A Turn-On Fluorescent Probe for Highly Selective and Sensitive Detection of Palladium

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A novel turn-on fluorescent probe for the detection of palladium has been designed. The probe can selectively and sensitively detect palladium in solution, and the limit of detection was calculated to be 11.4 nmol• L^{-1} . Furthermore, the probe was successfully used for fluorescence imaging of palladium in living cells.

Keywords fluorescent probe, palladium, living cell

Introduction

Palladium is the widely used precious metal in the fields of scientific research and material science such as drug discoveries and developments, organic catalytic reactions, and fuel cells *etc*.^[1-6] The frequent use of palladium in the pharmaceutical industry may lead to its significant accumulation in the final organic waste and even in the final medicinal products. Palladium ions can bind to thiol-containing amino acids, proteins (casein, silk fibroin and many enzymes), DNA or other macromolecules (*e.g.* vitamin B₆) and thereby may disturb a variety of cellular processes.^[7,8] The proposed maximum dietary intake of palladium is less than $1.5-15 \mu g$ per day per person, and its threshold in drugs is 5-10 ppm.^[9] Consequently, it is necessary to develop convenient and effective methods to detect palladium species in various samples.

Typical analytical methods used for quantification of palladium species include inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS), plasma emission spectroscopy (ICP-AES), solid phase micro extraction-high performance liquid chromatography (SPME-HPLC), and X-ray fluorescence (XRF).^[10-12] However, these methods often require complicated sample preparation steps, rigorous experimental conditions, sophisticated instrumentation and well-trained individuals. Thus, recent research activities on palladium detection have been focused on fluorescent methods^[13] due to the low cost, simplicity, sensitivity, selectivity, rapid response and high spatial resolution of fluorescence detection.^[14-25] Recently, many efforts have been devoted to developing fluores-

cent probes to detect palladium.^[26-51] The fluorescent probes for palladium are mostly based on two mechanistic pathways: chemical reaction catalyzed by palladium ions^[30-41] or the coordination between the palla-dium ions and the probes.^[42,45] However, the coordination-based probes may encounter selectivity issue because of interference from other transitional metal ions. In contrast, nearly all published fluorescent probes for palladium are based on Pd-catalyzed cleavage reactions which can recognize palladium with high sensitivity and selectivity. However, many reported sensing systems have been suffering from long response time (need several hours to achieve saturation point),^[31,41] rigorous test conditions (additional additives, *etc.*),^[30,36] which greatly restricted their practical applications. Koide and coworkers^[30] developed an innovative fluorescent sensing system for palladium species based on the Pd(0)catalyzed Tsuji-Trost allylic oxidative insertion reaction. This probe has been shown to be useful and selective for measuring low concentrations of palladium. Nevertheless, the sensing system requires initial conversion of Pd(II) to Pd(0) using a reducing agent such as PPh₃, tri-2-furylphosphine (TFP) or TFP-NaBH₄. More re-cently, Ahn and coworkers^[31] developed a probe carried propargyl ether moiety sensed palladium species in all the typical oxidation states without adding any additional reagents. However, this assay requires long reaction times (3 h).

Since recent efforts suggested that terminal propargyl ether moiety-functionalized probes are most selective for palladium recognization,^[31-33] we expected that a long excitation and emission resorufamine^[52] dye carrying a propargyl moiety may become a new palla-

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FULL PAPER

dium-selective probe. The masked long wavelength resorufamine dye may become a turn-on fluorescent probe for palladium with reduced background interference. To facilitate fast response to palladium, the propargyl moiety was connected to resorufamine through carbamate linkage to furnish a novel probe (probe 1) as shown below for palladium detection. As reported in this paper, such a probe shows excellent selectivity and high sensitivity for Pd^{2+} over other metal ions under physiological condition (at 37 °C in PBS-DMF, pH 7.4), and was successfully applied for palladium imaging in living cells.



Experimental

Materials and measurements

All reagents were purchased from commercial suppliers and used without further purification. Solvents used were purified by standard methods prior to use. ¹H NMR spectra were recorded on a Varian Model Mercury 400 MHz spectrometer. ¹H NMR chemical shifts (δ) are given (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet) downfield from Me₄Si, determined by chloroform (δ =7.26). ¹³C NMR spectra were recorded on a Varian Model Mercury 150 MHz spectrometer. Spectrometer UV-vis spectra were acquired on a Hitachi U-2900 double beam UV-visible spectrophotometer. Fluorescence spectra were measured by a Hitachi F-2500 fluorescence spectrophotometers. Electrospray ionization (ESI) mass spectra were acquired with Agilent 1100 Series LC/MSD and AB SCIEX Triple TOFTM 5600+ mass spectrometer. All spectra were recorded at room temperature, except for the confocal laser scanning microscopic images.

