

A Colorimetric and Fluorescent Sensor Based on Novel Iminocoumarin Precursor for Pd²⁺ Detection in Aqueous Solution

Lianqing Li^{1,2} · LeJun Gao³ · Junfeng Wang² · Zhengfeng Xiao² · Zhihong Liu¹

Received: 28 April 2015 / Accepted: 18 August 2015 / Published online: 29 August 2015
© Springer Science+Business Media New York 2015

Abstract A novel iminocoumarin precursor L was designed and well characterized. Sensor L showed high selectivity toward Pd²⁺ in aqueous solution (CH₃CN:H₂O, v/v, 1:1) with a detection limit is 2.1×10^{-7} M. Iminocoumarin was formed when added Pd²⁺ to the solution of L by removing the propargylic group.

Keywords Colorimetric sensor · Fluorescent sensor · Palladium detection

Introduction

Palladium plays a vital role due to its extensive use in many catalytic reaction and industrial applications [1]. However, Palladium compounds are hazardous to the environment and human health because palladium ions can bind to thiol-containing amino acids, proteins (casein, silk fibroin and many enzymes), DNA or other macromolecules (vitamin B6), it can cause severe primary skin and eye irritations [2]. Governmental restrictions on the levels of residual heavy metals in end

products are very strict. Typical contamination levels of palladium remaining in the drugs range from 5 to 100 ppm [3]. Therefore, the development of efficient methods for the detection of palladium in the environment is a very important issue. The traditional methods used for quantification of palladium species are atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), X-ray fluorescence. However these methods require complicated sample preparation steps, rigorous experimental conditions, sophisticated instrumentation, and well-trained individuals.

In contrast, fluorescent methods have high sensitivity, good selectivity, short response time, real-time monitoring [4, 5]. As a strong fluorescence quencher, Pd²⁺ could be detected by fluorescent ligands through fluorescence quenching. Many works have done for the exploring highly sensitive and selective fluorescent sensors for the Pd²⁺ ions detection [6–13]. As a work search high selective and sensitive fluorescent sensor for monitor Pd²⁺ in aqueous environment, a rhodamine derivative for Pd²⁺ detection was reported by our group [14]. Here we reported that we have developed a novel precursor of iminocoumarin with a propargyl group, which can be used as a colorimetric sensor for the detection Pd²⁺ in aqueous solutions.

✉ Zhihong Liu
lianqingli008@163.com; liuzh@snnu.edu.cn

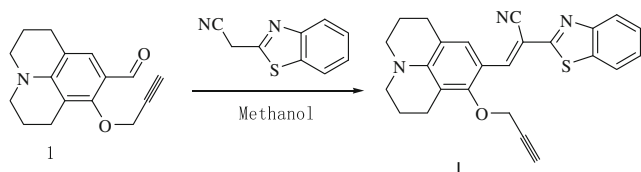
¹ Key Laboratory for Macromolecular Science of Shaanxi Province, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, People's Republic of China

² Department of Chemistry and Chemical Engineering, ShaanXiXueQian Normal University, Xi'an 710010, People's Republic of China

³ Binzhou Medical University Hospital, Binzhou 256600, People's Republic of China

Experimental

All reagents used were purchased from commercial suppliers and used without further purification. The solutions of metal ions were performed from their nitrate and chloride salts and the stock solution of L was prepared in DMSO. Double-distilled water was used



Scheme 1 The synthesis route for L

throughout the experiments. ^1H NMR and ^{13}C NMR measurements were performed with a Bruker Avance 300 (300 MHz) spectrometer with TMS as an internal standard and CDCl_3 as solvent. MS measurements were carried out on LC-Mass Spectrometer instrument (Bruker). Fluorescence spectra were measured on a Hitachi F-4500 with quartz cuvette (path length = 1 cm). The absorption spectra measurements were observed by a UV-6100s UV/Vis spectrometer (Mapada, China).

The fluorescent sensor L was designed and synthesized in one step as shown in Scheme 1. To a solution of compound 1 (2.55 g, 10 mmol) in anhydrous ethanol (30 mL) was added 2-Benzothiazoleacetonitrile (1.74 g, 10 mmol). The solution was refluxed for 5 h. After cooling, most solvent was removed under reduced pressure. The crude product was purified by recrystallization from ethanol to give 2.51 g pink solid in 54.8 % yield.

