

An Iridium(III) Complex that Exhibits Dual Mechanism Nonlinear Absorption

Kye-Young Kim, Richard T. Farley, and Kirk S. Schanze*

Department of Chemistry, University of Florida, P. O. Box 117200, Gainesville, Florida 32611-7200

Received: June 22, 2006; In Final Form: July 28, 2006

The photophysical properties of the complex $(\text{L})\text{Ir}(\text{ppy})_2^+$, where ppy = 2-phenylpyridine and L = 4,4'-(2,2'-bipyridine-5,5'-diylbis(ethyne-2,1-diyl))bis(*N,N*-dihexylaniline), have been investigated under one- and two-photon excitation conditions. In THF solution, the complex exhibits broad ground-state absorption with $\lambda_{\text{max}} \approx 500$ nm and weak photoluminescence with $\lambda_{\text{max}} \approx 730$ nm. Excitation of $(\text{L})\text{Ir}(\text{ppy})_2^+$ at 355 nm produces a long-lived excited state ($\tau \approx 1 \mu\text{s}$) that features a strong excited-state absorption in the near-infrared ($\lambda_{\text{max}} \approx 875$ nm, $\Delta\epsilon \approx 6.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Photoluminescence and transient absorption studies of $(\text{L})\text{Ir}(\text{ppy})_2^+$ carried out using 5 ns, 1064 nm pulsed excitation demonstrate that the same long-lived and strongly absorbing excited state can be efficiently produced by two-photon absorption. Solutions of the complex in THF display nonlinear absorption of 5 ns, 1064 nm pulses in a process that is believed to involve a combination of two-photon absorption and reverse saturable absorption.

Organometallic compounds are useful for optical applications requiring long-lived triplet excited states, because coupling of the transition metal to the organic chromophore significantly enhances the quantum efficiencies of singlet–triplet intersystem crossing and phosphorescence. Some applications of recent interest include light-emitting diodes based on electrophosphorescent chromophores,^{1,2} photovoltaic devices based on charge separation activated by triplet excited-state organometallic chromophores,^{3–5} and materials for nonlinear absorption. Among these applications, organometallic two-photon absorption (TPA)/reverse saturable absorption (RSA) chromophores are of particular interest because of their potential as nonlinear absorbing materials.^{6–10} Two-photon absorbers feature “instantaneous” nonlinear absorption in the short time regime (fs/ps), whereas reverse saturable absorbers exhibit nonlinear response on a longer time scale (ns/ μs). Thus, a molecule that contains both TPA and RSA chromophores will, in principle, give rise to a strong and broad temporal domain nonlinear absorption. In addition, the material will be transparent at the active wavelength, because the molecule is excited primarily by TPA.

There have been numerous reports concerning TPA or RSA in organic and organometallic materials, but to date, not much effort has been devoted to the study of chromophores that exhibit both TPA and RSA.^{11–13} We are interested in the design, synthesis, and characterization of organometallic complexes that exhibit “dual-mode” TPA/RSA nonlinear absorption. In particular, we seek to prepare organometallic oligomers that contain π -conjugated chromophores having large TPA cross sections (σ_2) that are strongly coupled to a transition metal chromophore that promotes intersystem crossing to a long-lived triplet excited state with a large cross section triplet–triplet absorption. As shown in the Jablonski diagram in Figure 1, such organometallic oligomers have the potential to exhibit nonlinear absorption by two mechanisms. First, due to the large σ_2 of the π -conjugated

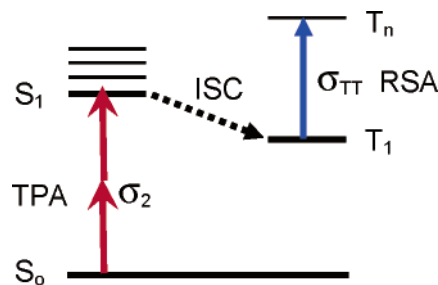
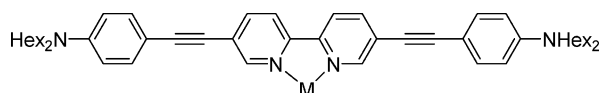


Figure 1. Jablonski diagram for a chromophore that exhibits two-photon absorption and reverse saturable absorption.

