



## Synthesis and two-photon up-conversion sensing property of pyridinylbenzothiadiazole-based chromophores



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### ABSTRACT

New two-photon up-conversion fluorescence (TPF) sensors, containing triphenylamine or carbazole as donor (D) and flanked pyridinylbenzothiadiazole as acceptor (A) to form D- $\pi$ -A<sub>n</sub> (n=1, 2 or 3) architecture, were synthesized and characterized. The investigation correlated molecular structure (acceptor number) with linear absorption, one-photon fluorescence (OPF) and two-photon fluorescence (TPF) detecting Cu<sup>2+</sup>, Ni<sup>2+</sup>, Hg<sup>2+</sup> and Ag<sup>+</sup> was carried out. Sensors containing more acceptor groups were found to exhibit greater sensitivity to both absorption and fluorescence detection. A comparison between OPF and TPF responses to the given metal ion (Cu<sup>2+</sup>) showed that the sensitivity of TPF quenching is larger than that of OPF quenching. This strongly supports the idea that pyridinylbenzothiadiazole-based chromophores with more acceptor groups possess potential application as two-photon up-conversion sensors.

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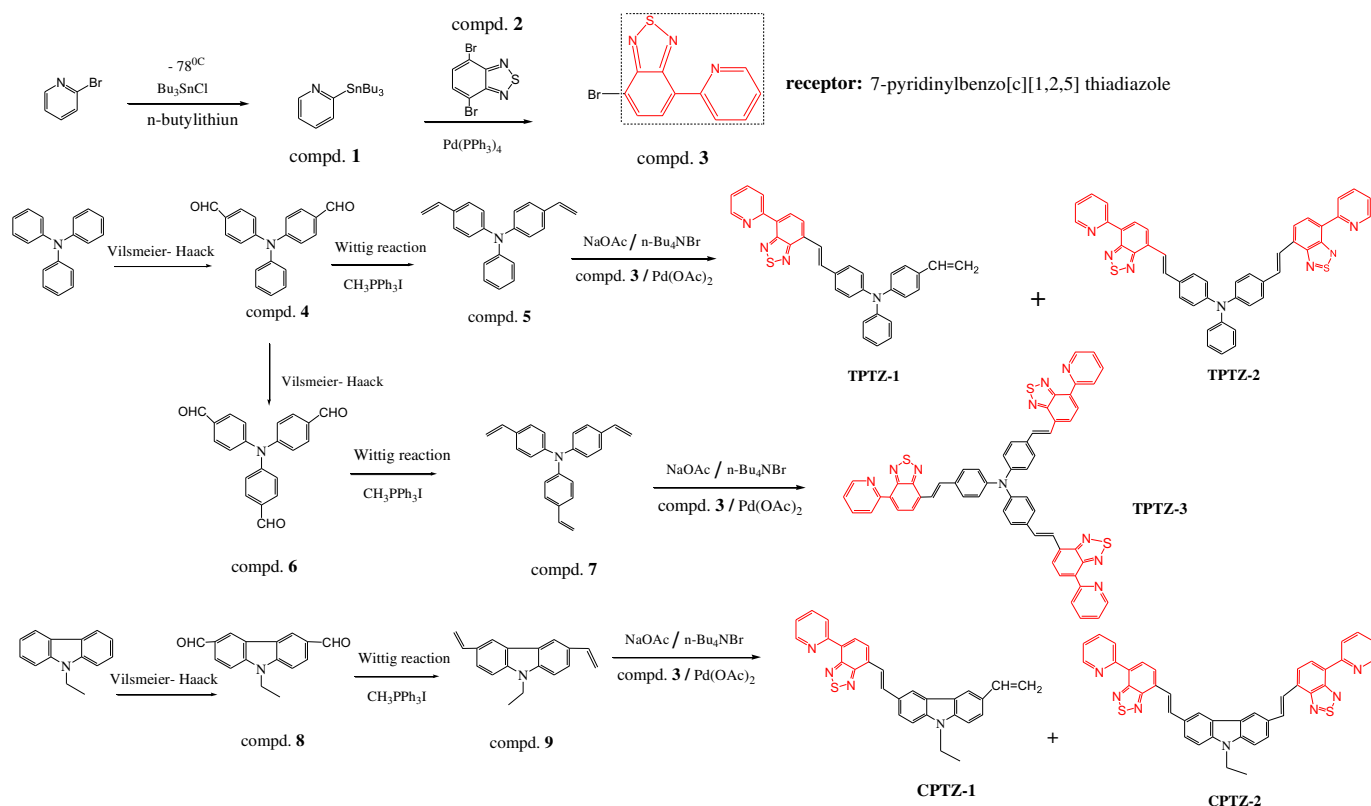
## 1. Introduction

