Studies of a fluorogenic probe for palladium and platinum leading to a palladium-specific detection method†

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Herein we demonstrate selective fluorescence detection of palladium in the presence of platinum by altering the pH of the reaction medium of a Pd^0/Pt^0-catalyzed Tsuji–Trost type reaction to yield a fluorescent compound.

Palladium and platinum are widely used precious metals in various materials such as dental crowns, catalytic converters, fuel cells, and jewelry. Despite the importance of these metals in such materials, a major downfall is the subsequent pollution of the environment that comes with their frequent use. Palladium and platinum intake occurs frequently because significant amounts of the metals are emitted due to automobile catalytic converter attrition[1] (0.1–0.8 μg/km/car[2]), and such pollution products may account for the presence of these metals in human bodies.[3] Thus, many samples, including environmental and geological samples, will contain a mixture of palladium and platinum. Since palladium and platinum are found in amounts of at least 100 ng g^{-1} in environmental samples such as road dust and roadside soil, it will become economically viable to recover these metals.[1c] As such, methods are urgently needed that not only provide sensitive detection of these metals but also specificity with respect to each metal in a high throughput fashion.

Current techniques of quantifying palladium or platinum rely on spectroscopic methods such as atomic absorption spectroscopy, X-ray fluorescence, and inductively coupled plasma emission spectroscopy, all of which are extremely sensitive to the matrix of the sample and prone to spectral interference.[4] These methods require large and expensive instruments and highly skilled individuals to operate them. In addition, such operations require great caution because an instrument can be cross-contaminated.[5] Due to the linear nature of these analyses, such techniques are not amenable to high throughput analysis. A fluorescent method would be more desirable because the measurement requires a far less expensive benchtop or handheld fluorometer. Moreover, the samples in fluorescent methods are not cross-contaminated because disposable cuvettes (~10 cents/cuvette; 340–800 nm) and multi-well plates are readily available, facilitating high throughput analysis.

Recently, our group reported a highly sensitive fluorescent probe for palladium and platinum based on the Tsuji–Trost[6] allylic oxidative insertion mechanism (Fig. 1).[7,8] Using this mechanism, M^0 oxidatively inserts into the allylic C–O bond of the nonfluorescent allylic ether **1** to form the putative complex **3**. This complex then reacts with a nucleophile to form the fluorescent compound **2** and an allylated nucleophile. Since this process is catalytic with respect to M^0, the analyte (Pd, Pt) amplifies fluorescence signal. This approach is conceptually new for metal detection[9] because this is the first example where the metal analyte amplifies fluorescence signal directly through a catalytic process in a well-defined system. Since Ph_3P reduces other metal species such as M^{II} to M^0 *in situ*, this method is capable of measuring total palladium and platinum quantities regardless of the oxidation states. Herein we report more in-depth studies concerning compound **1**. In addition, through further analysis of each of these systems, we now report the selective detection of palladium in the presence of platinum.

To determine the optimal pH of the palladium-catalyzed deallylation reaction, we examined the pH dependence in the optimal pH range for Pittsburgh Green **2** (pH = 4–10).[10] As Fig. 2(a) shows, a strong fluorescence signal was observed between pH 6–9.[11] The pH dependence results were then followed up with kinetic assessment. The initial rates were measured at pH 4, 7 and 10 using $PdCl_2$ (1 mol%) as a catalyst. As Fig. 2(b) shows, reaction occurs at all pHs tested. The rate at pH 10 is fastest, although the fluorescence intensity is lower at this pH, possibly due to nonfluorescent cyclic ether formation.[10] The rate at pH 7 was only ~10% slower and the rate at pH 4 was only ~30% slower. From these data, we deduced that pH 7 is best for palladium fluorescent analysis because it allows for optimal fluorescence intensity and rate;

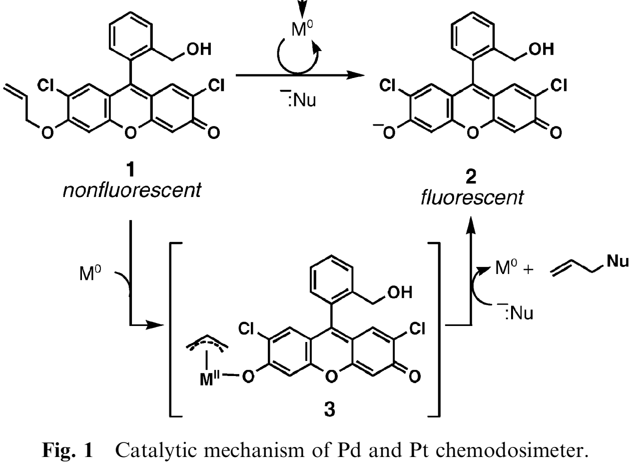

Fig. 1 Catalytic mechanism of Pd and Pt chemodosimeter.

