

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/23234878>

Photophysical Characterization of a Highly Conjugated Bipyridyl-Based Dye Synthesized by a Unique Two-Step Approach

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · OCTOBER 2008

Impact Factor: 3.3 · DOI: 10.1021/jp804975a · Source: PubMed

CITATIONS

4

READS

22

5 AUTHORS, INCLUDING:



Leonardo De Boni

University of São Paulo

103 PUBLICATIONS 1,141 CITATIONS

SEE PROFILE



Sheng Yao

University of Central Florida

37 PUBLICATIONS 650 CITATIONS

SEE PROFILE



Kevin D Belfield

University of Central Florida

225 PUBLICATIONS 4,279 CITATIONS

SEE PROFILE

ARTICLES

Photophysical Characterization of a Highly Conjugated Bipyridyl-Based Dye Synthesized by a Unique Two-Step Approach

Carlos Toro, Leonardo De Boni, Sheng Yao, Kevin D. Belfield,[†] and Florencio E. Hernández^{*,†}

Department of Chemistry, University of Central Florida, P.O. Box 162366, Orlando, Florida 32816-2366

Received: June 05, 2008; Revised Manuscript Received: July 31, 2008

In this article, we present a new and simple, yet efficient, two-step approach to synthesize 4,4'-bis(dibutylaminostyrylstyryl)-2,2'-bipyridine with high yield, as well as its linear and nonlinear optical characterizations in THF and toluene solutions. We show that its one- and two-photon absorption spectra are similar in both solvents. Nevertheless, the relaxation processes of this compound exhibit dependence on the solvent polarity. The one- and two-photon induced fluorescence signal of this molecule in solution reveals that its excited state is highly stabilized in THF solution rather than in toluene. Analysis of the fluorescence quantum yield, lifetime, and radiative and nonradiative decay rates are in agreement with Lippert's model for solute–solvent interactions. The optical measurements demonstrate that this dye is a promising candidate for multiphoton fluorescence imaging, optical limiting, and dye lasers.

Introduction

The necessity of developing new materials for photonic devices, such as optical switches,^{1,2} optical limiters,^{3,4} and dye lasers,⁵ and for medical and biological applications in photodynamic therapy⁶ and multiphoton fluorescence microscopy⁷ has strongly stimulated fundamental and applied research in the field of nonlinear optical phenomena during the past decades. Currently, the majority of research in these fields has focused on improving new materials with potential high nonlinearity. Among all available materials, organic compounds have been the most promising because of the ease of manufacturing and the capability in manipulating them to enhance the optical effects.

Despite the wide variety of known nonlinear optical phenomena, the so-called two-photon absorption (2PA) process has received significant attention from the scientific community because of its usefulness in a vast number of applications.^{8–11} 2PA was first predicted by Maria Goeppert-Meyer in the early 1930s¹² and involves the simultaneous absorption of two photons whose energies add up and match the energy required for an electronic transition. A special case of this process takes place when the two photons have half of the energy necessary for the corresponding transition, a mechanism referred to as “degenerate 2PA”. For most common dyes, this transition occurs in the red part of the visible spectrum, which represents a desirable transparency window in biomedical applications. Typically, the effectiveness of such a microscopic process is measured in terms of the 2PA cross section (σ_{2PA}) of individual molecules, which can then be related to the third-order macroscopic susceptibility, $\chi^{(3)}$. Molecular systems with relatively high values of σ_{2PA} are considered to be excellent candidates for applications in nonlinear optics.

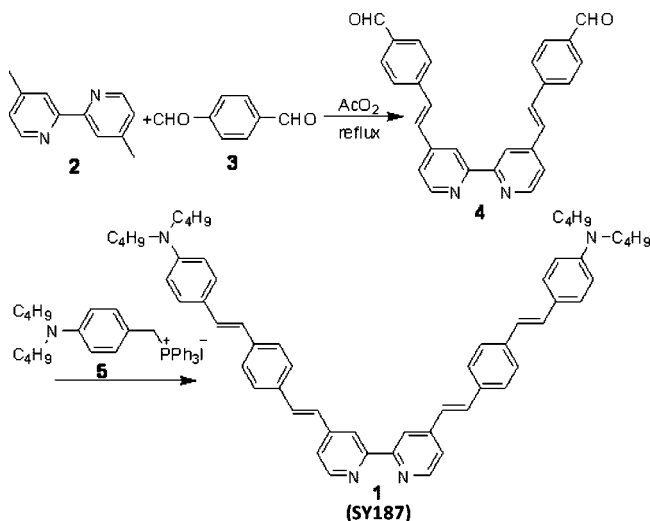
In terms of molecular design strategy, it is well-known that highly conjugated push–pull (donor–acceptor) systems show moderate to exceptional σ_{2PA} .¹³ Nevertheless, it has become evident after several studies that these archetypes inherently present two main disadvantages for macroscopic applications: (1) dipole–dipole interactions promote antiparallel molecular arrangement canceling out the nonlinear response in the bulk material, and (2) high π -electron delocalization leads to a red shift in the absorption band which compromises the transparency of the material in the desired region.¹⁴ With the aim of surmounting these drawbacks, Zyss et al.^{15–17} introduced in the early 1990s the concept of octupolar molecules. Conveniently, these systems present a rounded-off shape that suppresses dipole moments counteracting in the crystalline lattice, and it keeps the 2PA within the preferred transparency window.¹⁸ From this perspective, octupolar molecules have gained the interest of the material science community, and they have been successfully applied to several areas, with 2PA one of the most important.^{19,20}

