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A novel dual-mode turn-on optional chemodosimeter for the visualization of Pd⁰ with a low detection limit



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ABSTRACT

Rhodol is an ideal platform for fluorescent probes owing to its spirolactone framework and excellent photochemical properties. Herein, a novel rhodol-based colorimetric and fluorescent turn-on probe, **DER-1**, for the detection of Pd⁰, was rationally developed with an allyl carbamate group as the response unit. Base on the Pd⁰-triggered cleavage reaction and rhodol spiroring-opening mechanism, the proposed probe exhibited a high selectivity and sensitivity towards Pd⁰. Upon addition of Pd(PPh₃)₄, a significant fluorescence enhancement at 547 nm was observed with an obvious color change from colorless to pink, which can be easily identified by naked-eye. In addition, the fluorescence intensity at 547 nm was linearly proportional to the concentration of Pd⁰ in the range of 0–1.5 μ M, and the detection limit was calculated to be 1.14 nM. That is, probe **DER-1** can be quite a sensitive fluorescent turn-on probe for the quantitative detection of Pd⁰ in pretty low dose.

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1. Introduction

Palladium, which is widely distributed in the environment due to its use in alloys, fuel cells, chemical catalysts, and especially in automobile catalytic converters, is one of the most ubiquitous and poisonous heavy metals [1,2]. Available evidences indicated that palladium compounds originating from environmental matrices could be easily migrated to biological materials, thereby accumulating in the food chain [3]. Moreover, palladium, as a thiophilic element, can bind to thiol-containing amino acids, proteins, DNA and RNA, and other macromolecular, possibly impair various cellar processes, which may result in potential health hazards [4–6]. Even low doses of palladium are sufficient to cause allergic in susceptible individuals [7]. In view of this, effective assay methods for monitoring low levels of the palladium species are urgently required.

To determine the palladium concentration, various conventional techniques with low detection limits and multi-element

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http://dx.doi.org/10.1016/j.jphotochem.2017.01.007 1010-6030/© 2017 Elsevier B.V. All rights reserved. capabilities have been developed, such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), solid phase microextraction high-performance liquid chromatography (SPME–HPLC), X-ray fluorescence (XRF), time-of-flight resonance ionization mass spectrometry (TOF-MS), capillary zone electrophoresis (CZE) [8–12]. These methods do provide a rapidly and extremely accurate analysis of palladium; however, they need sophisticated sample-pretreatment procedures, complicated apparatus, and rigorous experimental conditions. Therefore, development of optical (colorimetric and fluorescent) methods is highly beneficial for the detection of palladium due to apparent advantages such as high selectivity and sensitivity, operational simplicity, rapidity, and low cost, over other methods [13–16].

Until now, various colorimetric and fluorescent chemosensors have been rationally reported for palladium sensing, and the detection of palladium is usually based on the complexation of palladium with the detector or the reaction between palladium and probe such as ring opening of rhodamine derivatives and palladium-catalyzed reactions [17–22]. Palladium detection based on coordination can always provide a reversible detection process



and signal change [23]. These chemosensors can thus be used to monitor the fluctuation of palladium content in various samples. However, their selectivity and sensitivity cannot always be guaranteed. Considering the low residue threshold of palladium in samples of drugs and biomaterials [24], a new strategy with high sensitivity and selectivity should be selected for low-dose palladium sensing. Investigations have indicated that a catalyzed mechanism based fluorescent probe usually exhibits high selectivity and sensitivity towards palladium species [25].

As we all know, rhodol fluorophore (also named rhodafluor) is the hybrid of fluorescein and rhodamine, and it is an interesting candidate for fluorescent probe since it inherit all the excellent photophysical properties, such as high extinction coefficient, quantum yield, photostability, and solubility in a variety of solvents, and low pH-dependence [26]. Owning to the spirolactone scaffold in rhodol fluorophore, which undergoes a conformational transformation from spirolactone (colorless and nonfluorescent) to an open-ring structure (colored and fluorescent), it is well considered to offer promise as fluorescent group to construct off-on optional probe [27].

In order to detect Pd⁰ in low dose, we have developed a novel optional Pd⁰-selective probe with a low detection limit. Herein, we present the design, synthesis and spectral properties of the fluorescent probe **DER-1** with a terminal allyl carbamate as the recognition unit (see ESI, Scheme S1). The designed probe exhibits prominent turn-on fluorescence response towards Pd⁰ in PBS buffer containing 50% THF, corresponding to the obvious color change from colorless to pink. Furthermore, the proposed probe shows high selectivity and sensitivity towards Pd⁰, especially with quite a low detection limit. Compared to our previous work, the probe of this work exhibited a more sensitive response with a lower detection limit.

