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A colorimetric and ratiometric fluorescence probe for detection of palladium in the red light region

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Developing probes for selective and sensitive detection of palladium in living organisms is of great importance. In this work, we synthesized a colorimetric and ratiometric fluorescence probe (Probe 1) with red light emission (λ_{em} = 643 nm) by employing isophorone based fluorescent dye as fluorophore and allylcarbamate group as response unit. Based on the Pd^0-triggered cleavage reaction, Probe 1 showed high response speed, selectivity, and sensitivity towards palladium species. Upon addition of palladium, the absorption and emission spectra of Probe 1 exhibited obvious red-shift, which can be easily discriminated by naked eyes. In terms of palladium, the detection limit is as low as 24.2 nM and the signal-to-noise ratio in fluorescence intensity can reach 85-fold. As a red emitting ratiometric sensor, Probe 1 can be potentially used for quantitative detection of palladium in living organisms.

Indruction

Palladium, a rare inner transition metal, is widely used in various materials such as dental crowns, catalytic converters, fuel cells, and jewellery as precious metal.[1–3] Despite the importance of palladium in such applications, subsequent damage to organisms with its frequent use (synthetic, medic inal and bioorthogonal organometallic chemistry) is a major downfall.[4] It can bind to DNA, protein, and other biomolecules, which disturbs biological processes.[5–7] Intracellular palladium is emerging as an exogenous metal that is of interest in recent years for those involved in BOOM chemistry (to unmask bioactive compounds upon the addition of palladium) and drug delivery.[8] Therefore, it is significant to develop some selective and sensitive methods for detection of palladium and its derivatives.[9] Several typical analytical methods, such as atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS), solid phase micro extraction-high performance liquid chromatography and X-ray fluorescence, have been used for the quantitative detection of palladium species.[10,11]

Among different analytical methods available, fluorescent imaging is considered to be the most sensitive approach because of its sensitivity and simplicity.[12] According to the recent reports, colorimetric and ratiometric fluorescent probes have many advantages such as the convenience and aesthetic appeal.[13–18] Particularly, ratiometric measurements have the important feature of permitting signal rationing, which can increase the dynamic range and provide built-in correction for environmental effects.[19,20] However, most of the palladium probes via fluorescence turn-on response have two main shortages: one is the single detection window, which always influences its quantitative detection because of environmental effects; the other is the short excitation wavelength, which limits their application in vivo.[21–26] Therefore, it is of significant importance to develop some ratiometric palladium probes that can emit in the red or NIR light region, because the longer wavelength fluorescence would not be disturbed by the auto-fluorescence taking place in indigenous biomolecules of the living systems.[27,28]

Isophorone based fluorescent dyes are well known for its excellent properties in Dye-sensitized solar cells and organic nonlinear optical crystals.[29–32] These dyes basically have typical donor-π-acceptor (D-π-A) structure, longer emission wavelength in the red (or NIR) region, and large Stokes shift from the ultrafast intramolecular charge transfer (ICT).[33] However, to the best of our knowledge, isophorone based fluorescent dyes have not been employed in fluorescence sensors. Herein, we designed a novel colorimetric and ratiometric palladium sensor (Probe 1) emitting in the red region (Scheme 1) by employing isophorone based fluorescent dye as the fluorophore and allylcarbamate group as the response unit. After reaction with palladium, the allylcarbamate group can cleave the carbamate linkage and release the amino group.[34] The probe can meet the criteria of both emitting in the red wavelength region and quantitative visual detection. At the same time, it showed high sensitivity and selectivity toward palladium.

Experimental

Synthesis of compound 3[35]

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Isophorone (5.0 g, 36.2 mmol) was dissolved in absolute EtOH (50.0 mL), followed by addition of malononitrile (2.87 g, 43.4 mmol) and piperidine (0.5 g, 4.8 mmol). Then, the mixture was refluxed for 12 h under N_2 atmosphere. After the solvent being removed, the precipitation was dissolved in CH_2Cl_2, washed with water, and dried over Na_2SO_4. Finally, the solvent was evaporated in vacuum, and the raw product was purified by silica column chromatography under Petroleum/Ethyl acetate = 5:1(v/v) to give a white solid (4.72g, 70%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.61(s, 1H), 2.51 (s, 2H), 2.19 (s, 2H), 2.04 (s, 3H), 1.01 (s, 6H) (Fig. S1). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 170.51, 160.06, 120.50, 113.22, 112.44, 78.04, 45.60, 42.61, 32.36, 27.79, 25.32 (Fig. S2).