To gain insight in the linear and nonlinear optical properties of octupolar systems, one should first understand the optical behavior of the individual molecules that comprise them. In this context, bipyridyl ligands have been commonly attached to transition-metal atoms to act as octupolar systems.²¹ The synthesis of these ligands usually requires tedious and time-consuming multistep procedures, which raise the cost of the final product. To overcome this problem, we designed a new and highly efficient strategy for the synthesis of one of these ligands, 4,4'-bis(dibutylaminostyrylstyryl)-2,2'-bipyridine (**1**) (hereafter, SY187). The same synthetic strategy is predicted to be applicable to other members of the bipyridyl ligand family. SY187 was fully characterized through linear and nonlinear spectroscopy, and a detailed analysis of the results are presented next in this article.

* Corresponding author. E-mail: florenzi@mail.ucf.edu.

[†] Also with CREOL-The College of Optics and Photonics.

CHART 1



Materials and Methods

The synthetic route followed in this section is portrayed in Chart 1. The experimental details are described in this section.

(a) **Synthesis of Intermediates 4 and 5.** 4,4'-Dimethyl-2,2'-bipyridine **2**, terephthalaldehyde **3**, and anhydrous DMF were purchased from Aldrich or Acros Organics and used as received. The intermediate 4,4'-(1*E*,1'*E*)-2,2'-(2,2'-bipyridine-4,4'-diyl)-bis(ethene-2,1-diyl)dibenzaldehyde **4** was synthesized by a slightly modified literature method.²² Briefly, **2** (2.2 g, 12 mmol) and **3** (4.8 g, 36 mmol) were refluxed for 48 h in 7 mL of acetic anhydride. The precipitate was collected by filtration and recrystallized from DMF to produce 2.47 g (49% yield). 4-(*N,N*-Dibutylaminobenzyl) triphenylphosphonium iodide **5** was synthesized according to literature methods.²³ NMR was collected using a 500 MHz Varian system. Melting point was uncollected.

(b) **Synthesis of Compound 1.** **4** (0.41 g, 0.98 mmol) and **5** (1.32 g, 2.16 mmol) were dissolved in anhydrous DMF by slight heating. KO^tBu was added to this solution, and the mixture was slowly cooled to room temperature. The reaction was completed in 16 h at room temperature. The product was precipitated from water and collected by filtration. Recrystallization from DMF gave 0.58 g of a yellow powder as pure product (72% yield). Mp: 234–236 °C, ¹H NMR (500 MHz, DMF-*d*₇): δ 8.90 (d, *J* = 5.0 Hz, 2H, Py-H), 8.83 (s, 2H, Py-H), 7.89–7.96 (m, 6H, Ph-H and Py-H), 7.89 (d, *J* = 16.0 Hz, 2H, CH=CH), 7.80 (d, *J* = 8.5 Hz, 4H, Ph-H), 7.66 (d, *J* = 8.5 Hz, 4H, Ph-H), 7.64 (d, *J* = 16.0 Hz, 2H, CH=CH), 7.45 (d, *J* = 16.0 Hz, 2H, CH=CH), 7.22 (d, *J* = 16.0 Hz, 2H, CH=CH), 6.91 (d, *J* = 8.5 Hz, 4H, Ph-H), 3.54 (m, 8H, CH₂), 1.75 (m, 8H, CH₂), 1.53 (m, 8H, CH₂), 1.12 (t, *J* = 7.2 Hz, 12H, CH₃). ¹³C NMR (75 MHz) Anal. Calcd for C₅₈H₆₆N₄ (819.17): C, 85.04; H, 8.12; N, 6.84. Found: C, 84.69; H, 7.96; N, 6.95.

(c) **Photophysical Characterization.** Solutions of SY187 (**1**) in toluene and THF (solvents were purchased from Aldrich and used as received) were prepared at concentrations of ca. 10^{−5} M and ca. 10^{−6} M for absorption and fluorescence emission measurements, respectively. Linear absorption spectra were collected with a single-beam spectrophotometer (Agilent 8453 diode array UV–vis) in a 1-cm quartz cell (contribution from the solvent and the quartz cell was subtracted). Steady-state fluorescence, fluorescence quantum yield, and excitation anisotropy were measured using a PTI Quanta Master spectrofluorimeter (model QM-3/2005) equipped with a 75 W xenon

lamp and two QuadraScopic monochromators (excitation and emission). Fluorescence quantum yield values were determined by using the standard method²⁴ with Coumarin 30 in acetonitrile as standard ($\phi_f = 0.67$).

