AOARD Research Project Final Report

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Submitted by:	National Central University
Principal Investigator:	Tzu-Chau Lin, Ph.D. Assistant Professor Department of Chemistry National Central University
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National Dong Hwa University,1, Sec. 2, Da-Hsueh Road,Shoufeng, Hualien 974,Taiwan,TW,974

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14. ABSTRACT
In this proposed research project, efforts have been focused on the synthesis and optical properties characterization of some multi-photon absorbing chromophores especially with frequency up-converted stimulated emission behavior. This research project was y aimed to study some structural parameters that may affect the multi-photon pumped stimulated emission properties in dye molecules. The structural parameters that was attempted to investigate include the substituent effets (types and/or positions) and chromophoric unit number density effect. Significant amount of time and man-power was spent to accomplish the synthesis and characterization of some of the designed model compounds. Most of these compounds possess strong two- and three-photon absorption (2PA & 3PA) induced up-converted emission covering various spectral regions. One of the synthesized stibazolium-type chromophore also shows strong 2PA-induced stimulated emission when pumped by femtosecond laser pulses at ~775 nm. Specifically, four stilbazolium chromophores have been stabilized for 2PP stimulated emission property studies. Only one of the synthesized compounds possesses 2PP-induced up-converted cavityless lasing when pumped by femtosecond laser pulses. To the best of author?s knowledge, this compound is so far the only stilbazolium salt with symmetrical di-substitution in its molecular structure that exhibits 2PP-induced stimulated emission in femtosecond regime. Although the currently collected data could not provide any clear picture of the relationship between molecular structure and stimulated emission property, using thiophene unit(s) as part of π-bridge in designing symmetrically di- ubstituted two-photon lasing dyes might be a direction that worthy to explore. On the other hand, the blueshifted forward lasing is an interesting phenomenon that worth to put more efforts on studying its origin.

15. SUBJECT TERMS
Nonlinear Optical Materials, Laser Materials Processing

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Abstract

In this proposed research project, we have planned to focus our efforts on the synthesis and optical properties characterization of some multi-photon absorbing chromophores especially with frequency up-converted stimulated emission behavior. This research project was originally aimed to study some structural parameters that may affect the multi-photon pumped stimulated emission properties in dye molecules. The structural parameters that we attempt to investigate include the substituent effets (types and/or positions) and chromophoric unit number density effect.

Due to the relocation of our research laboratory (from National Dong Hwa University to Natioanl Central University during Jul. 2005 to Oct. 2005), the re-establishment of the synthetic equipments in our laboratory seriously delayed the progress of the project, which also results in delay of this final research report. Nevertheless, as planned, we have devoted significant amount of time and man-power to accomplish the synthesis and characterization of some of the designed model compounds. Most of these compounds possess strong two- and three-photon absorption (2PA & 3PA) induced up-converted emission covering various spectral regions. One of the synthesized stibazolium-type chromophore also shows strong 2PA-induced stimulated emission when pumped by femtosecond laser pulses at ~775 nm. This report briefly presents the synthesis and characterization results of the proposed research project.

I. Objectives of the proposed research

Dye lasers are an important class of lasers as they offer the tunability over a comparatively wide spectral range. Dye lasers can be pumped by various excitation sources through one-photon pumping process and can emit in both pulsed and continuous wave (CW) forms. Frequency up-conversion, on the other hand, is another process to gain laser action from a dye medium through multi-photon excitation process. So far, for organic dyes, the major technique for obtaining frequency up-converted lasing is based on direct multi-photon (either two- or three-photon excitation) excitation.[1-9] The two-photon pumped (2PP) lasing technique is a special approach to frequency up-conversion lasing and the major advantages of 2PP lasing techniques for up-conversion are:

(i) There are no phase-matching requirements for 2PP lasing, which are necessary for harmonic generation,

(ii) It is feasible of using infrared (IR) lasers as the pumping sources to obtain laser action in UV to visible region (optical-to-optical conversion), and

(iii) It is capable of adopting film, waveguide and fiber configurations for compact and portable solid-state laser applications.

For the past few years, several attempts have been made to synthesize new chromophores which exhibit two-photon pumped lasing behavior[1-10] but the clear molecular design criteria is still lacking. In order to precisely control the molecular structures with various optimum absorption wavelength positions for different pumping source, a systematic synthesis work and cautious characterization should be performed.