Two-photon up-conversion fluorescence (TPF) on the excitation of the squared intense laser with low energy photons can be confined in an extremely small volume around the focal point [1,2], which brings about the desirable characteristics of deep penetration and high resolution [3]. TPF has attracted much attention due to its potential application in areas such as cell membrane microscopy [4,5], photodynamic therapy [6] and as chemo-sensors in biological systems [7–10]. Since conventional fluorescence (one-photon fluorescence, OPF) with blue emission can be disturbed by auto-fluorescence within the human body under excitation wavelengths in the 300–400 nm range which may cause substrate damage, two-photon up-conversion fluorescence (TPF) sensors with red emission using NIR photons as the excitation source offer a solution. Several papers have been published concerning TPF

sensors with benzoxazole [11], azacrown [12,13] and tris(picoly) amine [14] acceptors to detect cations, including calcium ion [15], zinc ion [16] and proton [17], but few reports have systematically studied the relationships between molecular structure (acceptor number) and detection sensitivity. It is known that large two-photon absorption cross-section can result in high TPF efficiency that provides sensors with high resolution character. However, there has been no report of the relationship of TPF response sensitivity and molecular structure (acceptor number). In addition, the sensitivity between TPF and OPF response to the given metal ion has not been reported yet. In this paper, we report the synthesis of a series of red emitting chromophores with a new acceptor (pyridinylbenzothiadiazole), and the investigation of their absorption/fluorescence response to metal ions such as Ni<sup>2+</sup>, Ag<sup>+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup>. These sensors contain triphenylamine or carbazole as the donor linking as the acceptor with an increasing number from 1 to 2 or 3, as shown in Scheme 1. Under the excitation of 470 nm and femto-second laser pulse at 800 nm, these chromophores presented an increasing two-photon absorption (TPA) cross-section from 121 to 254 GM with the acceptor number from 1, 2 to 3 for triphenylamine derivatives. The sensitivity to several metal ions

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**Scheme 1.** Synthetic routes of triphenylamine derivatives (TPTZ-1, TPTZ-2, TPTZ-3) and carbazole derivatives (CPTZ-1, CPTZ-2).

( $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Ag}^+$ ) on the linear absorption, one-photon fluorescence (OPF) and two-photon fluorescence (TPF) have been comparatively investigated.

## 2. Experimental section

### 2.1. Measurements

All chemicals used in the synthesis, with the exception of common solvents and reagents, were purchased from Acros Co. and used without further purification. IR spectra were measured by the Nicolet FT-IR 5DX instrument. Electron impact (Mode laser) mass spectra and EI mass spectra were obtained on a 4700 Proteome Analyzer (MALDI-TOF-TOF) produced by ABI Company and on an HP 5989 mass spectrometer, respectively.  $^1\text{H}$  NMR was performed on an INOVA-400 spectrometer.

Linear absorption measurements were made on a Hitachi U-3500 spectrophotometer. Interference from the quartz liquid cell and the solvent were subtracted. One-photon fluorescence (OPF) spectra were measured by an Edinburgh FLS 920 fluorimeter using a 1 cm path length cell. Two-photon fluorescence (TPF) spectra, obtained by Ti: sapphire femto-second laser tuned in the range of 700–850 nm, were recorded on a CD spectrograph. Two-photon absorption cross-section ( $\delta_{\text{TPA}}$ ) was calculated by the two-photon fluorescence method [18].

Titration procedures were as follows: to 2.0 mL of  $1 \times 10^{-4}$  M solution of sensors in THF was added 2  $\mu\text{L}$  aqueous metal salts ( $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ ) stock solutions of different concentrations. Upon each addition, the linear absorption and one-photon fluorescence (OPF) as well as two-photon fluorescence (TPF) spectra were monitored in real-time. A blank experiment (without metal

ions) was carried out via the same procedure to check the effects of adding water on the photophysical properties.

### 2.2. Synthesis

#### 2.2.1. Synthesis of components

**2.2.1.1. 2-Tributylstannylpyridine (comp. 1).** A solution of *n*-butyllithium (1.6 M) in hexane (39.2 mL, 0.062 mol) was slowly added to a solution of 2-bromopyridine (6 mL, 0.062 mol) in THF (120 mL) and cooled to  $-78^{\circ}\text{C}$  under argon. After 30 min, *n*- $\text{Bu}_3\text{SnCl}$  (16.8 mL, 0.062 mol) was added to give a dark solution which was stirred at  $-78^{\circ}\text{C}$  for one more hour. The solution was raised to room temperature and a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (60 mL) was added. The aqueous phase was extracted three times with ether (300 mL) and the combined organic layers were washed with brine (100 mL) and dried ( $\text{Na}_2\text{SO}_4$ ). The solvent was removed under reduced pressure to give yellow oil. The crude product was purified by chromatography on alumina (EtOAc/hexane 1:20) to give a pale yellow oil (22.1 g, 96%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  8.73–8.74 (d, 1H),  $\delta$  7.47–7.49 (t, 1H),  $\delta$  7.39–7.41 (d, 1H),  $\delta$  7.11–7.13 (t, 1H), 1.54–1.60 (m, 6H,  $\text{CH}_2$ ), 1.30–1.37 (m, 6H,  $\text{CH}_2$ ), 1.12–1.15 (m, 6H,  $\text{CH}_2$ ), 0.85–0.94 (t, 9H,  $\text{CH}_3$ ).

**2.2.1.2. 4,7-Dibromobenzo-*c*-1,2,5-thiadiazole (comp. 2).** To a stirred solution of benzo[*c*]-1,2,5-thiadiazole (12.17 g, 89 mmol) and 40% HBr (131 mL, 0.9 mol), a solution of 30%  $\text{H}_2\text{O}_2$  (66.7 mL, 0.65 mol) was added and then refluxed overnight until the solution color became dark red. Cooling the reaction solution, a brown solid was precipitated. After washing with  $\text{NaHSO}_3$  saturated solution, **comp. 3** was filtered and dried. It was used directly in the next step without further purification.

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