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A coumarin-based fluorescent probe for the fast detection of Pd^0 with low detection limit

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Abstract

A off-on coumarin-based fluorescent probe for the fast detection of Pd^0 is designed and synthesized. The probe shows not only good selectivity but also fast response to Pd^0 in phosphate buffered saline (PBS) solution. The absorption band at 412 nm rises sharply as well as the fluorescence at 450 nm after the addition of Pd^0 within few minutes. The detection limit is as low as 0.34 nM. The probe shows nonfluorescence when it conjuncted with allyl carbonate ester which destroys the Intramolecular Charge Transfer (ICT) system. The effect of Pd^0 to the probe can change the structure and make the departure of the conjuncted allyl carbonate ester. As a result, the fluorogen is exposed and it shows fluorescence.

Key words: Pd^0; fluorescent probe; coumarin; low detection limit

1. Introduction

With the development of modern industry, heavy and transition-metal(HTM) has been widely used in many fields such as chemistry, biology and environmental science.[1-6] Among all these heavy and transition-metal, palladium plays crucial roles in various fields because it is a perfect catalyst which has excellent ability of forming stable bonds. Recently, it is widely used in the synthesis of drugs[7] and disposing automobile exhaust. What's more, palladium is also widely used in the preparation of dental materials and fine jewellery[8]. However, even after purification of the final products, 300-2000 ppm of residual palladium is still left which is much higher than the specific threshold in drugs(5-10 ppm)[9]. It is well known that palladium can cause serious health hazard by forming palladium complex with thiol-containing proteins(such as casein, silk fibroin), DNA and RNA[10,11] and other macromolecules(Vitamin B_6)[12]. Therefore, governmental restriction for the threshold level of palladium in drugs is as low as 5-10 ppm[9]. Therefore, it seems to be urgent to develop sensors for the fast and selectively detection of palladium. Some methods such as atomic absorption spectroscopy(AAS), solid phase microextraction-high performance liquid chromatography, X-ray fluorescence, and plasma emission methods have been developed to test palladium, however, they all suffer from high cost of instruments and require good training individuals.

Fluorescent probe, on the other hand, has received much attention for the detection of palladium[13] and different metal ions[14,15] because of its obvious advantages. Their high sensitivity, relatively simple analysis protocols[16-20] and far less expensive makes it more adaptable in bioimaging analysis in vivo or even in living cells[21-24]. Consequently, many fluorescent probes for the detection of palladium have been designed. Zhu[25] etc. designed a naked eye and ratiometric probe which can detect palladium in the near-infrared region with the detection limit to be 0.3 ppb. Also, the modulation of the p-conjugated

electrons in cyanine dyes can result in a ratiometric fluorescence change with a large Stokes shift (270 nm). Liu[26] etc presented a reactive fluorescent probe for the colorimetric and ratiometric detection of palladium. The probe displays highly sensitive and selective response to palladium with the detection limit to be 6.1 nM. Likewise, another probe by Liu[27] was also reported. The probe has the similar structure but has good solubility in water which can be tested in phosphate buffer saline(PBS) containing less than 1% organic cosolvent without adding any additional reagents with the low detection limit of 25 nM. Ahn[28] etc synthesized a fluorescent probe for the detection of palladium species based on fluorescein. It is the first fluorescent probe which can be used in living organisms. Lin[29] etc designed a NIR fluorescent probe for the detection of palladium species based on a HD NIR fluorophore with high sensitivity and selectivity. Meanwhile, the probe can be introduced in cells for the detection of palladium species. Qian[30] etc designed a ratiometric probe for the detection of palladium species with large stoke shift while Yin[31] etc synthesized a ratiometric probe for the detection of palladium with the detection limit of 12 nM. Peng[32] etc described a turn-on fluoresent probe for the detection of palladium species by forming clathrate.

Herein, we design a fluorescent probe for the detection of Pd^0 with the high sensitivity and selectivity. What's more, the detection limit can reach to 0.34 nM. Like many papers[33-36], our probe is also based on the ICT system. The probe showed nonfluorescence when Connecting with allyl carbonate ester while the fluorescence appears when it reacts with Pd^0. The process makes the absorption at 412 nm increase sharply as well as the fluorescence at 450 nm. Palladium is the only metal which can react with the probe while the other metal ions can not.

2. Experiment

2.1 Chemicals and instrumentals

2, 4-dihydroxybenzaldehyde was purchased from Energy Chemical and used directly without any purification. The other chemicals were of the highest grade available and were used without further purification. All employed solvents were analytical pure and were employed without any further drying or purification.