Triggered by the fascinating 2PP lasing phenomenon and the advantages mentioned above for future potential applications, it is our interest to gain more insight of the detailed dye structure-laser action property relationships. Both synthesis efforts and photophysical characterization works will be involved in this study. Due to the relocation of our laboratory, some parts of the proposed molecular design, synthesis and linear optical properties characterization was conducted in National Dong Hwa University and others were continuously conducted in National Central University. The photophysical property studies such as two-photon pumped stimulated/up-converted emission was accomplished by our collaborator in the USA–the Institute for Lasers, Photonics and Biophotonics in State University of New York at Buffalo, USA (Professor Paras N. Prasad and Dr. Guang S. He)

II. Results and discussion

II-A. *Synthesis of the model compounds*

We have synthesized four model chromophores for this research project, one of them is multi-branched type and the others are linear type molecules. The chemical structures of these model compounds are shown in Fig. 1.

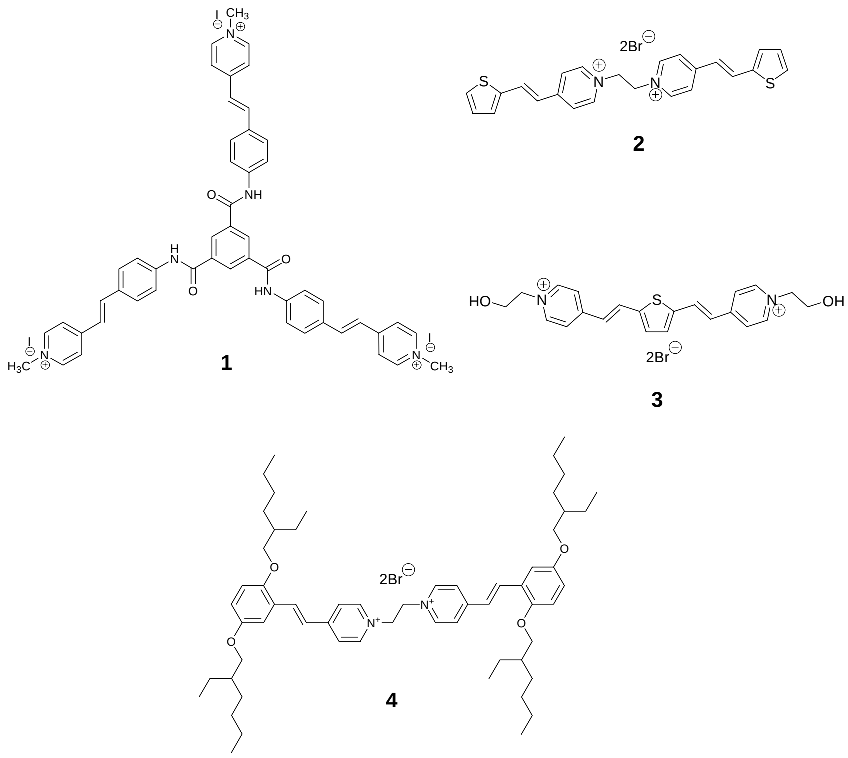
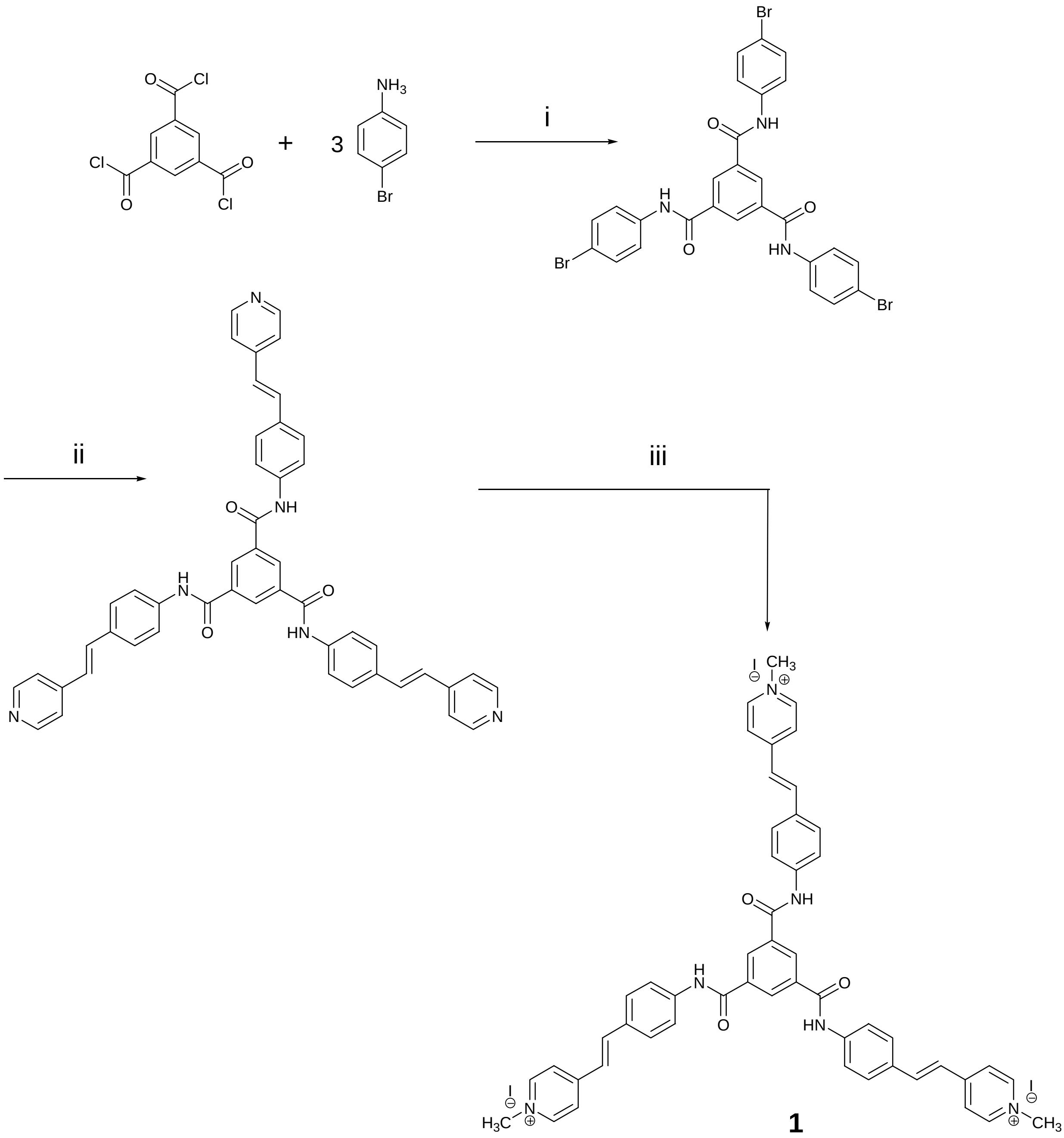


