond (left) and picosecond (right) pulses at 532 nm. The pair of excited-state absorption cross sections $(\sigma_S, \sigma_T) = (56, 780) \times 10^{-18}$ cm² generate all of the theoretical curves indicated by the solid lines.
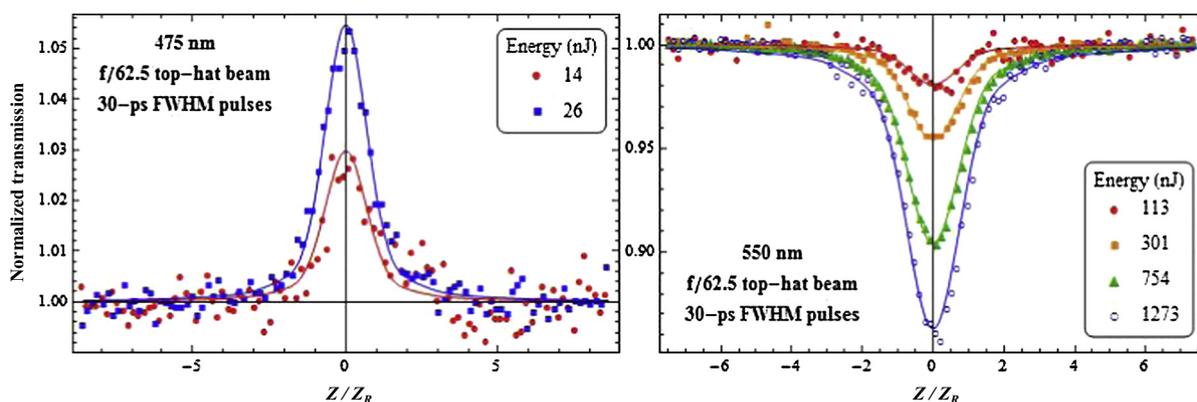

Fig. 3. Picosecond top-hat Z scans of 0.408-mM bpyPt(C≡C—F—C≡C—NI)₂ in toluene at two representative wavelengths: 475 nm (left) and 550 nm (right). The data at each wavelength were fit using $\sigma_S(\lambda)$ as the sole fitting parameter.

be described generically by the five-band rate equation model [5,25], which tracks the populations of the vibrational–rotational manifolds associated with the electronic ground state, S_0 (a singlet); with two singlet excited states, S_1 and S_m; and with two triplet excited states, T_1 and T_n. The differential equations for the populations of the relevant electronic states and for the attenuation and propagation of the beam are solved numerically using the procedure described in [26]. We analyze the Z-scan data in Fig. 2 in terms of this model, using the following independently measured parameter values: For $\sigma_G(532$ nm), the ground-state absorption cross section of bpyPt(C≡C—F—C≡C—NI)₂ in toluene at 532 nm, we employ the value $(1.19 \times 10^{-17}$ cm²) obtained from the UV–vis spectrum shown in Fig. 1; for the singlet excited-state lifetime τ_S, the triplet excited-state lifetime τ_T, and the triplet quantum yield Φ, we use the values reported above: 83.5 ps, 16.3 µs, and 0.06, respectively. We assume that decay from S_m to S_1 is ultra-fast (lifetime ~1 ps), as are decays to the lowest lying vibrational–rotational level in any band. The nanosecond Z-scan data display a diminution of induced absorption in the focal region that cannot be accounted for unless the lifetime of T_n is at least 100 ps; we therefore assume a T_n-lifetime of 100 ps, corresponding to a decay rate that falls at the lower end of the range of rates observed for internal conversions from an upper level to the lowest-lying excited state of the same multiplicity [25]. With these assumptions, we succeeded in finding a single pair of excited-state absorption cross-section values (σ_S, σ_T) that simultaneously fits the four nanosecond and six picosecond Z scans shown in Fig 2: $\sigma_S(532$ nm) $= 5.6 \times 10^{-17}$ cm² and $\sigma_T(532$ nm) $= 7.8 \times 10^{-16}$ cm².

The resulting ten theoretical curves, indicated by the solid lines in Fig. 2, are seen to fit the experimental data extremely well.

