



A highly selective and sensitive fluorescence probe with A- π -D- π -A structure for detection of Ag⁺

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ABSTRACT

A novel triphenylamine derivative, 4,4'-bis-([1,10]phenanthroline-2-yl)imidazo-triphenylamine (IPTPA) with an A- π -D- π -A structure, has been synthesized and characterized. The UV absorption, single and two-photon fluorescence spectra showed that IPTPA was highly sensitive to Ag⁺ with a lower detection limit of 3.97 nmol/L and a moderate binding constant of 2.16×10^5 /M at room temperature. The two-photon active cross-section of IPTPA was calculated with a value of 94.68 GM at 800 nm in the tris-HCl buffer solution. The binding mechanism between IPTPA and Ag⁺ were explored by the Job plot, ESI-MS and ¹H NMR. The A- π -D- π -A structure of IPTPA was substituted by the A- π -D- π -D structure of IPTPA-Ag to improve the fluorescence. Furthermore, the fluorescence microscopy images indicated that IPTPA could detect Ag⁺ in living cells.

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1. Introduction

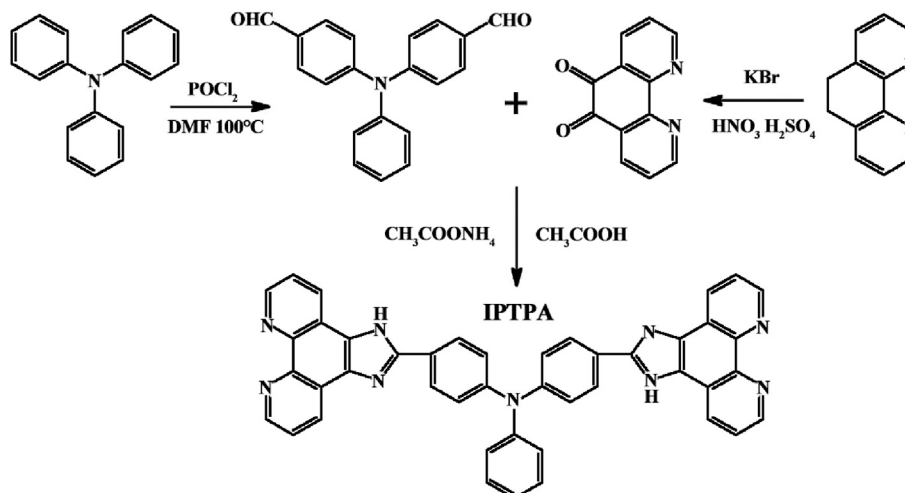
The contamination of heavy metal ions is harmful to human health and environment. In recent years, people pay more attention to heavy metal ions, such as Pb²⁺, Hg²⁺ and Cr³⁺. And now, due to the increasing demands of silver application in industry, severe silver (I) ion (Ag⁺) pollution has attracted much concern. Additionally, some of medication containing silver salt has been over-used, which will accumulate in liver tissues and originated liver cancer in the patient body [1,2]. Ag⁺ can also lead to organ failure and reduce the mitochondrial function by the elevated oxidative stress [3]. And it can cause the inactivation of enzymes and consequent health problems because of binding with sulfhydryl enzymes and various metabolites [4,5]. Hence, it is very important to find a simple and quick method to detect and analyze Ag⁺.

The fluorescence sensing method was widely applied in the detection of cations, anions and other chemical species because it is simple, cheap, rapid, highly selective and sensitive [6–13]. In recent years, many fluorescence probes of heavy metal ions like Zn²⁺, Pb²⁺

and Hg²⁺ have been reported [14–17], and the fluorescence probes of Ag⁺, such as rhodamine, quinolone and BODIPY derivatives have been developed [18–21]. But the probes of Ag⁺ detection with highlighted properties are still lack [22–25]. In view of the above, it is urgent to design and find some efficient fluorescence probes for Ag⁺ detecting, which are highly sensitive and selective, and larger two-photon active cross-sections (TPACS) [26,27]. For all we know, triphenylamine derivatives for Ag⁺ detection have not been reported. In triphenylamine structure, the three benzene rings linked with the nitrogen atom with obvious activity, good fluorescence and easily modified property, can be connected with external recognition groups at appropriate positions, and a series of fluorescence probes with certain functions can be produced. In this paper, a new fluorescence probe, 4, 4'-bis- ([1,10] phenanthroline-2-yl)imidazo-triphenylamine (IPTPA), was synthesized and used to detect Ag⁺ with A- π -D- π -A structure. Due to the good complexing ability of 1,10-phenanthroline to metal ions [28], IPTPA is capable of chelating silver ion by the two N in phenanthroline, which can effectively enhance fluorescence. So, IPTPA exhibited a pronounced fluorescence toward Ag⁺ versus other interfering metal ions. This probe possessed higher selectivity and sensitivity to Ag⁺ with better photon properties. Based on the above reasons, IPTPA may be applied as fluorescence probes of Ag⁺ detection by the single- and

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Scheme 1. The synthetic route of IPTPA.

two-photon excitation. Lastly, the fluorescence microscopy images of IPTPA in the presence and absence of Ag^+ were investigated by Olympus Fv300 confocal laser-scanning microscope exciting at the wavelength of 488 nm.

