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A highly sensitive and selective turn-on fluorescent chemosensor for palladium based on a phosphine–rhodamine conjugate†

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A fluorescent chemosensor with high sensitivity and selectivity for palladium species based on a conjugate of phosphine and rhodamine B has been developed. The chemosensor showed an excellent palladium selectivity with a detection limit down to the 10^{-9} M range, which is lower than the WHO limit for palladium content in drug chemicals.

The fluorescent chemosensors play pivotal roles in the detection of ionic species and small molecules, especially in monitoring heavy and transition metal ions.[1,2] As a rare transition metal, palladium plays a significant role in materials chemistry. The palladium species are widely used as catalysts in chemical transformations in the synthesis of various drugs and fine chemicals.[3] It is also widely used to prepare many dental materials, automobile exhaust catalysts, electric products, and jewellery. As a thiophilic element, however, the palladium species have an influence on human health and the environment in an adverse way as palladium ions can bind to thiol-containing amino acids, proteins, and other biomacromolecules.[4] Recently, Bradley *et al.* reported that palladium could mediate Suzuki–Miyaura cross-coupling reaction within cells.[5] Thus, palladium exposure may disturb a variety of cellular processes.[4] As a result, simple and reliable detection methods for palladium species with high substrate selectivity are vigorously pursued.

Some conventional methods for palladium detection, such as atomic absorption/emission spectrophotometry and ion-coupled plasma emission-mass spectrometry, are not only expensive and time-consuming in practice, but also require highly trained individuals.[6] In stark contrast, optical detection methods, particularly fluorescence methods, show unique potential for the development of highly sensitive and relatively simple analysis protocols. As a fluorescence quencher, Pd^{2+} could be detected by chemosensors through fluorescence quenching.[7] However, a fluorescence-enhanced chemosensor would be more efficient for Pd^{2+} detection. Recently, Holdt *et al.* designed a few fluorescence enhanced chemosensors for Pd^{2+} ions by using a new concept of photo-induced electron transfer (PET) fluoroionophores in fluorophore–spacer–receptor systems.[8] Koide *et al.* reported a turn-on fluorescent sensing system for palladium based on the catalytic Tsuji–Trost allylic oxidative insertion reaction of fluorescein derivatives.[9] Then, Ahn *et al.* extended the allylic oxidative insertion reaction in propargyl ether of fluorescein, which provided a more efficient way for palladium detection in practice.[10] Peng and co-workers developed a novel rhodamine chemosensor for palladium species by taking advantage of both the π-affinity of Pd to allyl groups and the well-known ring-opening process of the spirolactam of rhodamine B.[11] More recently, a cyclen-conjugated rhodamine hydroxamate was also reported with excellent Pd^{2+} selectivity.[12] Although the above excellent prototype devices have been developed for the detection of palladium species, some of them suffer from the disadvantage that the sensing system requires initial conversion of Pd(II) to Pd(0) using a reducing agent,[9] high temperature[13] or organic solvent.[8] Thus, fluorescent chemosensors with better sensitivity and selectivity for palladium species are still needed to be developed.

Enlightened by the fact that palladium is a strong phosphorus-affinity element,[14] we report herein a palladium specific chemosensor **L**, a conjugate of phosphine and rhodamine B. It was observed that **L** showed excellent selectivity and high sensitivity for Pd^{2+} ions over relevant competing metal ions and anions. A turn on ratio over 154-fold was triggered under saturated conditions. Furthermore, **L** was shown to be a promising potential fluorescent chemosensor for the direct qualitative determination of residual palladium in drug chemicals.

As shown in Scheme 1, chemosensor **L** was synthesized by treatment of rhodamine B with $POCl_3$, and then condensed with 2-(diphenylphosphino)benzenamine (**DPBA**), which was prepared in three steps starting from 2-chlorobenzenamine and triphenylphosphine according to the known procedure.[15]

In ethanol–H_2O (4 : 1, v/v) solution, **L** (10 μM) exhibited a very weak absorption band at 544 nm, which could be attributed to the presence of trace amounts of the ring-opened form of **L**. Addition of

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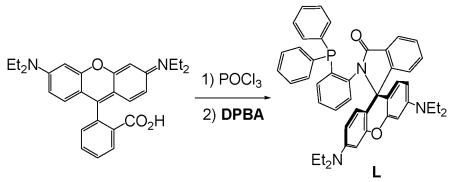


Scheme 1 Structure and the synthesis of the chemosensor **L**.