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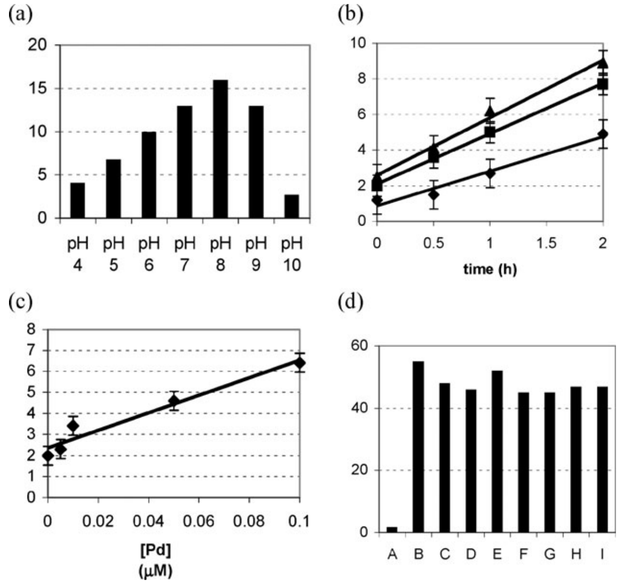

Fig. 2 Fluorescence analysis of Pd. In these graphs, the *y*-axis is fluorescence intensity (a.u. $\times 10^5$) at 525 nm. For example, "5" means 5×10^5. In all cases, [**1**] = 12.5 μM and [PPh_3] = 250 μM, and the assays were performed for 1 h at 24 °C. (a) The pH-dependent deallylation of **1** in the presence of $PdCl_2$ (0.625 μM) in 1 : 4 DMSO/buffer. (b) Initial rate analysis for deallylation of **1** in the presence of $PdCl_2$ (117 μM) in 1 : 1 DMSO/buffer. (◆) pH 4; $y = 1.94x + 0.880$; $R^2 = 0.969$; (■) pH 7; $y = 2.83x + 2.10$; $R^2 = 0.998$; (▲) pH 10; $y = 3.23x + 2.60$; $R^2 = 0.992$. (c) Correlation between fluorescence intensity and [$PdCl_2$] in 1 : 4 DMSO/pH 7 buffer after 4 h at 24 °C. $y = 41.6x + 2.37$; $R^2 = 0.952$. (d) Fluorescence induction by various Pd species and oxidation states. In samples B–I, [Pd] = 5.0 μM: A = no Pd, B = $Pd(PPh_3)_4$, C = $PdCl_2$, D = $Pd(OAc)_2$, E = $Pd(acac)_2$, F = $Pd(PPh_3)_2Cl_2$, G = $Pd(MeCN)_2Cl_2$, H = $Pd_2(dba)_3$, I = K_2PdCl_6.

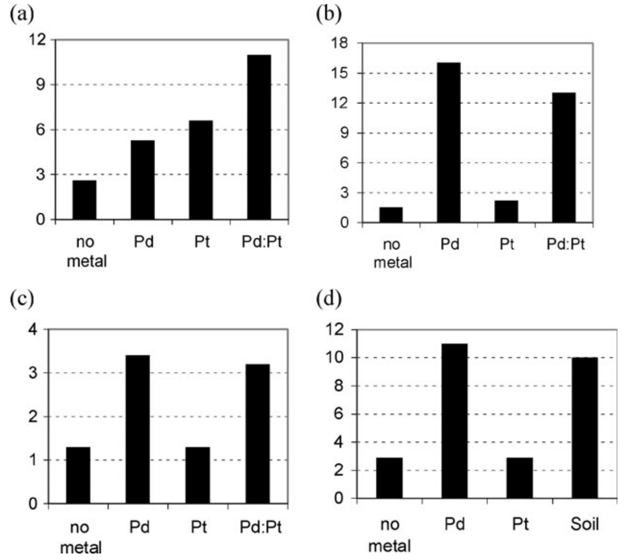

Fig. 3 Selective detection of palladium in the presence of platinum. In these graphs, the *y*-axis is fluorescence intensity (a. u. $\times 10^5$) at 525 nm. In all cases, [**1**] = 12.5 μM and [PPh_3] = 250 μM, and the assays were performed for 1–4 h at 24 °C. Concentrated pH 7 buffer (1.25 M) (1.0 mL) was added prior to fluorescence measurement to maximize signal. (a) Detection of 1 : 1 $PdCl_2/PtCl_2$ (0.100 μM each) in 1 : 4 DMSO/pH 7 buffer compared to positive controls. (b) Detection of 1 : 1 $PdCl_2/PtCl_2$ (5 μM each) in 1 : 4 DMSO/pH 4 buffer compared to positive controls. (c) Detection of 1 : 10 $PdCl_2/PtCl_2$ (0.500 μM Pd/5 μM Pt) in 1 : 4 DMSO/pH 4 buffer compared to positive controls. (d) Detection of soil spiked with 1 : 1 $PdCl_2 : PtCl_2$ (5 μM each) in 1 : 4 DMSO/pH 4 buffer compared to positive controls. No metal = soil with no Pd or Pt. Positive controls = metals in buffer without soil.

however, there is some flexibility with respect to pH as reaction occurs at each pH examined.