SCHEME 1: Structures of ML and L



ML: $\text{M} = \text{Ir}(\text{ppy})_2^+[\text{PF}_6]^-$ **L:** $\text{M} = \text{no metal}$ $\text{ppy} = 2\text{-phenylpyridine}$

chromophore, at moderate to high optical fluence, the first singlet excited state (S_1) of the oligomer will be populated by TPA. Second, due to the influence of the transition metal, rapid singlet–triplet intersystem crossing occurs ($S_1 \rightarrow T_1$), efficiently populating the triplet excited state. Due to the large cross section for the triplet–triplet absorption (σ_{TT}), the chromophore will exhibit additional nonlinear absorption via RSA.

In this communication, we report an investigation of the photophysics and nonlinear absorption properties of the Ir(III) complex **ML** (Scheme 1). This complex incorporates a heavy metal center into a donor- π -donor (D- π -D) type π -conjugated oligomer **L**. It is well-established that π -conjugated molecular structures containing electron donors (D) or acceptors (A) at both ends of a delocalized, π -electron system exhibit large TPA cross sections.^{14,15} In addition, iridium has the largest spin–orbit coupling constant of all the transition metals, and consequently, it is able to facilitate intersystem crossing to afford

* To whom correspondence should be addressed. Tel: 352-392-9133. Fax: 352-392-2395. E-mail: kschanze@chem.ufl.edu.

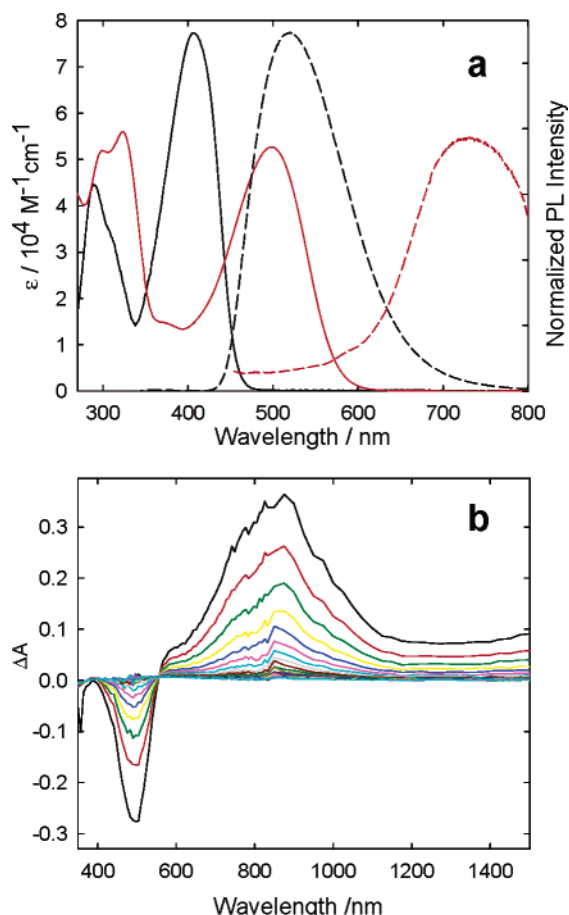


Figure 2. (a) Absorption (solid lines) and emission (dashed lines) spectra of **ML** (red) and **L** (black). (b) Transient absorption spectra of **ML** in deoxygenated THF solution obtained at 400 ns delay increments following 355 nm pulsed excitation.

a large triplet yield.¹⁶ Consequently, Ir complex **ML** is anticipated to exhibit nonlinear absorption via two mechanisms, TPA and RSA.

A series of investigations has been carried out to characterize the photophysics of the Ir(III) complex **ML** under conditions of one-photon and two-photon excitation. The results clearly show that (1) complex **ML** can be excited by TPA in the near-infrared region; (2) intersystem crossing is efficient, and the resulting triplet excited state is long-lived ($> 1 \mu\text{s}$) and absorbs strongly in the visible and near-infrared region; (3) the long-lived triplet excited state can be populated efficiently by TPA; and (4) nonlinear absorption of nanosecond, near-infrared pulses has been observed via the TPA/RSA mechanism. A selected set of results is presented below.

