



Ultrafast relaxation processes of multi-branched compounds based on 1,3,5-triazine: An investigation of the causes of a high fluorescence quantum yield after modification with perfluoroalkyl chains

Yaochuan Wang^{a,*}, Yihua Jiang^b, Dajun Liu^{a,*}, Yizhuo Wang^a, Guiqiu Wang^a, Jianli Hua^b

^a Department of Physics, Dalian Maritime University, Dalian 116026, People's Republic of China

^b Institute of Fine Chemicals, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, People's Republic of China

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ABSTRACT

The effect of modifying a 1,3,5-triazine-based multi-branched compound (T03-a) with perfluoroalkyl chains (T03-d) on the fluorescence and ultrafast dynamics was investigated by two-photon fluorescence and femtosecond transient absorption experiments. After modification, a significantly increased fluorescence quantum yield was observed. The fluorescence quantum yield of the perfluoroalkyl chain modified compound T03-d (0.86) was approximately 3.2 times greater than that of T03-a (0.27). The ultrafast dynamics experiments revealed the effect of the perfluoroalkyl chain modification on the intramolecular charge transfer (ICT) property. The ultrafast dynamics results agree with the changes in the fluorescent property. Our results indicate that the modification of compounds with perfluoroalkyl chains based on the 1,3,5-triazine tri-branched compound would be a very useful strategy for enhancement of the fluorescence, and the 1,3,5-triazine based multi-branched derivatives have the potential to be employed as molecular probes for biological fluorescence imaging.

1. Introduction

Two-photon fluorescent materials are essential for two-photon fluorescence microscopy [1]. For imaging, the materials must have both a large two-photon absorption (TPA) cross-section and a high fluorescence quantum yield [2,3]. Materials science has focused on the exploration of new TPA materials with improved properties [2–5]. Although some strategies effectively enhance the TPA cross-section, most strategies result in materials with relatively low fluorescence quantum yields, such as some dipole compounds and octupolar multi-branched molecules [6,7]. The excited state decay of a material contains many photophysical processes that can provide significant information about the excited state and the interaction between light and matter [8–10]. We have investigated the ultrafast dynamics of TPA compounds including dipolar, quadrupolar, multi-branched, and polymeric compounds [11–14]. These results have provided information that has assisted in the explanation of TPA.

In this study, the nonlinear optical (NLO) properties and ultrafast dynamics of the multi-branched compounds T03-a and T03-d were investigated by two-photon fluorescence and femtosecond (fs) pump-probe experiments to study the effects of introducing perfluoroalkyl chains to the end donor of a multi-branched compound. After modifica-

tion with perfluoroalkyl chains, the fluorescence quantum yield increased substantially. The ultrafast dynamics experiments revealed the effects of perfluoroalkyl chain modification on the fluorescent property and the intramolecular charge transfer (ICT) properties of the compounds. The fast process and subsequent long decay process were due to the formation of the ICT state and the relaxation of the ICT state, respectively. The 1,3,5-triazine based multi-branched derivatives have the potential to be molecular probes for biological fluorescence imaging in the life sciences.

2. Materials and experiments

The synthesis of the multi-branched compound T03-a and the perfluoroalkyl chain modified compound T03-d have been previously reported [15]. For this experiment, the compounds were dissolved in chloroform (CHCl₃), which was used without further distillation.

The tri-branched compounds investigated are shown in Fig. 1. In compound T03-a, the electron acceptor (A) group 1,3,5-triazine serves as the central core, and three electron donor (D) triphenylamine groups serve as the terminal ends, which forms a tri-branched structural configuration containing three D- π -A subunits. T03-d can be described with the electron-withdrawing perfluoroalkyl chains as side groups that

* Corresponding authors.

E-mail addresses: yewang@dmlu.edu.cn (Y. Wang), liudajun@dmlu.edu.cn (D. Liu).

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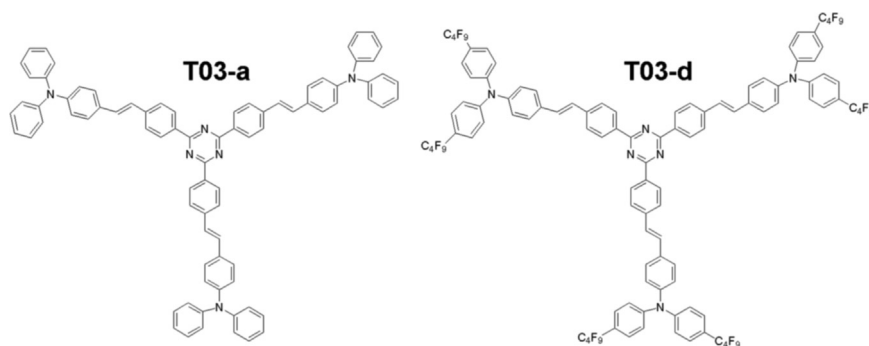


Fig. 1. The structures of the 1,3,5-triazine-based multi-branched compounds (T03-a and T03-d).

are linked to the terminal ends of the electron donor triphenylamines.

The UV–visible absorption spectra of the compounds in CHCl_3 were recorded on a Hitachi spectrophotometer with 2 nm spectral resolution, and the steady-state fluorescence spectra were recorded with dilute solutions (10^{-5} M) using an Edinburgh FLS 920 spectrometer with 1 nm spectral resolution.

