



A colorimetric and fluorescent sensor based on PBIs for palladium detection [☆]



Liang Zhang, Yefeng Wang, Jianjun Yu, Guanjin Zhang, Xiaofei Cai, Yue Wu, Limin Wang ^{*}

Shanghai Key Laboratory of Functional Materials Chemistry, Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, PR China

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ABSTRACT

A novel colorimetric and fluorescent sensor for Pd²⁺ has been developed based on the Pd-catalyzed deallylation. The sensor displays a highly sensitive and selective response with significant changes in both color (from orange to blue) and fluorescence (quenching).

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Introduction

With the wide use of palladium as catalysts in organic synthesis¹ and automobile exhaust purification,² the resulting high level of residual palladium in the final product and environment has raised great concern. Palladium influences our health and environment in an adverse way because it can bind to thiol-containing amino acids, proteins, DNA, and other biomolecules and thereby may disturb a variety of cellular processes. In the past few years, many analytic methods have been developed for the detection of palladium. The majority of the known methods include inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS), plasma emission spectroscopy (ICP-AES), solid phase microextraction–high performance liquid chromatography (SPME–HPLC), X-ray fluorescence (XRF), etc.³ However, these methods often require the complicated sample preparation steps, rigorous experimental conditions, sophisticated instrumentation, and well-trained individuals. Thus, current research has been focused on fluorescent methods, because of their low cost, simplicity, sensitivity, selectivity, rapid response, and high spatial resolution via microscopic imaging.⁴

Perylene-3,4:9,10-tetracarboxylic bisimide (PBI) and its derivatives are valuable functional dyes and have numerous potential applications.⁵ Particularly, for their extraordinary photoluminescence efficiency and high chemical and thermal stability, these compounds can be good platforms for the fluorescent sensors. Many works about fluorescent sensors based on the PBIs had been reported.⁶ According to some recent reports, palladium could be detected by a specific Pd-catalyzed deallylation reaction.⁷ Therefore, in this Letter we designed a novel PBI derivative as the fluorescence sensor for the detection of palladium. The results indicated that Pd²⁺ could be easily recognized from other cations through both colorimetric and fluorescence methods with high sensitivity and selectivity in the presence of KBH₄–PPh₃. Furthermore, the sensor can turn into blue from orange after the addition of Pd²⁺ in 0.5 h at room temperature, which can be observed by naked eyes.

Results and discussion

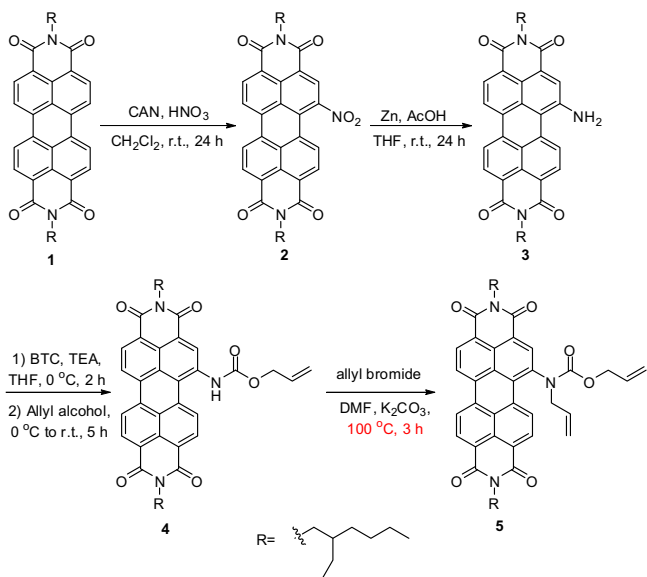
Sensor **5** was synthesized in four steps as shown in Scheme 1. Compounds **2** and **3** were synthesized as described in previous reports.⁸ Compound **3** was treated with BTC in THF at 0 °C and then reacted with allyl alcohol to form compound **4**.⁹ Finally, compound **4** was alkylated with allyl bromide to afford sensor **5** in 46% yield.¹⁰

The spectroscopic properties of the sensor **5** were rated in tetrahydrofuran–water solutions (THF:H₂O = 4:1, KBH₄ (10 mM), PPh₃ (10 mM)) at a micromolar concentration. As shown in Figure 1a, free sensor **5** (5 μM) showed an absorption wavelength with a maximum at 520 nm, owing to the electron-withdrawing effect of the

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^{*} Corresponding author. Tel.: +86 021 64253881.