Detection limits

The detection limit was calculated based on the fluorescence titration. In the absence of Pd^{2+} , the fluorescence emission spectrum of probe 1 was measured five times and the standard deviation of blank measurement was achieved. To gain the slop, the fluorescence intensity at 593 nm was plotted to the concentration of Pd^{2+} . So the detection limit was calculated with the following equation:

Detection limit = $3\sigma/k$

where σ is the standard deviation of blank measurement, k is the slop between the fluorescence intensity versus Pd^{2+} concentration.

Cell imaging experiments

HepG2 cells were incubated in DMEM with 10% (*V*/*V*) fetal bovine serum, 1% penicillin/streptomycin at

37 °C in 5% CO₂. HepG2 cells were seeded at a density of 5×10^4 cells per well (200 µL) in a 6-well plate. The cells were imaged by using a confocal laser scanning microscope (λ_{ex} =565 nm, OLYMPUS FV1000). HepG2 cells were incubated in DMEM with 10% (V/V) fetal bovine serum, 1% penicillin/streptomycin at 37 °C in 5% CO₂. HepG2 cells were seeded at a density of $5 \times$ 10^4 cells per well (200 µL) in a 96-well plate. Probe 1 (20 μ mol·L⁻¹, 2 mL) in PBS buffer (10 mmol·L⁻¹, pH 7.4, 1% DMSO) was added to HepG2 cells in a six-compartment cell culture plate that contained 2.0 mL culture medium, and was incubated at 37 °C for 30 min. After removing the culture medium and washing with PBS twice, the fluorescence images of cells were taken. Pd^{2+} (50 µmol•L⁻¹, 2.0 mL) in PBS buffer (10 mmol•L⁻¹, pH 7.4) was then added to the HepG2 cells, which were further incubated at 37 °C for 30 min. After washing with PBS twice, the fluorescence images of cells were taken.

Synthesis of probe 1

The synthetic approach for probe **1** is shown in Supporting Information (Scheme S1). The chemical structure of probe **1** was characterized by HRMS, ¹H NMR and ¹³C NMR spectroscopy.

Results and Discussion

With probe **1** in hand, the experiments for the detection of palladium were carried out following the procedures reported in the literatures.^[30-41]

Spectroscopic property of probe 1 and its response to Pd(II)

Initial spectroscopic properties of the probe 1 were measured in DMF/PBS solution (1 : 3, V : V, pH=7.4). PdCl₂ was selected as the representative palladium species in the following titration experiments since it is among the most toxic palladium compounds. As masked resorufamine, probe 1 (10 μ mol·L⁻¹) is observed to be non-fluorescent with a maximum absorption at 480 nm (Figure 1). However, upon the addition of PdCl₂ the solution of probe 1 exhibited a strong red-shifted absorption peak centered at 565 nm, and a dramatic increase in fluorescent intensity at the peak of 593 nm was noticed. It took about 1 h to reach the relative saturation point judged from the plot of time-dependent intensity change of fluorescence (Figure 2). Thus carbamate linkage allows amine-type fluorescent dye to be used to detect palladium and may facilitate faster response than most propargyl ether type probes reported.^[31-34] LC-MS spectroscopic evidences confirmed the formation of resorufamine, which led to the increase in fluorescence emission (Figures S1, S2). Therefore, the change of fluorescence is due to the palladium catalyzed depropargylation reaction including Pd(II)-promoted hydrolysis of the propargyl ether or Pd(0)-participated deprotection via allenylpalladium intermediate, followed by subsequent decarboxylation process (Figure S3).



Figure 1 Absorption spectral of probe **1** (10 μ mol·L⁻¹) in the presence of PdCl₂ (5 equiv.) in DMF-PBS (1 : 3, *V* : *V*) solution (10 mmol·L⁻¹, pH=7.4) at 37 °C.



Figure 2 Time-dependent fluorescence spectra of probe 1 (10 μ mol·L⁻¹) and the corresponding responses (inset) in the presence of 5 equiv. of PdCl₂ in DMF-PBS (1 : 3, *V* : *V*) solution (10 mmol·L⁻¹, pH=7.4) at 37 °C (E_x/E_m =565/593 nm).

