



## Review

## Aggregation enhanced two-photon fluorescence of organic nanoparticles



Xingrui Shi<sup>a</sup>, Zhenzhen Xu<sup>a, \*\*</sup>, Qing Liao<sup>a, \*\*</sup>, Yishi Wu<sup>b</sup>, Zhanjun Gu<sup>c</sup>, Renhui Zheng<sup>b</sup>, Hongbing Fu<sup>a, b, \*</sup>

<sup>a</sup> Beijing Key Laboratory for Optical Materials and Photonic Devices, Department of Chemistry, Capital Normal University, Beijing 100190, China

<sup>b</sup> Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

<sup>c</sup> Key Laboratory for Biomedical Effects of Nanomaterials and Nanosafety, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

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## ABSTRACT

Two-photon excited fluorescence bio-probes have obtained a great deal of interests in biological imaging and sensing applications. We synthesized a new donor– $\pi$ –acceptor molecular (BNSN) with strong intramolecular charge-transfer (ICT). Interestingly, different from conventional ICT compounds, BNSN molecules present an unusual ICT phenomenon, leading to a red-shifted emission and an increased fluorescence quantum yield ( $\Phi$ ) with increasing the polarity of solvents. Moreover, the fluorescence intensity and two-photon absorption cross-section all enhanced when the molecules aggregated. The nanoparticles of BNSN exhibit strong two-photon excited fluorescence in aqueous media, exhibiting the property of aggregation-enhanced two-photon fluorescence (AE-TPF). Our results demonstrate that the BNSN molecules with AE-TPF effect provide a new molecular type to construct efficient two-photon excited fluorescence nano-probes for bio-imaging.

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## 1. Introduction

In recent years, fluorescent nanoparticles (FNPs) have obtained a great deal of interests in biological imaging and sensing applications [1]. Besides inorganic FNPs, such as semiconductor nanocrystals and metallic nanoparticles, organic nanoparticles (ONPs) of low-molecular-weight functional compounds have inspired growing research efforts, due to their tailor-made chemical structure and their inherent bio-compatibility [2]. However, many of these ONPs are hydrophobic, and their fluorescence quantum yields ( $\Phi$ ) are greatly reduced as compared with the monomers due to aggregation caused fluorescence quenching (ACFQ) [3]. In 2001, an intriguing aggregation-induced emission (AIE) phenomenon was discovered by the Tang group, that is, chromophores in the

aggregate state exhibit a higher  $\Phi$  than that in the monomer state [4]. This opens a novel way to prepare highly emissive fluorescent ONPs (FONPs) [5,6] and a variety of AIE materials have been developed for applications, such as fluorescence sensors [7], biological probes, multistimuli-responsive nanomaterials, and active layers in the fabrication of organic light-emitting diodes. Nonetheless, these investigations have been mainly limited to single-photon AIE phenomena, while development of two-photon active AIE materials have met with limited successes [3,8].

Two-photon absorption (TPA) has attracted lots of attention since it was first proposed by M. Goppert-Mayer in her doctoral dissertation in 1931 [9]. Due to their potential applications in photonics [10,11], for example, two-photon-excited fluorescence microscopy, a lot of work are put into the manufacture of new two-photon materials in the recent years. Two-photon fluorescence (TPF) microscopy provides a great convenience for biological imaging and sensing applications, because of the use of near-IR laser light not only avoids auto-fluorescence from the biological background but also reduces undesired tissue photo-damage as a result of the near-transparency of many tissues in this spectral range [12]. For strong two-photon excited fluorescence (TPEF), a large TPF

\* Corresponding author. Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. Tel./fax: +86 10 6890 7107.

\*\* Corresponding authors.

E-mail addresses: [xuzhenzhen@cnu.edu.cn](mailto:xuzhenzhen@cnu.edu.cn) (Z. Xu), [hongbing.fu@iccas.ac.cn](mailto:hongbing.fu@iccas.ac.cn), [hbfu@cnu.edu.cn](mailto:hbfu@cnu.edu.cn) (H. Fu).

action cross-section and a high dye density ( $c$ ) are usually required. Since the TPF action cross-section can be expressed as a product of  $\delta \times \Phi$  [13], where  $\delta$  represents the TPA cross-section and  $\Phi$  is the fluorescence quantum yield. Moreover, according to the research efforts of scientists, the structure of molecules with ICT from donor groups to  $\pi$ -bridge can improve the TPA cross sections [14]. The molecular designs include symmetrical donor– $\pi$ -bridge–acceptor (D– $\pi$ -A), donor– $\pi$ -bridge–donor (D– $\pi$ -D) and donor– $\pi$ -bridge–acceptor– $\pi$ -bridge–acceptor– $\pi$ -bridge–donor (D– $\pi$ -A– $\pi$ -A– $\pi$ -D) [15]. In view of this, some TPA dyes with large  $\delta$  and AIE property were designed and synthesized by many groups using in series of fields [15–18]. For example, Tian et al., developed a new class of AIE active compounds with excellent TPA properties, which can be used as promising candidates for bio-sensing applications [8]. Liu et al. have reported the synthesis of an AIE fluorogen, 4,7-bis[4-(1,2,2-triphenylvinyl)phenyl]benzo-2,1,3-thiadiazole and the fabrication of the corresponding AIE dots for intravital TPF imaging of blood vessels [17]. However, we still urgently need to develop new approach to designing and synthesizing more TPA chromophores with the high  $\delta$  and  $\Phi$ , which show more potential applications in aqueous media, such as bio-imaging [18].

