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Synthesis and efficient three-photon excited green fluorescence of pyridine–triphenylamine conjugated dyes

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ABSTRACT

Pyridine-end-capped triphenylamine derivatives $(Py_2\text{-TPA})_n$ (n = 1,2,4) were synthesized using palladium-catalyzed Heck reaction and characterized by ^{1}H NMR, ^{13}C NMR, and HRMS-MALDI-TOF. Three-photon absorption and three-photon excited fluorescence properties of chromophores $(Py_2\text{-TPA})_n$ were studied using a femtosecond Ti:Sapphire laser system. These chromophores exhibit efficient three-photon excited green fluorescence peaking at 540–590 nm. The three-photon absorption cross-section of $\sigma_3 = 6.99 \times 10^{-79}$ cm^6 s^2 photon^{-2} in the femtosecond regime has been obtained from $(Py_2\text{-TPA})_4$. The ratio of 3PA cross-sections in CH_2Cl_2 solution σ_3 $(Py_2\text{-TPA})_4$:σ_3 $(Py_2\text{-TPA})_2$:σ_3 $(Py_2\text{-TPA})_1$ is 6.0:4.2:1. The ratio of conjugated π-electron numbers in $(Py_2\text{-TPA})_n$ is 4.4($n = 4$):2.6($n = 2$):1($n = 1$). The increasing the push–pull units of $(Py_2\text{-TPA})_n$ and π-electron conjugation length or increasing the extent of charge transfer from the ends to the middle aryl core results in an increase of the 3PA cross-section. The results indicate that large aromatic conjugated chromophores $(Py_2\text{-TPA})_n$ containing pyridine–triphenylamine D–A pairs and a conjugated aryl core provide a new opportunity for 3PA-materials and three-photon fluorophores for practical application.

1. Introduction

Three-photon absorption (3PA) is defined as the simultaneous absorption of three photons of the same or different energy in a single event through virtual states. 3PA is related to resonant fifth-order nonlinear processes induced by lasers [1,2]. The cubic dependence of 3PA process on incident light intensity provides stronger spatial confinement, so that a higher contrast in imaging can be obtained than with 2PA process. Three-photon absorption and three-photon pumped emission materials can be applied in the fields of three-photon pumped frequency-upconversion lasing, three-photon absorption based optical limiting, stabilization, and reshaping, short-pulse optical communications, and three-photon fluorescence imaging, and three-dimensional data storage [3–10].

He et al. first observed highly frequency-upconverted stimulated emission produced by direct three-photon absorption at 1300 nm in an organic chromophore [11]. Zheng et al. reported multiphoton pumped stimulated emission of a novel fluorophore IPPS with the three-photon absorption cross-section of 3.67×10^{-80} cm^6 s^2 by the femtosecond laser at 1197 nm [12]. Three-photon absorption and three-photon excited blue photoluminescence from oligophenylenes and oligofluorenes have been reported [13–15]. In recent years, donor-acceptor charge transfer molecules have been used to designed efficient 3PA materials [16–22].

In this articles, pyridine-end-capped triphenylamine derivatives $(Py_2\text{-TPA})_n$ (n = 1,2,4) were synthesized using palladium-catalyzed Heck reaction and characterized by ^{1}H NMR, ^{13}C NMR, and HRMS-MALDI-TOF. Three-photon absorption and three-photon excited fluorescence properties of chromophores $(Py_2\text{-TPA})_n$ were studied using a femtosecond Ti:Sapphire laser system. As shown in Fig. 1, large push–pull aromatic fluorophores $(Py_2\text{-TPA})_n$ (n = 1,2,4) contain pyridine–triphenylamine D–A pairs and a conjugated aryl core. The surface group of molecules is electron-withdrawing pyridine and the shell group is electron-donating triphenylamine. The triphenylamine–pyridine pairs are connected in the median core benzene or 2,5-diphenyl-1,3,4-oxadiazole with tetra- or bis-substitution.

These push–pull conjugated fluorophores $(Py_2\text{-TPA})_n$ contain one, or two, or four triphenylamine shell units and two, or four, or eight pyridine end-groups in the conjugated path. The absorption and emission wavelength/maxima of these pyridine-end-capped triphenylamine chromophores $(Py_2\text{-TPA})_n$ can be tuned by the conjugation length and the number of pyridine–triphenylamine D–A pairs. Because of the planar structure and the participation of π-electron delocalization of the building block, these compounds exhibit efficient three-photon absorption and three-photon excited