^1H -NMR: 8.36 (2H, s), 8.10 (1H, s), 8.03 (1H, d, $J = 3.9\text{Hz}$), 7.83 (1H, d, $J = 3.9\text{Hz}$), 7.46 (1H, t, $J = 3.6\text{Hz}$), 7.34 (1H, t, $J = 3.6\text{Hz}$), 4.57 (1H, s), 3.31 (4H, s), 2.79 (4H, s), 2.56 (1H, s), 1.96 (4H, s). ^{13}C NMR: 165.1154.6153.1, 152.4, 148.9, 145.0, 142.8, 133.0, 127.9, 127.5, 124.6, 123.3, 123.1, 117.9, 113.5, 108.1, 105.8, 98.4, 79.6, 74.8, 65.1, 61.4, 49.9, 49.6, 44.4, 27.3, 21.8, 21.2, 12.7.

HR-MS (ESI) :412.1452.

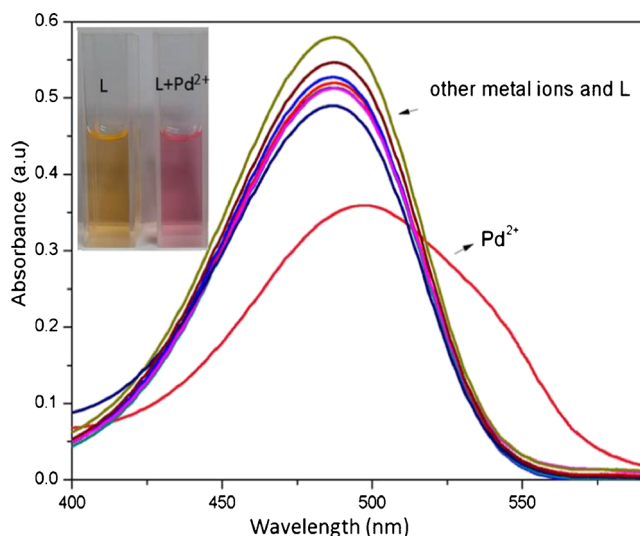


Fig. 1 UV-Vis changes of L (10 μM) in the present of various metal ions in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$. Inset: the color change of L in the present of Pd^{2+}

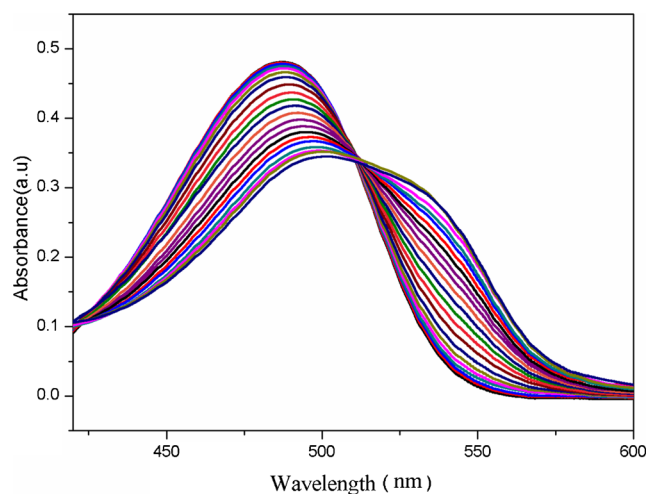


Fig. 2 UV-Vis changes of L (10 μM) with 5 equiv. of Pd^{2+} in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$

Results and Discussion

The selectivity of sensor L were first investigated by adding various metal ions (Pd^{2+} , Fe^{3+} , Ag^+ , Pb^{2+} , Cd^{2+} , Co^{2+} , Hg^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+}) to the aqueous solution ($\text{CH}_3\text{CN}/\text{H}_2\text{O}$, 1:1, v/v) of sensor L. Free sensor L showed an absorption at 487 nm in $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ solution, however, when 5 equiv. of Pd^{2+} was added, the absorption maximum has about a 36 nm red-shift and the intensity of the maximum exhibited a decrease (Fig. 1). Upon addition of other metal ions (Cd^{2+} , Cu^{2+} , Hg^{2+} , Mg^{2+} , Ni^{2+} , Pb^{2+} , Fe^{3+} , Zn^{2+} and Ag^+), no significant color or spectral changes were observed, therefore, sensor L can be considered as an effective colorimetric probe for Pd^{2+} . Thus, naked-eye detection of Pd^{2+} becomes possible.

