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Functionalized tetrafluorenylethylene-type chromophores: Synthesis, two-photon absorption and effective optical power-limiting properties in the visible-to-near IR region

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ABSTRACT

A series of novel multipolar fluorophores based on tetra-substituted olefinic scaffold using functionalized fluorenyl and indenofluorenyl units as the aryl substituents has been synthesized and investigated for their two-photon-related properties in the femtosecond and nanosecond time domains. When probed by the femtosecond pulses, these chromophores are found to possess appreciable intrinsic two-photon absorptivities with their local maxima very close to the short-wavelength end of the dynamic tuning range of a Ti: sapphire laser. While under the irradiation of nanosecond pulses, these dye molecules exhibit promising nonlinear optical-power-attenuation properties across the visible-to-near infrared region. Combining with their medium-high fluorescence quantum efficiencies, such archetype represents a new class of structures that could be utilized as effective broadband optical power-limiters and frequency up-converters especially with great potentiality to work in the visible regime.

1. Introduction

Just like the development path of many other science subjects, the theoretical prediction of two-photon absorption (2PA) made by Maria Göppert-Mayer in 1931 is far ahead of its experimental evidence [1] and the advent of lasers in 1960s has brought scientists appropriate excitation light sources to experimentally study this nonlinear optical phenomenon [2,3]. The intrinsic quadratic dependence of 2PA on the incident light intensity is one of the major characters that makes this third-order nonlinear optical phenomenon applicable in many photonics and biophotonics applications such as optical power-limiting, frequency up-converted lasing, 3-D data storage, 3-D microfabrication, nondestructive bio-imaging and tracking, and two-photon photodynamic therapy [4–11]. For the development of two-photon technologies, the exploration of new materials with strong 2PA plays an equally important counterpart as the advancement of high peak-power pulsed laser systems. Through rational molecular design, it is possible to construct organic structures that exhibit several orders of intensified 2PA with other desired molecular characteristics simultaneously integrated, which greatly compensates for the relatively poor performance of commercialized dyes for the aforementioned applications. Up to now, it has been realized that the combination of several structural parameters such as the efficiency of intramolecular charge-transfer, effective size of π-conjugation domain, and molecular dimensionality of a molecule is closely related to the molecular 2PA [12–29]. Therefore, the structural arrangement of the selected building units within a molecule is a hinge for the molecular design toward highly active 2PA-chromophores.

So far, various two-photon absorbing organic conjugated structures with different π-frameworks have been successfully demonstrated to show optical power-suppression function against high peak-power laser pulses in the nanosecond to femtosecond time domains [5,8,30–35] and most of the reported 2PA-based optical limiters are designed to attenuate laser pulses within near-IR region. In contrast, relatively fewer efforts focus on the molecular design toward nonlinear optical attenuation particularly in the visible range due to the challenge of nonlinearity/transparency trade-off. Nevertheless, several organic π-systems were explored and found to possess promising 2PA-based optical control of nanosecond and femtosecond laser pulses in the visible regime [36–38]. In addition, it has been experimentally shown that chromophores with branched π-frameworks could lead to strong multi-photon absorption while retaining wide range of linear

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transparency [39,40] and this is a valuable general guideline to design effective broadband optical-limiters based on 2PA. Following this motif of molecular design and our continuous efforts in developing multi-branched and dendritic π-structures for multi-photon absorption [25–29,41], in this paper we present a series of newly synthesized model chromophores based on functionalized tetrafluorenylethylene skeleton and the initial findings of their two-photon-related as well as effective optical power-limiting properties across the visible and near-IR regions.

2. Results and discussions

2.1. Model molecules and syntheses

The chemical structures and synthetic procedures for the targeted fluorophores (**1**–**3**) are illustrated in Fig. 1 and Scheme 1, respectively. The backbones of these dye molecules are conceptually based on the skeleton of tetraphenylethylene (TPE) but incorporate four identical functionalized fluorene and indenofluorene moieties as the aryl arms extended outward from the central ethylene unit. TPE-based molecules have been extensively studied recently owing to their unique emission behaviors in various physical states as well as their potential usage for fluorescent bio/chemosensors and electrochemical switching devices [42,43]. With the incorporation of beneficial structural units for the 2PA promotion (i.e. functionalized fluorenyl and indenofluorenyl units) and retention of the intrinsic non-coplanar nature of a TPE-type scaffold, we anticipate that these small multi-branched dyes may serve as another test system for the optimization study of nonlinearity/spectral transparency as well as exploration of their nonlinear absorption behavior within visible to near-IR region. The syntheses of these chromophores are relatively straightforward as outlined in Scheme 1, which mainly involve the preparation of properly functionalized fluorenyl/indenofluorenyl boronic acids (**7**–**9**) as the major synthons to couple with the commercialized tetraiodoethene through Pd-catalyzed Suzuki reaction protocol. Originally we did suspect that it would be difficult to attach four comparatively bulky fluorenyl/indenofluorenyl units to a central ethylene core and either low yield or incompletion of reaction due to such vicinal crowdedness may be encountered but neither these situations was observed in our case and chromophores **1**–**3** were successfully obtained in acceptable average yield of ~40%. All the model fluorophores are highly soluble in common organic solvents such as toluene, ethyl acetate, dichloromethane (DCM), and tetrahydrofuran (THF). The detailed synthetic procedures including the preparation of the key intermediates (**7**–**9**) and the final coupling reactions toward these model structures are described in the Experimental section.

