

Synthesis and two-photon induced fluorescence spectroscopy of a novel nonlinear optical chromophore

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A novel organic chromophore (A1) is designed and synthesized with a fine structure for two-photon absorption (TPA). The single-photon induced fluorescence spectra and the fluorescence lifetime have been studied for A1, excited respectively by 297-, 355-, 422-nm laser. And the two-photon induced fluorescence spectra were surveyed when A1 was excited by 820- and 910-nm laser. The results show that the curves of up-converted fluorescence spectra are almost same and have the same peak value at 518 nm. Accordingly, we can draw a conclusion that the TPA occurs when A1 is excited by 820- and 910-nm laser separately and though the absorption-transition pathway is different, the transition-emission pathway is the same.

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In recent years, considerable attention has been devoted to the organic molecules with up-converted fluorescence through two-photon absorption (TPA), owing to its connection with fundamental issues such as electronic conjugation, intramolecular charge transfer, hyperpolarizabilities, electron-phonon coupling, as well as to the numerous applications it offers in various areas such as telecommunications^[1,2], three-dimensional optical data storage^[3,4], information processing, optical power limiting^[5-7], microfabrication^[2,8], etc..

However, most of the organic molecules reported in recent years are designed to be composed by limited types of basic conjugated structural unit^[9,10]. In order to obtain organic molecules with high fluorescent quantum production rate and large TPA cross-section, the amelioration of these molecules is usually to change the donor/acceptor or the anion on the premise of connecting several basic conjugated structural units^[11]. Therefore, it is inevitably meaningful to design and synthesis new kind of basic conjugated structural unit, for the promotion of the molecules with two-photon induced up-converted fluorescence. In this experiment, one new type of basic conjugated structural unit (A1) was synthesized and its optical-physical properties were studied.

Synthesis of A1 is mainly by two steps. Firstly, 3-(dimethylamino) propionitrile and 4-bromo-1,8-naphthalic anhydride in equal amount were put into about 40-ml isoamy alcohol, stir and refluxing at the temperature of 130 °C for 15 hours. The products (molecule 1) of the first step should be distilled and purified before being used in the next step. Secondly, product 1 and 1,2-phenylenediamine in equal mole amount were put into about 50-ml ethyl alcohol, stir and refluxing at the temperature of 83 °C for 12 hours. The products of this step were purified by chromatogram to gain molecule 2. Synthesis process is shown as Fig. 1.

Chloroform was chosen as the solvent because A1 has a good solubility in it. Linear absorption spectrum of the dilute solution (1×10^{-4} mol/L) was surveyed, as shown in Fig. 2. The instrument used in the experiment is Ultraviolet-visible spectrophotometer (Tianjin Optics Instrument Plant, WFZ-25A) in the resolution of 1 nm. According to Fig. 2, two linear absorption bands can be recognized, with peaks value at 297 and 422 nm separately and an overlap around 355 nm. And in the scope above 500 nm, the linear absorption of A1 is very slight.

Fluorescence can be observed obviously in solution of A1 under natural light. According to the characteristic of A1's absorption spectrum, single-photon induced fluorescence spectra and fluorescence lifetime were studied at 297, 422, and 355 nm, respectively, corresponding to

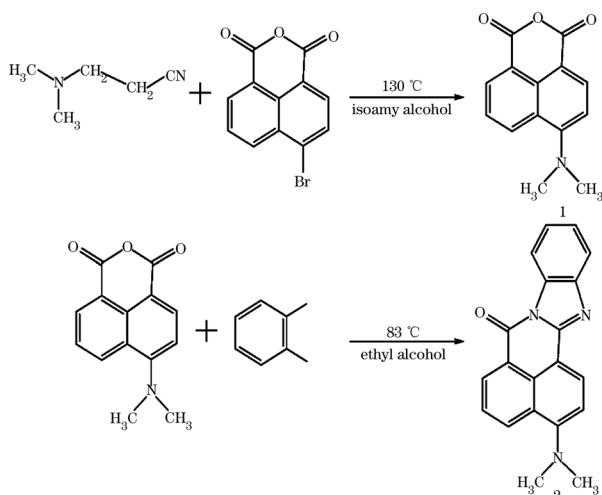


Fig. 1 Route of synthesizing A1.

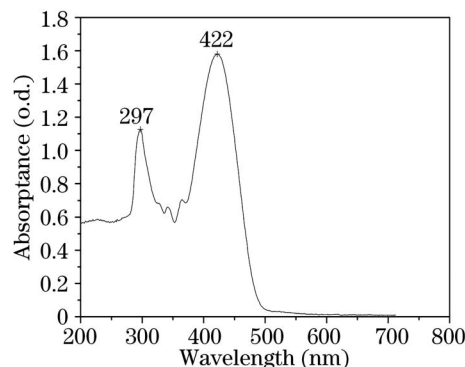


Fig. 2. Absorption spectrum of A1 in chloroform (concentration of the solution is 1×10^{-4} mol/L).