Reactions were monitored by TLC. ^{1}H NMR and ^{13}C NMR spectra were recorded on Brucker AM-400 MHz instruments with tetramethylsilane as internal standard. ESI was performed using a Waters LCT Premier XE spectrometer. Absorption spectra were carried out on a SHMADZU UV-Vis spectrophotometer. Fluorescence spectra were measured on a SHMADZU RF-5301PC Fluorescence spectrophotometer.

2.2 Preparation and characterization of 1

Compound 1 was synthesized according to the reported papers[37-39]. 2-4-dihydroxybenzaldehyde 2.76 g(20 mmol) and diethylmalonate 6.4 mL(40 mmol) were mixed together in 30 mL anhydrous ethanol. 1.5 mL piperidine was added to the above solution dropwise after that. The whole mixture was refluxed for 12 h after which the solvent was evaporated. The product was extracted with CH_2Cl_2, washed with brine and purified by column chromatography to give compound 1 as a white yellow solids(4.1 g 12.89 mmol). ^{1}HNMR(400 MHz, DMSO) δ 8.677(s,1H), 7.768(d, J=8, 1H) 6.84(dd, J=4, 1H), 6.73(d, J=1.2,1H), 4.26(q, 2 H), 1.29(t, J=8, 3H) (Fig.S1). ^{13}C NMR δ 164.03, 162.91, 157.07, 156.37, 149.41, 132.08, 113.97, 112.04, 110.39, 101.75, 60.77, 39.47, 14.10 (Fig.S2). HRMS: 257.0422 , calcd for: 257.0426 (Fig.S5). Yield: 64.5%.

2.3 Preparation and characterization of probe PC

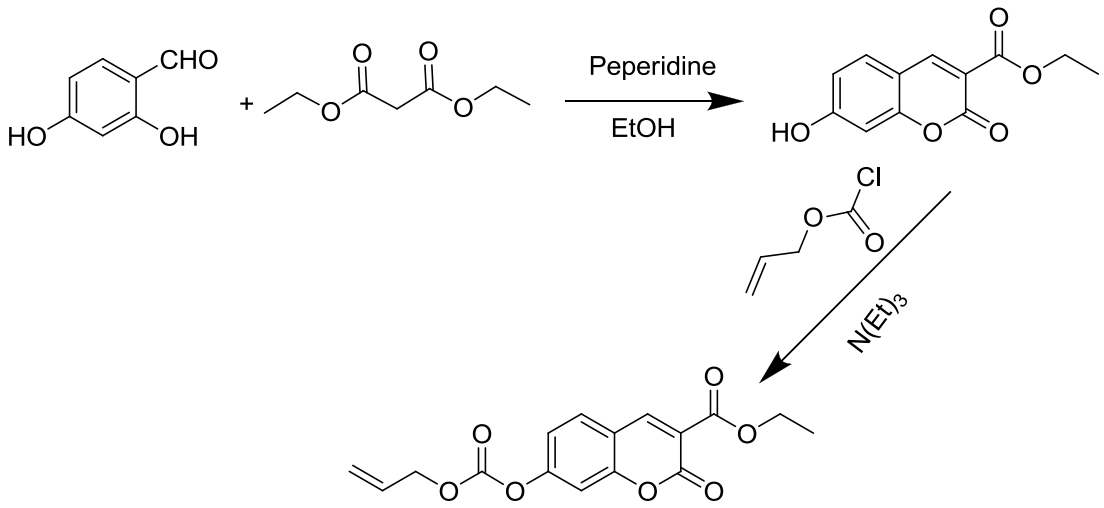
Using the method of the reported literature[40], probe PC was synthesized. A mixture of 0.234 g(1 mmol) compound 1 and triethylamine 0.27 mL (2 mmol) in 10 mL CH_2Cl_2 was stirred under an ice

bath. 65 μL(1.08 mmol) allyl chloroformate in 5 mL CH_2Cl_2 was added dropwise to the above solution. The whole mixture was stirred in an ice bath for 4 h and the solvents were evaporated after that. The solid was purified by column chromatography to give probe PC as a white solid(0.18 g, 0.56 mmol). ^{1}HNMR(400MHz, DMSO) δ 8.79(s, 1H), 8.00(d, J=8, 1H), 7.48(d, J=4, 1H), 7.45(dd, J=8, 1H), 6.0(m, 1H), 5.38(dd, J=4, 2H), 4.77(d, J=8, 2H), 4.3(q, 2H), 3.09(t, J=4, 3H) (Fig.S3). ^{13}C NMR 166.44, 155.65, 155.19, 154,65, 151.86, 148.18, 131.45, 119.15, 118.39, 116.99, 115.95, 109.38, 69.19, 61.23, 39.88, 14.01 (Fig.S4). HRMS: 342.0771, calcd for : 342.0775(Fig.S6). Yield: 56%.