E-mail address: wanglimin@ecust.edu.cn (L. Wang).



Scheme 1. The synthetic route of sensor 5.

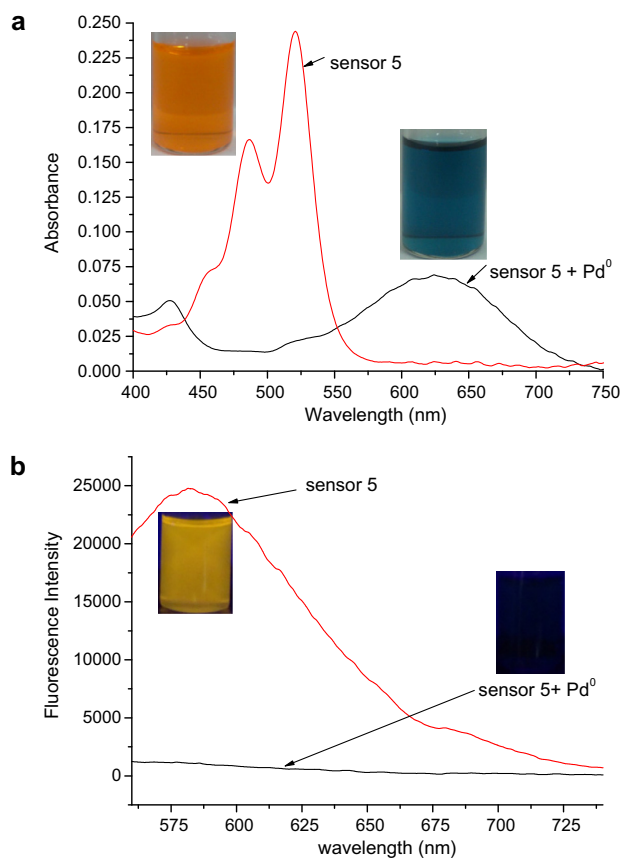


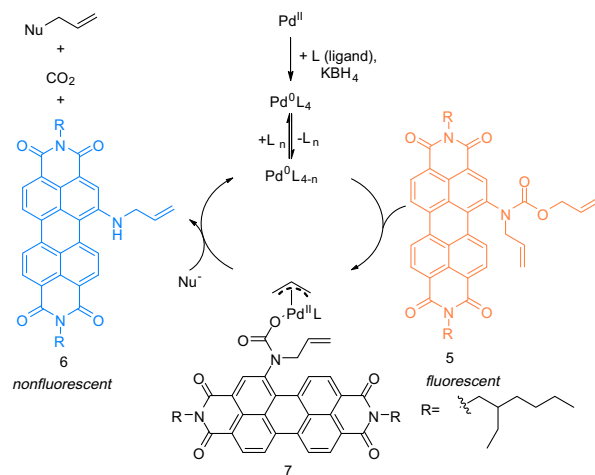
Figure 1. Absorption (a) and fluorescence (b) spectra change of sensor 5 (5 μ M) upon treatment with PdCl₂ (10 μ M), in tetrahydrofuran–water solutions (THF:H₂O = 4:1, KBH₄ (10 mM) and PPh₃ (10 mM)) at room temperature.

amide group. After being treated with PdCl₂ (10 μ M), the maximum absorption peak underwent a red shift to 620 nm, showing a colorimetric response. The marked color changes in the solutions (from orange to blue) could be distinguished by the naked eyes. This red shift in the absorption should be attributed to the strong electron-donating ability of the released allylamino in compound 6

(Scheme 2). An obviously fluorescence quenching was also detected (Fig. 1b). It took about 24 min to reach the relative saturation point as can be observed from the plot of the time-dependent fluorescence spectra (Fig. 2). Clearly, the results indicated that Pd²⁺ could be detected through both colorimetric and fluorescence methods by sensor 5 when a reducing agent, such as KBH₄–PPh₃, is added.

