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Synthesis and two-photon property studies of symmetrically substituted bisarylacetylene structures using functionalized quinoxalinoid units as the aryl substituents

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ABSTRACT

A series of symmetrically substituted multi-polar chromophores (**1**–**3**) based on the skeleton of bisarylacetylene using functionalized quinoxaline, indenoquinoxaline, and pyridopyrazine moieties as the aryl substituents has been synthesized and characterized for their two-photon absorption properties using femtosecond laser pulses as the probing tool. Under our experimental conditions, these model fluorophores are found to manifest strong and wide dispersed two-photon absorption in the near infrared (NIR) region. It is demonstrated that molecular structures with multi-branched π–frameworks incorporating functionalized quinoxalinoid units would possess large molecular nonlinear absorptivities within the studied spectral range. Optical power-limiting behavior in the femtosecond time domain of the indenoquinoxaline-derived dye molecule (**2**) from this model compound set was also investigated and the result indicates that such structural motif could be a useful approach for the molecular design towards strong two-photon absorbing material system for quick-responsive and broadband optical-control related applications.

1. Introduction

Similar to the development path of many other science subjects, the theoretical prediction of two-photon absorption (2 PA) made by Maria Göppert–Mayer in 1931 is far ahead of its experimental evidence [1]. After the advent of lasers in 1960, scientists started to have appropriate light sources to practically observe and study this nonlinear optical phenomenon [2,3]. For the past two decades, the availability of high peak power lasers has triggered the momentum to explore the two-photon technologies and many potential applications in the emerging field of photonics and biophotonics based on 2 PA have been demonstrated including optical power-limiting, frequency up-converted lasing, 3-D data storage, 3-D microfabrication, nondestructive bio-imaging and tracking, and two-photon photodynamic therapy [4–9]. In the course to develop two-photon technologies, the exploration of new materials with strong 2 PA plays an equally important counterpart as the advancement of laser systems. Through rational molecular design, it is possible to construct organic chromophores that exhibit several orders of intensified 2 PA with other desired molecular characteristics simultaneously incorporated, which greatly compensates for the relatively poor performance of commercialized dyes for the aforementioned applications. So far, it has been realized that the combination of several structural parameters such as intramolecular charge-transfer efficiency, effective size of π-conjugation domain, and molecular dimensionality of a molecule is closely related to the molecular 2 PA [10–32]. In other words, the arrangement of the selected building units within a molecule is a hinge for the molecular design toward highly active 2 PA-chromophores. In searching new strategies toward highly efficient 2 PA materials, we have been interested in the exploration of effective building units and structural arrangement that may enhance the molecular 2 PA. In this paper, we report our recent studies of degenerate two-photon absorption, up-converted emission and optical power-limiting properties of a series of newly synthesized quinoxalinoid chromophores by using ultrafast IR laser pulses working in the femtosecond regime as the major probing tools.

2. Results and discussion

2.1. Molecular structures and syntheses

The chemical structures of the studied model compounds in this work are illustrated in Fig. 1. These three structural congeners are

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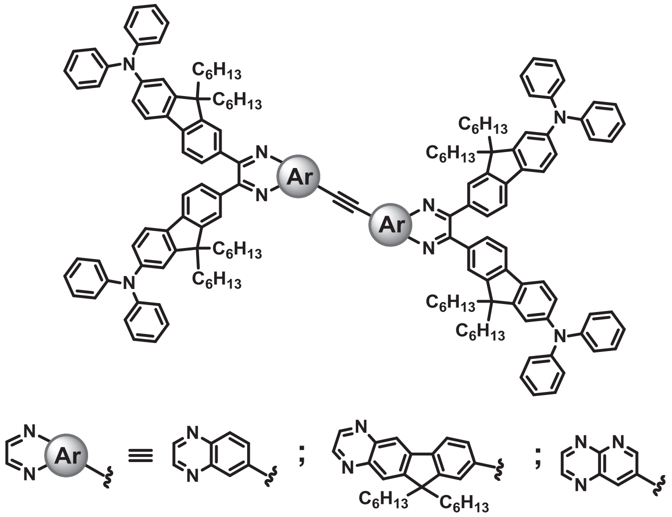

1 2 3

Fig. 1. Molecular structures of the studied model chromophores.

