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Synthesis and multi-photon absorption properties of symmetric bisarylacetylene chromophores using functionalized isomeric pyrazinoindenocarbazole units as the rigid aryl substituents

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ABSTRACT

A pair of isomeric chromophores based on the skeleton of bisarylacetylene using functionalized pyrazinoindenocarbazole moieties as the aryl substituents has been synthesized and characterized for their two- and three-photon-related properties in the femtosecond and nanosecond regimes. Our experiments have found that both model fluorophores manifest strong two-photon absorption in the near infrared region with one of the isomers exhibiting superior maximum two-photon absorptivity. It is realized that both the isomeric forms of functionalized pyrazinoindenocarbazoles are useful π-units for the construction of highly two-photon active materials but the effectiveness of the units is unequal, which is probably attributed to the difference of their conjugated structures. Two-photon-based optical power-limiting and stabilization against nanosecond laser pulses of one isomer was demonstrated. Additionally, these two chromophores exhibit strong three-photon-induced fluorescence when excited by the nanosecond laser with longer wavelengths ($\geq$1000 nm), implying their potential utility to serve as prototypes for the development of three-photon materials.

1. Introduction

Two-photon absorption (2 PA) is a nonlinear optical phenomenon, which involves a simultaneous absorption of two photons. Although the prediction of 2 PA was made by Maria Göppert-Mayer in 1931 [1], only after the advent of lasers in 1960 did the scientists start to have appropriate and significantly strong light sources in hands to practically investigate and explore the use of this third-order nonlinear optical process. Early works accomplished by Kaiser, Garret, Peticolas and Rieckhoff have revealed that many different molecular systems possess 2 PA behavior regardless of their organic or inorganic nature [2,3]. Due to its intrinsic square dependence of the incident light intensity, many potential applications in the emerging field of photonics and biophotonics based on 2 PA technology have been proposed and 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]. For the past years, the accumulated efforts on the rational molecular design has made it possible to construct organic chromophores that manifest several orders of intensified 2 PA along with other desired characteristics incorporated and this has greatly compensated for the relatively poor performance of commercialized dyes for the aforementioned applications. To this date, 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 important to the strength of molecular 2 PA. Therefore, the arrangement of the selected building units within a molecule plays a pivotal role for the molecular design toward highly active 2 PA-chromophores. Compared to the development of various types of two-photon materials and technologies, relatively fewer efforts were made in the systematic exploration of organic materials that exhibit strong three-photon absorption (3 PA) properties. In theory, any medium that possesses 2 PA may also manifests appreciable 3 PA provided that appropriate experimental conditions are adopted. 3 PA process offers an intriguing possibility for bio-imaging applications because longer excitation wavelengths in near-infrared region are used, which greatly reduces the scattered light losses and undesirable linear absorption within the living organism. Moreover, the intrinsic cubic dependence on the local optical intensity of the 3 PA

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process offers a superior spatial confinement so that a higher contrast and spatial resolution in imaging can be achieved consequently. On the other hand, this higher order nonlinear absorption process can also provide much better optical-limiting performance over broader spectral region under the same nonlinear transmission [10].

In searching for new structural moieties to construct highly efficient 2 PA materials, we have been interested in exploring the utility of fused-polyarenes when they are used as a part of the π-framework in the designed 2 PA dye molecules and in this paper, we present our recent studies of degenerate 2 PA, up-converted emission and optical power-limiting properties of a pair of newly synthesized isomeric chromophores with a bisarylacetylene scaffold derived from functionalized pyrazinoindenocarbazoles in the femotosecond and nanosecond time domains. Besides, the effective 3 PA properties of these two model chromophores were also tentatively probed by using nanosecond laser pulses within the spectral range of 1100–1500 nm, which may provide useful information about the molecular design for the 3 PA materials.