One-photon ground-state absorption and photoluminescence spectra for ligand **L** and Ir complex **ML** in THF are shown in Figure 2a. Ligand **L** exhibits absorption bands at 280 and 400 nm, arising from short- and long-axis polarized $\pi-\pi^*$ transitions, respectively. Ir complex **ML** features a broad absorption band at 500 nm arising from the long-axis polarized $\pi-\pi^*$ transition combined with an Ir \rightarrow ligand MLCT transition. The large absorption coefficient compared to Ir(ppy)₂(bpy)⁺ (where bpy = 2,2'-bipyridine) in which the visible absorption is exclusively due to an MLCT transition, indicates that the visible absorption of **ML** is dominated by the intraligand $\pi-\pi^*$ transition.^{17,18} The absorption maximum for **ML** is red-shifted by approximately 100 nm compared to ligand **L**. The red shift arises due to the effect of the cationic Ir(III) center on the π -electron system of the conjugated bipyridine ligand system.

In particular, the metal reduces the LUMO energy of the conjugated ligand, in part due to its positive charge, and in part due to the effect of coordination which forces the bipyridine unit into a planar conformation.¹⁹

Although ligand **L** is highly fluorescent with a band maximum at 520 nm, the emission of **ML** is dominated by a broad featureless luminescence band, with an emission maximum at 730 nm ($\phi_{\text{em}} = 0.003$, $\tau = 513 \text{ ns}$). The luminescence arises from an excited state having mixed character, consisting of intraligand $^3\pi-\pi^*$ and $^3\text{MLCT}$ configurations.^{18,20,21} This assignment is supported by the fact that the emission is strongly Stokes-shifted from the absorption, and it is comparatively long-lived.

Figure 2b displays transient absorption (TA) spectra of **ML** obtained in THF solution under one-photon excitation conditions (5 ns, 355 nm pulse, 10 mJ cm^{-2}). The TA spectrum features a ground-state bleaching centered at $\sim 500 \text{ nm}$ combined with a strong absorption band that extends throughout the visible and into the near-infrared region, with $\lambda_{\text{max}} \approx 875 \text{ nm}$ and $\Delta\epsilon_{\text{max}} \approx 6.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The transient absorption decays with $\tau = 1.2 \mu\text{s}$. An important question concerns the nature of the excited state that is responsible for the strong transient absorption. As noted above, on the basis of previous investigations of d⁶ transition metal complexes with π -conjugated ligands,^{18,20,21} we tentatively assign the long-lived excited state of **ML** to a state having mixed $^3\text{MLCT}-^3\pi-\pi^*$ character. This assignment is based on previous studies of Ir(III) and Ru(II) complexes with π -conjugated diimine ligands of varying conjugation length.^{18,21} In this work, we demonstrated that, as the energies of the $^3\text{MLCT}$ and $^3\pi-\pi^*$ states converge, the lowest excited state exhibits mixed $^3\text{MLCT}-^3\pi-\pi^*$ character. In **ML**, the $^3\text{MLCT}-^3\pi-\pi^*$ states are within 0.25 eV relative to one another,^{18,20} and therefore, the condition is correct for configuration mixing of the two states.

Given that the $\pi-\pi^*$ ground-state absorption maximum in complex **ML** is at 500 nm, it seemed reasonable that two-photon absorption would occur in the near-infrared at 1064 nm (the fundamental of a Q-switched Nd:YAG laser).²² To explore this possibility, we carried out a series of photophysical measurements on the complex in THF solution under two-photon excitation conditions at 1064 nm. The two-photon upconverted photoluminescence spectrum of **ML** produced by excitation with the 1064 nm beam is shown in Figure 3a. Note that the emission band shape and wavelength maximum are the same as those observed under one-photon excitation conditions. The observation of the 700 nm emission under 1064 nm excitation clearly indicates that **ML** can be excited by two-photon absorption. Indeed, the upconverted luminescence can be easily seen by eye as shown in Figure 3b.

In view of the fact that the phosphorescence quantum efficiency for **ML** is low, we conclude that the observation of phosphorescence suggests that two-photon excitation of the complex in the near-infrared affords a comparatively high yield of the triplet state. The observed emission is believed to arise by a sequence involving two-photon near-infrared absorption to populate the singlet excited state and intersystem crossing to populate the triplet state which relaxes by phosphorescence. The inset in Figure 3a shows that the emission intensity varies with the square of the infrared excitation intensity, consistent with the hypothesis that the triplet state is produced as a result of a two-photon absorption process. Transient absorption spectra obtained using an excitation wavelength of 1064 nm provide additional evidence for population of the triplet state via two-photon absorption. The band shape of the transient absorption

