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Synthesis and two-photon absorption properties of truxene-cored chromophores with functionalized pyrazine units fused as the end-groups

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ABSTRACT

A new set of model chromophores derived from a truxene core fused with varied number and size of functionalized pyrazine units was designed and synthesized for the tentative exploration of possible connections between the molecular structure and their linear/nonlinear optical properties. The initial experimental results have indicated that these model compounds not only possess strong and widely dispersed two-photon absorption (2 PA) within the near-IR region but also show the ascending overall 2 PA when the molecular structure varies with increase in complexity and molecular weight, which implies that both the number of branches and the size of π-framework are important factors to the molecular 2 PA in this model chromophore system. On the other hand, the studied model chromophores also manifest very good photostability within their two-photon active spectral region even under a prolonged irradiation of IR laser pulses. In addition, a representative chromophore is selected to demonstrate optical power-limiting and power-stabilization performance against nanosecond laser pulses.

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1. Introduction

In the recent years, the development of organic structures that exhibit strong two-photon absorption (2 PA) properties has drawn much attention owing to the utility of these organic compounds in many 2 PA-based potential applications in the emerging field of photonics and biophotonics such as optical power-limiting, frequency up-converted lasing, 3D optical data storage, 3D microfabrication, nondestructive bio-imaging and two-photon photodynamic therapy [1–4]. Through rational molecular design, it is possible to construct organic chromophores that simultaneously combine intensified 2 PA and other desired molecular characteristics, which greatly compensates the relatively poor performance of commercialized dyes for the aforementioned applications. Over the past two decades, much efforts have been devoted in understanding the general guidelines to enhance the molecular 2 PA by studying various π-conjugated chromophores with different molecular geometries and it is revealed that the combination of several major structural parameters such as the efficiency of intramolecular charge-transfer, the effective size of π-conjugation domain, and the molecular dimensionality is closely related to the molecular 2 PA. Nevertheless, in order to precisely engineer the molecular 2 PA behaviors at molecular level, further investigation of detailed connections between the structural arrangements of selected building units and 2 PA properties are needed. Following this concept, we believe that the exploration of new model structures derived from the cross-combination of those ever-reported 2 PA-enhancing building units may provide one of the efficient approaches toward this goal.

Among the rigid polyarene structures, truxene is frequently employed as the central unit to construct star-shaped π-conjugated skeletons with C_3-symmetry and octupolar characters for the investigation of their optoelectronic, mesogenic and two-photon-related properties [5]. Although truxene-cored two-photon active chromophores have been revealed to possess medium to strong two-photon absorptivities it should be noted that the majority of the reported structures to date are based on the same molecular design concept by attaching different π-branches of various electronic nature and conjugation lengths at the C2, C7, and C12 positions of a truxene core to build multi-branched scaffolds. In

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contrast, examples of adopting the structural motif of "fusing" peripheral branches to the central truxene moiety are very limited [6]. Our continuous efforts on the synthesis and study of 2 PA-dyes based on pyrazine-containing ring-complex systems have helped us to recognize some beneficial and some deleterious types of structural unit arrangement related to the molecular 2 PA [7–11]. Following this line of research, we attempt to evaluate the utility of pyrazine-fused truxene in the design of highly efficient 2 PA molecules, and to discern the impact of numbers and sizes of the π-conjugated peripheries on the two-photon activities. Therefore, in this paper we present the synthesis of a new series of multipolar two-photon-active model chromophores based on a functionalized pyrazine-fused truxene skeleton and the initial studies of their nonlinear optical properties in both the femtosecond and nanosecond time domains.

2. Results and discussion

The molecular structures of the studied chromophores in this work are illustrated in Fig. 1. Among the four members in this model compound set, compound **1** represents the smallest structure, in which a truxene is introduced as the central rigid core and a set of diphenylaminofluorene-functionalized pyrazine ring-complex is fused as the outward branch. Compounds **2** and **3** possess the same generic structure as **1** but bearing two and three pyrazine-lobes, respectively. Therefore, compounds **1**–**3** can serve as a group of model structures to investigate the impact of branch numbers on the molecular 2 PA in this model system. On the other hand, compound **4** represents the largest model chromophore in which an additional layer of indenoquinoxaline is inserted between the central core and peripheral units. Such a structure can be viewed as an "expanded" version of compound **3** and consequently may serve as a comparative model compound to elucidate the π-domain size effect on the molecular 2 PA. The synthetic procedures of these truxene-cored chromophores are illustrated in Scheme 1. The 5,10,15-hexaalkylated truxene (Compound **5**) was utilized as the prime starting material to perform consecutive functional group transformations for the preparation of the diamines (**9c**, **10c**, and **11c**) toward ring-complex formation with corresponding diketones (**12** and **13** [10]), by which the final chromophores (**1**–**4**) were obtained with medium to high yields. It is worthy to note that all the functional group transformations involved in this work were

