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A Colorimetric and Ratiometric Fluorescent Probe for Palladium

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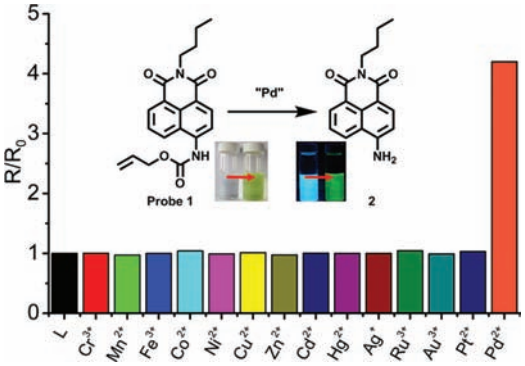
ABSTRACT



A colorimetric and ratiometric fluorescent probe for the palladium species has been developed based on the Pd^0-catalyzed cleavage of an allyoxycarbonyl group of amines under mild conditions. The probe displays a highly sensitive and selective response with significant changes in both color (from colorless to jade-green) and fluorescence (from blue to green), through the ICT process.

With the wide use of the palladium species in pharmacy and various materials,[1,2] the resulting high level of residual palladium in the final product has raised great concern.[3] Palladium can have adverse effects on our health and the environment, because it can bind to thiol-containing amino acids, proteins, DNA, and other biomolecules and disturb a variety of cellular processes.[1] Thus, the final threshold for palladium in the end products is strictly limited, with set governmental restrictions (no more than 5−10 ppm) and a proposed maximum dietary intake of palladium (as a crude estimate) of less than 1.5−15 μg per person per day.[4] This issue raises the urgent need to develop effective methods for palladium species sensing.

Conventional analytical methods for palladium species include atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), solid phase microextraction-high performance liquid chromatography, X-ray fluorescence, etc.[5] However, these methods

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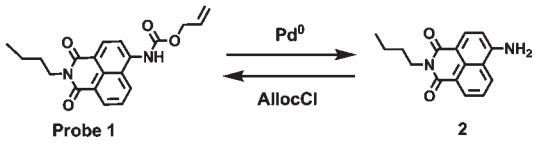
often need serious sample-preparation steps or expensive equipment. Thus, current research has been focused on fluorescent methods, because of their low cost, simplicity, and sensitivity.[6] Some fluorescent chemosensors[7] and chemodosimeters[8] for the palladium species have been reported in the literature recently. To the best of our knowledge, most of these sensors respond to palladium with changes only in fluorescence intensity (based on the ON−OFF[9] or OFF−ON mechanism[10]). However, a major limitation of the intensity-based sensor is that quantitative detection can be significantly influenced by the excitation power and detector sensitivity.[11] In contrast, ratiometric fluorescent measurement which uses the ratio of two fluorescent bands instead of the absolute intensity of one band, makes measuring the analyte more accurately and sensitively possible with minimization of the background signal.[12] Herein, we developed a ratiometric fluorescent probe for the palladium species with a perceived color change.

Scheme 1. Preparation of Probe **1** and Its Cleavage To Form **2**



In our scaffold, 4-aminonaphthalimide was chosen as the fluorophore because of its outstanding ICT structure[12c,13] and desirable photophysical properties, such as a large Stokes' shift, long emission wavelength, and insensitivity to pH (Scheme 1). Compound **1**, *N*-butyl-4-NHAlloc-1,8-naphthalimide, was prepared smoothly from *N*-butyl-4-amido-1,8-naphthalimide (**2**) and allyl chloroformat in a satisfactory yield. It can be easily cleaved with a quantitative conversion to the free amino compound **2** after being treated with $Pd(PPh_3)_4$ under mild reaction conditions.[14]

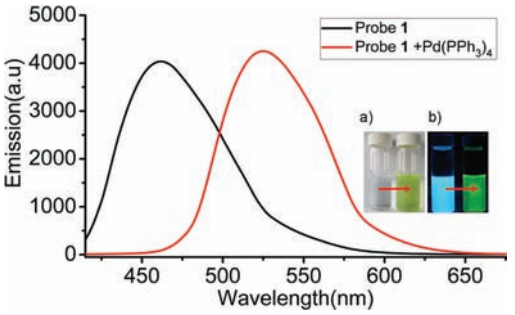


Figure 1. Fluorescence spectral changes of probe **1** (20 μM) upon treatment with $Pd(PPh_3)_4$ (10 μM), in acetonitrile−water solutions (CH_3CN:H_2O = 4:1, $NaBH_4$−PPh_3 (10 mM) and morpholine (10 mM)) at room temperature. Ex = 403 nm. Slit: 5.0 nm/5.0 nm. Inset: Photos showing (a) color and (b) fluorescence color changes upon addition of $Pd(PPh_3)_4$.

