



Four asymmetric bis-branched triphenylamine derivatives with charge transfer from one branch to the other: Two-photon emissions and bio-imaging applications



Xiaoping Gan^{a, b}, Xinping Ge^a, Chengkai Zhai^a, Jun Zheng^c, Xuguang Tang^a,
Yanchao Yang^a, Yupeng Tian^a, Xuanjun Zhang^d, Hongping Zhou^{a, *}

^a College of Chemistry and Chemical Engineering, Anhui University and Key Laboratory of Functional Inorganic Materials Chemistry of Anhui Province, 230601, Hefei, PR China

^b School of Science, Anhui Agricultural University, 230036, Hefei, PR China

^c Center of Modern Experimental Technology, Anhui University, Hefei, 230601, PR China

^d Faculty of Health Science, University of Macau, Taipa, Macau, SAR, PR China

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ABSTRACT

Four asymmetric bis-branched triphenylamine-cored compounds with different electron-withdrawing groups have been synthesized and their optical properties have been systematically investigated. The two-photon absorption cross-section (σ_{2PA}) values were measured by two-photon excited fluorescence which revealed that the four compounds possessed large σ_{2PA} values from 2011 to 4173 GM in the near-infrared region. Theoretical calculations revealed that the compounds were all provided with interesting intramolecular charge transfer generated from one branch to the other which contributed to the large σ_{2PA} values. Cytotoxicity tests indicated that all these compounds had good biocompatibility for living cells, both one- and two-photon fluorescence microscopy studies showed the potential application of the four new compounds in cell imaging due to the large σ_{2PA} and appropriate biocompatibility.

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1. Introduction

Small organic molecules with strong two-photon absorption (2PA) properties have attracted growing interest due to potential applications in the biomedical domain, including optical power limiting (OPL) [1], two-photon fluorescence bio-imaging (TPFI) [2], and photodynamic therapy (PDT) [3]. Among them, two-photon fluorescence bio-imaging has attracted considerable attention as a consequence of less photo bleaching, higher spatial resolution, and deeper light penetration [4,5]. There remains a need for excellent stains and dyes for two photon fluorescence bio-imaging. While an excellent dye/stain not only require a high signal-to-noise ratio which strongly relies on the large 2PA cross-sections (σ_{2PA}) of the precisely-engineered organic molecules, but also demand for a good biological compatibility which depends on the molecule volume. So design and synthesis of 2PA molecules with large σ_{2PA}

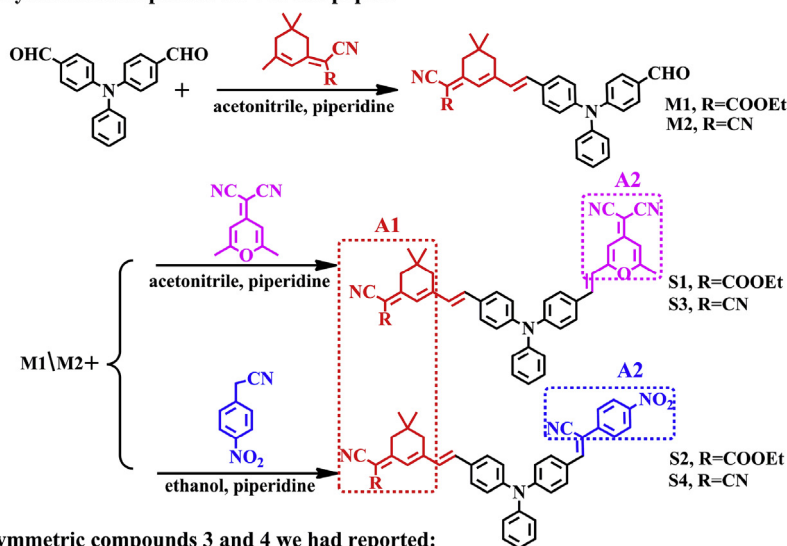
values and suitable biological compatibility are important factors in two-photon fluorescence bio-imaging.