The NLO fluorescence spectra were recorded on a TRISTAN light spectrometer. The fluorescence quantum yields of the compounds were measured with Rhodamine B in basic ethanol as a standard. The laser beam (370 nm, 1.4 mW) was slightly focused on the CHCl_3 solutions (10^{-5} M concentration). The spectra were measured and corrected. The detailed experimental conditions can be found in our previous publication [15]. The ultrafast responses of these compounds were investigated by femtosecond (fs) pump-probe experiments. The fs pulses for the NLO absorption and ultrafast transient absorption measurements were generated by the fs laser system (Spitfire, Spectra-Physics). The average output power of the Spitfire was approximately 300 mW. The pulse duration was 140 fs, the central wavelength was 800 nm, and the repetition rate was 1 kHz. The fs pump-probe experimental setup was described previously [16]. The fs pulses from the fs laser system (800 nm), were divided into two parts by a beam splitter. To efficiently pump the compounds into the excited state, a portion of the beam was frequency-doubled to 400 nm by a 0.5 mm thick β -barium metaborate (BBO) crystal. The other portion of the beam was focused on a 5 mm thick cell with flowing water to generate a supercontinuum in order to sample the photoinduced excited state at various wavelengths. A monochromator after the sample cell selected the probe wavelength. To detect dynamics without diffraction effects or coherent artifacts, the polarization of the pump beam was set perpendicular to that of the probe beam [11,17]. All of the measurements were performed at room temperature.

3. Results and discussion

3.1. Linear absorption and fluorescence emission of T03-a and T03-d

The absorption and normalized fluorescence spectra of the tri-branched compound T03-a and perfluoroalkyl chain modified compound T03-d dissolved in CHCl_3 in dilute concentrations (10^{-5} M) are shown in Fig. 2. The spectral results are shown in Table 1. Two major absorption bands are observed. The band located at approximately 311 nm is attributed to a localized multi-triazine aromatic π - π^* transition, and the band located at approximately 421 nm is attributed to the charge transfer state [18,19]. The charge transfer absorption maximum of T03-d is located at 395 nm, which has a 26 nm blueshift from the T03-a maximum due to the addition of the electron-withdrawing perfluoroalkyl chains as side groups to the end triphenylamine donors. These 1,3,5-triazine-based tri-branched compounds exhibit adequate fluorescence emission. The fluorescence peaks of T03-a and T03-d are located at 535 nm and 490 nm, respectively. These results indicate that modification with perfluoroalkyl chains may increase the

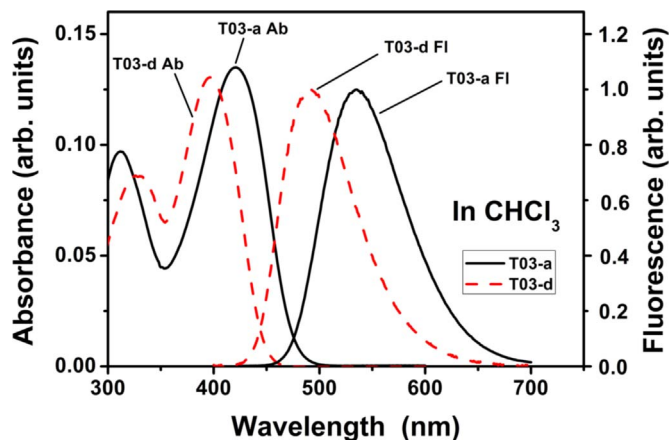


Fig. 2. The one-photon absorption spectra and normalized fluorescence spectra of T03-a and T03-d dissolved in CHCl_3 .

Table 1

A summary of the data for compounds T03-a and T03-d.

Compounds	Solvents	1PA-related optical properties			TPA-related optical properties	
		λ_{max}^a (abs)/nm	λ_{max}^b (fl)/nm	ϕ^c	λ_{max}^d (TPEF)/ nm	σ^e /GM
T03-a	CHCl_3	421	535	0.27	545	447
T03-d	CHCl_3	395	490	0.86	510	603

a λ_{max} is the wavelength for the maximum of the one-photon absorption spectra.

b λ_{max} is the wavelength for the maximum of the one-photon emission spectra.

c ϕ is the fluorescence quantum yield, which was determined by using Rhodamine B in ethanol as a standard.

d λ_{max} is the wavelength for the maximum of the two-photon fluorescence spectra.

e σ is the TPA cross-section.

band gap of the compound. Usually, in a conjugated system with delocalized π electrons, stronger ICT effects will cause a redshift in the absorption spectra. Thus, modification with perfluoroalkyl chains linked to the end of terminal triphenylamine groups may not lead to a stronger ICT effect. In the following investigations, the effect will be further discussed.

3.2. Fluorescence properties

Most two-photon imaging applications employ fs pulses at a wavelength of 800 nm. The two-photon fluorescence properties of the two compounds were investigated at this wavelength. Both T03-a and T03-d emitted intense fluorescence emission under irradiation of unfocused fs pulses with a pulse energy of several microjoules. Since no obvious linear absorption was observed at wavelengths longer than 750 nm, any absorption in this wavelength range would be attributed to

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