Fluorescence lifetime measurements were carried out by pumping the samples with a frequency-doubled visible light (410 nm) from an IR laser (Coherent Mira 900F) tuned at 820 nm, 240 fs (fwhm), and 76 MHz repetition rate, as the single-photon excitation source. A multimode fiber was used to couple the fluorescence emission from the sample solution into a single avalanche photodiode (APD) detector with wavelength-dependent instrument response function (IRF). Because of the dispersion of the multimode fiber used, the IRF of our APD-based system could be estimated to be better than 300 ps for 410 nm. Data acquisition and analysis were done with a combination of a stand-alone time-correlated single photon counting module TimeHarp 300 and a software package PicoHarp300, both from PicoQuant.

2PA and two-photon induced fluorescence (2PIF) were also studied in the same two solvents. 2PA cross sections were determined with the well-known open aperture Z-scan method.²⁵ All nonlinear measurements were performed using an EKSPLA 401 optical parametric generator system pumped by the third harmonic of a mode-locked, 25-ps (fwhm) EKSPLA PL-2143B laser, working at 10 Hz repetition rate. Typical concentrations in the order of 10^{−3} M were employed for 2PA measurements. The 2PIF spectra were collected using an Ocean Optics USB2000 system. Lasing in the SY187/toluene solution was achieved by pumping the sample with the third harmonic (355 nm) of the laser and collecting the stimulated emission spectrum with the same Ocean Optics system.

Results and Discussion

The synthesis of SY187 was already reported through complicated multistep procedures.^{26–28} Nonetheless, a novel and simplified synthetic line of attack was proposed in this article. In Chart 1, we show a highly efficient two-step synthetic route designed in our group, which consists of first preparing the key intermediate **4** and then coupling it with the phosphonium ylide **5** through a Wittig reaction. Through this route, we obtained 72% overall yield. This new synthetic strategy is envisaged as a simple and cost-efficient route for the systematic study of ligands commonly used in the design of octupolar molecules and fluorescent probes.

Once the synthesis of SY187 was accomplished, a thorough study of its photophysical properties was carried out. The normalized absorption and emission spectra of SY187 in toluene and THF solutions were measured (Figure 1). From Figure 1, it can be noticed that the absorption maximum is not affected by the polarity of the solvent. Conversely, the emission maximum is red-shifted in the solvent with higher polarity (THF). This behavior in Stoke's shift, $\Delta\tilde{\nu}_s = \tilde{\nu}_{\text{abs}} - \tilde{\nu}_{\text{fl}}$, of a chromophore in the presence of different solvents agrees with Lippert's model (eq 1):²⁴

$$\Delta\tilde{\nu}_s = \frac{2(\mu_e - \mu_g)^2}{hca^3} \cdot \Delta f + \text{constant} \quad (1)$$

Here, $\tilde{\nu}_{\text{abs}}$ and $\tilde{\nu}_{\text{fl}}$ are the wavenumbers (cm^{−1}) of absorption and emission, respectively. *h* is Planck's constant, *c* is the speed of light in vacuum, and *a* corresponds to the cavity radius in which the chromophore dwells (assumed to be 4 Å in our calculations). μ_e and μ_g represent the permanent dipole moment in the excited and ground states, respectively. The orientation

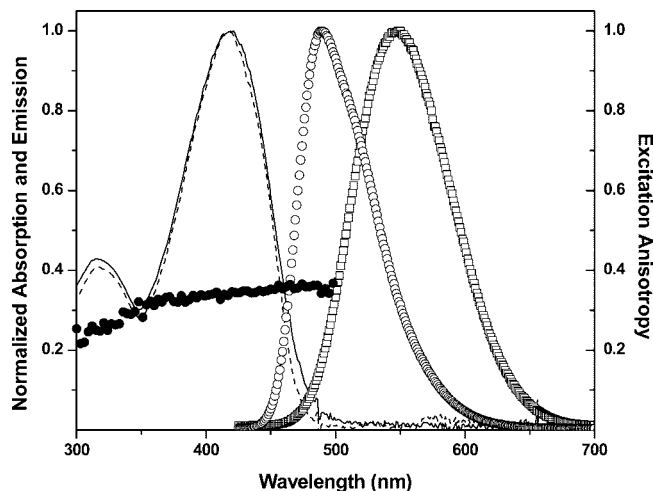


Figure 1. Normalized absorption of SY187 in toluene (solid line) and THF (dashed line) and its normalized fluorescence emission in toluene (○) and THF (□). Excitation anisotropy (●), measured in glycerol, is also depicted.

polarizability, Δf , a measure of solvent polarity, was estimated using eq 2:

$$\Delta f = f(\epsilon) - f(n) = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (2)$$

where $f(\epsilon)$ is the low-frequency polarizability of the solvent, which accounts for the molecular orientation of solvent molecules (slow process). $f(n)$ is the so-called high-frequency polarizability, which describes reorientation of electrons in the solvent (a nearly instantaneous process). ϵ is the dielectric constant of the solvent, and n is its corresponding refractive index.