The spectroscopic properties of the compound **1** were rated in acetonitrile−water solutions (CH_3CN:H_2O = 4:1, $NaBH_4$−PPh_3 (10 mM) and morpholine (10 mM)) at a micromolar concentration. As shown in Figure 1, free compound **1** (20 μM) showed a relatively short emission wavelength with a maximum at 462 nm (blue), owing to the electron-withdrawing effect of the amide group. After being treated with $Pd(PPh_3)_4$ (10 μM), the maximum emission peak underwent a red shift to 524 nm (green), showing a ratiometric response. This red shift in the emission should be attributed to the stronger ICT efficiency of the released amino compound **2** (Figure S1). A red shift from 370 to 430 nm of **1** was also detected in the maximum absorption spectrum. Additionally, marked color changes in the solutions, which ranged from colorless to jade-green, could be distinguished by the naked eyes. Clearly, the results indicated that Pd^0 could be detected through both ratiometric fluorescence and colorimetric methods by probe **1**.

To explore the reactivity of probe **1** toward other palladium metal sources, different initial oxidation states of palladium such as $PdCl_2$, $Pd(OAc)_2$, $Pd(CH_3CN)_2Cl_2$, and $Pd(PPh_3)_2Cl_2$ were examined (Figure S5). To our delight, all the samples gave similar responses to probe **1** as $Pd(PPh_3)_4$, indicating the response depends on palladium itself, regardless of its ligands or complex anions.

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(14) For detailed experimental procedures and the characterization of the new compounds, please see the Supporting Information.

Since $PdCl_2$ is the most toxic species, among the palladium compounds,[10a] we proceeded to study the detection of $PdCl_2$ in the following experiment.

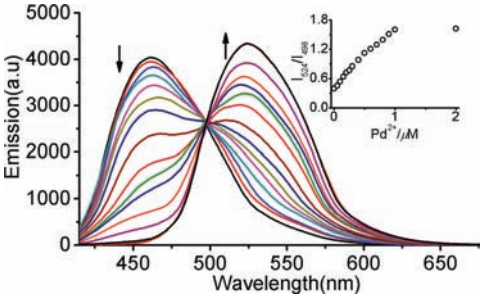

Figure 2. Fluorescence spectra of probe **1** upon titration of Pd^{2+} (0−2 μM) in acetonitrile− water solutions (CH_3CN:H_2O = 4:1, $NaBH_4$−PPh_3 (10 mM) and morpholine (10 mM)), taken after 5 min at room temperature. Ex = 403 nm. Slit: 5.0 nm/5.0 nm. [probe **1**] = 20 μM. Inset: Ratiometric calibration curve $I_{524\ nm}/I_{498\ nm}$ as a function of Pd^{2+}.

Upon titration of Pd^{2+} (Figure 2), a gradual decrease in fluorescence intensity at 462 nm and the simultaneous appearance of a new red-shifted emission band at 524 nm were observed with an isoemission point at 498 nm, indicating a clear ratiometric fluorescence change. The fluorescence intensity ratios of probe **1** at 524 and 498 nm ($I_{524\ nm}/I_{498\ nm}$) increased linearly with the amount of Pd^{2+} in the range of 0−1 μM (Figure 2, inset). The detection limit of probe **1** for $PdCl_2$ was determined as 6.1 nM (Pd content = 0.65 μg/L) (see the Supporting Information), much lower than the palladium content in persons found from samples of morning saliva (10.6 ± 7.4 μg/L).[1] That is, probe **1** can be a sensitive ratiometric fluorescent sensor for the quantitative detection of Pd^{2+}.