Herein, we demonstrated an AE-TPF in FONPs composed of donor– $\pi$ -acceptor (D– $\pi$ -A) type molecules of 2-bromo-6-(4-nitrostyryl) naphthalene (BNSN). Different from conventional ICT compounds, BNSN molecules presents an unusual ICT phenomenon, leading to a red-shifted emission and an increased fluorescence quantum yield ( $\Phi$ ) with increasing the polarity of solvents. Notably, we found that BNSN is AIE active because of the rotation of the bond attached to nitrobenzene. Meanwhile, their TPA cross-section is greatly enhanced when aggregated, about 18 times higher than those of monomers, probably due to exciton–vibration coupling. Moreover, the BNSN FONPs exhibit good water solubility, high photostability, and low cytotoxicity. All these features including the high TPA action cross-section, AIE properties and biocompatibility of BNSN FONPs make them attractive nano-probes for TPF imaging and sensing applications.

## 2. Experimental

### 2.1. Materials and instruments

All reagents for organic synthesis were purchased from Alfa Aesar and used as received without further purification. Other organic solvents (HPLC grade) were purchased from Beijing Chemical Agent Ltd., China. Ultrapure water with a resistivity of  $18.2 \text{ M}\Omega \text{ cm}^{-1}$ , produced using a Milli-Q apparatus (Millipore), was used in all experiments.

The steady-state absorption spectra were measured on a Shimadzu UV-3600 UV–VIS–NIR spectrophotometer. The stationary fluorescence spectra were performed on a Horiba FluoroMax-4-NIR spectrophotometer equipped with an integrating sphere. The relative fluorescence quantum yields of solutions and colloidal suspensions were measured by using 9,10-diphenylanthracene as a reference ( $\Phi = 0.95$ ), while the absolute fluorescence quantum

yield of BNSN FONPs was measured by using the integrating sphere equipped on FluoroMax-4-NIR spectrophotometer.

For measuring the temporally and spectrally resolved fluorescence spectra, the second harmonic (400 nm, 120 fs, 1 kHz) of a regenerative amplifier (Spitfire, Spectra Physics) seeded with a mode-locked Ti:sapphire laser (Tsunami, Spectra Physics) was used to excite the samples (liquid sample in a 10 mm cuvette or crystal sample mounted on a quartz plate) at the front surface with an incidence angle of  $45^\circ$ . Fluorescence collected along the sample surface normal direction was dispersed by a polychromator (250is, Chromex) and detected with a streak camera (C5680, Hamamatsu Photonics). The spectral resolution was 0.2 nm, and the temporal resolution was about 2 ps. For two-photon pumped single-crystal lasing experiment, the excitation light directly came from the fundamental (800 nm, 120 fs, 1 kHz) of the regenerative amplifier (Spitfire, Spectra Physics) seeded with a mode-locked Ti:sapphire laser (Tsunami, Spectra Physics) with the excitation fluence adjusted by using a set of neutral density filters.

### 2.2. Synthesis and characterization

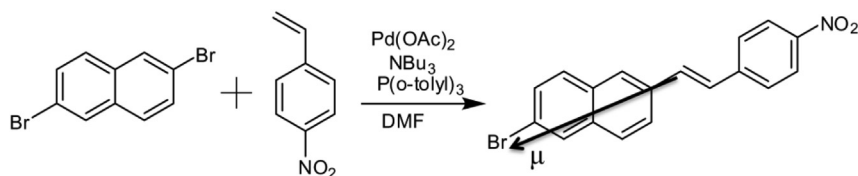
The synthetic routes of the compound of BNSN are shown in Scheme 1. The molecular were prepared by the Heck reaction and the molecular was characterized by MS (mass spectrometry),  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy. A mixture of 2,6-dibromonaphthalene (0.284 g, 1 mmol), 4-nitrostyrene (0.090 g, 0.6 mmol),  $\text{Pd}(\text{OAc})_2$  (15 mg, 0.07 mmol), triphenyl phosphate (200 mg, 0.64 mmol), tri-*n*-butylamine (1.7 g, 9 mmol), Dimethylformamide (20 mL) was introduced into a pressure tube, under argon atmosphere. The reaction mixture was heated for two days at  $130^\circ\text{C}$  and then poured into water. The phase was extracted with  $\text{CH}_2\text{Cl}_2$ . The pooled organic phases were washed with water, dried over anhydrous  $\text{MgSO}_4$ , filtered, and evaporated. The product was separated by flash chromatography on silica gel by means of  $\text{CH}_2\text{Cl}_2$ /petroleum ether (1:1). Finally a yellow powder (56 mg, 0.158 mmol) was obtained in 25% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (d, 1H), 8.24 (d, 1H), 8.00 (s, 1H), 7.88 (s, 1H); 7.77 (d, 2H), 7.74 (d, 1H), 7.72 (d, 1H), 7.70 (d, 1H), 7.67 (d, 1H), 7.39 (d, 1H), 7.299 (d, 1H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 115.4, 120.8, 124.5, 124.6, 127.2, 127.3, 127.9, 130.0, 130.1, 130.2, 132.2, 133.1, 134.0, 134.4, 134.7, 143.9, 147.1. MS (EI): 354.

## 3. Results and discussion

### 3.1. Solvent effects

Fig. 1a shows the absorption spectra of BNSN molecules in different solvents. It can be seen that the lowest  $S_0 \rightarrow S_1$  absorption of BNSN monomers in polar solvents, such as DCM, is a broad and structureless band (blue line (in the web version)), and become structured in nonpolar solvents, such as hexane (black line). Moreover, a slight red-shift of the absorption maximum of BNSN occurs when the polarity of solvents increase, which is the characteristic feature of ICT compounds [19]. Notably, we found that the emission color of BNSN can be tuned from blue to yellow with



Scheme 1. Synthetic routes to BNSN.

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