We further studied the sensing response of the sensor toward various concentrations of Pd²⁺ by absorption spectroscopy and fluorescence spectroscopy. Standard solution of PdCl₂ was gradually added to tetrahydrofuran–water solutions (THF:H₂O = 4:1, KBH₄ (10 mM), PPh₃ (10 mM), taken after 30 min at 20 °C). It can be found that the maximum absorption peak of the free sensor at 520 nm decreased and a new band at 620 nm increased (Fig. 3). The isosbestic points were at about 444 nm and 547 nm. The absorbance ratios of sensor 5 at 520 and 620 nm ($A_{520\text{ nm}}/A_{620\text{ nm}}$) increased linearly with the amount of Pd²⁺ in the range of 0–1 μ M. The fluorescence intensity also decreased linearly as shown in Figure 4.

In this Letter, the work on the selectivity of the sensor over other competing species was carried out under the same condition. As shown in Figure 5, the colorimetric response was detected only in the case of Pd²⁺; other metal species such as Ag⁺, Rh³⁺, Ru³⁺, Cr³⁺,



Scheme 2. Mechanism for selective recognition of palladium.

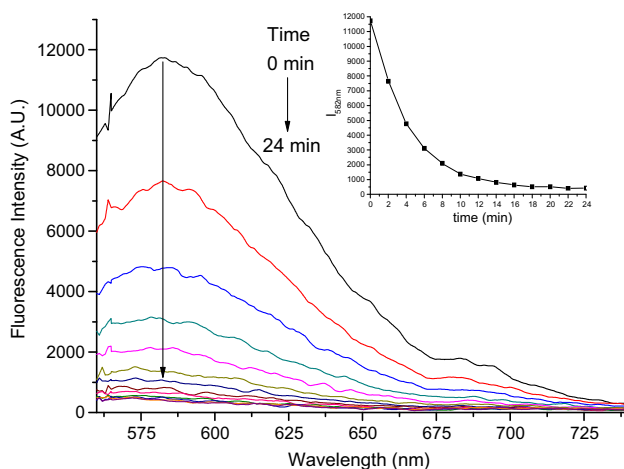


Figure 2. Time-dependent fluorescence change of the sensor 5 (5 μ M) upon treatment with PdCl₂ (10 μ M), in tetrahydrofuran–water solutions (THF:H₂O = 4:1, KBH₄ (10 mM) and PPh₃ (10 mM)) at room temperature. Inset: time-dependent intensity change.

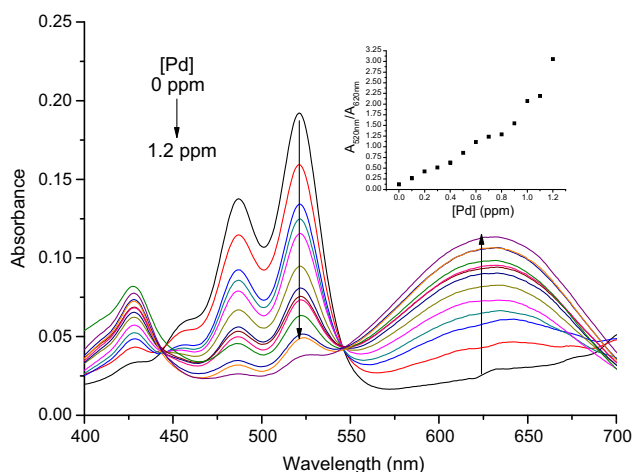


Figure 3. Absorption spectra of sensor **5** upon titration of Pd^{2+} (0–1.2 μM) in tetrahydrofuran–water solutions (THF:H₂O = 4:1, KBH_4 (10 mM) and PPh_3 (10 mM)), taken after 30 min at room temperature.