Using these conditions, we next examined the catalytic efficiency and sensitivity of our method. The TOF (turnover frequency) for Pd in pH 7 buffer under the high dilution and salt conditions ([**1**] = 12.5 μM; [Pd] = 50 nM; [PO_4^{3-}] = 50 mM) was determined as 3.1 h^{-1}. The fluorescent intensity correlated to the concentration of palladium in the 10 nM–100 nM (1–10 ppb) range after 4 h at 24 °C (Fig. 2(c)).

It is important to note that although excess Ph_3P is used to fully reduce the palladium species present, other ligands may initially be coordinated to the metal. To examine this, we tested the generality of our method using a variety of palladium reagents with oxidation states of 0, II and IV. As Fig. 2(d) shows, our method is general for many different palladium sources, and thus is successful at effectively converting all palladium to reactive $Pd(PPh_3)_n$ species regardless of other ligands present in the solution. A similar experiment involving various ligands surrounding palladium might be difficult with ICP-MS because it is sensitive to the chemistry within the coordination sphere of the metal. Using this method, samples are required to undergo rigorous pretreatment with concentrated acid, typically hydrochloric acid, which is necessary to stabilize the chloro-complexes of the metal to obtain a uniform signal.[12] Additionally, the presence of other non-halide ligands may cause undesired spectral interference.

As for platinum, we reported that the platinum-catalyzed deallylation was most effective using pH 7–9 buffers.[8] Further, the reaction at pH 7 was approximately 3.5 times faster than that at pH 10 and little reaction occurred at pH 4.[8] Thus, similar to palladium, signal enhancement was optimal at pH 7.

By examining the kinetic and pH data for both palladium and platinum, it is apparent that the Pd-catalyzed deallylation of **1** is 158 times faster than the Pt-catalyzed reaction at pH 4. As such, we set out to selectively detect palladium in the presence of platinum at pH 4. We first performed the reaction with a 1 : 1 mixture of palladium and platinum (0.100 μM each) in 1 : 4 DMSO/pH 7 buffer to confirm that the metals react independently of one another. As Fig. 3(a) shows, in fact this is the case and the fluorescence intensity in the 1 : 1 mixture is approximately additive with respect to the intensity of each metal alone. We then performed the reaction in 1 : 4 DMSO/pH 4 buffer. As Fig. 3(b) and (c) show, in this solution we were able to selectively detect palladium in the presence of platinum, even in the presence of excess platinum (10 : 1 platinum/palladium).

To demonstrate the potential application of this palladium-specific method, we carried out the following proof-of-concept experiment. Soil (heated in an oven at >100 °C for 24 h prior to this experiment; presumably this process can be accelerated by the use of a microwave oven) was suspended in 1 : 4 DMSO/pH 4 buffer (final: 10 mg mL^{-1}). We spiked the resulting mixture with a 1 : 1 mixture of palladium and platinum, which was left on a bench for 30 min. After filtering to remove insoluble materials,[13] the solution was then treated with Ph_3P (final concentration = 250 μM) and **1** (final concentration = 12.5 μM) and incubated for 4 h at 24 °C. As Fig. 3(d) shows, even without rigorous sample pretreatment, we were able to specifically detect palladium in this crude sample. Thus, although this experiment is somewhat artificial, this method could have potential application in platinum/palladium manufacturing because these metals are found together in mining sites (ores) and spectroscopic analyses of the individual metals typically require a complex series of purifications to eliminate molecular interferences.[12] Environmental samples, especially those collected from roadsides, contain both metals, and this method will allow the metals to be quantified differentially.

In conclusion, we have studied a sensitive fluorogenic probe for palladium and platinum based upon the Tsuji–Trost allylic oxidative insertion mechanism. Based upon the differences in pH dependence between palladium and platinum, we have demonstrated the selective detection of palladium in the presence of platinum by altering the pH of the reaction medium. This palladium-specific detection method can be applied even to crude samples such as soil. Thus, this detection method may change the paradigm of palladium analysis and find broad applications in materials, energy, the environment, and human health.

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