Synthesis of Compound 2[36]

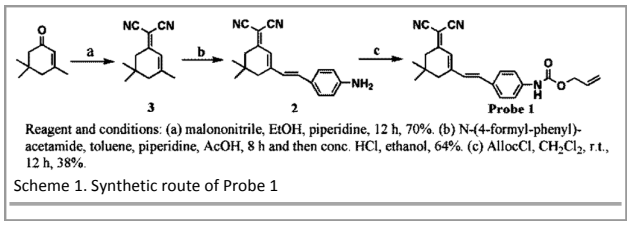
Under nitrogen atmosphere, compound 3 (300 mg, 1.6 mmol) and N-(4-formyl- phenyl) acetamide (263 mg, 1.6 mmol) were added to toluene (20 mL) containing piperidine (0.3 mL) and acetic acid (0.3 mL). Subsequently, the above mixture solution was refluxed for 8 h to give an orange precipitate. After filtration, the orange solid was refluxed in a mixed solution of concentrated HCl (20 mL) and ethanol (10 mL) for another 16 h. Then, the pH of the solution was adjusted to neutral and it was extracted with ethyl acetate. Finally, the organic layers were dried over Na_2SO_4, filtered, and concentrated to obtain the crude product, which was purified by silica column chromatography using CH_2Cl_2 as an eluent to yield Compound 2 (crimson solid, 340 mg, 64%). 1H-NMR (400 MHz, CDCl3): δ = 7.41 (d, J = 8 Hz, 2H), 7.10 (m, 2H), 6.70 (s, 1H),6.57 (d, J = 8 Hz, 2H), 5.87 (s, 2H), 2.55 (s, 2H), 2.49 (s, 2H), 1.00 (s, 6H) (Fig. S3). 13C-NMR (100 MHz, DMSO): δ = 169.80, 157.46, 151.34, 139.75, 130.12, 123.35, 119.94, 114.53, 113.76, 113.71, 72.69, 42.98, 39.69, 31.58, 27.43 (Fig. S4). HRMS (ESI): calcd. for $[C_{19}H_{19}N_3 + H]^+$ 290.1657; found 290.1657 (Fig. S5).

Synthesis of Probe 1

At 0 °C, a mixture of allocCl (1.0 mL) and CH_2Cl_2 (5 mL) was added dropwise to a solution of CH_2Cl_2 solution (15 mL), Compound 2 (200 mg, 0.69 mmol), and triethylamine (0.5 mL). After being stirred for 30 min, the mixture was heated to room temperature and stirred overnight. Then, the mixture was concentrated under vacuum and the crude product was purified by silica column chromatography under Petroleum/CH_2Cl_2 = 1:1 (v/v) to give a yellow solid (98 mg, yield: 38%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.99 (s, 1H), 7.64 (d, J = 8 Hz, 2H), 7.51 (d, J = 8 Hz, 2H),7.25 (m, 2H), 6.82 (s, 1H), 6.00 (m, 1H), 5.37 (dd, J = 4 Hz, J = 8 Hz, 1H), 5.25 (dd, J = 4 Hz, J = 8 Hz, 1H), 4.63 (d, J = 8 Hz, 2H), 2.59(s, 2H), 2.52 (s, 2H), 1.01 (s, 6H) (Fig. S6). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 170.21, 156.19, 152.98, 140.53, 137.49, 130.11, 122.02, 117.72, 113.96, 113.16, 75.70, 64.81, 39.68, 38.10, 31.62, 27.39 (Fig. S7). HRMS (ESI): calcd. For $[C_{23}H_{23}O_2N_3\text{-}H]^+$ 372.1712; found 372.1710 (Fig. S8).

Characterization and Detection

^{1}H NMR and ^{13}C NMR spectra were recorded on Brucker AM-400 MHz instruments with TMS as internal standard. HRMS was performed on Waters LCT Premier XE spectrometer. UV–Vis absorption spectra of the samples were conducted on a SHIMADZU UV–Vis spectrophotometer. The fluorescence spectra were measured with a SHIMADZU RF-5301PC fluorescence spectrophotometer by using 472 nm line of Xe lamp as excitation source at room temperature.



