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Two Dicyanostilbene-Derived Two-Photon Fluorescence Sensors for Ag^{+} and Zn^{2+}

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Two-photon excitation fluorescence microscopy (TPM), which uses two photons of lower energy as the excitation source, has rapidly evolved into a widely used tool in biological and biomedical research and is popular. Compared to traditional fluorescence microscopy, TPM offers intrinsic three-dimensional (3D) resolution combined with reduced phototoxicity and photo bleaching, increased specimen penetration, and negligible background fluorescence [1]. However, most fluorophores presently used as labels or sensor platforms in TPM belong to one-photon ones which have small two-photon absorption cross sections (δ) that limit their usage [2]. Therefore, to make TPM a more versatile tool in biology, researchers need a wider variety of two-photon probes with large δ for specific applications.

A stilbene-derived two-photon fluorescence sensor for Ag^{+} was synthesized and characterized. The UV-Vis, one-photon fluorescence and two-photon-induced fluorescence spectra of DAg were systematically researched. The values of its two-photon absorption cross sections are δ=950 GM in MeCN and δ=2410 GM in toluene. The fluorescence quantum yield (η) and two-photon excitation maximum wavelength (λ_{ex2}) of DAg are η=0.53 in MeCN and λ_{ex2}=790 nm, respectively. The binding constants of DAg for Ag^{+}, expressed as logK, are determined from the absorption, one- and two-photon emission titration curves to be 5.65 ± 0.03, 5.72 ± 0.07 and 5.76 ± 0.05 at 20°C in MeCN. The sensor has good two-photon absorption properties and can be used to detect trace Ag^{+} and Ag^{+}-imaging.

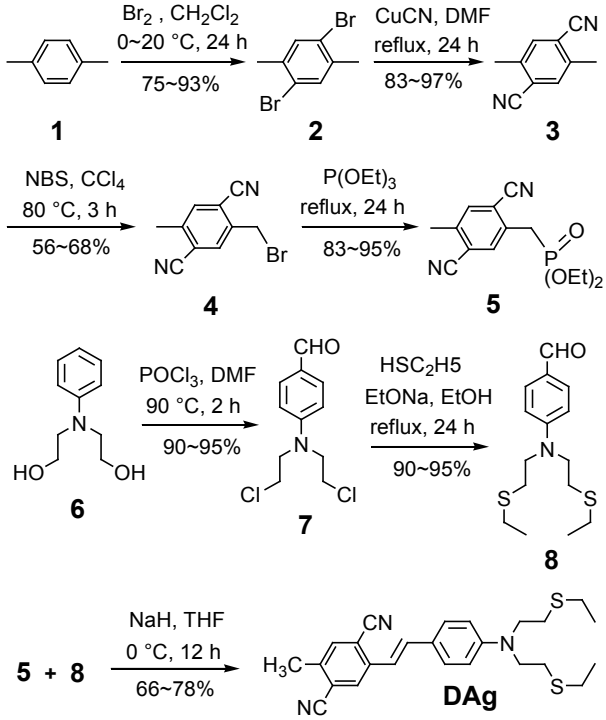

Figure 1: Synthetic procedures of Ag^{+} sensor.

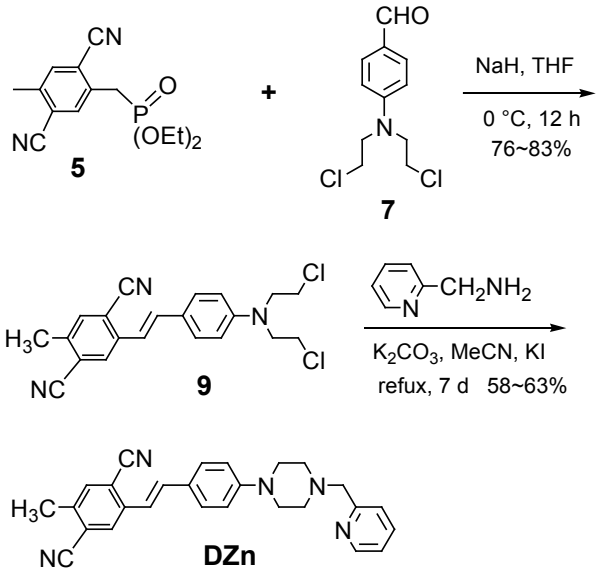

Figure 2: Synthetic procedures of Zn^{2+} sensor.

A stilbene-derived two-photon fluorescence sensor for Zn^{2+} was synthesized and characterized. The values of its Two-photon action cross sections (ηδ) and two-photon absorption cross sections (δ) are ηδ=580 GM and δ=935 GM in 3-(morpholino)propanesulfonic acid (MOPS) buffer aqueous solution, respectively. The fluorescence quantum yield and two-photon excitation maximum wavelength of complex DZn-Zn^{2+} are η=0.62 in MOPS buffer aqueous solution and λ_{ex2}=810 nm, respectively. DZn has a good selectivity for Zn^{2+}, and can still detect trace Zn^{2+} in the Presence of K^{+}, Ca^{2+}, Mg^{2+}, Ba^{2+} and Na^{+}, and is not disturbed by Cd^{2+}. The dissociation constants (KdOP and KdTP) for complex DZn-Zn^{2+} calculated from the one-photon and two-photon fluorescence titration curves are KdOP=0.51 ± 0.02 μM and KdTP=0.52 ± 0.01 μM, respectively. The two-photon action cross sections and two-photon absorption cross sections of DZn increased 72.5-fold from 8 to 580 GM and 2.3-fold from 400 to 935 GM upon saturation with Zn^{2+} in MOPS buffer aqueous solution, respectively. DZn can selectively detect

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intracellular free Zn^{2+} ions in live cells for 1500 s or so and in living tissues at a depth of 80–150 μm without interference from other metal ions and the membrane-bound probes (no fluorescence at 360–460 nm). DZn has noncytotoxic effect and excellent photostability (Figures 1 and 2) [1].

The main innovations in the article are as bellow: Firstly, The ICT (Intramolecular Charge Transfer)-based two-photon fluorescence sensor DAg for specific Ag^{+} recognition can quantitatively detect Ag^{+} and carry out microscopic Ag^{+}-imaging in live cells, resolving the international difficult question about the microscopic imaging for Ag^{+}, and being able to avoid such drawbacks as photobleaching and photodamage.

Secondly, The PET (Photoinduced Electron Transfer)-based two-photon fluorescence sensor DZn for specific Zn^{2+} recognition can quantitatively detect Zn^{2+} and carry out microscopic Zn^{2+}-imaging in live cells and in living tissues, further improving the sensitivity and precision of the microscopic imaging for Zn^{2+} in living tissues, and setting up a new record for the detection performances of the two-photon fluorescence sensors for Zn^{2+}, and breaking foreign technology monopoly in this area.

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