



A highly selective and sensitive colorimetric and near-infrared fluorescent turn-on probe for rapid detection of palladium in drugs and living cells

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ABSTRACT

Palladium contamination has attracted widespread attention due to the toxicity and the wide use of palladium species. Consequently, development of convenient and effective methods for palladium detection is of great importance. Herein, a new colorimetric and near-infrared (NIR) fluorescent turn-on probe based on the Tsuji-Trost reaction for palladium was developed. This probe can be used to detect palladium in aqueous solution (for example, in pH 7.4 PBS buffer with 0–20% DMSO) under mild conditions with high selectivity and sensitivity, giving rapid (within 2 min) and distinct dual colorimetric and NIR fluorescent turn-on signal changes with a detection limit as low as 2.2 nM. A paper test strip system was prepared with this probe for a convenient visual detection of palladium. In addition, MTT assays showed that this probe has low cytotoxicity and detection of palladium in real drug samples and living cells was successfully applied with this probe, indicating this probe has a good application prospect.

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1. Introduction

Palladium is a rare transition metal that plays very important roles in modern organic synthesis owing to its excellent catalytic performances for many reactions [1–3]. However, with the wide use of the palladium species such as Pd(PPh₃)₄, PdCl₂ etc in the industry over the past few decades, palladium contamination has raised great concerns due to the toxicity of palladium [4–6]. Studies have shown that palladium can bind to thiol-containing biomolecules such as protein, DNA, and RNA and disturb a variety of cellular processes, causing serious health problems to humans [7]. To prevent the health problems caused by palladium, the levels of residual palladium in end products have been strictly limited by the governmental regulations, for example, the threshold for palladium in active pharmaceutical ingredients is 5–10 ppm and the proposed dietary intake should be less than 1.5–15 µg per person per day in many countries [8]. Accordingly, effective methods for rapid detection of palladium are important. Several conventional methods such as atomic absorption spectroscopy (AAS), inductively

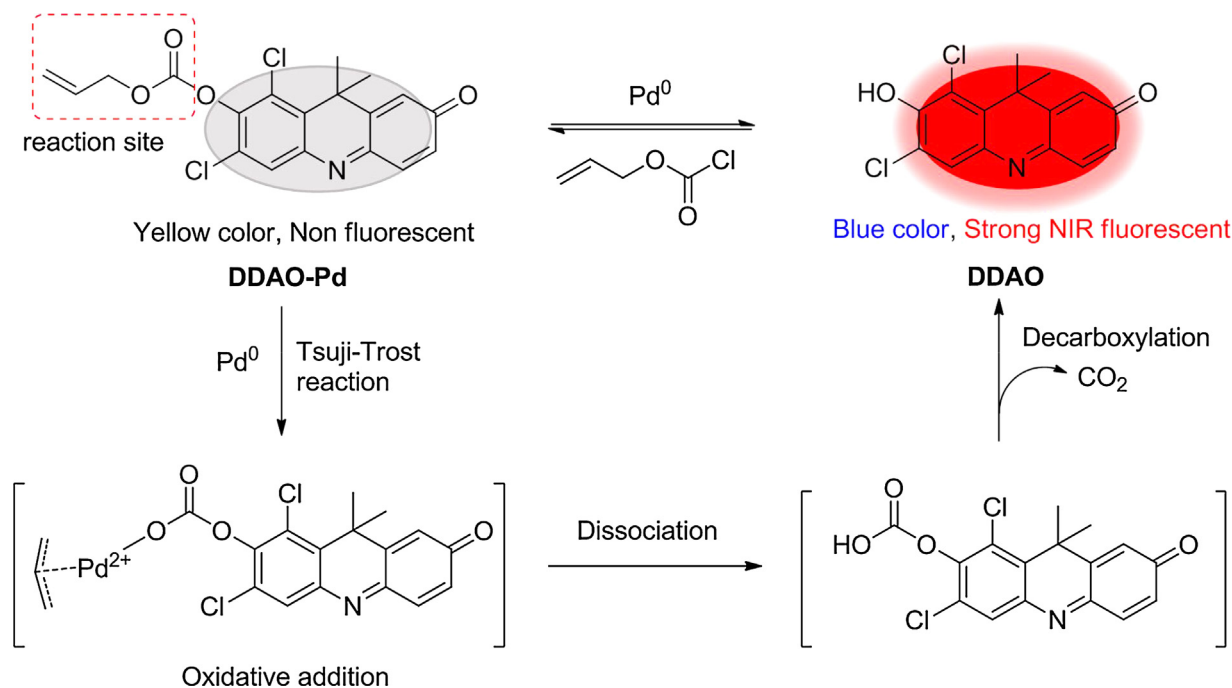
coupled plasma mass spectroscopy (ICP-MS) and plasma emission spectroscopy *etc.* have been developed for palladium detection [9–12], however, these methods are expensive, complicated and not suitable for real-time detection of palladium in living systems. Therefore, development of new methods for detection and imaging of palladium is of significance.