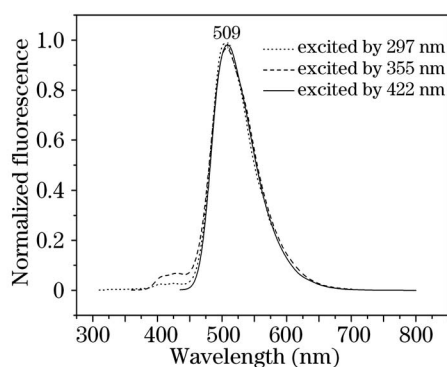


Fig. 3. Single-photon induced fluorescence (concentration of the solution is 5×10^{-6} mol/L) by stimulation lasers of 297, 355, and 422 nm.

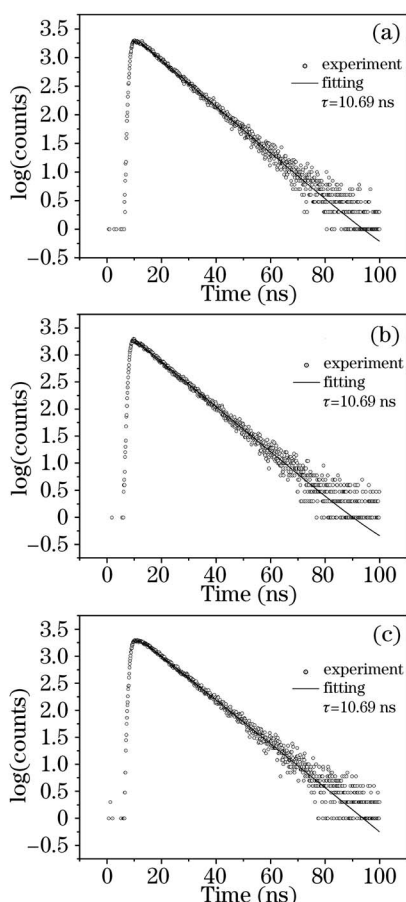


Fig. 4. Single-photon induced fluorescence lifetime decay curves (concentration of the solution is 5×10^{-6} mol/L) by the stimulation lasers of 297 (a), 355 (b), and 422 nm (c).

the two absorption peaks and one overlap. Instrument used in this experiment is manufactured by English Edinburgh Instrument Company's stable/transient state fluorescence spectroscope (Edinburgh FLS920). The fluorescence spectra of the solution (5×10^{-6} mol/L), shown in Fig. 3, are very similar under different stimulation lasers and the emission fluorescence peaks are all located at 509 nm. Figure 4 shows the fluorescence decay curves under the stimulation lasers of 297, 422, and 355 nm,

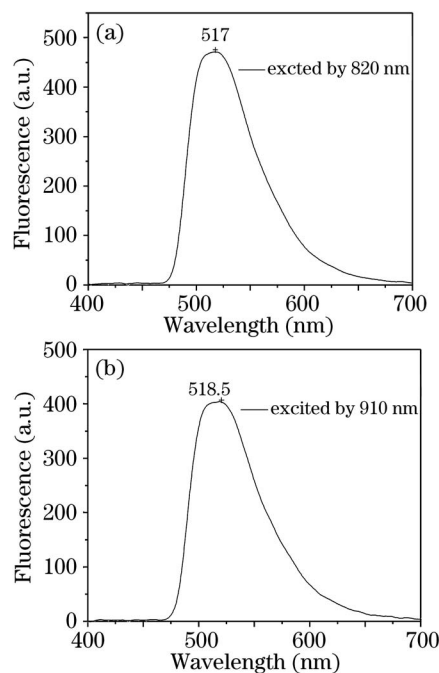


Fig. 5. Two-photon induced fluorescence by stimulation lasers of 820 (a) and 910 nm (b) (concentration of the solution is 0.01 mol/L).

respectively. The result of single exponential decay fit indicates that fluorescence lifetimes of three different stimulation lasers are almost same (about 10.5 ns). Thus, it can be concluded that it is from the same energy level that the stimulated molecules of A1 transfer to ground level during the process of radioactive transition.

Since the linear absorption of A1 has a peak value at 422 nm and is very slight in the scope above 500 nm, we choose the lights above 800-nm wavelength to stimulate A1. Green up-converted fluorescence is quite intense and can be observed obviously. The concentration of sample solution is 0.01 mol/L and the experimental data of fluorescence were recorded by optical fiber spectroscope (StellarNet Inc.EPP2000C UV-VIS), as shown in Fig. 5. Spectra of up-converted fluorescence, induced by 820- and 910-nm lasers respectively, have a emission band with a peak value around 518 nm. That phenomenon indicates that the TPA occurs when A1 is excited above 800 nm. Also, it is to draw a conclusion that the transition-emission pathway is same when excited A1 transfer to ground level, though the absorption-transition pathway is different when A1 is excited by different wavelength lasers.

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