To demonstrate the practical application of the probe, we carried out an experiment to monitor residul Pd in a reactor using probe **1**. A THF solution of $PdCl_2$ was stirred in four flasks for 1 h at room temperature. After the solution was poured out, the four flasks were treated with different washing procedures, respectively (no wash; brushing with detergent only; brushing with detergent and washing with water; and brushing with detergent, washing with water and acetone). Next, probe **1** solution (CH_3CN:H_2O = 4:1, $NaBH_4$−PPh_3 (10 mM) and morpholine (10 mM)) was added into the four flasks. After 5 min, obvious fluorescent and color changes were detected (Figure 3). Thus, probe **1** could be used for the quality control of reactors through convenient visual sensing.

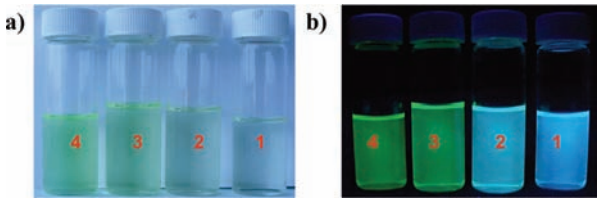

Figure 3. Color changes in probe **1** (20 μM) treated with the residual $PdCl_2$ on the surface of glassware. Left: Visible color on excitation at 365 nm using a hand-held UV lamp; Right: Visual fluorescence. From 1 to 4: Probe **1** solutions not exposed to $PdCl_2$ reagents (1) and exposed to $PdCl_2$ on the surface of glassware with different wash procedures (brushing with detergent, washing with water and acetone (2); brushing with detergent and washing with water (3); and brushing with detergent only (4)).

Furthermore, a proof-of-concept experiment for Pd^{2+} detection in the environment was also performed with pool and tap water. The water samples were collected and filtered, prepared as acetonitrile−water solutions (CH_3CN:H_2O = 4:1, $NaBH_4$−PPh_3 (10 mM) and morpholine (10 mM)), and then pretreated with different amounts of $PdCl_2$ (0−1 μM). After the addition of probe **1** (20 μM), $PdCl_2$ could be readily detected with a large fluorescence signal which was almost linearly dependent on the concentration of palladium (Figure 4). The results demonstrate that our detection system could function well in quantitative Pd^{2+} analysis in environmental samples.

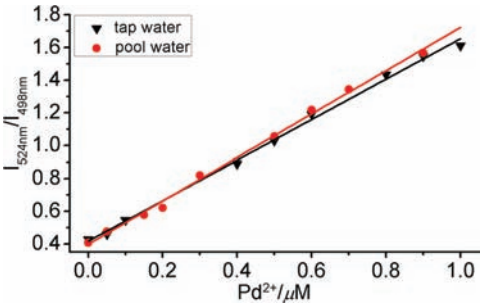

Figure 4. Proof-of-concept experiment with probe **1** (20 μM) for Pd^{2+} detection in acetonitrile−tap water (▼) and acetonitrile−pool water (●) solutions at μM levels. Ex = 403 nm. Slit: 5.0 nm/5.0 nm.

The selectivity experiment was conducted using different metal ions (Figure 5). Under modified conditions[15] in acetonitrile−water solutions (CH_3CN:H_2O = 4:1, PPh_3 (10 mM) and morpholine (10 mM)), the ratiometric response was detected only in the case of Pd^{2+}; other metal species such as Au^{3+}, Ag^{+}, Ru^{3+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+} had no or little effect on the emission of probe **1**. Remarkably, as one that coexists with Pd^{2+} in ores and also competes with it in the sensing studies,[10b] even Pt^{2+} did not show any influence on our sensor. Moreover, compared with various metal species

(15) Due to the similar π-electrophilicity between cationic Pd and Pt species, Pt^{2+} could also respond to probe **1** in acetonitrile−water solutions (CH_3CN:H_2O = 4:1, $NaBH_4$−PPh_3 (10 mM) and morpholine (10 mM) (Figure S9). In order to avoid the influence of Pt^{2+}, we optimized the conditions, in which $NaBH_4$ was deleted and the reaction time was prolonged (CH_3CN:H_2O = 4: 1, PPh_3 (10 mM) and morpholine (10 mM)). In this case, the sensor showed specific selectivity towards Pd^{2+}.