2. Experimental section

2.1. Materials and instruments

N,*N*-Diethylaminophenol and allyl chloroformate (AllocCl) were purchased from Energy Chemical and used directly without any purification. All other reagents were of the highest grade that available and used as received unless otherwise noted. All solvents were analytical pure and were without any dryness and purification prior to use. Twice-distilled water was used throughout all the experiments.

All reactions were monitored by TLC. The TLC analysis was performed on silica gel plates and column chromatography was conducted over silica gel (mesh 200–300), both of which were purchased from the Qingdao Ocean Chemicals. NMR spectra were recorded on a Bruker AV-400 spectrometer, while using TMS as an internal standard. All pH measurements were performed with a PHS-3C digital pH meter. High Resolution Mass Spectra (HRMS) were obtained by a Waters LCT Premier XE spectrometer. The UV-vis absorption spectra were carried out on a Varian CARY 100 spectrophotometer at 37 °C. Photoluminescent spectra were recorded with Varian Cary Eclipse spectrophotometer equipped with quartz cell of 1 cm path length at 37 °C. The fluorescence quantum yields were determined on a Horiba Fluoromax-4 fluorescence spectrophotometer.

2.2. Synthesis preparation of DER-1

N,N-Diethylrhodol was synthesized according to the procedures reported in the literature [28,29].

Synthesis of **DER-1**. To a stirred solution of *N*,*N*-diethylrhodol (97 mg, 0.25 mmol) in dry CH_2Cl_2 (10 mL) was added Et_3N (0.1 mL, 0.75 mmol) under ice bath, and the resulting mixture was stirred

for about 10 min. Then a solution of allyl chloroformate (60 mg, 0.5 mmol) in CH₂Cl₂ (5 mL) was added dropwise to the above mixture. After being stirred for 30 min at 0°C, the mixture was heated to room temperature and stirred for another 1.5 h. Eventually the solvent was evaporated under reduced pressure, and the pale pink crude product was purified by column chromatography (pure CH₂Cl₂) on silica gel, affording the desired **DER-1** as a white solid (65 mg, yield 51%). ¹H NMR (400 MHz, DMSO): 1.09 (t, /=6.9 Hz, 6H), 3.36 (q, /=6.9 Hz, 4H), 4.75 (d, *I* = 5.6 Hz, 2H), 5.32 (dd, *I* = 10.5, 1.0 Hz, 1H), 5.42 (dd, *I* = 17.2, 1.4 Hz, 1H), 6.01 (ddd, J = 22.7, 10.8, 5.6 Hz, 1H), 6.54–6.45 (m, 3H), 6.83 (d, J = 8.7 Hz, 1H), 7.01 (dd, J = 8.7, 2.3 Hz, 1H), 7.37–7.29 (m, 2h), 7.74 (t, I = 7.3 Hz, 1H), 8.03 (d, I = 7.5 Hz, 1H), 7.81 (t, I = 7.1 Hz, 1H). ¹³C NMR $(100 \text{ MHz}, \text{ DMSO}): \delta(\text{ppm}) = 168.58, 152.27, 152.14, 152.01, 151.77,$ 151.48, 149.33, 135.63, 131.57, 130.19, 129.14, 128.64, 126.14, 124.68, 124.06, 119.03, 117.25, 117.16, 109.77, 109.81, 104.07, 96.82, 82.69, 68.99, 43.76, 12.25. HRMS (ESI, m/z) calcd for $[C_{28}H_{25}NO_6 + H]^+$ 472.1760; found 472.1754.

2.3. Preparation of stock solutions of probe and metal ions

Stock solutions of **DER-1** and Pd(PPh₃)₄ were prepared in THF with a concentration of 0.5 mM. The PdCl₂ solution was also prepared in THF, but with a concentration of 1.0 mM. The solutions of LiClO₄, CuCl, Ce(NO₃)₃, SnCl₂, ZnCl₂, CrCl₃, MnCl₂, AlCl₃, CoCl₂, NaCl, NiCl₂, CaCl₂, Pb(NO₃)₂, CuCl₂, MgCl₂, FeCl₃, Bi(NO₃)₃, KCl, AgNO₃, BaCl₂, Hg(OAc)₂, PtCl₂ were prepared in with a concentration of 1.0 mM. The solution of NaBH₄ was also prepared in twice-distilled water, but with a concentration of 10^{-2} M.