Optical detection using probes with dual colorimetric and fluorescent signal changes has attracted increasing attention due to its high sensitivity, convenience, and capability of naked-eye on-site detection and noninvasive real-time detection in living systems [13,14]. So far, a number of colorimetric and fluorescent probes for palladium have been reported [14,15–30]. However, most of these probes showed absorption and emission within the UV or visible range (<650 nm), which limited their applications in biological systems. Compared to fluorescent probes in the visible region, near-infrared (NIR, 650–900 nm) fluorescent probes are known to be more suitable for living systems, because they produce fluorescence in the NIR region, which has less damage to living cells, better tissue penetration, and minimum interference from background autofluorescence of biomolecules in living systems [31–37]. So far, only several NIR fluorescent probes have been reported for the detection of palladium [38–42], and these probes used fluorophores with low fluorescence quantum yield and suffered

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Scheme 1. Probe **DDAO-Pd** for detection of palladium.

from long detection time, and/or poor water solubility, which also limited their applications. To overcome these shortcomings, development of new colorimetric and NIR fluorescent probes with better properties for palladium detection is still urgently needed.

Herein, we report a new colorimetric and NIR fluorescent probe (**DDAO-Pd**, Scheme 1) for detection of palladium. This probe uses the highly fluorescent 1,3-dichloro-7-hydroxy-9,9-dimethylacridin-2(9*H*)-one (**DDAO**) as the NIR fluorophore and an allylcarbonate as the reaction site for palladium. Notably, this probe not only can work in aqueous solution (for example, in pH 7.4 PBS buffer with 0–20% DMSO) under mild conditions, but also shows excellent sensing properties for palladium including high selectivity and sensitivity, low detection limit (2.2 nM), significant NIR fluorescence turn-on signal (~120-fold enhancement) changes together with distinct colorimetric (yellow to blue) signal changes and short response time (within 2 min). Moreover, this probe has low cytotoxicity and can be conveniently used for detection of palladium in real drug samples and living cells. In addition, an easy-to-use paper test strip system can be developed with this probe for a convenient visual detection of palladium.

2. Material and methods

2.1. Materials and instruments

All chemicals were purchased from commercial suppliers and used as received unless otherwise stated. Water was purified from a Millipore-Q ultrapurification system. The pH was measured using a PB-10 digital pH-meter (Sartorius). NMR spectra were collected on a Varian Mercury 600 or a Bruker Avance III 400 instrument. The low-resolution MS spectra were performed on a Waters LC-MS system (Waters E2695 with a Waters ACQUITY QDa mass detector). High-resolution mass spectrometry (HR-MS) spectra were obtained on a Bruker microTOF-Q instrument. UV-vis spectra were recorded on an Agilent Cary-100 UV-vis spectrophotometer and fluorescence spectra were obtained on an Agilent Cary Eclipse fluorescence spectrophotometer. Cell imaging was performed in an inverted fluorescence microscopy with a 20 \times objective lens.

2.2. Synthesis of probe **DDAO-Pd**

DDAO, the fluorophore of probe **DDAO-Pd**, was first synthesized according to the literature method [43] (see Supplementary Data). Then, it was used to synthesize probe **DDAO-Pd** as follows.

To a 50 mL of flask was added **DDAO** (400 mg, 1.3 mmol), dry dichloromethane (10 mL) and triethylamine (263 mg, 2.6 mmol). The mixture was cooled with an ice bath, and a solution of allyl chloroformate (188 mg, 1.56 mmol) in dry dichloromethane (2 mL) was added. After stirring for about 2 h, dichloromethane (30 mL) was added and the mixture was washed with saturated ammonium chloride solution. The organic phase was then dried over Na_2SO_4 . After removal of solvent, the crude product was purified via silica column chromatography using dichloromethane as eluent to afford of **DDAO-Pd** as a yellow solid (369 mg, yield 73%). Mp: 148–150 °C; TLC (silica plate): R_f ~0.83 (mobile phase: petroleum ether:ethyl acetate, 2:1, v/v). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.67 (dd, J = 8.6, 2.9 Hz, 1H), 7.65–7.62 (m, 1H), 7.35 (s, 1H), 7.24 (dt, J = 8.6, 2.3 Hz, 1H), 6.02 (ddt, J = 16.4, 7.1, 6.3 Hz, 1H), 5.47 (d, J = 17.1 Hz, 1H), 5.37 (dd, J = 10.4, 1.0 Hz, 1H), 4.78 (d, J = 5.8 Hz, 2H), 1.89 (s, 3H), 1.88 (s, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 173.22, 153.49, 152.83, 150.04, 140.34, 139.58, 139.50, 138.70, 137.52, 135.70, 133.22, 130.84, 120.94, 120.10, 119.37, 69.66, 39.19, 26.71. ESI-MS: 392.1 ($\text{M} + \text{H}^+$). HR-MS: calcd. for $\text{C}_{19}\text{H}_{16}\text{Cl}_2\text{NO}_4^+$ ($\text{M} + \text{H}^+$), 392.04509; found, 392.04592.

2.3. Optical studies

Stock solution of probe **DDAO-Pd** (1 mM) was prepared in DMSO (HPLC grade). Stock solution of $\text{Pd}(\text{PPh}_3)_4$ (2 mM) was prepared in THF (HPLC grade) as the source of Pd^0 and used freshly. Stock solutions of other analytes (2–10 mM) including different metal ions, common anions, amino acids and biothiols were prepared and diluted to desired concentrations with ultrapure water when needed. In a typical optical measurement, **DDAO-Pd** was diluted to 10 μM in a PBS buffer solution (10 mM, pH 7.4, with 20% DMSO, v/v, unless otherwise stated), and 3.0 mL of this solution was placed in a quartz cell. The UV-vis or fluorescent spectra were then recorded upon addition of an analyte (the change of total volume of the solu-

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