3. Results and discussion

3.1 Synthesis

The synthetic routine of probe PC is outlined in Scheme 1. By two simple steps, we can get probe PC with high yields. Coumarin derivate 1 is in high yields and it displays excellent fluorescence. The esterification reaction by connecting an allyl carbonate ester makes the disappearance of the strong fluorescence. The above reaction destroyed the ICT structure. When the probe encounters palladium, the interaction of palladium with double bond makes the separation of the allyl carbonate ester with coumarin. As a result, the fluorogen is exposed. The spectroscopic properties of probe PC were all tested in aqueous phosphate buffered saline (PBS) solutions(10mM, pH=7.4) containing 50% DMSO in the concentration of 10^{-5} M.



Scheme1. The synthesis procedure of the probe PC

3.2 The response time towards Pd^0

The time-dependent absorption and fluorescence intensity changes of probe PC after adding 5 equiv of Pd^0 is tested To confirm when will the probe get saturated after adding 5 equiv of palladium ($Pd(PPh_3)_4$ is the source of palladium). The probe PC is in the concentration of 10^{-5} M which is in the solution of phosphate buffered saline (PBS) containing 50% DMSO. 5 equiv of Palladium(Pd^0) is added to the above solution, and absorption spectra and fluorescence spectra are collected as shown in Fig.1. As it can be seen in Fig.1(a) that probe PC has nearly none absorption at 412 nm without Pd^0. However, the adding of Pd^0 makes the absorption at 412 nm increase a lot in one minute and grow gradually with time going on. Then the relationship between time and the changes of absorption at 412 nm is showed in Fig.1(b). The whole reaction can get saturation within 30 min as can be seen in Fig.1(b). The reaction rate is slowly decreased with the time going on corresponding to the smoothness of the curve in the figure. Likewise, the fluorescence is also collected in the same way with the excitation at 400 nm. The fluorescence shows the same tendency with the absorption as shown in Fig.1(c). The fluorescence at 452 nm increases gradually. Similarly, the relationship between time and the changes of fluorescence is collected as Fig.1(d). The difference is that the fluorescence intensity

changes more quickly. The fluorescence intensity increases obviously within 30 seconds and get saturation in 15 min which can be seen in Fig.1(d). All of this shows a rapid detection of Pd^0 which can be used in the practical application.