Not surprisingly, the dye in the solvent with the highest value of Δf , THF ($\Delta f_{\text{THF}} = 0.210 > \Delta f_{\text{tol}} = 0.013$), presents the greatest Stoke's shift. By using the experimental values of $\Delta \tilde{\nu}_s$, that is, 3515 cm^{-1} ($\sim 70 \text{ nm}$) for SY187/toluene and 5500 cm^{-1} ($\sim 130 \text{ nm}$) for SY187/THF, along with data available for the same compound in dichloromethane²⁶ ($\Delta \tilde{\nu}_s = 7088 \text{ cm}^{-1}$; $\Delta f_{\text{CH}_2\text{Cl}_2} = 0.220$), we estimated (using eq 1) the difference between the permanent dipole moments of the excited and ground states, $\Delta \mu = \mu_e - \mu_g$, to be approximately 9.4 D. It should be pointed out that a better evaluation of this parameter would require a more reliable estimation of the cavity radius. Quantum mechanical methods, such as the polarizable continuum model,²⁹ should provide a more reliable value of a in each particular solvent. Nevertheless, because of the size of SY187, this calculation would be computationally expensive.

To fully characterize the linear optical properties of SY187, we performed measurements of its molar absorptivity (ϵ'), fluorescence quantum yield (ϕ_f), and fluorescence lifetime (τ_f) in toluene and THF. We also calculated the radiative decay rate, $\Gamma = \phi_f/\tau_f$, and the nonradiative decay rate, $k_{\text{nr}} = (1 - \phi_f)/\tau_f$, in both solvents. Table 1 summarizes the photophysical properties of SY187 in the solvents of interest. It is worth noticing that most of the parameters remain virtually identical, with the exception of ϕ_f and Γ . In toluene, the former is 3.5 times greater than that in THF, whereas Γ is almost 5 times greater. The chromophore, when dissolved in toluene, tends to remain rigid and planar, leading to a significant reduction of losses due to nonradiative pathways. The observed overwhelming radiative

TABLE 1: Photophysical Properties of SY187 in THF and Toluene Solutions

property	solvent	
	THF	toluene
molar absorptivity, ϵ' ($\text{M}^{-1} \text{cm}^{-1}$)	34000	30100
fluorescence quantum yield, ^a Φ_f	0.10	0.35
fluorescence lifetime, ^a τ_f (ns)	1.6	1.2
radiative constant, Γ ($\times 10^7 \text{ s}^{-1}$)	6.1	29
nonradiative constant, k_{nr} ($\times 10^8 \text{ s}^{-1}$)	5.8	5.4

^a Excitation wavelength was 410 nm.

decay rate of SY187 in toluene is responsible for the lasing effect observed in this particular solution (see discussion below).

In addition to the absorption and emission properties of SY187 in toluene and THF, Figure 1 shows the excitation anisotropy (r_0) of this dye measured in glycerol. Glycerol was chosen because of its high viscosity, which avoids rotational diffusion. The excitation anisotropy²⁴

$$r_0 = \frac{2}{5} \left(\frac{3 \cos^2 \beta - 1}{2} \right) \quad (3)$$

provides valuable information concerning the angle (β) between the absorption and emission dipole moments. Higher values of r_0 correspond to virtually collinear dipole moments that can be related, in most common dyes, to $S_0 \rightarrow S_1$ transitions. Variations in values of r_0 , usually found at shorter wavelengths of the absorption band, correspond to transitions to higher excited states. For the sake of clarity, it is important to emphasize that contributions to the excitation anisotropy from "pure" electronic transitions is an ideal case. Frequently, inhomogeneous broadening and overlapping between excited states are essential aspects to be considered. In our particular case, r_0 remains almost constant from 350 to 500 nm. This suggests that such an absorption band corresponds mainly to a transition to the first excited state $S_0 \rightarrow S_1$. According to symmetry selection rules, $S_0 \rightarrow S_1$ is a one-photon allowed transition but two-photon forbidden.³⁰ In the spectral range from 300 to 350 nm, r_0 values decrease, without leveling off, implying that, for the most part, simultaneous excitation to the first two excited states have been reached rather than pure $S_0 \rightarrow S_2$. Therefore, overlapping between excited states is more likely occurring, and the values of excitation anisotropy correspond to contributions from that mixing. These remarks were confirmed by applying the Gaussian deconvolution method to the linear absorption spectrum of SY187 in THF. Because of its similarity with the linear absorption spectrum of SY187/toluene, we only show the Gaussian deconvolution method in one solvent. Figure 2 depicts the outcome of the deconvolution method employing three Gaussian curves centered at different wavelengths. A substantial overlapping between the bands corresponding to the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions, from 300 to 400 nm, is evident. Additionally, a transition to a higher excited state ($S_0 \rightarrow S_n$) lies on top of the $S_0 \rightarrow S_2$ transition in the spectral region between 250 and 350 nm. Further interpretation of these findings was pursued by means of 2PA.