The value of $\sigma_T(532$ nm), determined from simultaneous fitting of nanosecond and picosecond Z scans in the manner just described, was next used in conjunction with the fs TA spectra reproduced in Fig. 1 to provide an estimate of $\sigma_T(\lambda)$ at various wavelengths of interest in the visible: $\sigma_T(\lambda)$ was determined from the fs TA spectrum at "long" (5912-ps) time delay and the value of $\sigma_T(532$ nm), 7.8×10^{-16} cm². Since the time delay is significantly longer than τ_S, the measured optical density change should be due entirely to the population of the lowest-lying triplet excited state T_1. The values of $\sigma_T(\lambda)$ obtained in this way are reported in Table 1.

Finally, at wavelengths other than 532 nm, the value of $\sigma_T(\lambda)$ estimated from the fs TA spectrum was employed as a fixed parameter in the five-band model, and the picosecond Z scans were fit using $\sigma_S(\lambda)$ as the single fitting parameter. Table 1 displays the results, and the fits at two representative wavelengths are indicated by the solid lines in Fig. 3.

The fs TA spectra appearing in the right-hand panel of Fig. 1 provide a qualitative check of the consistency of these results: The spectra recorded at 0, 2, 7.6, and 100 ps after excitation are all seen to lie more or less on top of one another over the range 500–700 nm; only in the spectrum at 5912-ps time delay can one discern any significant decay. It can be shown that in a low-polarity solvent like toluene, in which one would expect solvent reorientation effects to be negligible, the observed optical density change at times t exceeding the time scale for internal conversions within the singlet manifold is given by

Table 1
Absorption cross sections of bpyPt(C≡C—F—C≡C—NI)$_2$ in toluene.

λ (nm)	$\sigma_G(\lambda)$ (10^{-18} cm^2)[a]	$\sigma_S(\lambda)$ (10^{-18} cm^2)[b]	$\sigma_T(\lambda)$ (10^{-18} cm^2)[d]
450	249	185	–
475	118	83	3
480	90	67	175
490	55	66	465
500	36	55	578
510	25	53	704
520	18	54	796
532	12	56[c]	780[c]
540	7.7	51	763
550	3.8	52	831
560	1.5	58	905
570	0.49	75	919
580	0.081	200	866

[a] From UV–vis absorption spectrum.
[b] Obtained by fitting ps top-hat Z scans, except where otherwise noted.
[c] Determined from combined fitting of ns and ps Z scans.
[d] For wavelengths other than 532 nm, $\sigma_T(\lambda)$ is determined from the value of $\sigma_T(532\ \text{nm})$ and the fs TA spectrum at 5.9 ns time delay.

$$\Delta OD(\lambda,t) \propto \{\sigma_S(\lambda) - \sigma_G(\lambda) - \eta\Phi[\sigma_T(\lambda) - \sigma_G(\lambda)]\}e^{-t/\tau_S} + \eta\Phi[\sigma_T(\lambda) - \sigma_G(\lambda)]e^{-t/\tau_T}, \tag{1}$$

where $\eta = \tau_T/(\tau_T - \tau_S) \approx 1$. Computing the coefficients of $\exp[-t/\tau_S]$ and $\exp[-t/\tau_T]$ from the cross section values in Table 1, one obtains, for instance at $\lambda = 532$ nm, values of -2×10^{-18} cm^2 and 46×10^{-18} cm^2, respectively. At other wavelengths, there is a similar disparity in the relative magnitudes of the two coefficients, which serves to suppress the effects of the decay at time scale τ_S relative to those at the longer time scale τ_T.

4. Conclusions

We report the following photophysical parameter values for bpyPt(C≡C—F—C≡C—NI)$_2$ in toluene: 83.5 ps for the singlet excited-state lifetime τ_S, obtained by fitting fs TA decay data; 16.3 μs for the triplet excited-state lifetime τ_T, obtained from ns TA decay data; and 0.06 for the triplet quantum yield Φ, measured using relative actinometry. By simultaneously fitting 532-nm picosecond top-hat and nanosecond Gaussian Z scans at multiple energies to a five-band model, we obtain the following values of the absorption cross sections at 532-nm wavelength: 5.6×10^{-17} cm^2 for the singlet excited-state absorption cross section $\sigma_S(532\ \text{nm})$, and 7.8×10^{-16} cm^2 for the triplet excited-state absorption cross section $\sigma_T(532\ \text{nm})$. Combined analysis of the fs TA spectrum at 5.9-ns time delay and top-hat picosecond Z scans at other wavelengths in the visible provides values of $\sigma_S(\lambda)$ and $\sigma_T(\lambda)$ at those wavelengths.