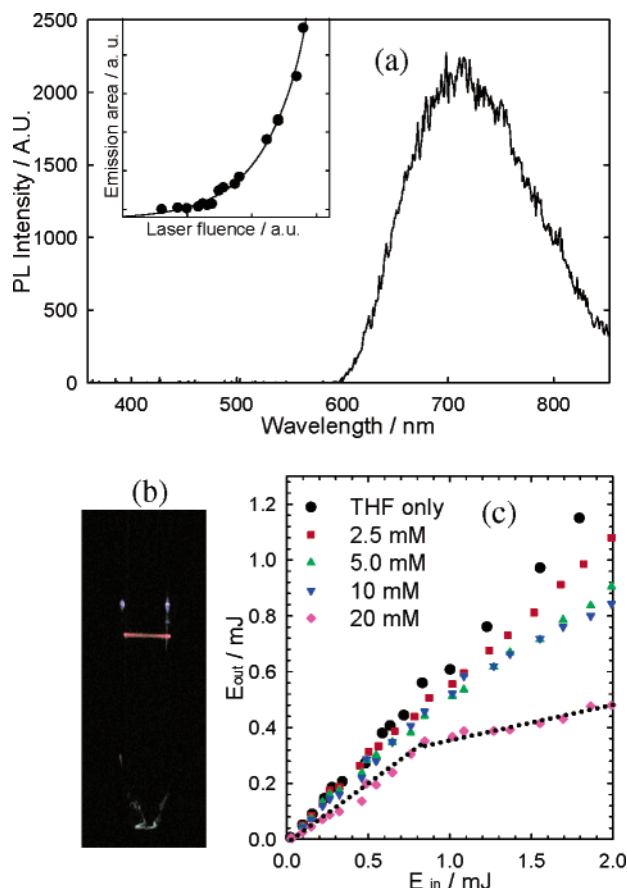


Figure 3. (a) Emission spectrum of a solution of **ML** in THF ($c = 5$ mM) obtained using 1064 nm pulsed excitation. (b) Photograph of the visible emission under 1064 nm excitation. (c) Transmittance of 1064 nm pulsed beam at various concentrations of **ML** in THF.

spectrum observed under two-photon excitation conditions is similar to that obtained using one-photon excitation (see Supporting Information).²³ The fact that strong transient absorption is seen for the triplet state under two-photon excitation conditions clearly indicates that a relatively large triplet excited-state population can be produced via TPA, even with a nanosecond pulsed laser.

The observation of the strongly absorbing triplet excited state of **ML** produced under two-photon excitation conditions suggests that this material will exhibit dual-mode optical limiting via RSA and TPA. To provide a proof of principle for this concept, we carried out preliminary studies to examine the nonlinear absorption of **ML** using 1064 nm, 5 ns pulses. These experiments were carried out with the liquid sample placed at the focal plane of a 10 cm plano convex lens. Figure 3c shows the laser power dependence of the transmittance of **ML** at a range of concentrations in THF solution. While the blank THF solution responds linearly to the incident energy, it is evident that the THF solutions of Ir(III) complex **ML** exhibit nonlinear absorption, the extent of which increases with the concentration of **ML**. Notably, for a 20 mM solution of **ML**, the transmitted energy is significantly reduced above an input energy of 0.8 mJ. Importantly, the observed nonlinear absorption of the nanosecond 1064 nm pulses is believed to arise by the mechanism shown in Figure 1, i.e., two-photon absorption followed by intersystem crossing and then reverse saturable absorption due to strong triplet–triplet absorption.

Taken together, the results of the work carried out on organometallic TPA/RSA chromophore **ML** demonstrate that it is possible to produce a long-lived triplet excited state in high

yield by near-infrared two-photon absorption. Because the triplet excited state has a large absorption cross section, this molecular system displays nonlinear absorption via the dual-mode TPA/RSA mechanism. We believe that it will be possible to synthesize a series of organometallic chromophores that make it possible to tune the wavelength and optimize the cross sections for the two-photon and triplet–triplet absorptions. This will result in a “toolbox” of chromophores that feature efficient nonlinear absorption over a broad wavelength region for long and short laser pulses.

Acknowledgment. We thank the Air Force Office of Scientific Research (grant no. FA9550-06-1-1084) for support of this work.