2.4. General spectrophotometric experiments

Both the fluorescence and UV–vis absorption experiments were conducted in PBS buffer solution (20 mM, pH = 7.4, 50% THF, v/v). Test solutions were prepared by placing 30.0 μ L of **DER-1** solution (0.5 mM), 1470.0 μ L of DMSO, and an appropriate aliquot of each analyte stock solution into a 3.0 mL test tube, and diluting the resulting solution to 3.0 mL with PBS buffer solution (20 mM, pH = 7.4). The slight pH variations of the solutions were achieved by adding the minimum volumes of NaOH (0.1 M) or HCl (0.2 M). The resulting solutions were well-mixed and kept at 37 °C for 60 min, and then the fluorescence spectra or UV–vis absorption spectra were recorded. For all the measurements of fluorescence spectra, excitation was performed at 500 nm with slit widths for excitation and emission of 5.0 and 5.0 nm, respectively.

2.5. Determination of detection limit

The detection limit was calculated by $3\delta/k$ method [30,31], where δ is the standard deviation of blank measurement and k is the slope between the fluorescence intensity versus **DER-1** concentration. In the absence of Pd⁰, the fluorescence emission spectrum of **DER-1** was measured 5 times and the standard deviation (δ) was achieved. To get the slope, the fluorescence intensity at 547 nm was plotted as a concentration of Pd(PPh₃)₄.

3. Results and discussion

3.1. Probe design and synthesis

It is well-known that the protection of the hydroxyl group of fluorophores can quench their fluorescence and the removal of functionalized reactive site can recover the fluorescent signals of the fluorophores [32]. Such phenomenon can be attributed to the remarked changes in electronic properties that induced by the protection-deprotection of functional groups. This strategy has been widely employed to develop reaction-based turn-on fluorescent probes.

A suitable protectable group is of quite importance. As is known to all that Pd⁰-catalyzed Tsuji-Trost allylic reaction was often adopted as an admirable mechanism to develop fluorescent probes for sensing of Pd⁰. To employ the mechanism for the selective and quantitative determination of Pd⁰, a terminal allyl carbamate was usually incorporated to a fluorescent group as the recognition unit. In our previous work, allyl carbamate moiety was incorporated to a coumarin derivative and the fluorescent molecule perform excellent selectivity and sensitivity towards Pd⁰ [33].

In order to further develop and improve the sensitivity and detection limit, we constructed **DER-1** for Pd⁰ sensing in mixed aqueous solution. In our scaffold, allyl carbamate was selected as the trigger moiety and *N*,*N*-diethylrhodol (**DER**) was the fluorescent emission group. **DER** was selected to be the fluorophore because they inherit all the excellent photophysical properties from fluorescein and rhodamine, such as high extinction coefficients, quantum yields, photostability, and good solubility, yet low pH-dependence. Moreover, convention of the O-substituted rhodol to O-free rhodol would induce an increase in fluorescence intensity, which is an ideal scaffold for developing turn-on fluorescent probes [34,35].

The desired probe **DER-1** was conveniently prepared according to the synthetic routine that outlined in Scheme 1. Firstly, *N*,*N*-diethylrhodol (**DER**) was prepared by the reaction of 2-(4-diethylamino-2-hydroxybenzoyl) benzoic acid with resorcinol following the reported procedure. Then, probe **DER-1** could be easily synthesized in a satisfactory yield by treating **DER** with allyl chloroformate in dry dichloromethane under basic conditions at room temperature, and its structure was confirmed by ¹H NMR, ¹³C NMR, and HRMS spectra(see ESI, Figs. S1–S3).



Fig 1. Absorption spectra of **DER-1** (5 μ M) in PBS buffer solution (20 mM, pH = 7.4) containing 50% THF in the absence (black) or presence (red) of Pd(PPh₃)₄ (2.0 equiv). Insert: color change of **DER-1** upon addition of Pd(PPh₃)₄. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2. Spectroscopic properties of DER-1 towards Pd⁰

The spectral properties of probe DER-1 were firstly examined in the absence and presence of Pd⁰ in PBS buffer (20 mM, pH = 7.4) containing 50% THF at 37 °C. Pd(PPh₃)₄ was selected as the resource of Pd⁰ in all experiments. The absorption spectrum of free probe **DER-1** shows no absorption bands beyond 400 nm, as shown in Fig. 1. However, treatment of **DER-1** (5 μ M) with 2.0 equiv. of Pd (PPh₃)₄ resulted in a remarkable change in the absorption spectrum. A new, high absorption peak at 520 nm with a shoulder around 491 nm appeared. Meanwhile, the solution color changed



Scheme 1. Preparation of probe DER-1.



