



Ultrafast responses of dipolar and octupolar compounds with dipicolinate as an electron acceptor

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HIGHLIGHTS

- Octupolar compound gain 12-fold enhancement of two photon absorption.
- Dynamic properties of intra-molecular charge transfer state are determined.
- Cooperative effect is responsible for great increase of two photon character.

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ABSTRACT

Two dipolar compounds with dipicolinate as electron acceptor group named *trans*-dimethyl-4-[4'-(*N,N*-dimethylamino)-styryl]-pyridin-2,6-dicarboxylate (**M-1**), *trans*-dimethyl-4-[4'-(*N,N*-diphenylamino)-styryl]-pyridin-2,6-dicarboxylate (**P-1**) as well as a **P-1** based multi-branched octupolar compound {4-[(*E*)-2-(2,6-dimethoxycarbonylpyridin-4-yl) vinyl]}-*N,N*-bis{4-[(*E*)-2-(2,6-dimethoxycarbonylpyridin-4-yl)vinylphenyl]}aniline (**P-3**) with intense two-photon fluorescence emission properties are systematically investigated by using steady-state absorption and fluorescence spectroscopy, Z-scan, and two-photon excited fluorescence (TPF) method. The two-photon absorption cross section of octupolar compound **P-3** in THF solution is determined to be 376 GM, which is approximately 12 times greater than that of dipolar counterpart **P-1** (32 GM). Transient absorption spectroscopy is employed to investigate the excited state dynamics of the dipolar and octupolar compounds. The formation and relaxation lifetimes of the intra-molecular charge transfer (ICT) state are determined to be in the ranges of several picoseconds and several-hundreds of picoseconds, respectively, for all the three compounds in THF solutions. An extended π -conjugated system and increased intra-molecular cooperative effect are responsible for the observed large two-photon absorption character.

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1. Introduction

Multi-photon absorption (MPA) materials have been extensively investigated due to their promising applications in many fields, including 3-dimensional fluorescence imaging [1,2], optical data storage and fabrication [3–5], optical limiting [6,7], multi-photon photodynamic therapy [8] and so on. These potential applications have stimulated research on the relationship between the molecular structure and the two-photon absorption (TPA) property. Prasad and co-workers showed first that the TPA cross section value

of a multi-branched molecule is nearly proportional to the square of the branch numbers, which shows there is some cooperative enhancement originating from inter-branch coupling [9,10]. Subsequently, many octupolar or multi-branched molecules with similar structural property were synthesized, among which are molecules with very large TPA cross-section values. The extensively employed cores of these multi-branched systems are either an electron rich group, such as triphenylamine [11–15], or an electron deficient group, such as 1,3,5-triazine [16], 2,4,6-tricyanobenzene [17], and the pyridine cation [18]. Among these cores, triphenylamine is an electron-rich, propeller-shaped molecule exhibiting a C_3 symmetry, thus displaying an octupolar feature. By introducing electron-withdrawing groups on the three positions para to the central nitrogen, very efficient TPA chromophores were obtained

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[19,20].

Pyridine-2,6-dicarboxylic(dipicolinic) acid and its derivatives are highly useful tridentate ligands, as they can form nine-coordinating complexes with lanthanides. To the best of our knowledge, there have been only a few reports on dipicolinate and its derivatives as an acceptor in D- π -A chromophores.

To design and synthesize new compounds with larger TPA properties, a proper understanding of the dynamics of the TPA excitation process is of great importance. In our previous work, we reported the synthesis and optical properties of a series of dipolar and octupolar TPA chromophores containing dipicolinate [21–23]. These TPA dyes possess strong chelating ability and good water solubility and these good properties are apparently due to the two methoxycarbonyl groups in pyridine ring. Among these groups, *trans*-dimethyl-4-[4'-(*N,N*-diphenylamino)-styryl]-pyridine-2,6-dicarboxylate (**PASPD/P1**, see Fig. 1) has high quantum yield and a large TPA cross-section, which is probably due to the strong triphenylamine donor. In this paper, we present the ultrafast response, fluorescence properties and TPA properties of triphenylamine-cored dipolar/octupolar dyes containing dipicolinate (**M-1**, **P-1** and **P-3**, see Fig. 1).