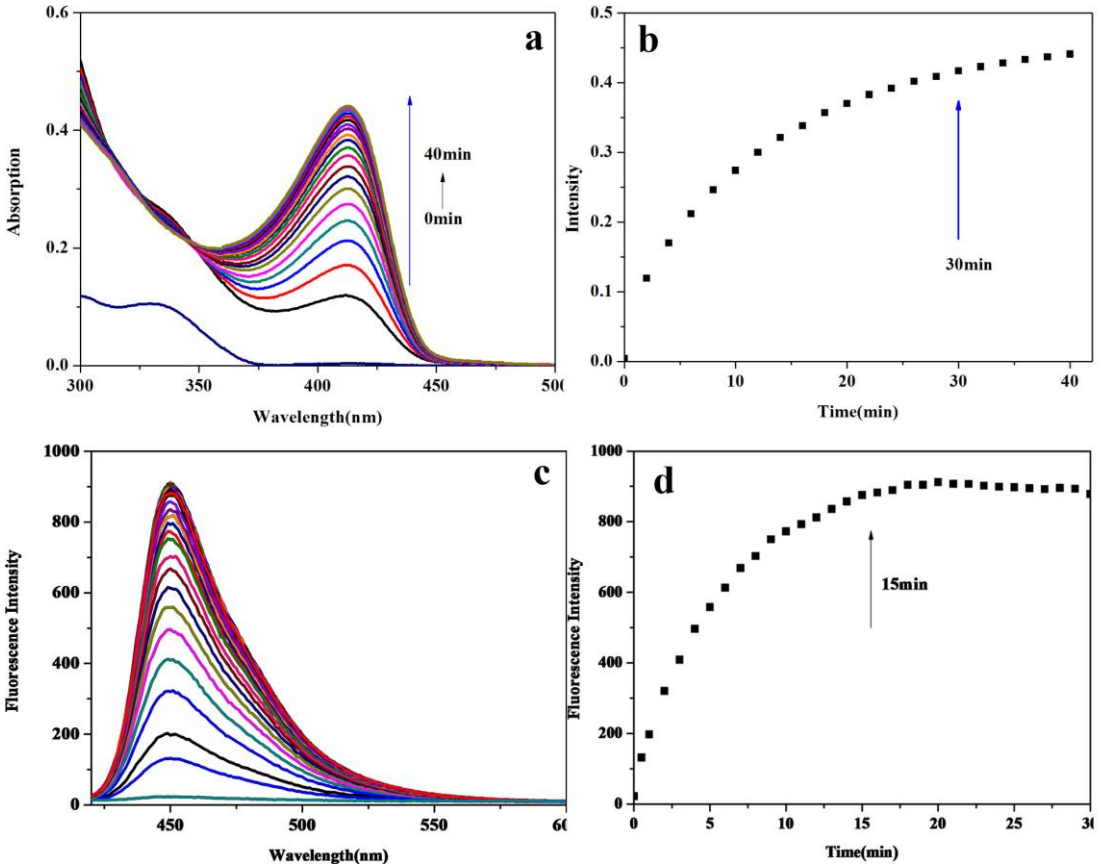


Fig.1. (a) Time-dependent absorption changes of probe PC after adding 5 equiv. of Palladium($Pd^{0)}$. (b) The changes of absorption intensity at 412 nm in the time range of 0 min-40 min. (c) Time-dependent changes of fluorescence intensity of probe PC after adding 5 equiv. Palladium(Pd^0) when excited with 400 nm. (d) The changes of fluorescence intensity at 452 nm in the time range of 0 -30 min. The spectroscopic properties of probe PC were tested in aqueous phosphate buffered saline (PBS) solutions(10mM, pH=7.4) containing 50% DMSO in the concentration of 10^{-5} M.

3.3 The selectivity towards different metal ions

As we all know, the selectivity towards only one ion is of vital importance for a good probe. Then the selectivity towards different ions is tested. The selectivity towards different ions is shown in Fig.2. $CaCl_2$, $CuCl_2$, $FeCl_3$, $HgCl_2$, $CoCl_2$, $NiCl_2$, $ZnCl_2$, $PbCl_3$, NaCl, KCl, $AgNO_3$, $MnCl_2$, $AlCl_3$, $BaCl_2$,

$Cr(NO_3)_3$ are used as the source of other metal ions and $Pd(PPh_3)_4$ is the source of palladium which is dissolved in water and THF, respectively. The probe is dissolved in the concentration of 10^{-5} M in the solution of phosphate buffered saline (PBS) containing 50% DMSO. 100 equiv of other ions and 5 equiv of palladium(Pd^0) is added to the above solutions respectively. The spectra of absorption and fluorescence are tested 30 min later after the adding of different ions. It can be found from the absorption spectra that only Pd^0 can cause the increase in 412 nm(Fig.2(a)) while the other ions can not. The fluorescence changes is also tested with the same conditions(Fig.2(b)). It can be seen that nearly no fluorescence can be found with other metal ions while Pd^0 can cause the fluorescence increase obviously. All these data demonstrate that the probe PC has a good selectivity towards Pd^0 over other metal ions. Thus, the probe has metal ion specificity. However, only metal ion specificity for a good probe is not enough. Many metal ions are mixed together whether they are in river or in other places. Therefore, it is very important for the detection of a specific ion without the interference of other metal ions, especially when the other metal ions are in good quantity. Then, the effect of other metal ions is tested. First, the probe PC is dissolved in phosphate buffered saline (PBS) containing 50% DMSO in the concentration of 10^{-5} M. 100 equiv of different metal ions are added to the above solution respectively. The fluorescence is tested and collected after 30 min, which is shown in Fig.3. The fluorescence intensity after adding 100 equi of other metal ions is corresponding to the left bar in the figure. All the solutions show nearly nonfluorescence. 5 equiv of palladium(Pd^0) is added to the above solutions respectively. The fluorescence is investigated and collected after 30 min as shown in Fig.3. The fluorescence intensity after adding 5 equiv of palladium(Pd^0) is corresponding to the right bar in the figure. It can be seen that the probe PC can still detect Pd^0 even with adding quantity of metal ions. All this proved that this sensing for Pd^0 is hardly interfered by other metal ions as can be seen in Fig.3.