Reagent and conditions: (a) malononitrile, EtOH, piperidine, 12 h, 70%. (b) N-(4-formyl-phenyl)-acetamide, toluene, piperidine, AcOH, 8 h and then conc. HCl, ethanol, 64%. (c) AllocCl, CH_2Cl_2, r.t., 12 h, 38%.

Scheme 1. Synthetic route of Probe 1

The detection limit of Probe 1 was calculated according to the previous report.[37-40] The fluorescence emission spectrum of Probe1 was measured by five times to achieve the standard deviation (σ) of blank measurement.[21] In order to obtain the slope (S), the ratio of the fluorescence intensity at 570 nm and 643 nm were plotted as a function of palladium concentration (0−1 μM). The detection limit was calculated with the following formula: 3σ/S.

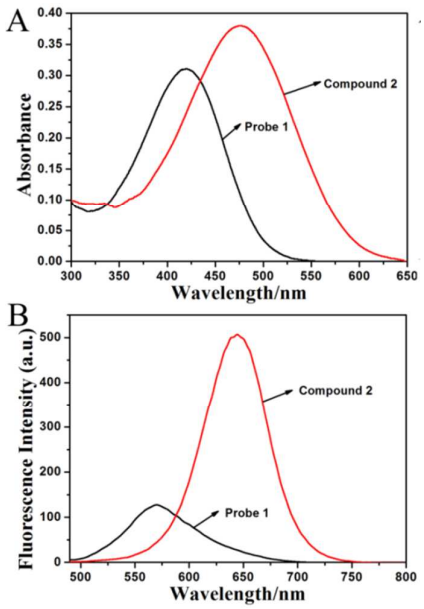


Fig. 1. (A) UV–vis absorption and (B) Fluorescence spectra of Probe 1 and Compound 2. All spectra were recorded in DMSO/PBS buffer solution (50/50, v/v, pH = 7.4, 20 mM). λ_{ex} = 472 nm. Slit: 5 nm/5 nm.

Result and discussion

Synthesis route

The synthetic route of Probe 1 is illustrated in scheme 1. Firstly, compound 3 was synthesized by the reaction of isophorone and malonitrile in EtOH. Then, compound 3 reacted with N-(4-formyl-phenyl)acetamide in presence of acetic acid and piperidine, followed by treatment with concentrated HCl to generate Compound 2 in EtOH. Finally, Probe 1 was obtained by the reaction of Compound 2 and AllocCl in DCM at room temperature.[28] Structural identification of Probe 1, compound 3,