constructed based on the scaffold of a bisarylacetylene by using electron-donor-functionalized quinoxalinoid units as the aryl substituents. We have selected pyrazine-containing ring complexes as the heterocyclic parts in this model compound system since the involvement of electron-withdrawing hetero-atoms is expected to alter the electronic nature of the resulting chromophores compared to the all-carbon analogues. From the standpoint of molecular structure, each functionalized quinoxalinoid moiety of the studied model compound can be assumed to be dipolar because of its push–pull nature and skeletal geometry. Therefore, the connection between the presented structural arrangement and molecular 2 PA would be an interesting subject to study. Furthermore, we have attached alkyl chains at C9 positions of all the fluorenyl units in order to improve the molecular solubility in common organic solvents, which is another important issue to be considered in the molecular design from both the aspect of experiments and applications. The syntheses of the target model compounds are relatively straightforward as illustrated in Scheme 1, which mainly include the preparation of various precursors with appropriate functional groups for either conventional or modified Pd-catalyzed Sonogashira reactions to accomplish final chromophores. In brief, compound **1** was synthesized in one-step fashion by using a more reactive aryl iodide (**5**) and bis(methylsilyl)acetylene as the synthons while compound **2** was accomplished through another recently developed one-step coupling method that involves decarboxylative processes [33]. Differently, the typical multi-step Sonogashira reaction was finally found to be the most effective protocol to construct compound **3** instead of using either the aforementioned one-step cross-coupling conditions after several attempts. All the new dyes were obtained in acceptable yields and the details for the syntheses of these model compounds are presented in Section 5.

2.2. Optical properties characterization

2.2.1. One-photon absorption (1 PA) and fluorescence-related measurements

Linear absorption and fluorescence spectra of the studied compounds in toluene solutions (with concentration of 1×10^{-6} M) are shown in Fig. 2 and the related photophysical data are collected in Table 1. The 1 PA spectra were recorded through a Shimadzu 3501 PC spectrophotometer and the 1 PA-induced fluorescence spectra were measured utilizing a Jobin-Yvon FluoroMax-4 spectrometer. All these chromophores exhibit intense linear absorption in the UV–Vis region with the lowest-energy peaks located at 428 nm for **1** ($\varepsilon \sim 6.11 \times 10^4$ cm^{-1} M^{-1}), 445 nm for **2** ($\varepsilon \sim 1.50 \times 10^5$ cm^{-1} M^{-1}), and 466 nm for **3** ($\varepsilon \sim 6.83 \times 10^4$ cm^{-1} M^{-1}), respectively. These compound solutions also emit intense fluorescence under the irradiation of a common UV-lamp with blue-greenish color for **1** and **2** and green-yellowish color for **3**, which is in agreement with the measured emission spectra as illustrated in Fig. 2b.

The photostability of the studied dye compounds in solution phase was tentatively evaluated by continuously monitoring the decay of the fluorescence intensity during the course of UV-irradiation. We have utilized a set of UV-lamps as the excitation light source to provide ∼350 nm radiation with total output of 120 W for this experiment. The detailed experimental arrangement is described in the Supporting information. A commercialized laser dye, Coumarin 307, was selected as the reference and the results are illustrated in Fig 3. It can be seen that during the first 1-h consecutive exposure of UV-light, both compounds **1** and **2** retain >97% of their original emission intensity while compound **3** exhibits an observable decline (∼15%) of the original fluorescence intensity. Prolonged irradiation further deteriorates the emissive property of these model chromophore solutions and it is found that compound **3** shows a larger fluorescence intensity decrease (∼55%) whilst those of 1 and 2 are kept within ∼12% after 3 h of UV-light exposure. On the other hand, it is also found that compounds **1** and **2** possess better photostability compared to Coumarin 307. Overall, model compounds **1** and **2** manifest fairly good resistance of photodamage which is comparable to that of Coumarin 307 and is superior to that of compound **3** under our experimental condition. We suspect that the weak photo-resistance of compound **3** may be originated from the pyridine unit but the clarification of this issue is currently beyond the scope of this work.

2.2.2. Two-photon excited fluorescence (2PEF) emission properties

The studied model chromophores manifest strong two-photon excited upconversion emission which can be easily sighted even under low power of excitation by an unfocused femtosecond laser beam at ∼800 nm. Fig. 4a illustrates the 2 PA-induced fluorescence spectra of the model chromophores **1**–**3**. The sample solutions were freshly prepared at concentration of 1×10^{-4} M in toluene for this measurement and the excitation source utilized for this two-photon induced fluorescence study is from a mode-locked Ti:Sapphire laser (Chameleon Ultra II, Coherent) which delivers ∼140 fs pulses with the repetition rate of 80 MHz and the beam diameter of 2 mm. The intensity level of the excitation beam was carefully controlled to avoid the saturation of absorption and photodegradation. Besides, the relative position of the excitation beam was adjusted to be as close as possible to the wall of the quartz cell (10 mm × 10 mm cuvette) so that only the emission from the front-surface of the sample was recorded in order to minimize the re-absorption or inner-filter effect. It is noted from Fig. 4a that for each model chromophore the shape and spectral position of the measured 2 PA-induced emission is basically identical to its corresponding 1 PA-induced fluorescence band in Fig. 2b, which implies that in our dye system the radiative relaxation processes occurred within the studied samples are from the same final excited states regardless of the excitation method.

The power-squared dependence of the 2 PA-induced fluorescence intensity on the excitation intensity of the studied fluorophores was also examined. Fig. 4b–d are logarithmic plots of the measured data and the results (i.e. the fitting slope ≈2) validate that 2 PA process is responsible for the observed up-converted fluorescence emissions in all cases.