Since bipyridyl ligands are commonly used in the synthesis of organometallic octupolar molecules,²¹ the nonlinear optical characterization of SY187 was an attractive target for study. Under this premise, we measured the 2PA spectra of SY187 in THF and toluene, spanning from 500 to 900 nm. The experimental normalized transmittance curves (Z-scan signatures), at several wavelengths and different energies, were adjusted with equations reported elsewhere,³¹

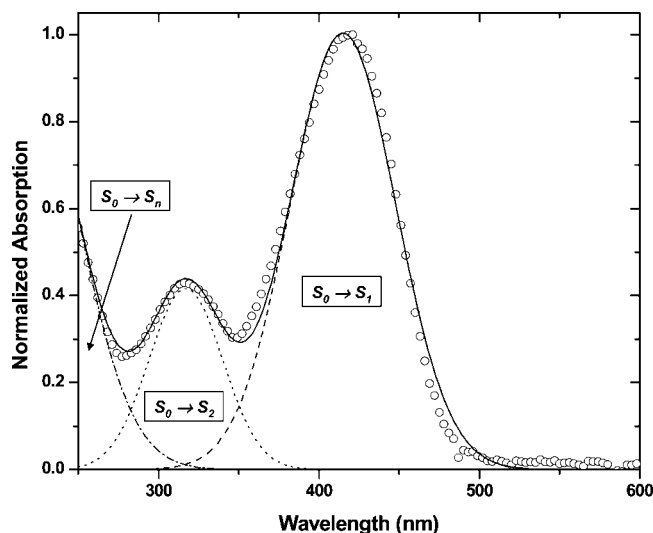


Figure 2. Experimental normalized absorption spectrum of SY187 in THF (○) adjusted with three Gaussian curves (dashed, dotted, and dashed-dotted lines) representing electronic transitions to different states. Solid line corresponds to the overall contribution to the absorption band.

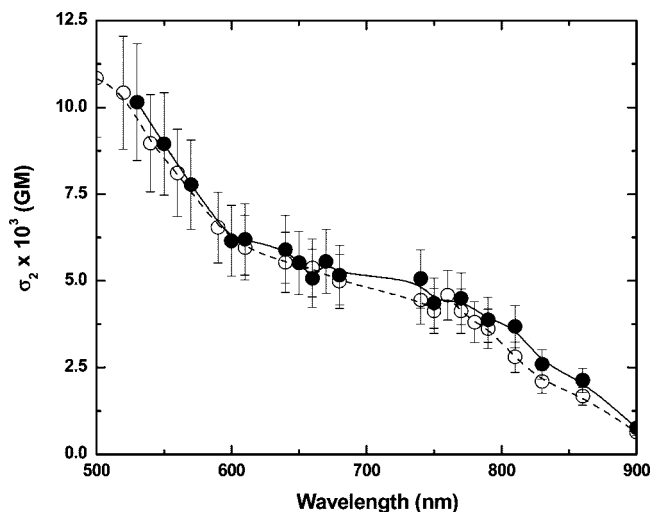


Figure 3. Two-photon absorption spectra of SY187 in THF (●, solid line) and toluene (○, dashed line).

$$T(z) = \frac{1}{\sqrt{\pi} \cdot q_0} \int_{-\infty}^{+\infty} \ln(1 + q_0 e^{-\delta^2}) d\delta \quad (4)$$

where $q_0 = I_0 \cdot \alpha_2 \cdot L \cdot w_0^2 / w^2(z)$, from which the two-photon nonlinear absorption coefficient (α_2) can be extracted. The latter relates to the two-photon absorption cross section through $\sigma_2 = \alpha_2 \cdot (h\nu) / N_0$. In the previous equations, I_0 represents the pulse intensity at the focal plane, L is the sample thickness, and w_0 and $w(z)$ are the beam waist at the focal plane and at a z -position, respectively. $h\nu$ is the energy of the excitation photons, and N_0 is the concentration of the dye in solution.

In Figure 3, we portray the experimentally determined 2PA cross section of SY187 (points) in both solvents as a function of the wavelength. Lines are depicted to guide the reader and are not meant to be a fitting. From this figure, it is evident that the nonlinear process is independent of the solvent polarity. Furthermore, three well-defined spectral regions can be clearly distinguished. (a) From 500 to 600 nm, the values of σ_2 are quite high and monotonically decreasing. This is a typical feature of enhanced 2PA due to one-photon absorption when pumping

relatively close to the linear absorption band.³² (b) From 600 to 700 nm, the two-photon cross section remains fairly constant, with an average value of 5000 GM (1 GM = 1×10^{-50} cm⁴·s·photon⁻¹·molecule⁻¹). This spectral region matches with the $S_0 \rightarrow S_2$ spectral segment, predicted by excitation anisotropy (300–350 nm) and the absorption spectrum deconvolution for 2PA allowed transition, though overlapping between the first two excited states cannot be totally discarded within this region. Finally, (c) from 750 to 900 nm, where σ_2 monotonically diminishes as expected for a forbidden 2PA transition, where $S_0 \rightarrow S_1$ is the main contribution to the absorption band in this region. This was evidenced by the values of r_0 and absorption spectrum deconvolution. Although SY187 is centrosymmetric, cross section values are not zero in this range because of geometry relaxation and symmetry breaking in solution that makes transition selection rules more relaxed.³³ In this context, our experimental results are in agreement with the theoretical calculations of 2PA spectra recently reported by Zhang et al.¹⁴ for a family of bipyridyl ligands and complexes. Even though such calculations were performed in gas phase and using semiempirical methods (ZINDO-SOS), the spectral behavior is still reproducible. At this point, it is necessary to specify that this chromophore presents a main feature for nonlinear optical applications, this is, a high 2PA cross section. Unquestionably, the magnitudes of the σ_2 , reported in our work, are slightly enhanced because all measurements were performed using picosecond pulses (i.e., excited-state absorption could still be relatively important).³⁴