2. Experimental

2.1. Chemicals

1,10-phenanthroline was obtained from Aladdin. Triphenylamine, triphenylphosphine and other reagents were got from commercial sources. Other chemicals were AR grade. Organic solvents were further purified to anhydrous grade. The stock solutions (1×10^{-3} mol/L) of silver nitrate in tris-HCl buffer solution were prepared. IPTPA was dissolved in ethanol to form the stock solution (1×10^{-3} mol/L), which will be diluted the concentrations of 1×10^{-5} mol/L for single-photon measure and 1×10^{-4} mol/L for two-photon measure.

2.2. Instruments

Nuclear magnetic resonance spectra were recorded on a Bruker Avance 400 spectrometer operating at 400 MHz. A Thermo Fisher IS10 spectrometer was used to get Infrared spectra. The samples

were grinded with KBr to form a wafer. Elemental analyses were recorded on a Perkin 2400 (II) autoanalyser. Electrospray ionization mass spectrometry (ESI-MS) was obtained on LCQ Fleet. The UV–visible–near IR absorption spectra were obtained on a SHIMADZU UV-2550 spectrophotometer. Single and two-photon fluorescence spectra were noted on a HITRCHIF-4500 fluorescence spectrometer and on an OOIBASE32 spectrophotometer, respectively. The pump laser beam was from a mode-locked Ti: sapphire laser system (Coherent Mira900-D) with a wavelength range of 700–1000 nm. The pulse duration and the repetition rate were 200 fs and 76 MHz, respectively. A confocal laser-scanning microscope (Olympus Fv300) was used to get the fluorescence images in living cells with an objective lens ($\times 40$).

2.3. Synthesis

The expected compound (IPTPA), whose synthetic route is depicted in [Scheme 1](#).

The preparation process of 1,10-phenanthroline-5,6-dione and 4, 4'-diformyltriphenylamine can refer the relative literature [[29,30](#)].

The synthetic procedure of 4, 4'-bis- ([1,10] phenanthrolin-2-yl) imidazo -triphenylamine (IPTPA).

A mixture of 1,10-phenanthroline-5,6-dione (0.314 g, 1 mmol),

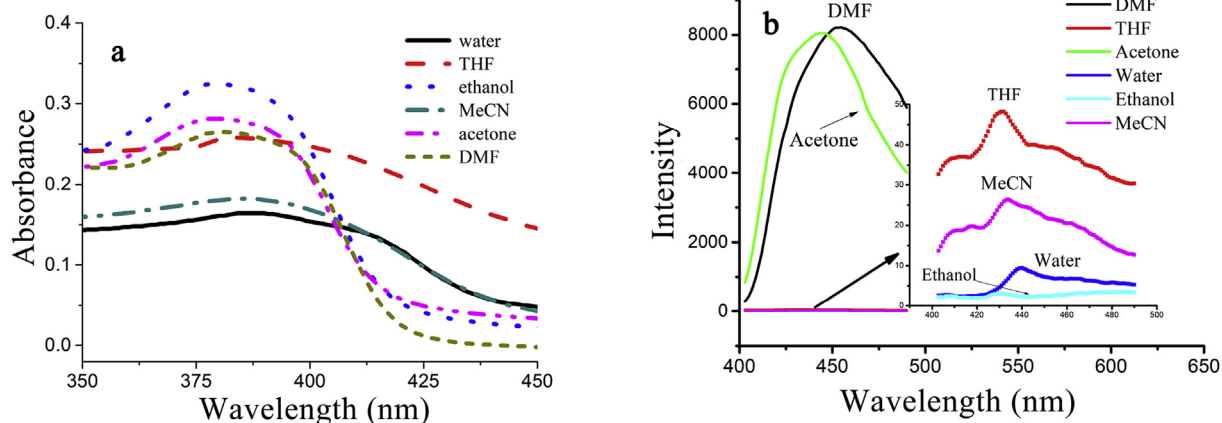


Fig. 1. The UV–vis absorption spectra (a) and single-photon fluorescence spectra (b) of IPTPA in various solvents with a concentration of 1×10^{-5} mol/L⁻¹.

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