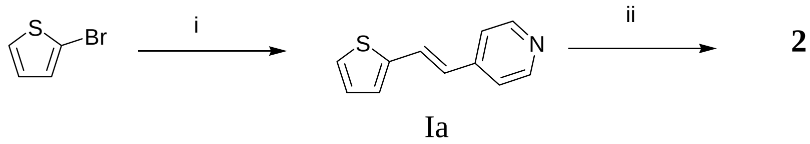
Fig. 1. Chemical structures of the studied dye molecules.

All these model compounds are with the genetic nature of stilbazolium salt, which are varied in the type, positions and strength of electron-donors. The synthetic routs utilized to approach these dye compounds are depicted in Schemes 1-2.

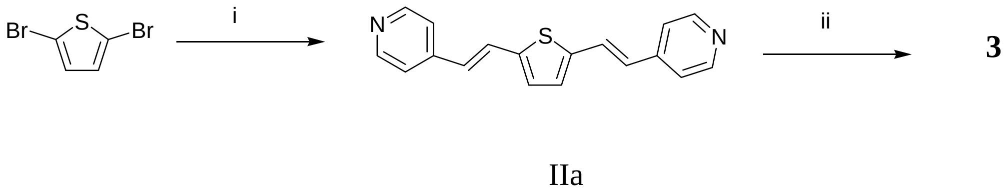


Reagents and conditions: (i) THF, R.T.;
(ii) $Pd(oac)_2$, $Ph_3(o\text{-tol})_3$, 4-Vinylpyridine, $MeCN/Et_3N$,48hr;
(iii) CH_3I, Acetone,reflux

