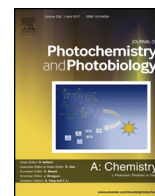




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Invited paper

## A theoretical investigation of a series of novel two-photon zinc ion fluorescent probes based on bipyridine

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## ABSTRACT

In this work, a series of bipyridine core D(A')-π-A-π-D(A') type two-photon absorption (TPA) fluorescence probe molecules for recognition of Zn<sup>2+</sup> have been studied by the density functional theory (DFT) and time dependent-DFT (TD-DFT). Furthermore, the TPA properties of these novel chromophores are explored by using DALTON program. The results of our study show that these probe molecules have the obvious TPA in the range of 600–672 nm. After combining with Zn<sup>2+</sup>, the fluorescence spectra red-shift and the TPA cross-section ( $\delta$ ) increase for most probes. These studied molecule probes, except for molecule T-8 and T-9, possess the potential to become excellent TP fluorescence imaging agents for rapid detection of Zn<sup>2+</sup>. More importantly, this work presents structure modification strategies for increasing two-photon response. The analysis of the relationship between structure and properties indicates that, the substitutions on the 5,5' site are more favorable to obtain larger  $\delta$  and longer emission wavelength than the modification on 4,4' site and 6,6' site, and the increase of electron-donating ability of end group is benefit to the red-shift of spectra and the increase of  $\delta$  value. These substitutions and modifications do not affect the ability of probes to bind Zn<sup>2+</sup>. We hope this detailed study can provide help for the design and synthesis of new Zn<sup>2+</sup> fluorescent probes.

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### 1. Introduction

Zinc is the second most abundant transition-metal; it plays an important role in biological systems, such as apoptosis, gene expression, neurotransmission, and enzyme regulation [1–3]. Most biological zinc ions are tightly bound to proteins, functioning as catalytic or structural cofactors. In contrast, a small percentage of zinc is weakly bound to endogenous ligands and considered chelatable or mobile [4–6]. Mobile forms of zinc occur throughout the body and are capable of producing unique “zinc signals” critical to the physiological functions of the endocrine/exocrine, immune, nervous, and reproductive systems [7,8]. In the reproductive system, zinc is linked to male fertility, oocyte maturation, and cancer [7,9–11]. The healthy prostate contains large stores of Zn<sup>2+</sup> within the epithelium of the peripheral zone. In cancerous prostate tissue and near sites of inflammation, Zn<sup>2+</sup> levels are significantly

reduced [7,8,12]. These observations suggest that zinc is intimately involved with oncogenesis, and if inflammation may be ruled out or treated, zinc could be used as a cancer-specific biomarker [12]. Understanding the physiology of prostatic zinc requires tools that can rapidly detect and quantify mobile zinc in complex environments such as cell lysate and biological fluids. So, there is great demand for the real-time detection and imaging of zinc ion concentrations with sensitive and non-invasive techniques. However, due to the colorlessness and magnetic silence of Zn<sup>2+</sup>, it is difficult to accurately understand the biological roles of Zn<sup>2+</sup> [13,14]. Fluorescent probe can meet these requirements. Therefore, it is the top priority of chemists to design the efficient and selective Zn<sup>2+</sup> target imaging fluorescent probes.

Two-photon (TP) active Zn<sup>2+</sup> responsive fluorophores have been focused greatly due to its own advantages. Two-photon absorption (TPA), simultaneous absorption of two lower-energy photons, results in initiation of the same photophysical processes as one high-energy photon absorbed. Taking advantage of TPA molecules can avoid from tissue auto-fluorescence, self-absorption, and photo-damage/photo-bleaching effects. Second, the quadratic

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dependence of TPA on intensity causes photochemistry reaction to take place in a small focal region, allowing for more control in microfabrication and imaging applications [15]. It has been found that molecules possessing good two-photon properties have either an asymmetrical D- $\pi$ -A (donor- $\pi$ -conjugated group-acceptor) or a symmetrical D- $\pi$ -A- $\pi$ -D or A- $\pi$ -D- $\pi$ -A structural motif [16–19]. A generally accepted TPA material design strategy is to develop chromophores with large changes in polarization upon excitation [16], including increasing conjugation length and attaching strong electron donor-acceptor group to the chromophore backbone. This strategy is beneficial to design and synthesis a ratiometric Zn<sup>2+</sup>-selective TP active probe that exhibits high absorption cross section, enhanced fluorescence intensity upon complexation with the metal ion, good pH- and photo-stability and a better tissue penetration depth.

There are several reports on TP active fluorophores for the sensing and imaging of Zn<sup>2+</sup> [20–25]. However, most of them show a nonratiometric fluorescence response and their TPA cross section ( $\delta$ ) and TP action cross section ( $\delta\Phi$ ) values are relatively low. Ajayaghosh' group reported a D- $\pi$ -A- $\pi$ -D type Zn<sup>2+</sup>-selective fluorescent probe (named GBC) by employing a D-A-D quadrupole possessing a bipyridine core as the Zn<sup>2+</sup> binding site, two carbazole moieties as electron donors. In a 1:1 MeCN/H<sub>2</sub>O solution, GBC showed red-shifted emission spectra (from 530 to 610 nm) upon binding to Zn<sup>2+</sup> along with a 9-fold increase in the TP brightness [26]. However, the intrinsic reason of that zinc ion can enhance spectral shift and TP brightness has been unclear. At the same time, the relationship between the GBC molecular structure and fluorescence properties, TPA properties and the influence factors of fluorescence and TPA properties also have not been revealed. Based on these questions, a series of GBC derivatives have been designed and studied, aim to expound recognition zinc ions mechanism of the GBC, find out the structure-property relationship, and further optimize the fluorescence and TPA properties, provide some useful information for synthesis and design novel ratiometric TP fluorescence probe of zinc ions.