With the aim of confirming the nature of the two-photon absorption process and taking advantage of the fluorescent ability of the dye, we carried out typical 2PIF measurements in both solvents. Figure 4a,b portrays the 2PIF signal as a function of input energy, pumping at 840 nm for SY187/THF and 760 nm for SY187/toluene. A slope value close to 2 (in the log–log plots) confirms that the process is indeed due to the simultaneous absorption of two photons of the same energy.

Seeking new alternatives and more efficient materials for nonlinear optical applications, our group has engaged in systematic research of a structure–property relationship leading to a rational design of materials with extraordinary two-photon and three-photon absorption properties.^{35,36} Unarguably, SY187 lies within such a group, meeting one of the most important requirements for high two-photon cross section: long π -electron conjugation through the structure. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of SY187 are portrayed in Figure 5. Calculation of these frontiers orbitals was performed by using Hyperchem. First, the structure was optimized with the semiempirical method AM1,³⁷ and then the energy of the orbitals was estimated with the ZINDO/S method.³⁸ The HOMO is evenly and highly delocalized through the entire structure, suggesting that the charges are capable of moving without relative effort. The LUMO, however, remains relatively localized at the center of the structure. This hints that pyridyl moieties (acceptors) are mainly responsible for such behavior, as expected for a system that undergoes intramolecular charge transfer from the amine groups (donors).

Finally, additional fluorescence studies were carried out on compound SY187 with the purpose of completely exploiting its potential as an optical material. The quest for efficient dye lasers still remains a field of active research because of the variety of applications of these types of systems.⁵ Because SY187 shows high one-photon induced fluorescence, a study of lasing ability of this dye in toluene and THF was undertaken.

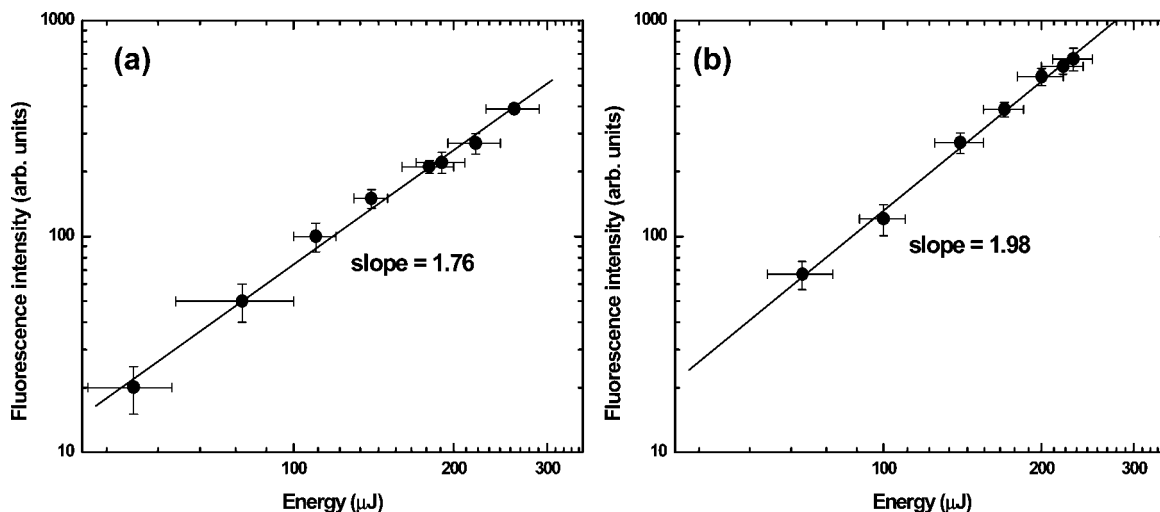


Figure 4. Two-photon fluorescence intensity as a function of input energy. (a) SY187 in THF pumping at 840 nm. (b) SY187 in toluene pumping at 760 nm.

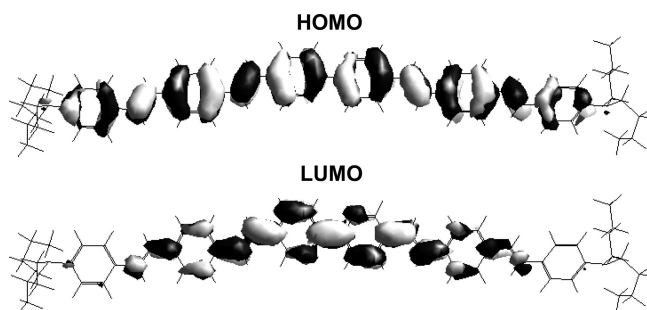


Figure 5. Frontier orbitals, HOMO and LUMO, of SY187 in gas phase calculated with the ZINDO/S method.