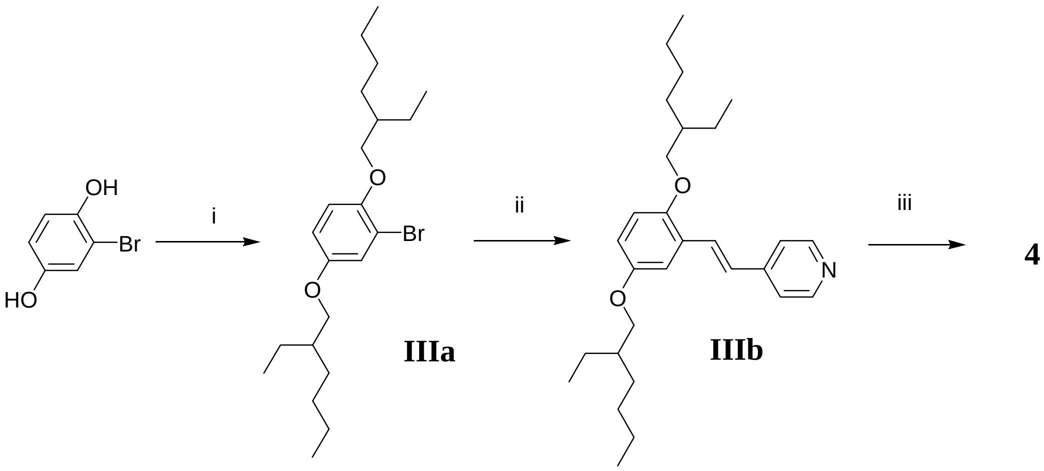
Scheme 1. The synthetic route for multi-branched stilbazolium compound **1**.



Reagents and conditions: (i) $Pd(oac)_2$, Ph_3(*o*-tol)$_3$, 4-Vinylpyridine, $MeCN/Et_3N$,48hr;
(ii) BrCCBr, Acetone,reflux



Reagents and conditions: (i) $Pd(oac)_2$, Ph_3(*o*-tol)$_3$, 4-Vinylpyridine, $MeCN/Et_3N$,48hr;
(ii) BrCCOH, DMF, ~50 ^{0}C



Reagents and conditions: (i) CCCC(C_2H_5)CCBr, K_2CO_3,KI / DMF,N_2
(ii) $Pd(oac)_2$, Ph_3(*o*-tol)$_3$, 4-Vinylpyridine, $MeCN/Et_3N$,48hr;
(ii) BrCCOH, Acetone,reflux

Scheme 2. The synthetic procedures for linear stilbazolium compound **2-4**.

II-B. ***Optical properties characterization***

Linear absorption spectra measurement. Linear absorption spectra of the synthesized model compounds in solution phase were measured by a UV-3150PC UV-VIS-NIR Scanning Spectrophotometer from Shimadzu. All the sample solutions were freshly prepared in the same manner with concentration of 1×10^{-5} M in DMSO for this measurement. Fig. 2 shows the recorded linear absorption spectra of these chromophore solutions. The linear absorption maxima of these dyes range from 336 nm to 447 nm and their extinction coefficients vary from 3162 to 4773 M^{-1} cm^{-1}.

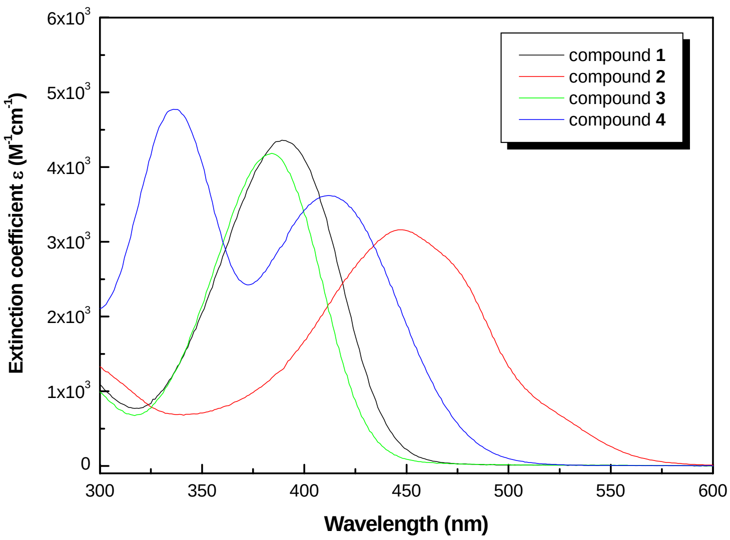


Fig. 2 Linear absorption spectra of the model compounds in DMSO at concentration of 1×10^{-5} M