## 2. Computational method

In this study, the ground-state geometries of the all studied molecules were fully optimized by the density functional theory (DFT) applying the M06-2X functional and the 6-31G(d, p) basis set on all atoms [27]. At the same level, the natural bond orbital (NBO)

analyses have been calculated. On the basis of the optimized structures, the electronic structure and UV-visible absorption spectra are systematically investigated by the time dependent-DFT (TD-DFT) method combine with CAM-B3LYP hybrid functional and 6-31G(d, p) basis set [28]. The emission spectra and the first excited geometries of all molecules were obtained by TDDFT/mPWb1k/6-31G (d, p) in acetonitrile solvent, which is better at dealing with weak interactions and charge transfer interactions [29]. To evaluate the solvent effects, acetonitrile solvent was simulated using the polarizable continuum model (PCM) including in the program of Gaussian 09 program package [30]. All these calculations were performed using the Gaussian 09 program package [31].

The TPA characteristics, especially the TPA cross sections ( $\delta_{TPA}$ ), are evaluated by utilizing the quadratic response theory combined with CAM-B3LYP exchange–correlation functional and 6-31G (d, p) basis set as implemented in the DALTON program [32]. The acetonitrile solvent was considered by the PCM in the DALTON program.

From the sum-over-state formulas, the two-photon matrix elements for the resonant absorption of two photons with identical energy are expressed as [33]

$$S_{\alpha\beta} = \sum_i \left( \frac{\langle 0|\mu_\alpha|i\rangle\langle i|\mu_\beta|j\rangle}{\omega_i - \omega_j/2} + \frac{\langle 0|\mu_\beta|i\rangle\langle i|\mu_\alpha|j\rangle}{\omega_i - \omega_j/2} \right) + \left( \frac{\Delta\mu_\alpha^{0j}\langle 0|\mu_\beta|j\rangle}{\omega_j/2} + \frac{\Delta\mu_\beta^{0j}\langle 0|\mu_\alpha|j\rangle}{\omega_j/2} \right) \quad (1)$$

Here,  $\omega_i$  is the excitation energy from the ground state  $|0\rangle$  to the excited state  $|i\rangle$ ,  $\omega_j$  stands for the excitation energy associated with the transition from the ground to the final excited state  $|j\rangle$ ,  $\mu_\alpha$  and  $\mu_\beta$  denote to the Cartesian components of the electric transition dipole moment operator along the molecular x, y, and z axes ( $\alpha, \beta = \{x, y, z\}$ ),  $\Delta\mu$  corresponds to each component of the difference between the dipole moments of the excited and ground states.

For molecules in gas phase and solution, the TPA cross section is given by orientational averaging over the two-photon absorption probability: [34]

$$\delta_{tp} = \sum_{\alpha\beta} \left[ F \times S_{\alpha\alpha}S_{\beta\beta}^* + G \times S_{\alpha\beta}S_{\alpha\beta}^* + H \times S_{\alpha\beta}S_{\beta\alpha}^* \right] \quad (2)$$

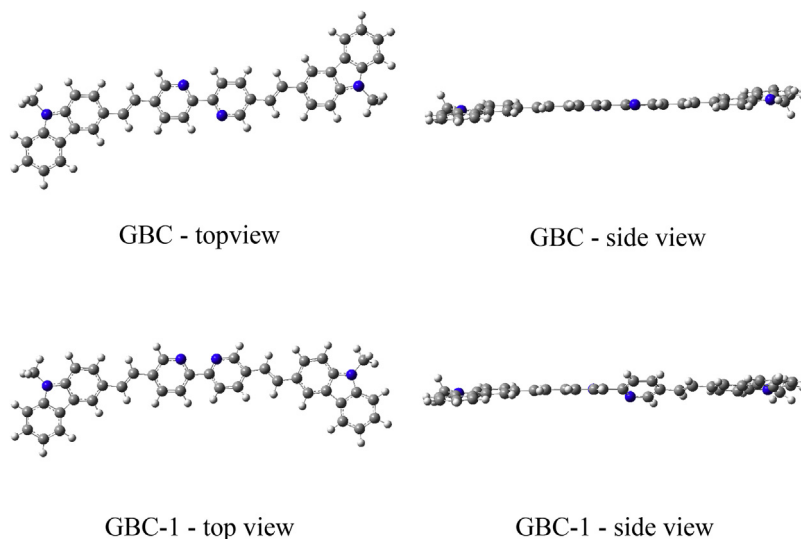


Fig. 1. Optimization geometry of GBC and GBC-1.

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