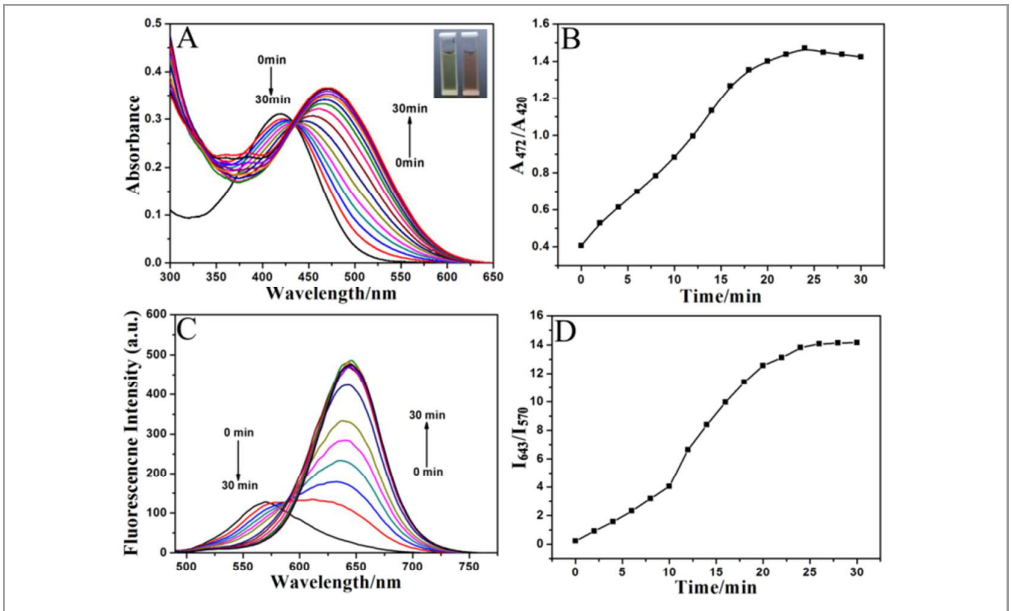


Fig. 2. (A) Time dependent UV–vis absorption spectra and (B) A_{472}/A_{450} evolution of Probe 1 upon addition of palladium (0) (50 μM). (C) Time dependent fluorescence spectra and (D) I_{643}/I_{570} evolution of Probe 1 upon addition of Palladium (50 μM). A_{472} and A_{472} are the absorbance of Probe 1 at 450 nm and 472 nm, respectively, while I_{570} and I_{643} are the fluorescence intensities at 570 nm and 643 nm. All spectra were recorded in DMSO/PBS buffer solution (50/50, v/v, pH = 7.4, 20 mM). λ_{ex} = 472 nm. Slit: 5 nm/5 nm. The inset of Fig. 2A shows the color change of Probe 1 upon addition of Palladium (50 μM).

and Compound 2 was confirmed by NMR and HRMS spectroscopy (Fig. S1–Fig. S8).

Properties of Probe 1

Fig. 1 shows the UV–vis absorption and fluorescence spectra of Probe 1 and Compound 2. As shown in Fig. 1A and 1B, Probe 1 exhibits a typical ICT broad absorption peak at 420 nm (Fig. 1A) and weak fluorescence emission peak at 570 nm (Fig. 1B), while Compound 2 presents a red-shifted absorption peak at 472 nm and a strong fluorescence at 643 nm. The fluorescence quantum yields of Probe 1 and Compound 2 were determined to be 0.003 and 0.016, respectively, by using Rh 6G (Φ = 0.94, in EtOH) as reference (Table S1). Both Probe 1 and Compound 2 show large Stokes shifts (150 nm for Probe 1 and 170 nm for Compound 2), which is relative to the D-π-A structures of Probe 1 and Compound 2. The distinct difference between Compound 2 and Probe 1 in the spectroscopic properties can be explained as follows: For Compound 2, due to the strong electron donating ability of amino group, the donor-π-acceptor (D-π-A) structure shows high dipole moment, resulting in evident red-shifts of absorption and emission spectra. In the case of Probe 1, the electron donating ability of the nitrogen atom was deprived by the electron-withdrawing carbonyl group,[28] thus the dipole moment of donor-π-acceptor (D-π-A) structure would dramatically decline. As a result, the absorption and emission peaks would shift to shorter wavelength.

To investigate the reaction property of Probe 1, initial spectroscopic studies were conducted by monitoring the changes of the absorption and fluorescence spectra upon addition of $Pd(PPh_3)_4$ in DMSO/PBS buffer solution (50/50, v/v, pH = 7.4, 20 mM). As shown in Fig. 2A and 2B, after adding palladium (50 μM) to Probe 1, the absorption at 472 nm increases gradually, along with the depression of absorption at 420 nm ($\Delta\lambda_{abs}$ = 52 nm), corresponding to a color change from yellow to pink (the inset of Fig. 2A). Meanwhile, the emission band at 570 nm decreases gradually and a new band at 643 nm emerges ($\Delta\lambda_{em}$ = 73 nm). With a palladium concentration of 50 μM, the ratio of fluorescence intensities at 643 nm and 570 nm (I_{643}/I_{570}) reaches 85 (Fig. 2C and 2D), revealing that Probe 1 has a high signal-to-noise ratio. It is worth noting that the observed fluorescence intensity increased after Probe 1 was totally transformed to Compound 2. The reason can be explained as follows: Possessing two electron-withdrawing groups (EWG), dicayano group and carbonyl moiety, Probe 1 as a "pull-pull" system blocks the ICT process. After addition of Pd, the amide moiety will be converted into amino moiety. As an electron-donating group (EDG), the amino moiety can increase the fluorescence intensity by forming a "push-pull" system.[41–44]

Additionally, both absorption and emission spectra reach a plateau within 30 min (Fig. 2B, D), indicating that the response rate of Probe 1 to palladium is very fast.