Two-photon excited fluorescence measurement. All these chromophore solutions manifest two-photon absorption induced up-converted fluorescence emission. Fig. 3 presents two-photon induced fluorescence spectra of these four compounds. These sample solutions were prepared in DMSO at concentration of 1×10^{-3} M for this measurement. The excitation laser pulses with wavelength of ~775 nm and average pulse energy of ~5μJ were generated from a Ti:sapphire laser oscillator/amplifier system. The fluorescence spectral measurements were accomplished by using a HoloSpec CCD-array spectrometer in conjunction with a fiber coupler head. Fig. 3

presents the recorded 2PA-induced fluorescence spectra of the studied chromophores.

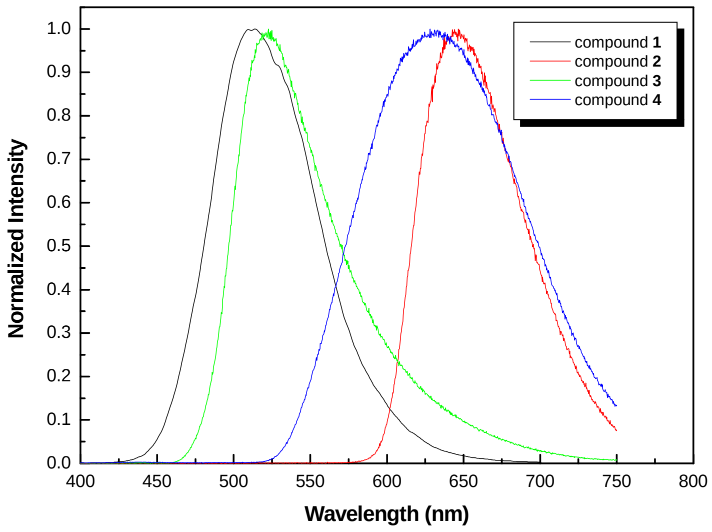


Fig. 3 Normalized two-photon absorption induced up-converted emission. (sample concentration: 1×10^{-3} M in DMSO)

Two-photon pumped cavityless lasing. Originally, we intended to utilize nanosecond laser pulses generated either from a dye laser pumped by a Q-switched Nd:YAG pulsed laser or the Q-switched Nd:YAG pulsed laser itself with different IR wavelengths and various repetition rate (from1 to 10 Hz) for this study. After several careful experiments, we have found that none of the prepared dye solution (0.02M/DMSO) shows two-photon pumped stimulated emission under our experimental condition. This might be due to the relatively low local pumping intensity. In order to effectively increase the local pumping intensity, we have employed femtosecond laser pulses as the pumping tool. These laser pulses are from a mode-locked Ti-sapphire oscillator/amplifier system (CPA-2010 from Clark-MXR) producing ~160-fs-duration, ~775-nm wavelength, and ~8-nm spectral-width laser output with a repetition rate of 1 kHz. The laser beam was focused via an f = ~ 5-cm lens onto the center of the sample cell. If the sample possess 2PP stimulated emission, our optical set-up (in conjunction with appropriate spectrometer and streak camera) as described in Fig. 4 can readily characterize the spectral (and/or temporal) properties of 2PP fluorescence emission, 2PP-based stimulated emission, temporal profiles of the pumping beam and stimulated emission beams. The experimental set-up for two-photon pumped frequency up-conversion lasing property study is illustrated in Fig. 4. We have carefully checked all the above-mentioned sample solutions and found that compound **2** exhibit blue-green stimulated emission. The measured spectral profile of the stimulated emission from this dye compound was recoded by the same grating spectrometer (HoloSpec from Kaiser Inc.) mentioned above and is illustrated in Fig. 5.