There's little influence to the detection of Pd^0 even with quantity of other metal ions.

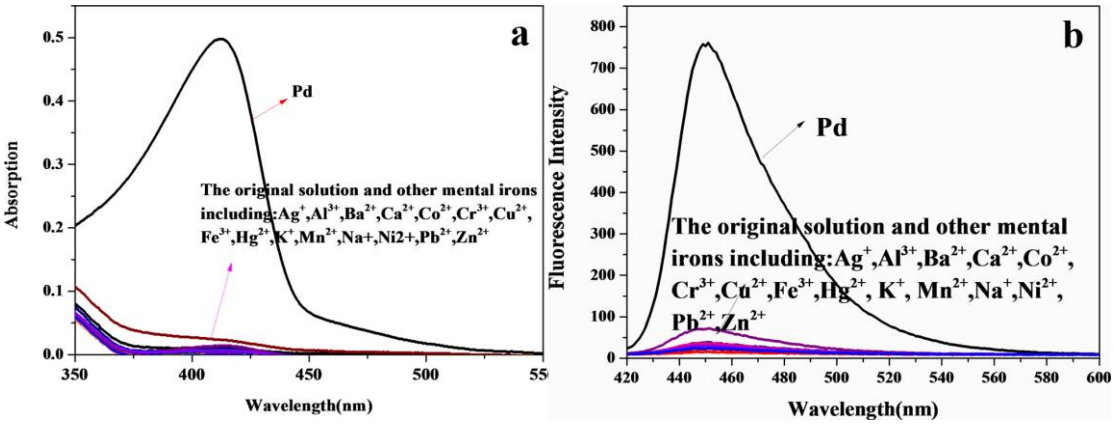


Fig.2. (a) Absorption of probe PC and probe PC in the presence of different ions including Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, K^+, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+} and Zn^{2+}; (b) Fluorescence intensity of probe PC and probe PC in the presence of different ions including Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, K^+, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+} and Zn^{2+} with excitation at 400 nm. Other metal ions are in the quantity of 100 equiv and Pd^0 is in the quantity of 5 equiv. The spectroscopic properties of probe PC were measured in aqueous phosphate buffered saline (PBS) solutions(10mM, pH=7.4) containing 50% DMSO in the concentration of 10^{-5} M.

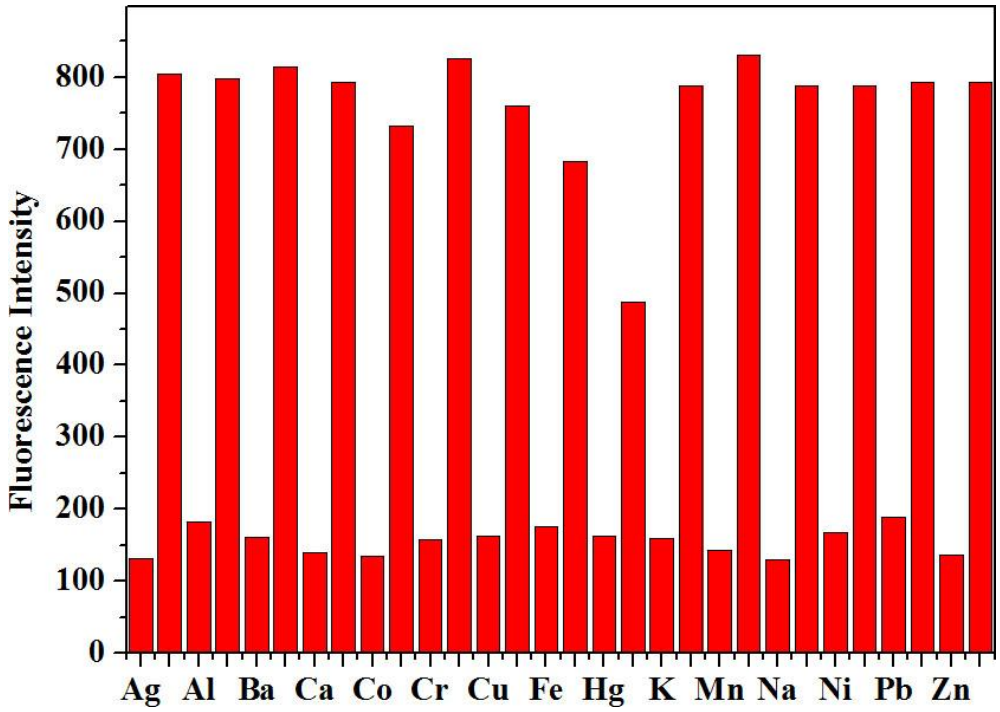


Fig.3. Effect of metal ions. The fluorescence intensity changes of probe PC in the presence of 100 equiv of various of cations. The short bar in the left is the fluorescence intensity of probe PC with other ions in the concentration of 1μM. The ions including Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Hg^{2+},