The ratio of absorption cross sections $\sigma_T(532\ \text{nm})/\sigma_G(532\ \text{nm})$ for bpyPt(C≡C—F—C≡C—NI)$_2$ in toluene is only 66, compared to the value of 754 reported in [16] for bpyPt(C≡C—F—BTZ)$_2$ in dichloromethane, a more polar solvent. However, this large reported value of the cross-section ratio reflects not the strength of the latter complex's triplet excited-state absorption, but rather the weakness of its ground-state absorption at 532 nm resulting from the negative solvatochromic effect of the dichloromethane solvent. Indeed, the value of $\sigma_T(532\ \text{nm})$ reported here for bpyPt(C≡C—F—C≡C—NI)$_2$ in toluene, 7.8×10^{-16} cm^2, is significantly *larger* than that reported in [16] for bpyPt(C≡C—F—BTZ)$_2$ in dichloromethane, 4.6×10^{-16} cm^2. In toluene, where bpyPt(C≡C—F—BTZ)$_2$ exhibits a measured $\sigma_G(532\ \text{nm})$ of 9.6×10^{-18} cm^2, one would expect the ratio $\sigma_T(532\ \text{nm})/\sigma_G(532\ \text{nm})$ to be comparable for the two complexes. Most significantly, the reported triplet excited-state lifetime of bpyPt(C≡C—F—C≡C—NI)$_2$ in toluene, 16.3 μs, represents an almost twenty-fold improvement over the triplet excited-state lifetime of

bpyPt(C≡C—F—BTZ)$_2$, measured in deoxygenated, 0.005-mM toluene solution to be 827 ± 50 ns.