Solutions of the chromophore (concentrations in the order of ca. 10^{-2} to 10^{-3} M) were pumped by the third harmonic beam (355 nm) of a Nd:YAG laser, which was focused by a cylindrical lens ($f = 5$ cm) into a 1-cm quartz cell containing the solutions. Dye laser emission signal was coupled to an Ocean Optics spectrometer. Lasing signal was only observed for the SY187/toluene solution. This attention-grabbing advancement was sustained by the observations already discussed related to fluorescence quantum yield and radiative decay rates for this particular molecule. Both parameters overwhelm the ones measured in SY187/THF.

Figure 6 represents the lasing efficiency of SY187/toluene measured as the stimulated emission output energy (lasing) as a function of input energy (pumping energy). Additionally, the inset depicts a normalized emission spectrum of the same solution along with the normalized lasing spectrum. From the latter, it can be observed that maximum emission occurs at around 510 nm, while the laser peaks at 520 nm with a very narrow emission band (fwhm ≈ 12 nm). In the main plot, it must be realized that lasing signal linearly increases with respect to the input energy up to approximately $150 \mu\text{J}$. This corresponds to an estimated lasing efficiency of 5%. Further increment in the pumping energy induces a change in the lasing emission slope. Perhaps other mechanisms, such as thermal effects and photodegradation, become important at high irradiances.

Conclusions

4,4'-Bis(dibutylaminostyrylstyryl)-2,2'-bipyridine was synthesized by an exceedingly efficient procedure that shortens the number of steps required to afford this bipyridyl derivative and

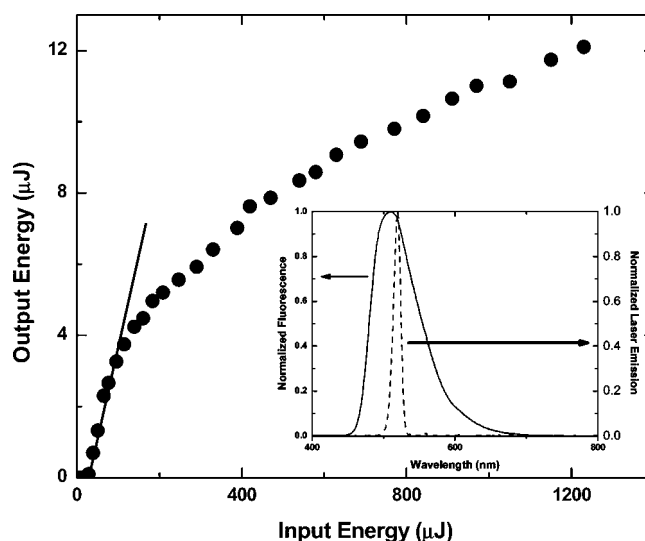


Figure 6. Lasing efficiency (output energy as a function of input energy) of SY187 in toluene pumping at 355 nm. Inset shows the normalized fluorescence emission of this compound in toluene along with the lasing spectrum. Lasing threshold is approximately $30 \mu\text{J}$.

can be extended to larger systems. We proved SY187 to be an excellent fluorescent probe for both single and multiphoton excitation. Also, we showed that its radiative decay rate changes with the host solvent polarity. Finally, the stimulated emission and laser effects observed in this molecule in toluene makes this system particularly attractive for dye laser applications. Applications of SY187 in nonlinear optics are anticipated because of its relatively high two-photon absorption cross sections over a broad spectral range.

Acknowledgment. This research was supported by the Department of Chemistry, University of Central Florida. L.D.B. acknowledges CAPES (Brazil) for financial support through Project 4169/06-9. K.D.B. acknowledges the financial support of the Civilian Research and Development Foundation (UK-C2-2574-MO-04) and the National Science Foundation (ECS-0524533 and ECS-0621715).

References and Notes

- (1) Raymo, F. M.; Tomasulo, M. *Chem.—Eur. J.* **2006**, *12*, 3186–3193.