K^+, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+} and Zn^{2+}. The high bar in the right is the fluorescence intensity of probe PC with the adding of 5 equiv Pd^0 to the above solutions. The spectroscopic properties of probe PC were measured in aqueous phosphate buffered saline (PBS) solutions(10 mM, pH=7.4) containing 50% DMSO in the concentration of 10^{-5} M.

3.4 pH effect to the probe and probe PC

In our surrounding atmosphere, the pH is varied in a wide range and it also has slight variation in human bodies. Therefore, it is very important for a fluorescent probe to be stable in a wide range of pH. At least, it must be stable in physiological environment. Therefore, pH effect on the fluorescence behavior of Probe(PC) and Probe PC with Pd^0 is investigated. A wide pH range from 2 to 12 is adjusted using phosphate buffered saline (PBS) solutions(10 mM, pH=7.4). Then, probe PC is dissolved in the prepared phosphate buffered saline (PBS) solutions(10 mM, pH=7.4) using 50% DMSO as good solvent and then 5 equiv of Pd^0 is added to the above solutions. The spectra of probe PC and probe PC with Pd^0 are measured after 30 min and the fluorescence spectra are collected as shown in Fig.4. In a wide range of pH from 2 to 12, it can be seen that Probe PC is stable in a wide pH range from 2 to 10. When the pH is higher than 10, hydrolysis is occurred which results in the increase of fluorescence. This prove that probe PC can be used in physiological environment. What's more, in a pH range of 6 to 12, probe PC can detect Pd^0 with slight interference of the pH changes which can be used in physiological environment.

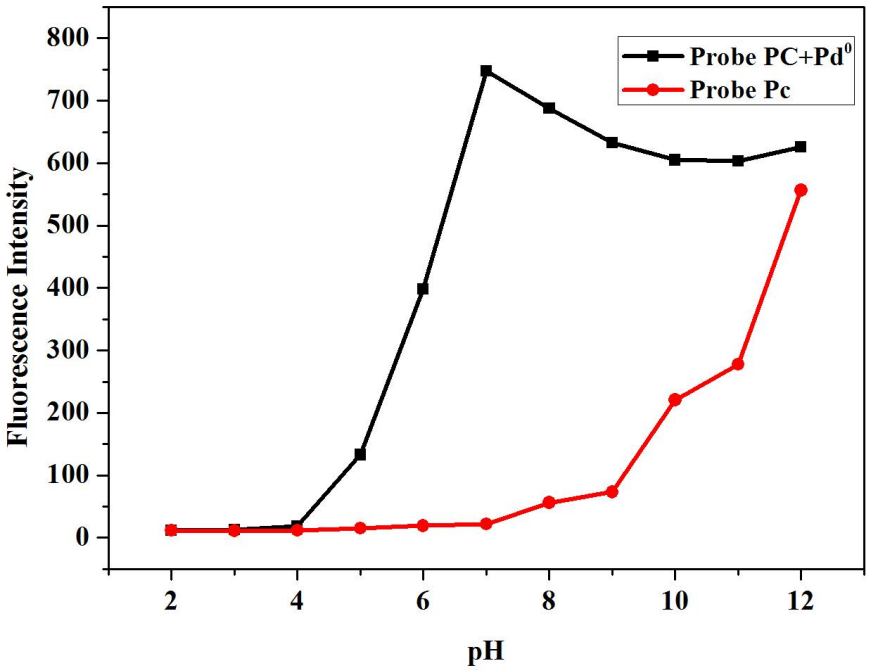


Fig. 4. pH effect on the fluorescence behavior of probe PC(red line) and probe PC with Pd^0(black line). The fluorescence spectra were collected with the excitation at 400 nm. The spectroscopic properties of probe PC were tested in aqueous phosphate buffered saline (PBS) solutions(10 mM, pH=7.4) containing 50% DMSO in the concentration of 10^{-5} M.

