



Synthesis, two-photon absorption properties and bioimaging applications of mono-, di- and hexa-branched pyrimidine derivatives



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ABSTRACT

A series of mono-, di- and hexa-branched pyrimidine derivatives possessing two-photon absorption have been synthesized. The spectral features of the dyes showed solvatochromic with significant bathochromic shifting of the emission spectra and large Stokes shifts in more polar solvents mainly due to the intramolecular charge-transfer. The two-photon absorption cross-section values were measured by two-photon excited fluorescence and open aperture Z-scan methods. The results revealed that the two-photon absorption cross-section values were enhanced with increasing electron-donating strength of the end group and branch number. The photophysical properties of the dyes were further investigated with the aid of theoretical calculations. In addition, the di-branched dyes has the largest values of two-photon absorption cross-section per molecular weight, low cytotoxicity and can be internalized by human liver cancer cell line and accumulates in the cytoplasm, allowing for live cell two-photon fluorescence imaging, so it is promising for *in vitro* and *vivo* cellular imaging applications.

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1. Introduction

In recent years, materials displaying large two-photon absorption (2PA) have attracted considerable interest owing to the potential applications including two-photon photodynamic therapy, three-dimensional optical data storage, up-converted lasing, optical power limiting materials and bioimaging [1–5]. The applications have significantly depended on the advantage of these materials with low energy excitation in the near-IR region, which can effectively prevent damage to the materials. Consequently, it has become the technique of choice for non-invasive biological imaging in thick tissue and in living animals, due to the above features [6].

The majority of currently used fluorescent imaging reagents are mainly designed for one-photon microscopy, however, not suitable for two-photon microscopy, because of their small σ_{2PA} values and

low brightness [7]. Therefore, there is a pressing need to synthesize materials with large 2PA cross-sections for *in vivo* imaging. Some efficient molecular design strategies were put forward to provide guidelines for the development of materials with large 2PA cross-sections [8,9]. Generally, molecular structures containing a π -center with electron donors or acceptors on the terminal sites of the conjugation system are expected to exhibit good 2PA response. Particularly, the conjugation length, π -electron center, and chemical functional groups at the end of electron conjugation are recognized as three important factors for structure-property optimization [10]. Additionally, designing a multi-branched backbone molecular structure is one of the effective strategies to obtain a large 2PA cross-section, as the branched architecture not only provides a way to incorporate several 2PA-enhancing parameters into a single system, but also allows material chemists to optimize a dye molecule by combining various desired characteristics together for specific purposes [11]. For example, the molecules consisting of triazine unit as a strong electron-accepting center and a terminal electron-donating group linked through a π -conjugated bridge have been shown to be excellent 2PA materials [12–14]. Recently, a series of pull–push type pyrimidine derivatives with large σ_{2PA} have been reported [15–20]. However, according to our knowledge, there is no systematic research on the relationships between σ_{2PA}

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and the branch number, as well as the application in bioimaging for the pyrimidine derivatives.

Relying on above consideration, we were motivated to design a series of dyes based on the pyrimidine unit containing both a styryl and 1,3,5-triazine unit and investigate their optical properties as 2PA materials (Fig. 1). This idea is also based on the following considerations: (1) Pyrimidine has a high electron affinity and good planarity making it an appropriate building block in construction of chromophores for nonlinear optical materials [15–19]. On the other hand, pyrimidine ring has well-known reactivity in the position 4 and 6, which can easily undergo reactions with an aromatic aldehyde in solvent-free conditions. Moreover, the styryl group is an effective building block for 2PA chromophores. Therefore, pyrimidine derivatives with a styryl group as π -conjugation may serve as a kind of effective 2PA materials. (2) 1,3,5-triazine-based compounds show good optical properties, because of high planarity of the conjugated system, strong intramolecular charge transfer, and additional cooperative enhancement between the branches [21].

The synthetic procedure of pyrimidine derivatives were shown in Fig. 2.

2. Experimental section

2.1. Materials and apparatus

All chemicals and solvents were dried and purified by standard methods. IR spectra ($4000\text{--}400\text{ cm}^{-1}$), as KBr pellets, were recorded on a Nicolet FT-IR 870 SX spectrophotometer. The ^1H NMR and ^{13}C NMR spectra recorded on at $25\text{ }^\circ\text{C}$ using Bruker 400 Ultrashield