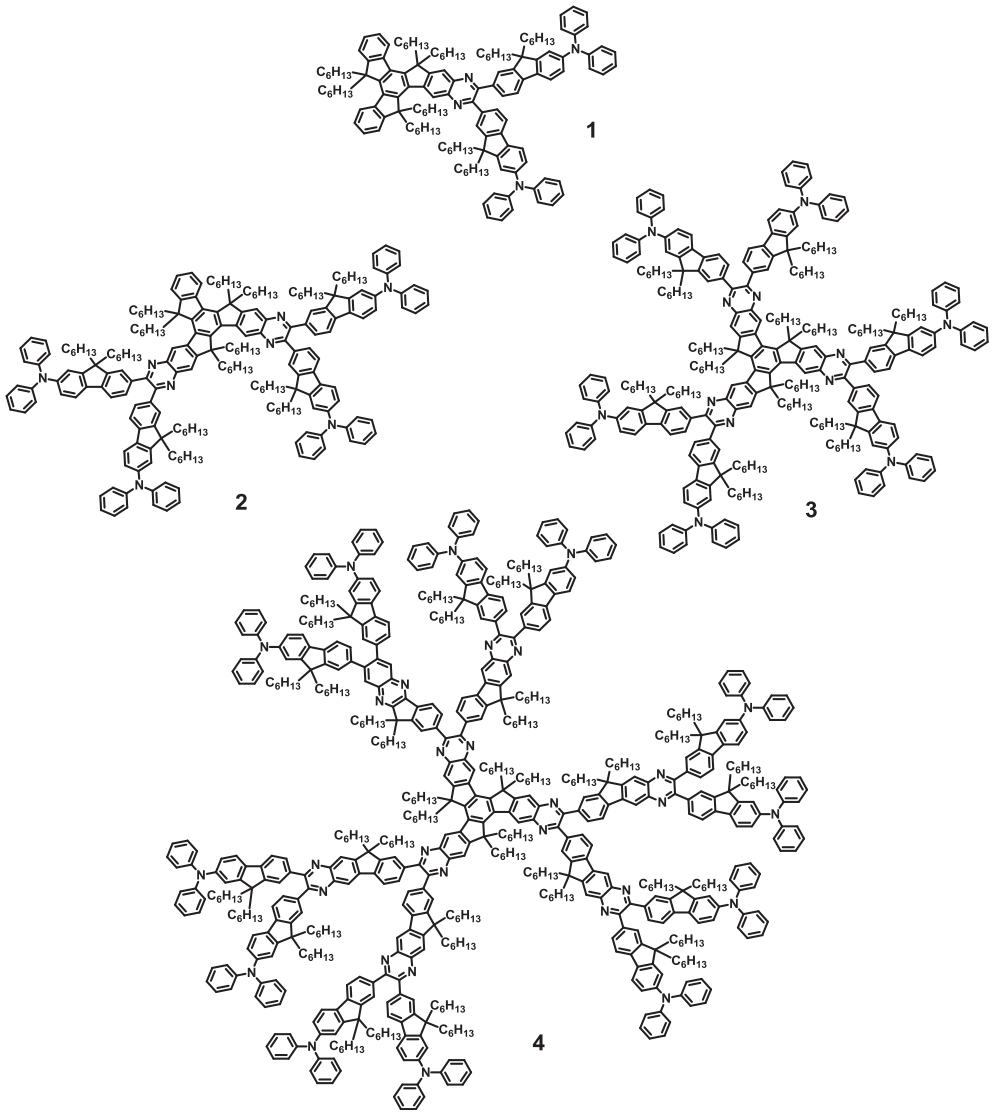

Fig. 1. Molecular structures of the studied model chromophores.

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