3.5 Determination of the detection limit

To calculate the detection limit, titration of of Pd^0 (0-0.18 μmol) to the probe PC solution is investigated. Probe PC is dissolved in phosphate buffered saline (PBS) solutions(10 mM, pH=7.4) containing 50% DMSO in the concentration of 10^{-5} M. 0.2 μmol, 0.4 μmol, 0.6 μmol, 0.8 μmol, 1 μmol, 1.4 μmol, 1.8 μmol and 2 μmol Pd^0 were added to the solution respectively. Upon the titration of Pd^0(Fig.5(a)), the fluorescence at 450 nm increases gradually. The detection limit is calculated based on the fluorescence titration and is calculated by the equation: detection limit=3σ/k. Where σ is the standard deviation of blank measurement, k is the slope between the fluorescence intensity versus Pd^0 concentration. The fluorescence intensity of probe PC is measured by 15 times and the standard deviation(σ) of blank measurement is obtained. To get the slope, the fluorescence intensity at 450 nm is

plotted as a concentration of Pd^0 as shown in Fig.5(b). And the detection limit is calculated to be 0.34 nM which is much lower than the Pd^0 concentration of threshold in drugs.

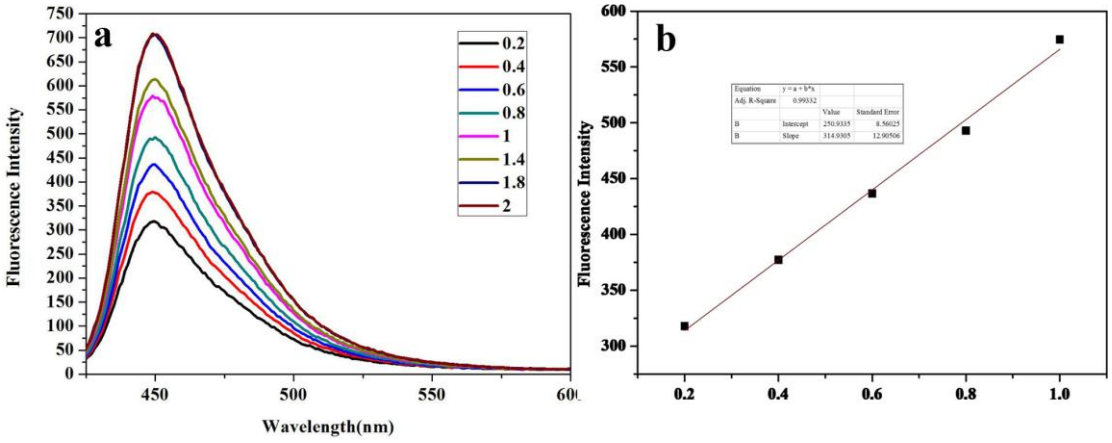


Fig.5. (a) Fluorescence response upon titration of Pd^0 (0-0.18 μmol) with excitation at 400 nm taken after 30 minutes. It is from 0.2 equiv to 2 equiv from the bottom to the top. (b) Fluorescence intensity versus concentration of Pd^0(pd: 0-0.18 μmol) at 450 nm with excitation at 400 nm taken after 30 minutes. The spectroscopic properties of probe PC were measured in aqueous phosphate buffered saline (PBS) solutions(10 mM, pH=7.4) containing 50% DMSO in the concentration of 10^{-5} M.

3.6 The proposed mechanism for the detection of Pd^0

Pd^0 is capable of catalyzing the allylic oxidative insertion to cleave the allylic C-O bond of allylic ethers to complex. These complexes then react with various nucleophiles which is know as Tsuji-Trost reaction[41,42]. The excellent selectivity towards Pd^0 should be attributed to the highly specific Pd^0-triggered cleavage process. As shown in Fig.6, the probe shows no fluorescence when conjugated with an allyl carbamate group. However, when Pd^0 is added, they will react with the allyl carbamate group of the probe PC and ionize to form π-allylpalladium(II) complex 2 and further transferring the allyl unit to morpholine as the nucleophile, and then producing carbamate 3. Finally, decarboxylation of the compound delivers the compound 1 with strong blue fluorescence. To further prove the mechanism of the reaction, the reaction of probe PC with $Pd(PPh_3)_4$ was conducted under the same conditions and the products were subjected to mass spectral analysis. The peak at m/z 257.0442

corresponding to compound 1 was observed, which proved the proposed mechanism(Fig.S7).