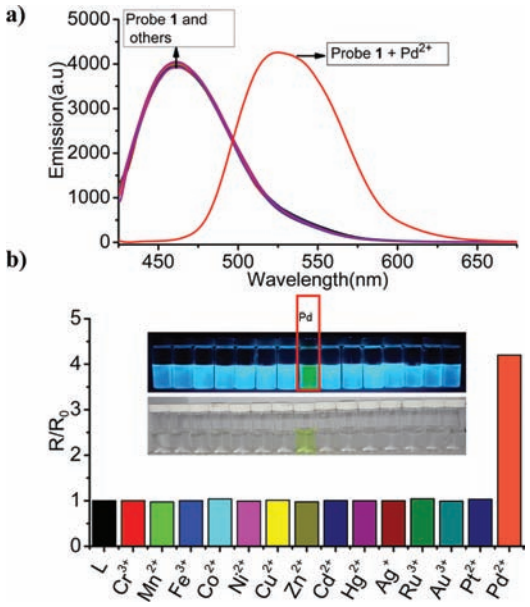

Figure 5. (a) Fluorescence spectra of probe **1** in the absence and presence of different metal ions Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ag^{+}, Pt^{2+}, Au^{3+}, Ru^{3+}, and Pd^{2+} (as their ClO_4^- or Cl^- salts) in acetonitrile–water solutions (CH_3CN:H_2O = 4:1, PPh_3 (10 mM) and morpholine (10 mM)), measured after 30 min; (b) Metal ion selectivity of probe **1** ($R = I_{524\ nm}/I_{498\ nm}$). Inset: Fluorescence changes excited by UV lamp (365 nm) and color changes in probe **1** upon addition of various metal cations. Ex = 403 nm. Slit: 5.0 nm/5.0 nm. [probe **1**] = 20 μM, [M^{n+}] = 10 μM.

tested, the only color change in probe **1** with Pd^{2+} made it convenient to detect the palladium species through colorimetric method.

Different anion-induced influences on the sensing behavior of the probe **1**–Pd^{2+} system were also investigated. As shown in Figure S7, the sensing for Pd^{2+} hardly experienced interference from commonly coexistent anions, such as F^-, Cl^-, Br^-, I^-, CNS^-, HSO_4^-, $H_2PO_4^-$, NO_3^-, ClO_4^-, and AcO^-. Furthermore, competition experiments of metal ions showed that the addition of various metal ions promoted a negligible effect on Pd^{2+} sensing (Figure S8).

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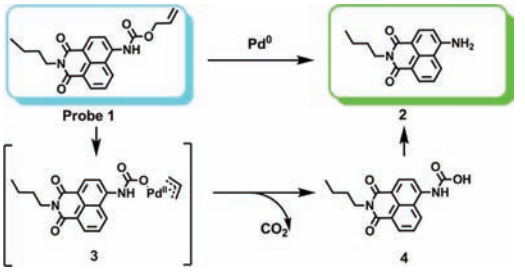
Scheme 2. Mechanism for Selective Recognition of Palladium



The excellent selectivity should be attributed to the highly specific Pd^0-triggered cleavage process. A feasible fluorescence sensing mechanism is shown in Scheme 2.[16] Pd^0 reacts with the allyl carbamate group of compound **1** to yield π-allylpalladium(II) complex **3**, further transferring the allyl unit to morpholine as the nucleophile, and then producing carbamate **4**. Finally, decarboxylation of the compound delivers the compound **2** with the green fluorescene. In this case, the sensor could operate through the cleavage reaction triggered by Pd^0 with fluorescence changes at two different wavelengths. Furthermore, Pd^{2+} can also be detected by the same principle, when a reducing agent, such as $NaBH_4$–PPh_3, is added.

In conclusion, we have rationally developed a sensitive and selective fluorescent probe for the palladium species based on the Pd^0-triggered cleavage reaction under mild conditions. Probe **1** displayed specific and ratiometric fluorescent responses toward palladium, with a marked color change from colorless to jade-green. Moreover, with the ratiometric fluorescent signal and a low detection limit, the probe may be favorable for the quantitative detection of palladium in environmental and chemical settings.

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Supporting Information Available. Experimental details, characterization for the compounds, and additional spectroscopic data are reported. This material is available free of charge via the Internet at http://pubs.acs.org.