Fig. 2. Fluorescence spectra of **DER-1** (5 μ M) in PBS buffer solution (20 mM, pH = 7.4) containing 50% THF in the absence (black) or presence (red) of Pd(PPh₃)₄ (2.0 equiv). Insert: fluorescent emission change (under UV light) upon addition of Pd(PPh₃)₄. λ_{ex} = 500 nm; slits: 5 nm/5 nm. (For interpretation of the references to colur in this figure legend, the reader is referred to the web version of this article.)

obviously from colorless to pink, which could facilitate naked-eye visual detection of Pd⁰ (inset Fig. 1).

Probe **DER-1** also exhibited excellent fluorescent signaling for Pd⁰. In the emission spectrum, **DER-1** (fluorescence quantum yield $\Phi < 0.001$) displays no fluorescence at 547 nm as expected when excited at 500 nm. The low fluorescent background was reasonably attributed to that **DER-1** existed predominantly in spirolactone form, and the spirocyclic form of rhodol was always colorless and nonfluorescent. However, treatment of probe **DER-1** with Pd (PPh₃)₄ triggered a dramatic turn-on fluorescence enhancement (>330-fold, Φ = 0.4182) at 547 nm and correspondingly an obvious bright green-yellow fluorescence was clearly observed (Fig. 2). Furthermore, Pd²⁺ species containing PdCl₂, Pd(PPh₃)₂Cl₂, Pd (OAc)₂ and Pd(CH₃CN)₂Cl₂ gave the similar responses under reducing conditions (NaBH₄-PPh₃) (see ESI, Fig. S4). Evidences available above meant that the designed probe possessed the



Fig. 3. Time-dependent fluorescence spectra of **DER-1** (5 μ M) upon addition of Pd (PPh₃)₄ (2.0 equiv.). The spectra were recorded in PBS buffer solution (20 mM, pH = 7.4) containing 50% THF at 37 °C. λ_{ex} = 500 nm; slits: 5 nm/5 nm.

potentiality of sensing both ${\rm Pd}^0$ and ${\rm Pd}^{2+}$ under reducing conditions.

For better understanding of the sensing ability of the designed probe towards Pd^0 , the time-dependent fluorescence intensity changes of probe **DER-1** in the absence and presence of $Pd(PPh_3)_4$ were studied. The fluorescence intensity of free probe **DER-1** displayed no noticeable changes with time, indicating that the proposed probe is quite stable under sensing environment. However, upon addition of 2.0 equiv. $Pd(PPh_3)_4$ to probe **DER-1** (5 μ M), it was obviously observed that the solution of **DER-1** afforded an initial fast, followed by gradual increase in emission intensity and it reached a plateau in about 75 min (Figs. 3 and S5). However, it could reach about 90% of the saturation in 60 min at established condition. In this work, 60 min was selected as the assay time for the evaluation of the sensitivity and selectivity of **DER-1** towards Pd^0 .

3.3. Ion selectivity and competitiveness

It is well known that the most important property of a probe is high selectivity towards the targeted analyte over other competitive species. To investigate the selectivity of probe **DER-1** towards Pd⁰ and other metal ions, the UV-vis absorption and emission spectra after addition of different metal ions such as Na⁺, K⁺, Cu⁺, Li⁺, Ag⁺, Mn²⁺, Co²⁺, Ba²⁺, Mg²⁺, Ca²⁺, Hg²⁺, Zn²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Pd² ⁺, Fe²⁺, Sn²⁺, Ce³⁺, Fe³⁺, Cr³⁺, Al³⁺, Bi³⁺, and Pd⁰ were recorded in PBS buffer. As shown in Fig. 4, only the addition of Pd⁰ induced remarkable signal changes in the UV-vis absorption and emission spectra. However, nearly no or little absorption and emission fluorescence changes were observed even in the presence of 10.0 equiv of above-mentioned metal ions. Specifically, a 330-fold fluorescence intensity enhancement at 547 nm was observed in the presence of Pd⁰, corresponding with the color change from colorless to pink that could be easily distinguished by naked eye (see ESI, Fig. S6). To further examine the selectivity of probe DER-1 towards Pd⁰, competitive experiments involving the effects of other mentioned metal ions in the determination of Pd⁰ were carried out, which indicated that the addition of various abovementioned metal ions promoted a negligible effect on Pd⁰ sensing (Fig. 5).