Supporting Information Available: Experimental section including: compound synthesis and characterization; ¹H and ¹³C NMR spectra of **ML** and **L**; description of methods used for one-photon and two-photon excited photophysical studies; and transient absorption spectrum of **ML** obtained under two-photon excitation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature (London)* **1998**, *395*, 151–154.
- (2) Kwong, R. C.; Sibley, S.; Dubovoy, T.; Baldo, M.; Forrest, S. R.; Thompson, M. E. *Chem. Mater.* **1999**, *11*, 3709–3713.
- (3) Kalinowski, J.; Stampor, W.; Szymtowski, J.; Cocchi, M.; Virgili, D.; Fattori, V.; Di Marco, P. *J. Chem. Phys.* **2005**, *122*.
- (4) Shao, Y.; Yang, Y. *Adv. Mater.* **2005**, *17*, 2841–2844.
- (5) Guo, F.; Kim, Y.-G.; Reynolds, J. J.; Schanze, K. S. *Chem. Commun.* **2006**, 1887–1889.
- (6) Powell, C. E.; Humphrey, M. G. *Coord. Chem. Rev.* **2004**, *248*, 725–756.
- (7) Ehrlich, J. E.; Wu, X. L.; Lee, I. Y. S.; Hu, Z. Y.; Rockel, H.; Marder, S. R.; Perry, J. W. *Opt. Lett.* **1997**, *22*, 1843–1845.
- (8) He, G. S.; Xu, G. C.; Prasad, P. N.; Reinhardt, B. A.; Bhatt, J. C.; Dillard, A. G. *Opt. Lett.* **1995**, *20*, 435–437.
- (9) Bhawalkar, J. D.; He, G. S.; Prasad, P. N. *Rep. Prog. Phys.* **1996**, *59*, 1041–1070.
- (10) Spangler, C. W. *J. Mater. Chem.* **1999**, *9*, 2013–2020.
- (11) Powell, C. E.; Morrall, J. P.; Ward, S. A.; Cifuentes, M. P.; Notaras, E. G. A.; Samoc, M.; Humphrey, M. G. *J. Am. Chem. Soc.* **2004**, *126*, 12234–12235.
- (12) Joshi, M. P.; Swiatkiewicz, J.; Xu, F. M.; Prasad, P. N. *Opt. Lett.* **1998**, *23*, 1742–1744.
- (13) McIlroy, S. P.; Clo, E.; Nikolajsen, L.; Frederiksen, P. K.; Nielsen, C. B.; Mikkelsen, K. V.; Gothelf, K. V.; Ogilby, P. R. *J. Org. Chem.* **2005**, *70*, 1134–1146.
- (14) Reinhardt, B. A.; Brott, L. L.; Clarson, S. J.; Dillard, A. G.; Bhatt, J. C.; Kannan, R.; Yuan, L. X.; He, G. S.; Prasad, P. N. *Chem. Mater.* **1998**, *10*, 1863–1874.
- (15) Kannan, R.; He, G. S.; Lin, T. C.; Prasad, P. N.; Vaia, R. A.; Tan, L. S. *Chem. Mater.* **2004**, *16*, 185–194.
- (16) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry: A Comprehensive Text*; Wiley: New York, 1980.
- (17) Ichimura, K.; Kobayashi, T.; King, K. A.; Watts, R. J. *J. Phys. Chem.* **1987**, *91*, 6104–6106.
- (18) Glusac, K. D.; Jiang, S. J.; Schanze, K. S. *Chem. Commun.* **2002**, 2504–2505.
- (19) Manas, E. S.; Chen, L. X. *Chem. Phys. Lett.* **2000**, *331*, 299–307.
- (20) Walters, K. A.; Ley, K. D.; Cavaleiro, C. S. P.; Miller, S. E.; Gosztoła, D.; Wasielewski, M. R.; Bussandri, A. P.; van Willigen, H.; Schanze, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 8329–8342.
- (21) Liu, S. X.; Schanze, K. S. *Chem. Commun.* **2004**, 1510–1511.
- (22) In all of the one- and two-photon excited studies reported herein, we observed no photochemical degradation of **ML** or **L**, even after long-term irradiation with ultraviolet or near-infrared laser pulses. While this is not a quantitative result, it strongly implies that **L** and **ML** have very low quantum yields for photodecomposition.
- (23) The two-photon excited transient absorption spectrum was obtained on a different instrument than the one-photon excited spectrum shown in Figure 2b. The detector used for the two-photon excited studies is not sensitive beyond 850 nm, and therefore, it is not possible to observe the maximum of the triplet–triplet absorption that occurs at ~875 nm.