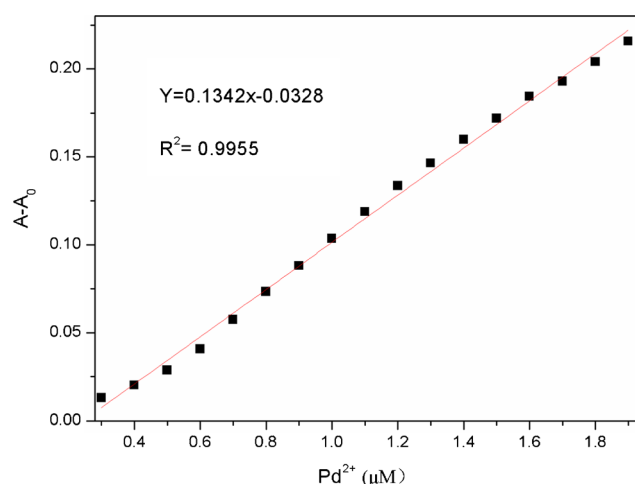


Fig. 3 linear correlation between the relative absorption intensity at 540 nm and Pd^{2+} concentration

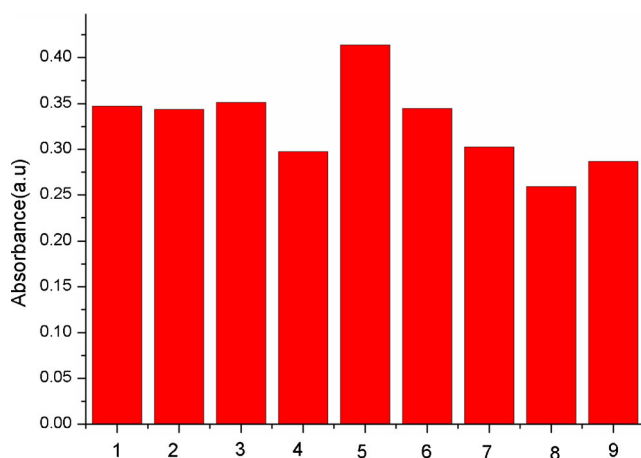


Fig. 4 Metal ions selectivity of L (10 μ M) toward Pd²⁺ in CH₃CN-H₂O. 1. Pd²⁺ only 2. Pd²⁺+Pb²⁺ 3. Pd²⁺+Ag⁺ 4. Pd²⁺+Cd²⁺ 5. Pd²⁺+Hg²⁺ 6. Pd²⁺+Co²⁺ 7. Pd²⁺+Zn²⁺ 8. Pd²⁺+Fe³⁺ 9. Pd²⁺+Cu²⁺

Figure 2 showed the results of absorption titration of L with Pd²⁺ ions. Upon the addition of Pd²⁺, the absorbance at 487 nm was gradually decreased and a new peak at 523 nm was observed. This absorbance change reached saturation point upon the addition of 2 equiv. of Pd²⁺. It is note worthy that further addition of the Pd²⁺ ion solution caused no significant change in the spectral patterns. Moreover, there was a good linear correlation ($R = 0.9955$) between relative absorbance intensity at 540 nm and Pd²⁺ concentration in the range from 3.0×10^{-7} to 1.8×10^{-6} M, as depicted in Fig. 3. The detection limits for Pd²⁺, at a signal to noise ratio of 3, was estimated to be 2.1×10^{-7} M.