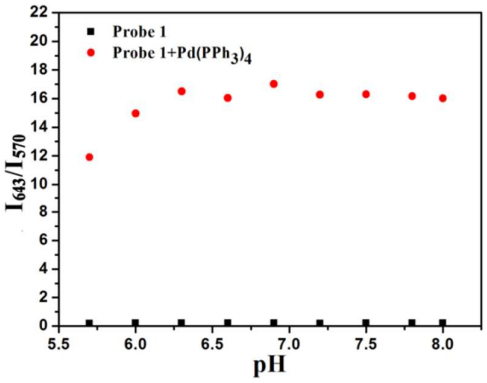


Fig. 3. Effect of pH on I_{643}/I_{570} of Probe 1 (10 μM) in DMSO/NaH_2PO_4-Na_2HPO_4 solution (1/1, v/v). λ_{ex} = 472 nm. Slit: 5 nm/5nm.

Effect of pH

To explore the applicability of Probe 1 in real biological systems, the effect of pH on the fluorescence response of Probe 1 to palladium was evaluated in the pH range of 5.7–8.0. As shown in Fig. 3, I_{643}/I_{570} shows a slight increase in the pH range of 5.7–6.2 and almost keeps unchanged in the pH range of 6.2–8.0. This result indicates that Probe 1 is stable in biological systems and can be employed as a capable candidate for palladium detection.

Sensitivity

The recognition ability of Probe 1 to palladium in DMSO/PBS buffer solution (50/50, v/v, pH = 7.4, 20 mM) was also investigated by the UV–vis absorption and fluorescence titration experiments. As shown in Fig. 4A, The absorption at 420 nm decreases gradually with increasing the concentration of $Pd(PPh_3)_4$ from 0 to 20 μM, together with the enhancement of absorption at 472 nm. The absorbance ratio at 472 nm and 420 nm (A_{472}/A_{420}) has a good linearity (R = 0.9957) as a function of palladium concentration (0–20 μM) (Fig. 4B). Similarly, the intensity of fluorescence emission at 570 nm decreases gradually, along with the evident increase of fluorescence emission at 643 nm (Fig. 4C). Fig. S9 shows the plot of fluorescence intensity ratio at 643 nm and 570 nm as a function of palladium concentration. Obviously, the plot fits linearly with a correlation coefficient of 0.9694 in the palladium concentration range of 0−1 μM. The detection limit of Probe 1 was estimated to be as low as 24.2 nM. This result indicated that Probe 1 is quite suitable to quantitatively detect low concentration of palladium, similar to the previous reports (Table S2).

Reaction mechanism

The excellent selectivity should be attributed to the highly specific Pd0-triggered cleavage process.[23,45] A feasible fluorescence sensing mechanism is shown in Scheme 2. Firstly, as a trigger moiety, allylcarbamate conjugates with palladium and ionizes to form Probe 1-Pd. Next, carbamate 2 is formed by dissociation. Finally, carbamate 2 transforms into Compound 2 by decarboxylation. Because Probe 1 and Compound 2 have different absorption and emission wavelengths, the presence/or absence of Pd can be easily identified. Moreover, the conversion rate of probe 1 is positively relative to Pd content, so, we can estimate the Pd concentration in solution by analyzing the variation of fluorescence intensities at 570 nm and 643 nm. To confirm this mechanism, the product after the reaction between Probe 1 and palladium was isolated and checked via TLC. The result showed that the reaction product is Compound 2 (Fig. S10), which was further proved by the peak at 290.1653 in the HRMS (theoretical mass: 290.1657) (Fig.