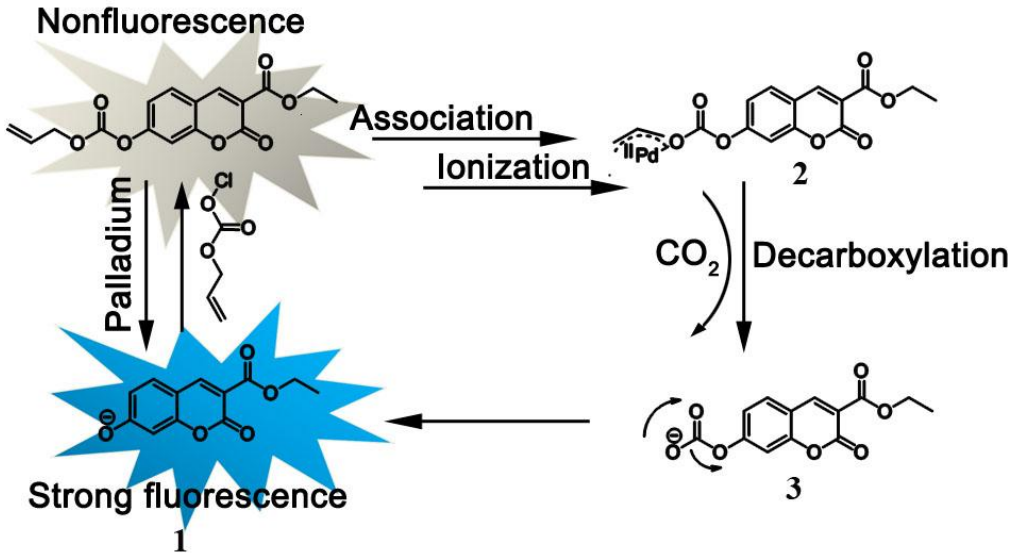


Fig. 6. Mechanism for the detection of palladium

4. Conclusions

In summary, we have designed and synthesized a fluorescent probe for the fast detection of Pd^0 based on coumarin. The synthesized probe shows not only good selectivity but also fast response to Pd^0 in phosphate buffered saline (PBS). The absorption at 412 nm rises sharply as well as the fluorescence intensity at 450 nm after the addition of Pd^0 within few minutes. The detection limit can be as low as 0.34 nM. The probe shows nonfluorescence when connected with allyl carbonate ester which destroys the ICT system. The effect of Pd^0 to the probe can change the structure. As a result, the fluorophore is exposed and it shows fluorescence.

Acknowledgment

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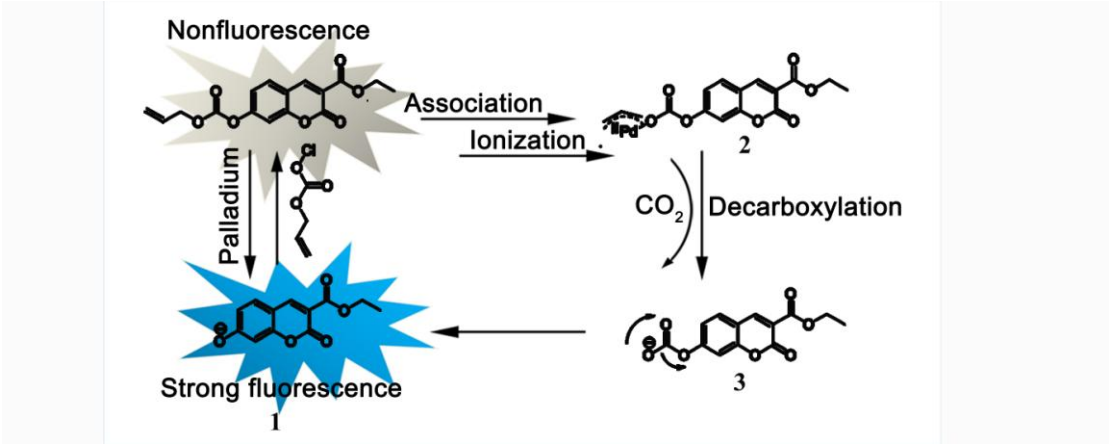
Graphical abstract



We design a fluorescent probe for the detection of palladium with the high sensitivity and selectivity. The probe shows nonfluorescence when connected with allyl carbonate ester which destroys the ICT system. The effect of palladium to the probe can change the structure. As a result, the fluorophore is exposed and it shows fluorescence.

Highlights:

1. A coumarin-based fluorescent probe for the detection of Pd^0 is designed and synthesized.

2. The probe shows good selectivity towards Pd^0 compared with many other ions

3. The probe can detect Pd^0 even with the disturbance of quantity of other metal ions.

4. The detection limit is as low as 0.34 nM which is lower than the specific threshold in drugs.