Selectivity of probe 1

An exceptional feature of probe 1 is its high selectivity towards the target analyte over other potential competitive species. The selectivity of probe 1 toward various metal ions was investigated and the results are shown in Figure 3 (black bars). The results indicate that the probe 1 displays selective response toward palladium ion. Under the same conditions, nearly no responsive changes are observed in the presence of 100 µmol•L⁻¹ (10-fold) of Ag⁺, Co²⁺, Cu²⁺, Fe³⁺, Hg²⁺, Mg²⁺, Ni²⁺, Zn²⁺, Ca²⁺, Mn²⁺, Pb²⁺, Li⁺, Na⁺, K⁺, Ba²⁺ and Al³⁺ in DMF/PBS solution (1 : 3, V : V, pH =7.4). A small enhancement in the fluorescence was observed only in the case of Au³⁺ (50 µmol•L⁻¹, 5 equiv.) that has high *p*-electrophilicity.^[31] Thus, according to the obvious spectroscopy changes, the designed probe 1 can detect Pd²⁺ with high selectivity.

To further verify the selectivity of probe 1 for Pd^{2+} , interference experiments involving the effects of other metal ions (Figure 3, red bars) in the identification of Pd^{2+} ions were also performed. Compared with the intensity of probe 1 responded toward Pd^{2+} in the absence of any interference ions, the presence of other metal ions caused only tiny variations on the fluorescence intensity except Au^{3+} and Hg^{2+} which resulted in low to moderate quenching of the fluorescence. Thus, these free metal ions would have little influence towards probe 1 and do not hamper the fluorogenic detection of Pd^{2+} .



Figure 3 Fluorescence intensity changes of probe 1 (10 μ mol·L⁻¹) for Pd²⁺ in the presence of various metal ions in DMF-PBS (1 : 3, *V* : *V*) solution (10 mmol·L⁻¹, pH=7.4) at 37 °C. Black bars represent the addition of a single analyte including: (0) None, (1) Ag⁺, (2) Co²⁺, (3) Cu²⁺, (4) Fe³⁺, (5) Hg²⁺, (6) Mg²⁺, (7) Ni²⁺, (8) Zn²⁺, (9) Ca²⁺, (10) Mn²⁺, (11) Pb²⁺, (12) Li⁺, (13) Na⁺, (14) K⁺, (15) Ba²⁺, (16) Al³⁺, (17) Au³⁺, (18) Pd²⁺. *c*(Au³⁺)=50 μ mol·L⁻¹, *c*(Pd²⁺)=50 μ mol·L⁻¹, *c*(other metal ion)=100 μ mol·L⁻¹. Red bars represent the subsequent addition of Pd²⁺ (50 μ mol·L⁻¹) to the mixture (*E_x*/*E_m*=565/593 nm).

Detection limit

Figure 4 shows the fluorescence spectra of probe 1 upon titration with PdCl₂. The fluorescence spectrum of probe 1 (10 μ mol·L⁻¹) in the absence of palladium in DMF/PBS solution (1:3, V:V, pH=7.4) exhibits very weak fluorescence emission at 593 nm. With continuous addition of PdCl₂, the fluorescence intensity at 593 nm increased in accordance with the increasing concentration of PdCl₂. About 110-fold fluorescence enhancement was observed after 60 min when the concentration of Pd^{2+} ions was 50 μ mol·L⁻¹. The observed fluorescence intensity is nearly proportional to the Pd²⁺ concentration up to 8 μ mol·L⁻¹ (Figure 4). The detection limit of PdCl₂ was calculated to be 11.4 nmol \cdot L⁻¹ (2.1 ppb), which is far below the allowable level of palladium ions (5-10 ppm) from the European Agency for the Evaluation of Medicinal Products (EMEA).^[9]

Probe 1 response to different palladium complexes

To demonstrate the potential application of the probe to detect various sources of palladium species, we tested whether it could respond to different initial oxidation states of palladium with various kinds of ligand. Thus typical commercially available palladium species such