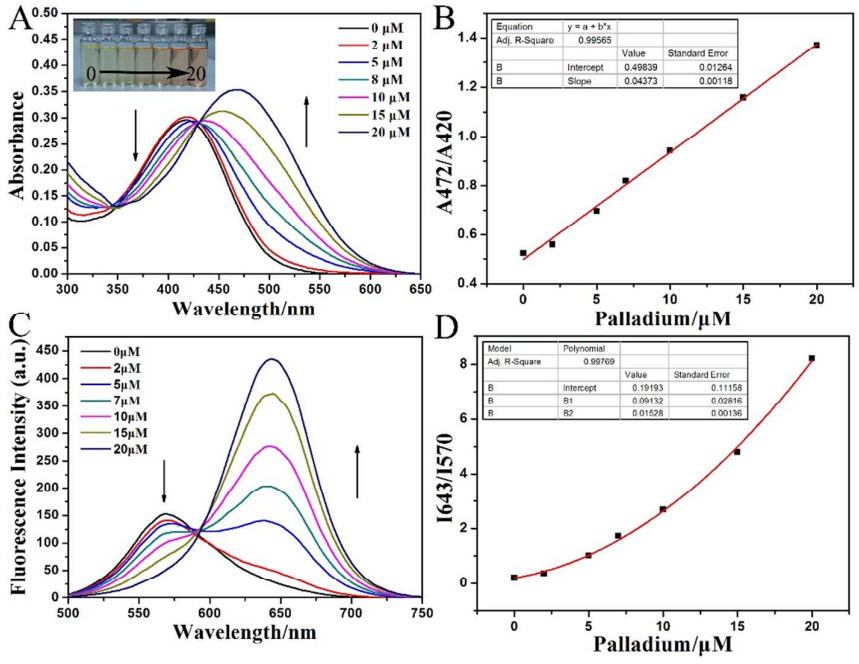
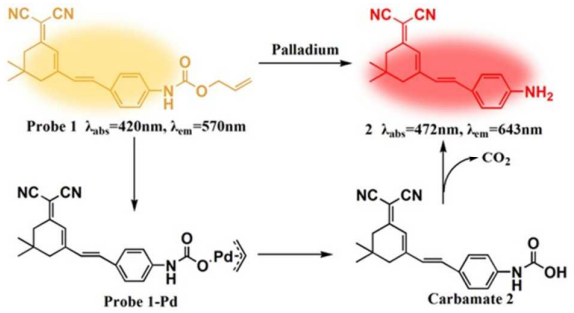


Fig. 4. (A) UV–vis absorption spectrum evolution of Probe 1 (10μM) in terms of palladium concentrations (0–20 μM). (B) Ratiometric calibration curve of A_{472}/A_{420} as a function of palladium (0) concentration. (C) Fluorescence spectrum evolution of Probe 1 (10μM) in terms of palladium concentrations (0–20 μM). (D) Ratiometric calibration curve of I_{643}/I_{570} as a function of palladium concentration. Spectra were recorded in DMSO/PBS buffer solution (50/50, v/v, pH = 7.4, 20mM). The Inset of Fig. 4A shows color change of Probe 1 in different concentrations of palladium (0–20 μM). λ_{ex} = 472 nm. Slit: 5 nm/5 nm.

S11). Moreover, the changes of both UV–vis absorption and fluorescnece spectra upon addition of palladium further confirmed the above-mentioned reaction mechanism (Fig. S12).



Scheme 2. Mechanism for selective recognition of palladium (0).

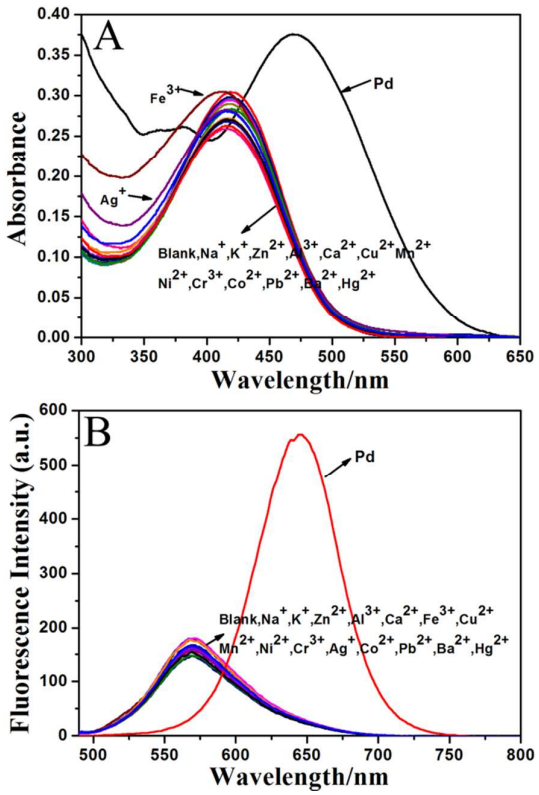


Fig. 5. (A) UV–vis absorption and (B) fluorescence spectra of Probe 1 upon addition of various metal ions: Na^+, K^+, Zn^{2+}, Al^{3+}, Ca^{2+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Cr^{3+}, Ag^+, Co^{2+} , Pb^{2+}, Ba^{2+} and Hg^{2+} (50 μM). All spectra were recorded in DMSO/PBS buffer solution (50/50, v/v, pH = 7.4, 20 mM). λ_{ex} = 472 nm. Slit: 5 nm/5 nm. Note: Pd represents palladium (0).