- (2) Mancois, F.; Rodriguez, V.; Pozzo, J. L.; Champagne, B.; Castet, F. *Chem. Phys. Lett.* **2006**, *427*, 153–158.
- (3) Albert, I. D. L.; Marks, T. J.; Ratner, M. A.; Rauh, R. D. *J. Phys. Chem. A* **2000**, *104*, 837–844.
- (4) Sun, Y. P.; Riggs, J. E. *Int. Rev. Phys. Chem.* **1999**, *18*, 43–90.
- (5) Duarte, F. J.; Hillman, L. W. *Dye Laser Principles with Applications*; Academic Press: San Diego, CA, 1990.
- (6) Wilson, B. C.; Patterson, M. S. *Phys. Med. Biol.* **2008**, *53*, R61–R109.
- (7) Gratton, E.; Barry, N. P.; Beretta, S.; Celli, A. *Methods* **2001**, *5*, 103–110.
- (8) Makarov, N. S.; Rebane, A.; Drobizhev, M.; Wolleb, H.; Spahni, H. *J. Opt. Soc. Am. B* **2007**, *24*, 1874–1885.
- (9) Yang, D.; Jhaveri, S. J.; Ober, C. K. *MRS Bull.* **2005**, *30*, 976–982.
- (10) Plakhotnik, T.; Walser, D.; Pirotta, M.; Renn, A.; Wild, U. P. *Science* **1996**, *271*, 1703–1705.
- (11) Birch, D. J. S. *Spectrochim. Acta, Part A* **2001**, *57*, 2313–2336.
- (12) Goepfert-Meyer, M. *Ann. Phys.* **1931**, *9*, 273–294.
- (13) Lee, S.; Thomas, K. R. J.; Thayumanavan, S.; Bardeen, C. J. *J. Phys. Chem. A* **2005**, *109*, 9767–9774.
- (14) Zhang, X. B.; Feng, J. K.; Ren, A. M. *J. Phys. Chem. A* **2007**, *111*, 1328–1338.
- (15) Ledoux, I.; Zyss, J.; Siegel, J.; Lehn, J.-M. *Chem. Phys. Lett.* **1990**, *172*, 440–444.
- (16) Zyss, J.; Ledoux, I. *Chem. Rev.* **1994**, *94*, 77–105.
- (17) Ledoux, I.; Zyss, J. C. R. *Phys.* **2002**, *3*, 407–427.
- (18) Zhou, X.; Feng, J. K.; Ren, A. M. *Chem. Phys. Lett.* **2005**, *403*, 7–15.
- (19) Seo, J. W.; Jang, S. Y.; Kim, D.; Kim, H. J. *Tetrahedron* **2008**, *64*, 2733–2739.
- (20) Liu, K.; Wang, Y.; Tu, Y.; Agren, A.; Luo, Y. *J. Phys. Chem. B* **2008**, *112*, 4387–4392.
- (21) Feuvrie, C.; Maury, O.; Le Bozec, H.; Ledoux, I.; Morrall, J. P.; Dalton, G. T.; Samoc, M.; Humphrey, M. G. *J. Phys. Chem. A* **2007**, *111*, 8980–8985.
- (22) Chapurlat, R.; Kuntz, E.; Kuntz, E. U.S. Patent 3,810,873, 1974.
- (23) Porres, L.; Bhatthula, B. K. G.; Blanchard-Desce, M. *Synthesis* **2003**, *10*, 1541–1544.
- (24) Lakowicz, J. *Principles of Fluorescence Spectroscopy*; Kluwer Academic: New York, 1999.
- (25) Sheik-Bahae, M.; Said, A.; Wei, T.; Hagan, D.; Van Stryland, E. *IEEE J. Quantum Electron.* **1990**, *26*, 760–769.
- (26) Viau, L.; Maury, O.; Le Bozec, H. *Tetrahedron Lett.* **2004**, *45*, 125–128.
- (27) Maury, O.; Viau, L.; Senechal, K.; Corre, B.; Guegan, J. P.; Renouard, T.; Ledoux, I.; Zyss, J.; Le Bozec, H. *Chem.—Eur. J.* **2004**, *10*, 4454–4466.
- (28) Jang, S. R.; Lee, C.; Choi, H.; Ko, J. J.; Lee, J.; Vittal, R.; Kim, K. J. *Chem. Mater.* **2006**, *18*, 5604–5608.
- (29) Cossi, M.; Barone, V.; Mennucci, B.; Tomasi, J. *Chem. Phys. Lett.* **1998**, *286*, 253–260.
- (30) Mortensen, O. S.; Svendsen, E. N. *J. Chem. Phys.* **1981**, *74*, 3185–3189.
- (31) Correa, D. S.; De Boni, L.; Misoguti, L.; Cohanoschi, I.; Hernandez, F. E.; Mendonca, C. R. *Opt. Commun.* **2007**, *277*, 440–445.
- (32) De Boni, L.; Misoguti, L.; Zilio, S. C.; Mendonca, C. R. *ChemPhysChem* **2005**, *6*, 1121–1125.
- (33) Antonov, L.; Kamada, K.; Ohta, K.; Kamounah, F. S. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1193–1197.
- (34) Belfield, K.; Bondar, M.; Hernandez, F. E.; Przhonska, O.; Yao, S. J. *Phys. Chem. B* **2007**, *111*, 12723–12729.
- (35) Cohanoschi, I.; Hernandez, F. E. *J. Phys. Chem. B* **2005**, *109*, 14506–14512.
- (36) Cohanoschi, I.; Belfield, K. D.; Toro, C.; Yao, S.; Hernandez, F. E. *J. Chem. Phys.* **2006**, *124*, 194707.
- (37) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.
- (38) Ridley, J.; Zerner, M. *Theor. Chim. Acta* **1973**, *32*, 111–134.

JP804975A