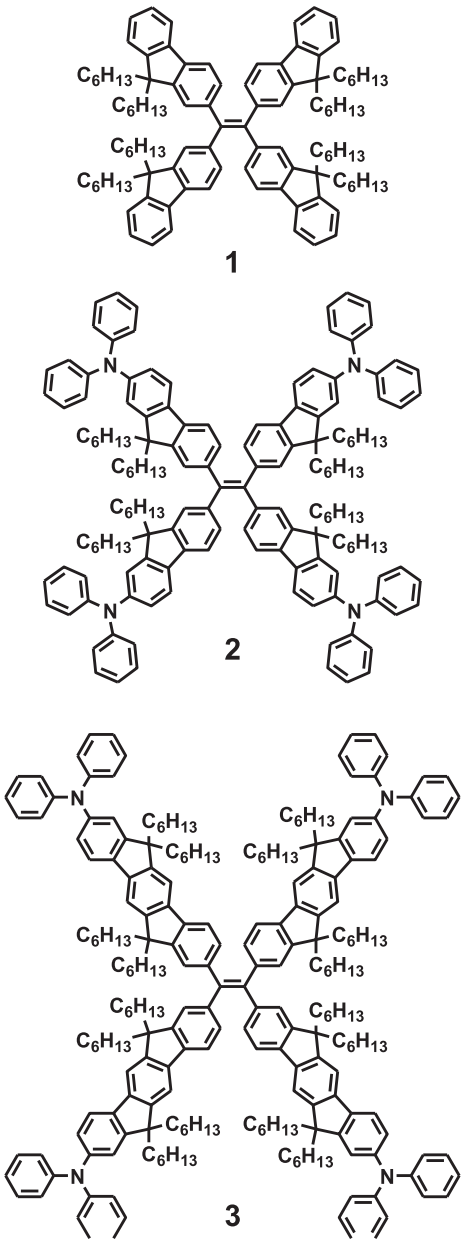

Fig. 1. Chemical structures of the studied model chromophores.

2.2. Optical properties characterization

2.2.1. Linear absorption and fluorescence properties

Fig. 2 presents the linear absorption and fluorescence spectra of compounds **1**–**3** in THF. All these chromophores exhibit intense linear absorption in the UV–Vis region with the lowest-energy peaks located at 325 nm for **1** ($\varepsilon \sim 2.04 \times 10^5$ cm^{-1} M^{-1}), 379 nm for **2** ($\varepsilon \sim 2.38 \times 10^5$ cm^{-1} M^{-1}), and 402 nm for **3** ($\varepsilon \sim 3.01 \times 10^5$ cm^{-1} M^{-1}), respectively. It is noted that the lowest-energy absorption bands are bathochromically shifted and the molar absorption coefficients are increased monotonically when the molecular π-skeletons are expanded from **1** to **3**. Additionally, all these model compounds possess a wide window of linear transparency stretching over the visible and the near-IR spectral region, which indicates that the originally expected structural crowdedness around the central ethylene units should cause an interruption of the molecular π-conjugation to certain extent in these dye molecules, rendering larger energy gaps between corresponding electronic ground-states and excited-states. Therefore, the major absorption bands of these chromophores are all located at the high-energy end of spectra. Such feature also implies that these chromophores would manifest two-photon absorption within the visible region and could be potential candidates for broadband optical-limiting and frequency up-conversion applications particularly operated in the visible. These dye molecules also emit strong visible fluorescence in their solution phase (in THF) under the irradiation of a common UV-lamp with purple-blue color for **1** and cyan color for **2** and **3**, which is in agreement with the measured emission spectra (see the inset of Fig. 1). The combined photophysical data of the studied model chromophores in solution phase are collected in Table 1.