Selectivity

Selectivity is a very important performance for a fluorescence probe. To investigate the selectivity of Probe 1 to different metal ions, we compared the UV–vis absorption and fluorescence spectra of Probe 1 after addition of different metal ions (Na^+, K^+, Zn^{2+}, Al^{3+}, Ca^{2+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Cr^{3+}, Ag^+, Co^{2+}, Pb^{2+}, Ba^{2+}, and Hg^{2+}). As shown in Fig. 5, UV–vis absorption and fluorescence spectra almost have no change in the presence of Na^+, K^+, Zn^{2+}, Al^{3+}, Ca^{2+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Cr^{3+}, Ag^+, Co^{2+}, Pb^{2+}, Ba^{2+}, and Hg^{2+} ions except for palladium, indicating that Probe 1 has an excellent selectivity toward palladium. Remarkably, the fluorescence intensity ratio I_{643}/I_{570} increases 85-fold in the presence of palladium. The corresponding color change from yellow to pink can be easily observed by naked eye (Fig. 6). Moreover, as shown in Fig. S13, Probe 1 exhibits the same sensitivity to both Pd(0) and Pd(II), which indicates that Probe 1 has generality for detecting palladium species. Fig. S14A presents the time dependent fluorescence spectrum of Probe 1 for Pd^{2+} ions. From Fig. S14B, it can be seen that the fluorescence intensity ratio I_{643}/I_{570} keeps unchanged after 25 min. So, 30 min can be used as an appropriate reaction time for Pd^{2+} detection.

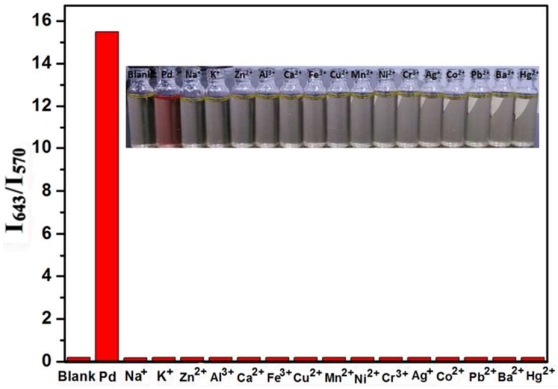


Fig. 6. Relative emission intensity ratios of Probe 1 at 643 nm and 570 nm (I_{643}/I_{570}) upon addition of different metal ions: Na^+, K^+, Zn^{2+}, Al^{3+}, Ca^{2+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Cr^{3+}, Ag^+, Co^{2+} , Pb^{2+}, Ba^{2+} and Hg^{2+} (50 μM). λ_{ex} = 472 nm. Slit: 5 nm/5 nm. Inset: Color changes of Probe 1 after addition of different metal ions. Note: Pd represents palladium (0)

Conclusion

We successfully synthesized a new colorimetric and ratiometric fluorescence probe (Probe 1) with red emission by using isophorone based fluorescent dye as fluorophore and allylcarbamate group as response unit. Based on the Pd^0-triggered cleavage reaction under mild conditions, Probe 1 showed high response speed, selectivity, and sensitivity towards palladium species under room temperature. Moreover, Probe 1 displayed colorimetric and ratiometric responses toward palladium species. Upon addition of palladium, the absorption and emission spectra of Probe 1 exhibited obvious red-shift, corresponding to a color change from yellow to pink which can be differentiated by naked eye. In terms of palladium, the detection limit is as low as 24.2 nM and the signal-to-noise ratio in fluorescence intensity can reach 85-fold. As a ratiometric red emitting sensor, Probe **1** can be potentially used for quantitative detection of palladium in living organisms. Moreover, this work also presented a new application field for isophorone based fluorescence dyes.

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