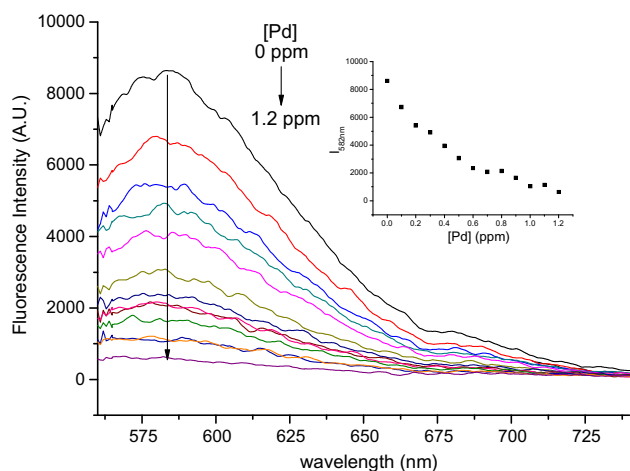


Figure 4. Fluorescence spectra of sensor **5** upon titration of Pd^{2+} (0–1.2 μM) in tetrahydrofuran–water solutions (THF:H₂O = 4:1, KBH_4 (10 mM) and PPh_3 (10 mM)), taken after 30 min at room temperature. Inset: plot of the concentration of Pd^{2+} versus the fluorescence intensity of the sensor toward various concentrations of Pd^{2+} at $\lambda_{\text{em}} = 582 \text{ nm}$.

Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , Ba^{2+} , and Hg^{2+} had no or little effect on the absorption of sensor **5**. Moreover, compared with various metal species which were tested, only Pd^{2+} could cause a fluorescence quenching (Fig. 6). Thus, the designed PBI derivative as the fluorescence sensor can successfully detect Pd^{2+} with high selectivity and sensitivity.

The excellent selectivity should be attributed to the highly specific Pd-catalyzed deallylation.⁷ We had run a large-scale reaction between **5** and PdCl_2 under the identical condition that has been used for the chemical sensing studies and got compound **6**.¹¹ Then, we compared the UV–vis spectrum of compound **6** and that of compound **5** after addition of PdCl_2 (Fig. S1). The slight differences could be due to the unreacted sensor **5**. A feasible sensing mechanism is shown in Scheme 2. First Pd^{II} is reduced to Pd^0 by KBH_4 . Then reacts with the allyl carbamate group of sensor **5** to yield π -allylpalladium(II) complex **7**, further transferring the allyl unit to a nucleophile and decarboxylation to afford compound **6**. In this case, the sensor can detect Pd^{2+} when a reducing agent, such as KBH_4 – PPh_3 , is added.

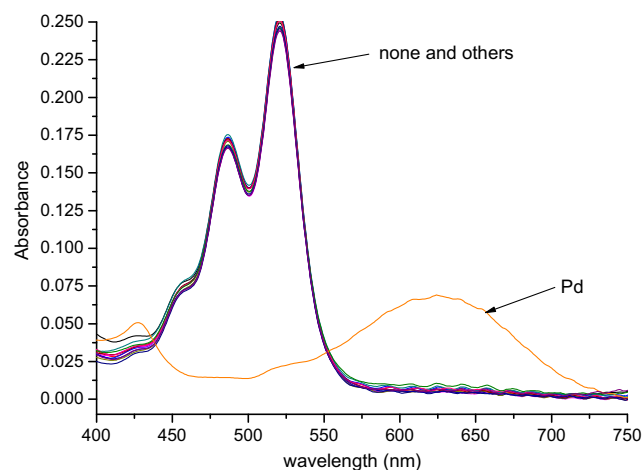


Figure 5. Absorption spectra of sensor **5** in the absence and presence of different metal ions Ag^+ , Rh^{3+} , Ru^{3+} , Cr^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , Ba^{2+} , Hg^{2+} , and Pd^{2+} (as their SO_4^{2-} , NO_3^- or Cl^- salts) in tetrahydrofuran–water solutions (THF:H₂O = 4:1, KBH_4 (10 mM) and PPh_3 (10 mM)), taken after 30 min at room temperature.