Furthermore, to validate the high selectivity of L for Pd²⁺, the competitive experiments were studied. As shown in Fig. 4, cations such as Cd²⁺, Cu²⁺, Hg²⁺,

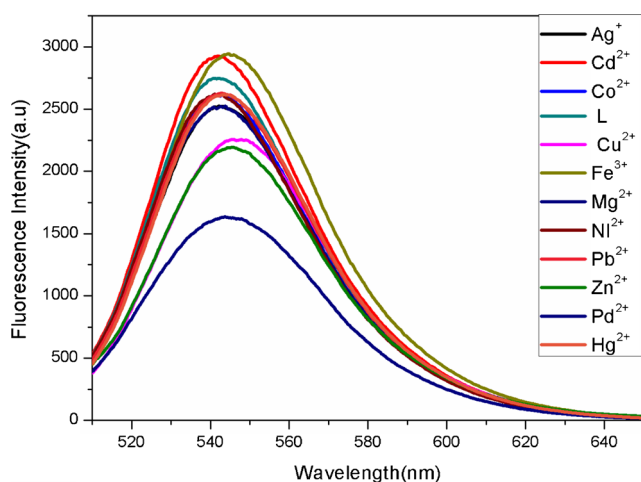


Fig. 5 Fluorescence spectra of L (10 μ M) in the present of various metal ions (5 eq) in CH₃CN-H₂O, Ex = 485 nm

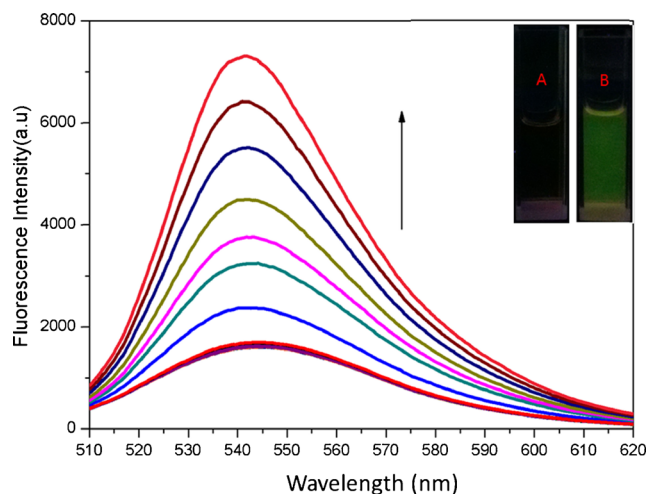


Fig. 6 Fluorescence spectra of L (10 μ M) in the present of various amount of Pd²⁺ (0-5 eq) in CH₃CN-H₂O after addition of equal amount of EDTA, Ex = 485 nm. Inset: A: L + Pd²⁺. B: L + Pd²⁺+EDTA under 365 nm lamb

Ni²⁺, Pb²⁺, Fe³⁺, Zn²⁺ and Ag⁺ have slight influence on the absorbance intensity. It means that the detection of Pd²⁺ by L is hardly affected by these common co-existent metal ions.

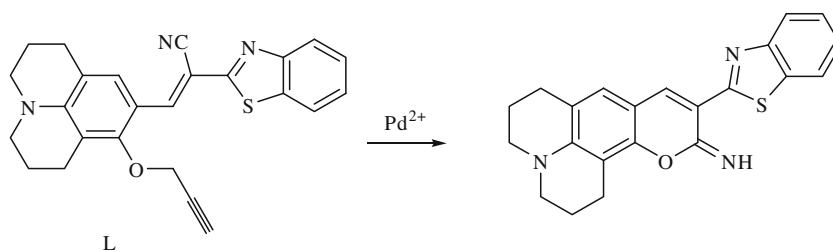
To further explore the sensing behavior of L for Pd²⁺ ion, fluorescent spectra of L in CH₃CN-H₂O were examined. As shown in Fig. 5, free L shows an emission at 545 nm, upon addition of 5 equiv. of Pd²⁺, the fluorescence was quenched due to the paramagnetic properties of Pd²⁺. To gain deeper insight into the sensing behavior of L with Pd²⁺, the prepared Pd²⁺-L complex was treated with EDTA-2Na for 1 min, a strong green fluorescence was observed. The quantitative nature of the sensing of Pd²⁺ ion by L was elucidated by fluorescence titration of probe L in aqueous solution in the present of equal amount of EDTA, as shown in Fig. 6, the fluorescence at 545 nm was enhanced with the concentration of the Pd²⁺ increased.

The competitive experiment was studied by addition of various competitive cations in the present Pd²⁺. The Pd²⁺ induced fluorescence intensity was unaffected by 2 equiv. of other metal ions. The excellent selectivity should be attributed to the highly specific Pd²⁺ catalyzed depropargylation [15, 16]. The proposed mechanism for L as shown in Scheme 2, iminocoumarin was formed after removed propargylic group by introduced Pd²⁺, however, due to the paramagnetic properties of Pd²⁺, the fluorescence was quenched and the fluorescence was recovered after the addition of EDTA.