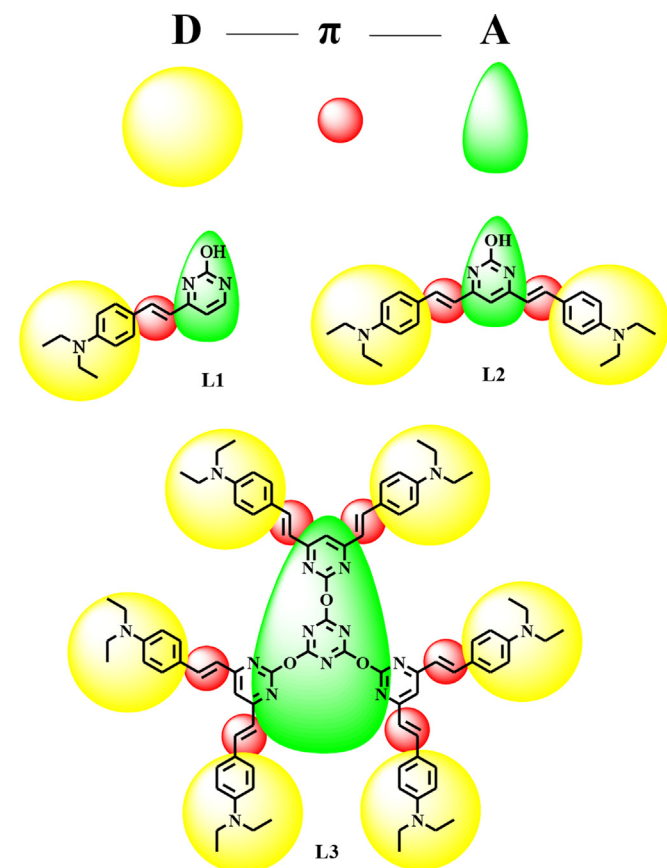


Fig. 1. The molecular structure of L1, L2 and L3.

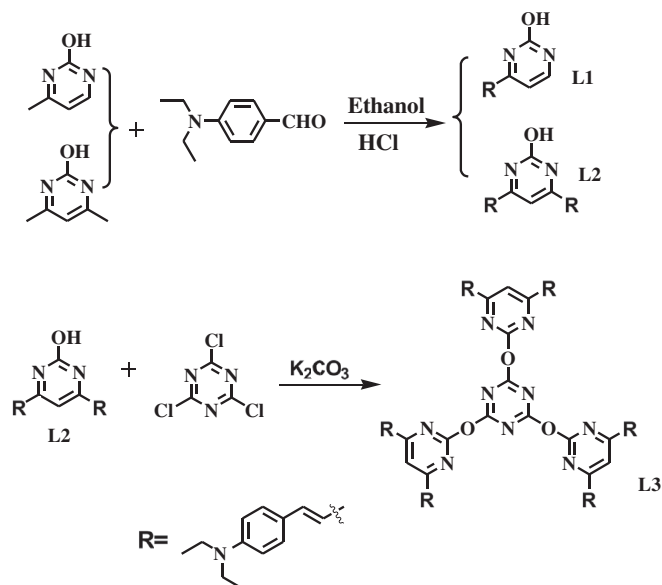


Fig. 2. Synthesis of the chromophores L1, L2 and L3.

spectrometer were reported as parts per million (ppm) from TMS (δ). MALDI-TOF mass spectra were recorded using Bruker Autoflex III Smartbeam. Elemental analyses were carried out on a Perkin–Elmer 240 analyzer. Melting point is measured on FP62 instruments.

UV spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. The fluorescence spectra measurement was performed with use of a HITACHI F-2500 Spectrofluorophotometer. The concentration of a sample solution was 5.0×10^{-6} mol/L 2PA cross-section of the samples were obtained by the two-photon excited fluorescence (2PEF) method with femtosecond laser piles and a Ti:sapphire system (680–1080 nm, 80 MHz, 140 fs) as the light source.

2.2. Measurements

2.2.1. The fluorescence quantum yields (Φ)

The fluorescence quantum yields (Φ) were determined by using fluorescein as the reference according to the literature method [22].

2.2.2. 2PA cross-section (σ_{2PA})

Two-photon absorption (2PA) is a nonlinear optical process in which a molecule simultaneously absorbs two photons of an energy $h\nu$ (or of energy $h\nu_1$ and $h\nu_2$) to access an excited state of $2h\nu$ (or $h\nu_1 + h\nu_2$). The two techniques for 2PA cross-sections are measured by two-photon excited fluorescence (2PEF) and Z-scan methods, respectively.

The molecular 2PA cross-section (σ_{2PA}) has been measured using the 2PEF method with the following equation [23]:

$$\sigma = \sigma_{\text{ref}} \frac{\Phi_{\text{ref}} c_{\text{ref}} n_{\text{ref}} F}{\Phi c n F_{\text{ref}}} \quad (1)$$

Here, the subscripts ref stands for the reference molecule. σ is the 2PA cross-section value, c is the concentration of solution, n is the refractive index of the solution, F is the integrated area of the detected two-photon-induced fluorescence signal, and Φ is the fluorescence quantum yield. The σ_{ref} value of reference is taken from the literature [24].

The Z-scan measurement is described as follows. For the open aperture Z-scan $|q_0(z,0)| < 1$, the normalized energy transmittance

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