References

[1] V. Eckhouse, I. Cestier, G. Eisenstein, S. Combrié, G. Lehoucq, A. De Rossi, Kerr-induced all-optical switching in a GaInP photonic crystal Fabry–Perot resonator, Opt. Ex. 20 (2012) 8524–8534.
[2] A.M.C. Dawes, L. Illing, S.M. Clark, D.J. Gauthier, All-optical switching in rubidium vapor, Science 29 (2005) 672–674.
[3] J. Clark, G. Lanzani, Organic photonics for communications, Nat. Photonics 4 (2010) 438–446.
[4] K.B. Manjunatha, R. Dileep, G. Umesh, M.N. Satyanarayan, B. Ramachandra Bhat, All optical nonlinear and switching characteristics of a novel ruthenium complex, Opt. Mat. 36 (2014) 1054–1059.
[5] J.W. Perry, Organic and metal-containing reverse saturable absorbers for optical limiters, in: H.S. Nalwa, S. Miyata (Eds.), Nonlinear Optics of Organic Molecules and Polymers, CRC Press, Boca Raton, Florida, 1997.
[6] M. Hissler, W.B. Connick, D.K. Geiger, J.E. McGarrah, D. Lipa, R.J. Lachicotte, R. Eisenberg, Platinum diimine bis(acetylide) complexes: synthesis, characterization, and luminescence properties, Inorg. Chem. 39 (2000) 447–457.
[7] C.E. Whittle, J.A. Weinstein, M.W. George, K.S. Schanze, Photophysics of diimine platinum(II) bis-acetylide complexes, Inorg. Chem. 40 (2001) 4053–4062.
[8] T.J. Wadas, R.J. Lachicotte, R. Eisenberg, Synthesis and characterization of platinum diimine bis(acetylide) complexes containing easily derivatizable aryl acetylide ligands, Inorg. Chem. 42 (2003) 3772–3778.
[9] W. Sun, B. Zhang, Y. Li, T.M. Pritchett, Z. Li, J.E. Haley, Broadband nonlinear absorbing platinum 2,2′-bipyridine complex bearing 2-(benzothiazol-2′-yl)-9,9-diethyl-7-ethynylfluorene ligands, Chem. Mater. 22 (2010) 6384–6392.
[10] B. Zhang, Y. Li, R. Liu, T.M. Pritchett, A. Azenkeng, J.E. Haley, Z. Li, M.R. Hoffmann, W. Sun, Synthesis, structural characterization, photophysics and broadband nonlinear absorption of platinum(II) complex bearing 6-(7-benzothiazol-2′-yl-9,9-diethyl-9h-fluoren-2-yl)-2,2-bipyridinyl ligand, Chem. Eur. J. 18 (2012) 4593–4606.
[11] F.N. Castellano, I.E. Pomestchenko, E. Shikhova, F. Hua, M.L. Muro, N. Rajapakse, Photophysics in bipyridyl and terpyridyl platinum(II) acetylides, Coord. Chem. Rev. 250 (2006) 1819–1828.
[12] T.M. Pritchett, W. Sun, F. Guo, B. Zhang, M.J. Ferry, J.E. Roger-Haley, W. Shensky III, A.G. Mott, Excited-state absorption in a terpyridyl platinum(II) pentynyl complex, Opt. Lett. 33 (2008) 1053–1055.
[13] Z. Ji, Y. Li, T.M. Pritchett, N.S. Makarov, J.E. Haley, Z. Li, M. Drobizhev, A. Rebane, W. Sun, One-photon photophysics and two-photon absorption of 4-[9,9′-di(2-ethylhexyl)-7-diphenylaminofluoren-2-yl]-2,2′:6′,2″-terpyridine and their platinum chloride complexes, Chem. Eur. J. 17 (2011) 2479–2491.
[14] V.W.-W. Yam, R.P.-L. Tang, K.M.-C. Wong, K.-K. Cheung, Synthesis, luminescence, electrochemistry, and ion-binding studies of platinum(II) terpyridyl acetylide complexes, Organometallics 20 (2001) 4476–4482.
[15] I.E. Pomestchenko, C.R. Luman, M. Hissler, R. Ziessel, F.N. Castellano, Room temperature phosphorescence from a platinum(II) diimine bis(pyrenylacetylide) complex, Inorg. Chem. 42 (2003) 1394–1396.
[16] T.M. Pritchett, W. Sun, B. Zhang, M.J. Ferry, Y. Li, J.E. Haley, D.M. Mackie, W. Shensky III, A.G. Mott, Excited-state absorption of a bipyridyl platinum(II) complex with alkynyl-benzothiazolylfluorene units, Opt. Lett. 35 (2010) 1305–1307.
[17] I.C. Khoo, J.-H. Park, J. Liou, All-optical switching of continuous wave, microsecond lasers with a dye-doped nematic liquid crystal, Appl. Phys. Lett. 90 (2007) 151107.
[18] H. Guo, M.L. Muro-Small, S. Ji, J. Zhao, F.N. Castellano, Naphthalimide phosphorescence finally exposed in a platinum(II) diimine complex, Inorg. Chem. 49 (2010) 6802–6804.
[19] R. Liu, A. Azenkeng, Y. Li, W. Sun, Long-lived platinum(II) diimine complexes with broadband excited-state absorptions: efficient nonlinear absorbing materials, Dalton Trans. 41 (2012) 12353–12357.
[20] C.V. Kumar, L. Qin, P.K. Das, Aromatic thioketone triplets and their quenching behaviour towards oxygen and di-t-butylnitroxy radical. A laser-flash-photolysis study, J. Chem. Soc. Faraday Trans. 2: Mol. Chem. Phys. 80 (1984) 783–793.
[21] P.A. Firey, W.E. Ford, J.R. Sounik, M.E. Kenney, M.A.J Rodgers, Silicon naphthalocyanine triplet state and oxygen. A reversible energy-transfer reaction, J. Am. Chem. Soc. 110 (1988) 7626–7630.
[22] M. Sheik-Bahae, A.A. Said, T.-H. Wei, D.J. Hagen, E.W. Van Stryland, Sensitive measurement of optical nonlinearities using a single beam, IEEE J. Quantum Electron. 26 (1990) 760–769.
[23] W. Zhao, P. Palffy-Muhoray, Z-scan technique using top-hat beams, Appl. Phys. Lett. 63 (1993) 1613–1615.
[24] W. Zhao, P. Palffy-Muhoray, Z-scan measurement of $\chi^{(3)}$ using top-hat beams, Appl. Phys. Lett. 65 (1994) 673–675.
[25] C.R. Giuliano, L.D. Hess, Nonlinear absorption of light: optical saturation of electronic transitions in organic molecules with high intensity laser radiation, IEEE J. Quantum Electron. 3 (1967) 358–367.
[26] Y. Li, T.M. Pritchett, J. Huang, M. Ke, P. Shao, W. Sun, Photophysics and nonlinear absorption of peripheral-substituted zinc phthalocyanines, J. Phys. Chem. A 112 (2008) 7200–7207.