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 two constitutional isomers have the same generic scaffold based on a bisarylacetylene using electron-donor-functionalized pyrazinoindenocarbazole units as the aryl substituents. We have selected pyrazine-fused indenocarbazole ring systems as the heterocyclic parts in this model compound system since the involvement of electron-attracting hetero-atoms is expected to alter the ground-state electronic nature of the resulting chromophores compared to their all-carbon analogues. On the other hand, these fused-polyarenes are expected to possess better conjugation condition due to their rigidity and coplanar nature and consequently provide larger area of π-delocalization upon light excitation. Besides, from the viewpoint of overall molecular structure, the studied compounds manifest a symmetrically substituted skeletal geometry as well as a multi-branched framework, which are both believed to be the beneficial structural parameters for the enhancement of molecular 2 PA. Therefore, a conjugated system that combines all the above-mentioned structural characteristics would serve as an interesting model for investigation of multi-photon absorption properties. In addition, in order to increase the solubility and hence the processibility of these model chromophores, we have attached alkyl chains at C9 positions of all the fluorenyl units and on the nitrogen atoms of carbazole moieties. The syntheses of the target model compounds are relatively straightforward as illustrated in Scheme 1, which mainly involve the preparation of various precursors with appropriate functional groups for Pd-catalyzed Suzuki and Sonogashira reactions to accomplish final chromophores. In brief, we have used a previously reported brominated-fluorenothiadiazole compound [11] (i.e. **3**) as the starting material and perform the borylation to prepare compound **4** for the Suzuki coupling in the next step. Compounds **4** and **5** were obtained in the yields of 65% and 50%, respectively. Compound **5** was then used as the initial synthon for the triphenylphosphine-mediated reductive cyclization [12] to construct the isomeric thiadiazoloindenocarbazole precursors (i.e. **6a** and **6b**). To our delight, these two constitutional isomers were separable through column chromatography and were obtained in serviceable yields of 43% and 30% for **6a** and **6b**, respectively. Alkyl chains were then attached to the nitrogen atoms of the carbazole units via a common alkylation method to afford **7a** (78%) and **7b** (76%). In order to accomplish the desired bisarylacetylene scaffold, a recently developed one-step Sonogashira type coupling which involves a Pd-catalyzed decarboxylative process was employed [13] and both compounds **8a** and **8b** were obtained in the same yield of 78%. Finally, $LiAlH_4$ (LAH) was utilized as the reducing agent to recover the diamine functional groups from the fused [1,2,5]thiazole rings of compounds **8a** and **8b** to afford **9a** and **9b**, which were used directly for the next step without purification. Through acid-catalyzed pyrazine formation with a corresponding diketone (compound **10**), the target model chromophores were prepared in the yields of 33% and 37% for **1** and **2**, respectively. The chemical structures of all of the new compounds were confirmed by the corresponding methods and the details for the syntheses of these compounds are presented in the Experimental section. As illustrated in Fig. 1, a previously reported chromophore [14] that possesses the same generic scaffold but using functionalized indenoquinoxaline as the aryl substituent has been selected as a reference compound (**R**) for the purpose of comparison.

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 and THF (at a 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 by a Shimadzu 3501 PC spectrophotometer and the 1 PA-induced fluorescence spectra were measured utilizing a Jobin-Yvon FluoroMax-4 spectrometer. Both these isomeric chromophores exhibit intense linear absorption in different solvents with the lowest-energy peaks located around ~445 nm for **1** and ~455 nm for **2**. It is noted that there is no apparent solvent effect in the linear absorption spectra of these compounds while solvent polarity does possess salient solvatochromic effect on their fluorescence behavior, which implies that the (relaxed) excited-states of these model chromophores manifest more dipolar characters than their ground-states. Similar properties have been reported for other symmetrically substituted multi-polar molecules and the symmetry-breaking phenomenon caused by electron-vibration coupling and dipolar solvation effects were proposed to account for this behavior [15–19].

2.2.2. Two-photon-related properties in the femtosecond regime

Both the studied isomeric chromophores exhibit strong two-photon-excited fluorescence which can be easily observed even under the radiation of an unfocused femtosecond laser beam with wavelength of 800 nm at low power level. Fig. 3(a) illustrates the 2 PA-induced fluorescence spectra of these compounds. The sample solutions were freshly prepared at concentration of 1×10^{-4} M in corresponding solvents for this measurement and a mode-locked Ti:Sapphire laser (Chameleon Ultra II, Coherent) was employed as an excitation source to provide ~140 fs pulses with the repetition rate of 80 MHz and the beam diameter of 2 mm for the experiment. The intensity level of the excitation beam was carefully controlled to avoid the saturation of absorption and photodegradation. Moreover, in order to minimize the re-absorption or inner-filter effect, 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. From Fig. 3(a), it is noted that for each model molecule the shape and spectral position of the measured 2 PA-induced emission is virtually identical to its corresponding 1 PA-induced fluorescence band in Fig. 2(c) and (d), which reveals that the radiative relaxation processes occurred within the studied samples are from the same final emissive