Branched molecules possessing quadrupole or octupole electron structures usually possess large σ_{2PA} values due to the synergetic enhancement effect on 2PA cross-sections brought from different branch numbers. For example, since Prasad [6] reported a series of multi-branched 2PA compounds with triphenylamine as the central core possessed large 2PA cross-sections (587 GM) at wavelength of 796 nm, many groups [7–11] have investigated the triphenylamine-cored multi-branched two-photon materials, which showed excellent 2PA properties and can be applied in bio-imaging. In our previous work [12], we have synthesized a series of symmetric branched triphenylamine derivatives which exhibited gradually enhanced 2PA cross-section values with the branch number. While the fact is not that the larger the 2PA cross-section is, the better the two-photon fluorescence bio-imaging becomes. We found that the bis-branched molecules (Scheme 1, compounds 3 and 4) possessed the best ability of two-photon fluorescence bio-imaging because they possessed the optimum balance of 2PA performance and suitable biocompatibility. So the bis-branched

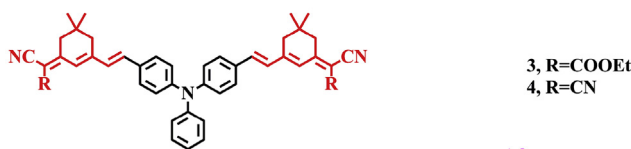
* Corresponding author.

E-mail address: zhpzhp@263.net (H. Zhou).

The asymmetric compounds S1-4 in this paper:



The symmetric compounds 3 and 4 we had reported:



Scheme 1. Preparation of S1-4.

compounds with appropriate 2PA properties will be the effective candidates in two-photon fluorescence bio-imaging domain.

However, most of the previously described bis-branched compounds are symmetric, which only possessed partial intramolecular charge transfer (ICT) [13,14] in each branch thus resulting in a modest σ_{2PA} value, hence research focused on bis-branched compounds for two photon bio-imaging is rare. It is well known that a wide range of ICT benefits the fluorescence emission, so constructing branched compounds with ICT distributed over the whole molecule is another way to enhance the two-photon fluorescence emission ability in a small organic molecule. Thus we postulated that constructing an asymmetric bis-branched molecule ($A_1 - \pi - D - \pi - A_2$, Scheme 1, S1-4) through adjusting the acceptor in one branch on the basis of the existing bis-branched molecule ($A - \pi - D - \pi - A$, Scheme 1, compounds 3 and 4) might combine the synergetic enhancement effect of the branch numbers with the ICT and could be more favorable for fluorescence emission.

Herein, we synthesized four asymmetric $A_1 - \pi - D - \pi - A_2$ model triphenylamine-cored bis-branched quadrupolar molecules (S1-4) (Scheme 1) to apply on two-photon fluorescence bio-imaging. Considering the isophorone derivatives were often used to prepare red emitting materials because they could construct a large conjugate system and be easily modified, we selected isophorone as an electron acceptor in one branch and either 2-(2,6-dimethyl-4H-pyran-4-ylidene)malononitrile [15] or 4-nitrophenylacetonitrile [16] as the other electron acceptor to construct asymmetric model quadrupolar molecules, in which we changed the terminal groups (cyano group or ester group) to fine tune the polarity of the molecules and expected them to generate more outstanding 2PA performance with the same biocompatibility. Then we systematically investigated their one- and two-photon optical properties through a series of spectroscopic methods and the results showed that they were all provided with excellent 2PA properties. The highest 2PA cross-section of S2 was 4172 GM in benzene and higher

about 2-fold than that of the previously reported compounds 3 and 4 (Scheme 1). Meanwhile, we successfully carried out the two-photon fluorescence bio-imaging applications according to their excellent 2PA properties and favorable biocompatibility.

2. Experiments

2.1. General procedures

All commercially available chemicals were of analytical grade or chromatographic grade. Every solvent was purified using conventional methods beforehand. IR spectra were recorded with a Nicolet FT-IR NEXUS 870 spectrometer (KBr Disc) in the 4000 - 400 cm^{-1} region. Melting points (uncorrected) were determined on an XT4 MP Apparatus (Taikē Corp., Beijing, China). ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 400 Ultrashield spectrometer using $\text{DMSO}-d_6$ as solvents. Chemical shifts were reported in parts per million (ppm) relative to internal TMS (0 ppm) and coupling constants in Hz. Splitting patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), or multiplet (m). The mass spectra were obtained on a LTQ-Orbitrap XL mass spectrometer.

2.2. Optical measurements

One-photon absorption (OPA) spectra were recorded on a SPECORD S600 spectrophotometer. The one-photon emission fluorescence (OPEF) spectra were performed using a Hitachi F-7000 fluorescence spectrophotometer. In the measurements of emission spectra, the slit pass width was 10 nm for all compounds. OPA and OPEF of S1-4 were measured in five different polar organic solvents with the concentration of 1×10^{-5} M. The path length of quartz cuvettes were of 1 cm.

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