Conclusion

In summary, a novel precursor of iminocoumarin was developed. Sensor L showed highly selectivity for Pd²⁺ detection

Scheme 2 Proposed mechanism of Pd²⁺ depropargylation of sensor L



both in colorimetric and fluorescence method due to Pd²⁺ catalyzed depropargylation reaction. Sensor L can be used for Pd²⁺ recognition in potential.

Acknowledgments This work was supported by Scientific Research Program Funded by Shaanxi Provincial Education Department (Program No.14JK1181) and Scientific Foundation of Shaanxi Xue Qian Normal University (Program No. 2015ZDKJ016).

References

- Iwasawa T, Tokunaga M, Obora Y, Tsuji Y (2004) Homogeneous palladium catalyst suppressing Pd black formation in air oxidation of alcohols. *J Am Chem Soc* 126: 6554–6555
- Kielhorn J, Melber C, Keller D, Mangelsdorf I (2002) Palladium – a review of exposure and effects to human health. *Int J Hyg Environ Health* 205:417–432
- Buchwald SL, Mauger C, Mignani G, Scholze U (2006) Industrial-scale palladium-catalyzed coupling of aryl halides and amines – a personal account. *Adv Synth Catal* 348:23–39
- F. Yu, X. Han, L. Chen, Fluorescent probes for hydrogen sulfide detection and bioimaging. *Chem Commun*, (2014).
- Wang R, Yu C, Yu F, Chen L, Yu C (2010) Molecular fluorescent probes for monitoring pH changes in living cells. *TrAC Trends Anal Chem* 29:1004–1013
- L. Duan, Y. Xu, X. Qian, Highly sensitive and selective Pd²⁺ sensor of naphthalimide derivative based on complexation with alkynes and thio-heterocycle. *Chem. Commun. (Cambridge, U. K.)*. (2008) 6339–6341.
- H. Li, J. Fan, J. Du, K. Guo, S. Sun, X. Liu, X. Peng, A fluorescent and colorimetric probe specific for palladium detection. *Chem. Commun. (Cambridge, U. K.)*. 46 (2010) 1079–1081.
- Li H, Fan J, Peng X (2013) Colourimetric and fluorescent probes for the optical detection of palladium ions. *Chem Soc Rev* 42: 7943–7962
- He J, Zha M, Cui J, Zeller M, Hunter AD, Yiu S-M, Lee S-T, Xu Z (2013) Convenient detection of Pd(II) by a metal-organic framework with sulfur and olefin functions. *J Am Chem Soc* 135:7807–7810
- Jiang J, Jiang H, Liu W, Tang X, Zhou X, Liu W, Liu R (2011) A colorimetric and ratiometric fluorescent probe for palladium. *Org Lett* 13:4922–4925
- Kaur P, Kaur N, Kaur M, Dhuna V, Singh J, Singh K (2014) ‘Turn-on’ coordination based detection of Pd²⁺ and bioimaging applications. *RSC Adv* 4:16104–16108
- Li H, Cao J, Zhu H, Fan J, Peng X (2013) Optical Pd²⁺ sensing by rhodamine hydrazone ligands: different stoichiometries in aqueous/nonaqueous environments. *Tetrahedron Lett* 54:4357–4361
- LQ. Li, ZH Liu, A colorimetric and fluorescent turn on chemodosimeter for Pd²⁺ detection. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 138(2015) 954–957.
- S. Cai, Y. Lu, S. He, F. Wei, L. Zhao, X. Zeng, A highly sensitive and selective turn-on fluorescent chemosensor for palladium based on a phosphine-rhodamine conjugate. *Chem. Commun. (Cambridge, U. K.)*. 49 (2013) 822–824.
- Song F, Garner AL, Koide K (2007) A highly sensitive fluorescent sensor for palladium based on the allylic oxidative insertion mechanism. *J Am Chem Soc* 129:12354–12355
- Wei G, Wang L, Jiao J, Hou J, Cheng Y, Zhu C (2012) Cu²⁺ triggered fluorescence sensor based on fluorescein derivative for Pd²⁺ detection. *Tetrahedron Lett* 53:3459–3462