Figure 4 Fluorescence spectra changes and fluorescence intensities of probe 1 (10 μ mol·L⁻¹) in the presence of increasing concentrations of Pd²⁺ (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0 equiv.) in DMF-PBS (1 : 3, *V* : *V*) solution (10 mmol·L⁻¹, pH=7.4) at 37 °C. Inset: A linear calibration curve between the fluorescent intensity changes of probe 1 and the concentration of PdCl₂ in the range of 1 to 8 μ mol·L⁻¹. Each spectrum was recorded 60 min after addition of PdCl₂ (E_x/E_m =565/593 nm).

as $Pd(PPh_3)_4$, $PdCl_2$, $Pd(OAc)_2$, $PdCl_2(dppf)_2$, $Pd(PPh_3)_2Cl_2$, and $Pd_2(dba)_3$ were selected and the results are shown in Figure 5. According to the fluorescence intensity increment, sensitivities of probe 1 to palladium species were in the following order: $Pd_2(dba)_3 > Pd(OAc)_2 > PdCl_2 > Pd(PPh_3)_2Cl_2 >$ $Pd(PPh_3)_4 > PdCl_2(dppf)_2$.^[33] The results revealed that probe 1 remarkably responds to the different oxidation states of palladium. These results indicated that the depropargylation reaction can be catalyzed via Pd(II)- catalyzed hydration intermediates, but also via allenyl palladium resulting from the oxidative addition of Pd(0).^[33,53,54]



Figure 5 Comparison of the fluorescence intensity changes on different palladium complexes, measured for a mixture of probe **1** (10 μ mol·L⁻¹) and the palladium species (50 μ mol·L⁻¹) in DMF-PBS (1:3, *V*: *V*) solution (10 mmol·L⁻¹, pH=7.4) at 37 °C. (0) probe only; (1) PdCl₂(dppf)₂; (2) Pd(PPh₃)₄; (3) Pd(PPh₃)₂Cl₂; (4) PdCl₂; (5) Pd(OAc)₂; (6) Pd₂(dba)₃ (*E_x/E_m*= 565/593 nm).

Effect of pH

The potential pH effects on probe 1 in the absence or presence of PdCl₂ were subsequently evaluated (Figure 6). The fact that fluorescence remained almost unchanged for the free probe over pH range of 6.0-8.0 indicated that the probe 1 is very stable in such pH range. In stark contrast, remarkable fluorescent signal enhancement was observed within the pH range 6.0-8.0 when the probe 1 was treated with PdCl₂, suggesting that the novel probe was promising for biological applications.



Figure 6 Effect of pH on the fluorescence intensity (λ_{em} =593 nm) of probe **1** (10 µmol•L⁻¹) in DMF/phosphate buffer (1 : 3, *V* : *V*) upon addition of 50 µmol•L⁻¹ Pd²⁺ after incubation at 37 °C.

Imaging Pd²⁺ in living cells

To demonstrate the practical applicability of the probe in biological systems, fluorescence imaging experiments in living cells (HepG2 cells) were carried out. HepG2 cells were incubated with 10.0 μ mol·L⁻¹ of probe 1 for 30 min, and then treated with 50.0 μ mol·L⁻¹ of PdCl₂. The fluorescence images of HepG2 cells were recorded before and after addition of Pd²⁺. As shown in Figure 7, in the absence of Pd²⁺, free probe 1 provided no detectable fluorescence signals in living cells (Figure 7A). However, after incubation with Pd²⁺, red fluorescence was observed in living cells (Figure 7B). Thus, these experimental images suggested that the probe 1 is cell membrane permeable and capable of sensing palladium in living cells.

Conclusions

In conclusion, we have developed a chemical reaction-based fluorescent probe 1 selective for recognition of palladium species. The results demonstrate that probe 1 exhibits a high sensitivity and selectivity for Pd^{2+} detection, with detection limit of 11.4 nmol•L⁻¹. Moreover, such a probe is able to respond to different oxidation states of palladium among other transition metal ions without additional reagents. The current work provides a new mild and promising strategy for the detection of palladium species in biological and environ



Figure 7 Confocal fluorescence images of $PdCl_2$ in HepG2 cells incubated at 37 °C with 10 µmol•L⁻¹ of probe 1. Representative fluorescence images of HepG2 cells treated with probe 1 (10 µmol•L⁻¹) in the absence of Pd^{2+} (A) and in the presence of 50 µmol•L⁻¹ Pd^{2+} (B) for 30 min at 37 °C; (A2) and (B2) are bright-field image of cells shown in panel; (A3) merged images of (A1) and (A2); (B3) merged images of (B1) and (B2).

mental systems.

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