Nickel and Platinum exist in the same group in the periodic table as palladium, so they may possess similar chemical and physical properties. In other words, Ni (0) and Pt (0) have the highest possibilities to interfere the Pd⁰ detection process, if any. Considering all these above, the selectivity of **DER-1** to Ni²⁺, Pt²⁺, Ni (0), Pt (0) were also investigated. As shown in Fig. S7, nearly no or little changes were observed in their absorption and emission spectra even in the presence of 10.0 equiv. of these four species. These results did demonstrate that the proposed probe show an excellent selectivity towards Pd⁰ over other competitive metal ions. Clearly, the outstanding selectivity should be attributed to Pd⁰-triggered cleavage progress.

3.4. Effect of pH on the detection of Pd^{0}

It is generally known that ester group is susceptible to pH change and easily hydrolyzed under both acid and basic conditions. Therefore, studies of the pH effect on the fluorescent responses of probe **DER-1** were examined in the absence and presence of Pd(PPh₃)₄, respectively. As shown in Fig. 6, the designed probe was stable for quite a long time (over 60 min) in a wide pH range of 2.0–10.0 monitored at 547 nm. However, an obvious fluorescence intensity enhancement was observed above pH of 10.0, which should be attributed to hydrolysis of the probe under strong basic conditions. Once the probe **DER-1** (5 μ M) was incubated with 2.0 equiv Pd(PPh₃)₄, negligible fluorescence were



Fig. 4. UV-vis absorption (a) and fluorescence (b) spectra of **DER-1** (5 μ M) only and in the presence of Pd⁰ (2 equiv.), Na⁺, K⁺, Cu⁺, Li⁺, Ag⁺, Mn²⁺, Ca²⁺, Bg²⁺, Ca²⁺, Hg²⁺, Zn²⁺, Cu²⁺Ni²⁺, Pb²⁺, Pd²⁺, Fe²⁺, Sn²⁺, Ce³⁺, Fe³⁺, Cr³⁺, Al³⁺, and Bi³⁺ (10 equiv., respectively). The spectra were recorded at 1 h after addition of Pd⁰ in PBS buffer solutions (20 mM, pH = 7.4) containing 50% THF at 37 °C. $\lambda_{ex} = 500$ nm; slits: 5 nm/5 nm.

observed within the pH range 2.0–5.0, and weak fluorescence signal was obtained at pH 6.0. It suggested that $Pd(PPh_3)_4$ couldn't convert probe **DER-1** to ring-opening form **DER** in strong acid solutions. However, the fluorescence intensity at 547 nm showed distinct changes over a wide pH range of 7.0–11.0. The results indicated that the response of probe **DER-1** towards Pd⁰ were favorable at a wide pH range of 7.0–11.0 containing the physiological conditions, and that the probe **DER-1** could be selected as a candidate for Pd⁰ detection.

3.5. Sensitivity study

To further explore the recognition ability of probe **DER-1** towards Pd^0 , the absorption and emission titration experiments were carried out in PBS buffer (20 mM, pH=7.4) containing 50%

THF at 37 °C. As proposed, the probe **DER-1** (5 μ M) was incubated with different concentrations of Pd(PPh₃)₄ (0–3 μ M) under abovementioned condition and the absorption and fluorescence spectra were recorded after an interval of 60 min, respectively. The absorption band at 520 nm enhanced gradually with the increase of the concentration of Pd(PPh₃)₄, accompanied with an obvious color change from colorless to pink (Fig. 7a and Fig. S8a). Also, there was a good linearity of the absorption at 520 nm versus the Pd (PPh₃)₄ concentration (0–1.5 μ M) with R² = 0.98815 (Fig. 7b). Similarly, the addition of Pd(PPh₃)₄ to probe **DER-1** also led to significant fluorescent emission spectra changes; the fluorescence intensity recorded at 547 nm greatly enhanced with the increase of Pd(PPh₃)₄ concentration (Figs. 7 c and S8b). Furthermore, the plots of the fluorescence intensity at 547 nm fit linearly with the Pd (PPh₃)₄ concentration range of 0–1.5 μ M with a correlation