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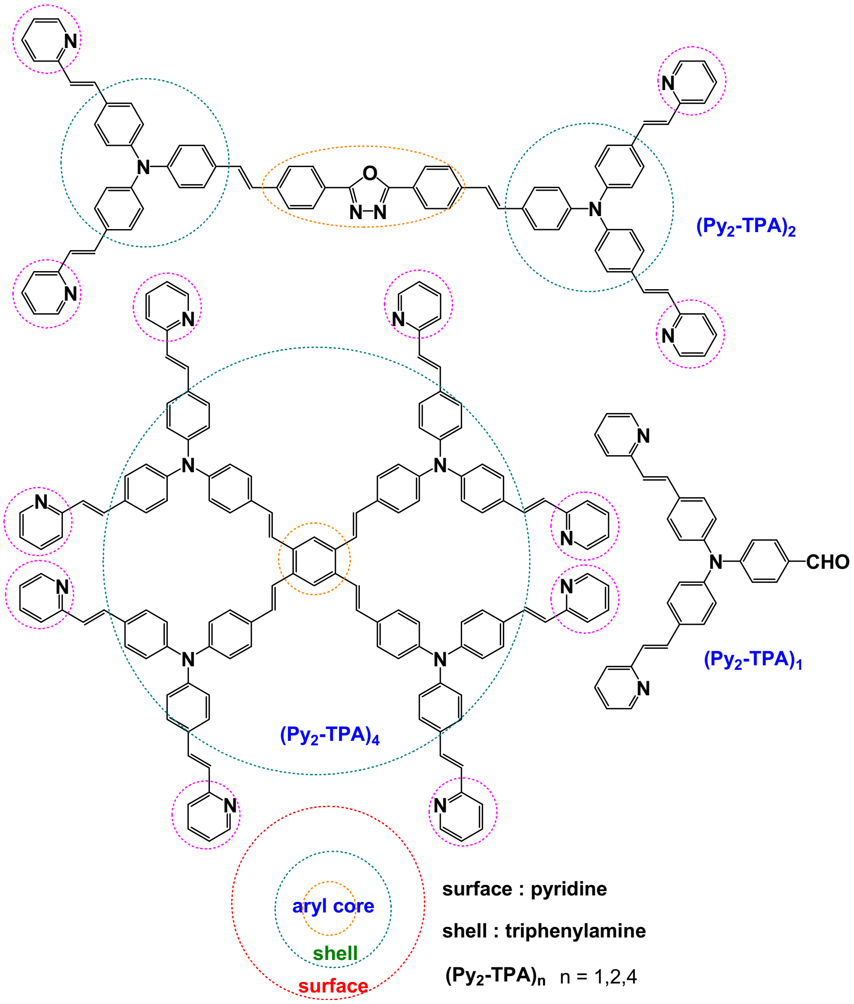

Fig. 1. Molecular structures of pyridine–triphenylamine conjugated dyes (Py$_2$-TPA)$_n$ (n = 1,2,4).

green fluorescence emission. The three-photon absorption cross-section of 6.99×10^{-79} cm^6 s^2 in the femtosecond regime has been obtained from (Py$_2$-TPA)$_4$.

The Three-photon absorption cross section is related to resonant fifth-order molecular susceptibility. Pyridine–triphenylamine conjugated chromophores (Py$_2$-TPA)$_n$ would facilitate π-electron delocalization and thus improve three-photon absorption response. This allowed us to derive structure–property relationships aiming at optimization of large push–pull aromatic chromophores for 3PA.

2. Experimental

2.1. Experimental section

2.1.1. General

Solvents were purified and dried using standard protocols. Three starting materials N,N-di(4-iodophenyl) amino benzaldehyde (M1), 2,5-bis{4-[N,N-di(4-iodophenyl)aminostyryl]phenyl}-1,3,4-oxadiazole (M2), and 1,2,4,5- tetra[4-N,N-di(4-iodophenyl) aminostyryl]benzene (M3), were prepared by our laboratory. All other chemical reagents were obtained commercially and were used as received without further purification.

Chemical structures were identified by high resolution mass spectrometry (HRMS) and nuclear magnetic resonance (NMR). HRMS were recorded on an UltraflexIIMALDI-TOF mass spectrophotometer. ^{1}H NMR measurements were determined with a Bruker 500 MHz spectrometer, with TMS (tetramethyl silane) as the internal standard. ^{13}C NMR measurements were determined with a Bruker 300 MHz spectrometer.

UV–visible absorption spectra were determined on a Shimadu UV-3600 spectrophotometer. Fluorescence spectra were measured on an HORIBA FL-4 max spectrometer.

The excitation sources used for 3PA studies were a Ti:sapphire oscillator/amplifier and an optical parameter amplifier (OPA) system (model Mira900-F from Coherent), the latter produced ~80-fs duration, 1300 nm wavelength laser output with a repetition rate of 1 kHz. The output divergence angle after collimation is around 0.6 mrad. The incident laser pulses were focused via a f = 15 cm lens onto the center of the sample cell which is a 1 cm-length quartz cuvette. The pulse duration after the OPA was measured by an autocorrelator system (model SSA from Coherent Inc.) The samples' frequency up-conversion fluorescence spectra are obtained by OMA (model: SpectraPro-300i, from Acton Research Corporation) in the sample detect condition. Three-photon absorption cross-section values of all the chromophores in solution were investigated by a direct nonlinear transmission (NLT) method [12,23–25] with femtosecond pulse.

The excitation sources used for 2PEF studies were a Ti:sapphire oscillator/amplifier and an optical parameter amplifier (OPA)