2. Materials and experimental section

2.1. Synthesis

The synthesis method of **M-1**, **P-1**, and **P-3** was reported in detail elsewhere [21,22]. As shown in Fig. 1, dipolar D- π -A compounds **M-1** and **P-1** employ dipicolinate as the electron acceptor group, C=C double bond as the conjugation bridge, and different electron donating groups (**M-1**: *N,N*-dimethylbenzenamine and **P-1**: triphenylamine). A **P-1** based octupolar multi-branched compound **P-3** with triphenylamine as the central core was also studied. It was found that **P-3** with octupolar tribranched structural property exhibits excellent TPA and TPF properties. In the experimental investigation, tetrahydrofuran (THF) has been used without further distillation.

2.2. Experimental

The UV-visible absorption spectra in THF solutions were recorded on a Hitachi spectrophotometer with spectral resolution of 2 nm, and the one-photon fluorescence spectra was recorded in dilute solutions (10^{-5} M) by using an Edinburgh FLS 920 spectrometer with spectral resolution of 1 nm.

The results of TPA cross section were measured by using the

open-aperture Z-scan method [24]. The two-photon fluorescence (TPF) spectra was recorded by a TRISTAN light spectrometer. The ultrafast responses of the dipicolinate derivatives were investigated via femtosecond (fs) pump-probe experiments, the setup of which has been described in Ref. [25]. The fs pulses employed in ultrafast dynamics measurements were generated by amplification stage of the used fs laser system (Spitfire, Spectra-Physics). The average output power from the Spitfire was approximately 300 mW. The pulse duration was 140 fs, the wavelength was 800 nm, and the repetition rate was 1 kHz. All the experiments were performed at room temperature.

3. Results and discussions

3.1. Linear absorption and fluorescence spectra

The normalized UV-vis absorption spectra of compounds **M-1**, **P-1**, and **P-3** in THF solutions at a concentration of 10^{-5} M are shown in Fig. 2, and the linear optical and fluorescence properties are summarized in Table 1. The maximum peaks of one-photon absorption corresponding to charge-transfer bands of the π -conjugated molecules are at 409 nm and 416 nm for compounds **M-1** and **P-1**, respectively. The result could be explained by the fact that lone pair electrons on the nitrogen of **P-1** may have delocalized onto the terminal phenyls [26]. However, the maximum peak of the octupolar derivative **P-3** is located at 427 nm, showing an 11-nm red-shift compared with linear counterpart **P-1**. The absorption band is ascribed to the charge-transfer band of the molecules [27], whereas the absorption peaks are located at a shorter wavelength (**M-1**: 287 nm, **P-1**: 295 nm, and **P-3**: 301 nm) and are assigned to the n - π^* transition [28]. The linear fluorescence spectra was measured under excitation of 365 nm. One can see that maximum peaks of one-photon fluorescence were red shifted as the number of branches increased; this behavior is a clear indication of some interactions occurring between the chromophore moieties in the molecule, resulting in charge redistribution and extended delocalization [29]. These compounds show obvious down-converting emission property. The Stokes shifts are 105 nm, 101 nm, and 101 nm, for **M-1**, **P-1**, and **P-3**, respectively.

3.2. Two-photon fluorescence and two-photon absorption

All of the three dipicolinate derivatives exhibit intense fluorescence emission under the excitation of fs pulses at the wavelength of 800 nm. The fluorescence can be observed with the naked eye even under excitation of unfocused laser pulses with a pulse energy

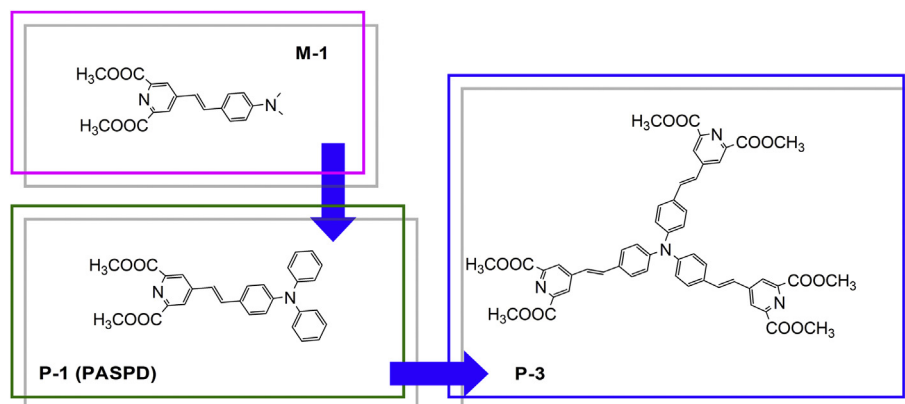


Fig. 1. Structures of **M-1**, **P-1**, and **P-3**.

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