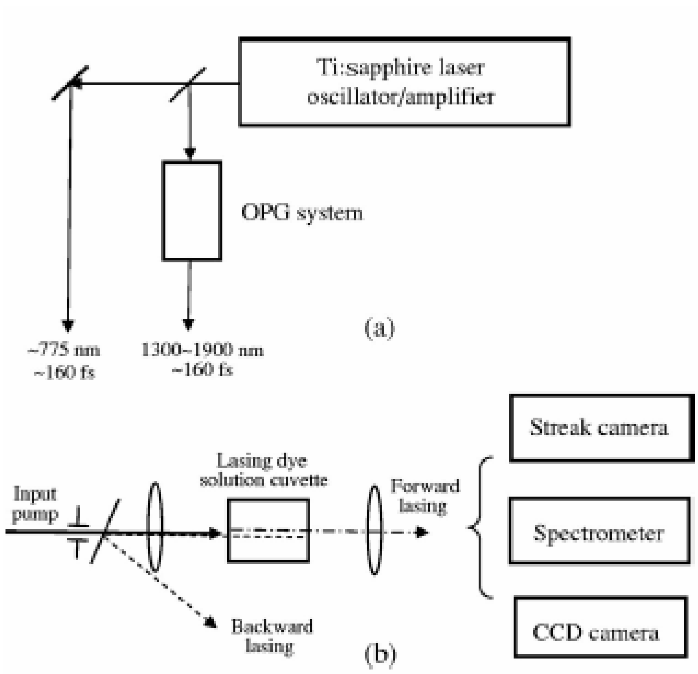


Fig. 4 Pump-laser source(s) and optical setup for two-photon pumped lasing behavior study.

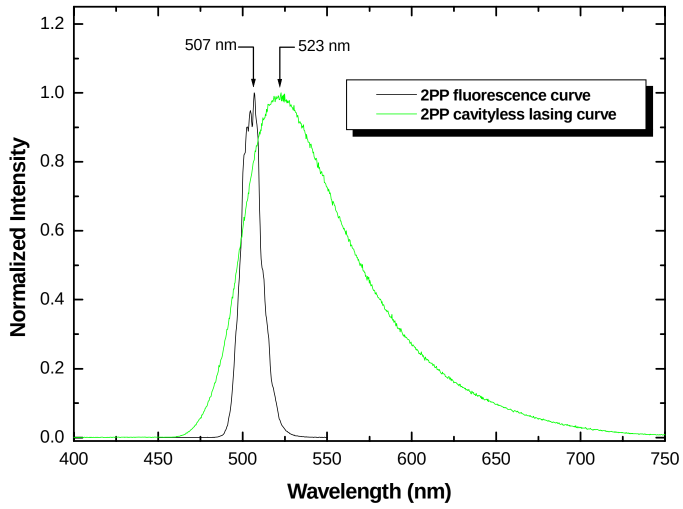


Fig. 5 Normalized spectra of two-photon excited fluorescence and forward 2PP cavityless lasing from compound **3**/DMSO solution at the pump energy level of ~20μJ.

From Fig. 5 one can see that (1) the peak wavelength position of the forward 2PP lasing is located at higher energy end compared to the fluorescence curve; (2) the lasing spectral bandwidth (~14nm) is much smaller than the corresponding fluorescence bandwidth (~73 nm). The mechanism for the cause of blueshifted forward lasing is not clear at current stage and this issue will be the subject of our future investigation.

III. Conclusion

We have synthesized four stilbazolium chromophores for 2PP stimulated emission property studies. Unfortunately, only one of the synthesized compounds possesses 2PP-induced up-converted cavityless lasing when pumped by femtosecond laser pulses. To the best of our knowledge, this compound is so far the only stilbazolium salt with symmetrical di-substitution in its molecular structure that exhibits 2PP-induced stimulated emission in femtosecond regime. Although the currently collected data could not provide any clear picture of the relationship between molecular structure and stimulated emission property, using thiophene unit(s) as part of π-bridge in designing symmetrically di- ubstituted two-photon lasing dyes might be a direction that worthy to explore. On the other hand, the blueshifted forward lasing is an interesting phenomenon that worth to put more efforts on studying its origin.