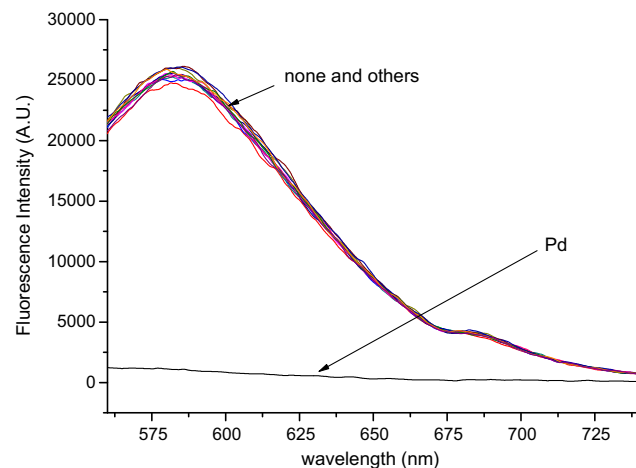


Figure 6. Fluorescence spectra of sensor **5** in the absence and presence of different metal ions Ag^+ , Rh^{3+} , Ru^{3+} , Cr^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , Ba^{2+} , Hg^{2+} , and Pd^{2+} (as their SO_4^{2-} , NO_3^- or Cl^- salts) in tetrahydrofuran–water solutions (THF:H₂O = 4:1, KBH_4 (10 mM) and PPh_3 (10 mM)), taken after 30 min at room temperature.

Conclusion

In summary, a novel PBI derivative fluorescence sensor was designed and synthesized. According to the specific Pd-catalyzed deallylation reaction it could exhibit highly selective and sensitive detection of Pd^{2+} in the presence of KBH_4 – PPh_3 as a reducing agent. Both colorimetric and fluorescence methods could be used.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2013.05.076>.

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- Compound **3** (0.252 g, 0.4 mmol) and BTC (0.356 g, 1.2 mmol) were mixed in 10 mL anhydrous THF and cooled to 0 °C. Then TEA was added dropwise. After stirred at 0 °C for 2 h under nitrogen atmosphere, aryl alcohol (1.5 mL) was added. The resulted mixture was warmed to room temperature and stirred overnight. At the end of the reaction, the solvent was removed in vacuum. After purification by column chromatography (200–300 mesh silica gel, DCM/methanol = 100:1), the desired product was obtained as red solid (0.170 g, yield 60%). Since the solubility of compound **3** in common organic solvents is very low, it is impossible to perform NMR characterization directly on the this product obtained.
- A mixture of compound **4** (0.142 g, 0.2 mmol), aryl bromide (0.256 g, 2.0 mmol) and potassium carbonate (0.276 g, 2.0 mmol) in 30 mL dry DMF was stirred at 100 °C for 3 h. At the end of the reaction, the solvent was removed in vacuum. After purification by column chromatography (200–300 mesh silica gel, DCM), the desired product was obtained as red solid (0.136 g, yield 90%). ¹H NMR (400 MHz, CDCl₃) δ ppm: 0.88–0.97 (m, 12H), 1.29–1.44 (m, 16H), 1.89–1.97 (m, 2H), 3.73–3.79 (m, 1H), 4.10–4.16 (m, 4H), 4.65–4.87 (m, 3H), 5.02–5.12 (m, 3H), 5.32–6.03 (m, 3H), 8.46–8.84 (m, 7H). ¹³C NMR (100 MHz, CDCl₃) δ ppm: 10.6, 14.1, 23.1, 24.1, 28.7, 29.8, 30.7, 37.9, 44.2, 67.4, 118.6, 120.1, 123.0, 123.3, 123.6, 126.5, 128.0, 130.1, 131.1, 131.9, 135.3, 163.3, 163.6. HRMS calcd for C₄₇H₅₂N₃O₆ 754.3856, found 754.3859.
- Compound **6**: ¹H NMR (400 MHz, CDCl₃) δ ppm: 0.87–0.96 (m, 12H), 1.30–1.38 (m, 16H), 1.88–1.92 (m, 2H), 3.94–4.04 (m, 4H), 4.08 (t, *J* = 5.6 Hz, 2H), 5.38–5.46 (m, 2H), 6.03 (t, *J* = 5.2 Hz, 1H), 6.07–6.16 (m, 1H), 7.97 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8 Hz, 1H), 8.27 (d, *J* = 8 Hz, 1H), 8.39 (d, *J* = 8 Hz, 1H), 8.68 (d, *J* = 8 Hz, 1H). HRMS calcd for C₄₃H₄₈N₃O₄ 670.3645, found 670.3644.