Fig. 5. Fluorescence intensity of **DER-1** at 547 nm in the presence of single metal ion (black) and a mixture of Pd⁰ (2 equiv.) and various metal ions (10 equiv.) (red). Data were acquired at 1 h after addition of various metal ions in PBS buffer solutions (20 mM, pH = 7.4) containing 50% THF at 37 °C. λ_{ex} = 500 nm; slits: 5 nm/5 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 6. The effect of pH on the fluorescence intensity changes of **DER-1** (5 μ M) at 547 nm in absence (black) and presence (red) of Pd(PPh₃)₄ (2 equiv.) in PBS buffer solution (20 mM, pH = 7.4, 1:1, v/v) at 37 °C. λ_{ex} = 500 nm; slits: 5 nm/5 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

coefficient of 0.9969 (Fig. 7d). The detection limit of **DER-1** (5 μ M) for the sensing of Pd⁰ was calculated to be as low as 1.14 nM according to a 3 δ method. This is sufficient sensitive for Pd⁰ detection in common chemical and industrial samples. Taking all these results together, **DER-1** displayed promising application prospects for the selective and sensitive detection of Pd⁰ with colorimetric and emission outputs.

3.6. Proposed sensing mechanism for the Pd⁰ detection

The excellent selectivity can be ascribed to the highly specific Pd⁰-triggered cleavage process. According to previously well-received sensing mechanism for Pd⁰ probes with an allyoxy allyoxycarbonyl group, it is expected that the trigger moiety of the allyl chloroformate unit is initially conjugated with palladium and ionized to form π -allylpalladium(II) **complex 1**, and then dissociating and decarboxylating to release the ring-opening **DER** under basic condition (Scheme 2) [36]. The presence or absence of Pd⁰ can be easily identified according to the absorption and fluorescence spectrum of testing samples, because **DER-1** and **DER** have different spectroscopic properties. Moreover, the fluorescence intensity at 547 nm is positively



Fig. 7. (a) UV-vis absorption spectra evolution of **DER-1** (5μ M) in terms of palladium concentrations ($0-3 \mu$ M). (b) Absorption intensity at 520 nm of probe DER-1 versus increasing concentrations of Pd⁰. (c) Fluorescence spectra evolution of probe **DER-1** (5μ M) in terms of palladium concentrations ($0-3 \mu$ M). (d) Fluorescence intensity at 547 nm of probe **DER-1** versus increasing concentrations of Pd⁰. All spectra were acquired at 1 h after Pd⁰ addition at 37 °C in PBS buffer solutions (20 mM, pH = 7.4) containing 50% THF. λ_{ex} = 500 nm; slits: 5 nm/5 nm.



Scheme 2. A proposed mechanism for Pd⁰ sensing by DER-1.

relative to Pd^0 concentration, and then the Pd^0 content can be determined. To confirm the proposed sensing mechanism, the reaction product of **DER-1** with $Pd(PPh_3)_4$ was isolated by column chromatography ($CH_2Cl_2:EtOH = 20:1$). The ¹H NMR and HRMS analysis indicated the free **DER** was produced during the detection process. (see ESI, Figs. S9 and S10). Moreover, the fact that both the absorption and fluorescence spectra of the test system after addition of $Pd(PPh_3)_4$ resembled those of free fluorophore **DER** further confirmed the above-mentioned sensing mechanism (see ESI, Fig. S11).

4. Conclusion

In this work, a novel reaction-based fluorescent probe with allyl carbamate as the recognition unit was rationally designed and synthesized for Pd⁰ sensing. The Pd⁰-triggered cleavage of allyl N, *N*-diethylrhodol carbonate to the parent rhodol was used as the basis of **DER-1** for colorimetric and fluorescent signaling of Pd⁰. Based on the Pd⁰-triggered cleavage reaction, the designed probe shows high sensitivity and selectivity towards Pd⁰ in PBS buffer solution under mild condition at 37 °C. Upon addition of 2.0 equiv. Pd(PPh₃)₄ into DER-1 (5 µM), a 330-fold fluorescence enhancement was observed, and corresponding to a marked color change from colorless to pink which can be identified by naked-eye. Meanwhile, the detection limit of **DER-1** for Pd⁰ sensing was calculated to be as low as 1.14 nM. Moreover, the probe is guite stable in a wide pH range. All these above demonstrate its potential usefulness as a molecular probe for Pd⁰ detection in industry, laboratory, and environment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2017.01.007.

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