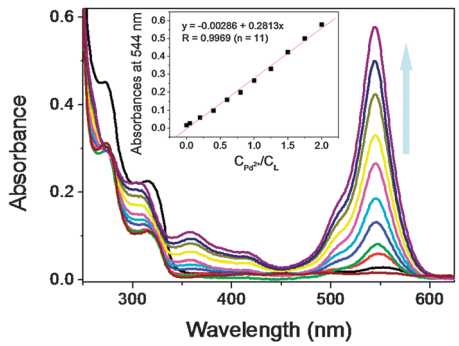


Fig. 1 UV-vis titration spectra of **L** (10 μM). Upon titration of Pd^{2+} (0–2 equiv.) in ethanol–water (4 : 1, v/v), $C_{Pd}{}^{2+}/C_L$ = 0, 0.05, 0.2, 0.4, 0.6, 0.8, 1.0, 1.25, 1.5, 1.75, 2. Inset: the absorbances at 544 nm of **L** as a function of $C_{Pd}{}^{2+}/C_L$.

1 equiv. of Pd^{2+} into the solution, however, immediately induced a significant absorbance enhancement (27-fold) at 544 nm (Fig. S1, ESI†). Only a very weak increase of absorbance at 544 nm was observed with the same amount of Cu^{2+}, Fe^{3+} and Hg^{2+}. No obvious response could be observed upon the addition of other ions. Meanwhile, upon the addition of Pd^{2+}, the color of the solution immediately changed from colorless to pink-red, indicating that **L** can serve as a "naked-eye" probe for Pd^{2+}. As shown in Fig. 1, the absorbance at 544 nm increased smoothly in the presence of different concentrations of Pd^{2+}, which indicated the formation of a new complex between **L** and Pd^{2+}. A linear dependence of the absorbance at 544 nm as a function of $[Pd^{2+}]/[\mathbf{L}]$ was observed (inset of Fig. 1). Stoichiometry for **L** and the Pd^{2+} complex was evaluated on the basis of the Job's plot and was found to be 1 : 1 (Fig. S2, ESI†).

Fig. 2 shows the fluorescence spectrum of **L** and those in the presence of different concentrations of Pd^{2+}. The free chemosensor

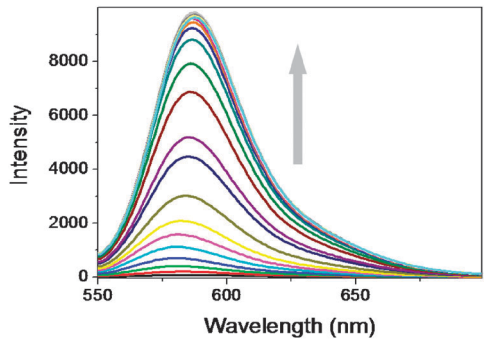
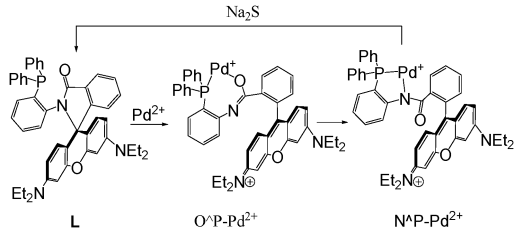


Fig. 2 Fluorescent titration spectra of **L** (1 μM) in the presence of different concentrations of Pd^{2+} in ethanol–water (4 : 1, v/v), $C_{Pd}{}^{2+}/C_L$ = 0, 1, 2.5, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 100. λ_{ex} = 530 nm. Slit: 5.0 nm; 10.0 nm.

L (1 μM) exhibited a very weak fluorescence (Φ = 0.003; λ_{ex} = 530 nm) at 587 nm. The titration of Pd^{2+} with **L** led to a rapid increase of the emission intensity (Φ = 0.45; λ_{ex} = 530 nm) at 587 nm. Over 150-fold fluorescence enhancement was observed under saturated conditions (*ca.* 50 equiv.). The increase of the fluorescence intensity at 587 nm followed the sigmoidal curves and the fluorescence turn-on constant ($K_{turn\text{-}on}$) was calculated as 32.0 ± 0.3 μM (with correlation coefficient R = 0.999) (Fig. S3, ESI†).[16] From the changes in Pd^{2+}-dependent fluorescence intensity at 587 nm (Fig. S4, ESI†), the detection limit was estimated to be 1.49×10^{-9} M, indicating that the limit of detection of **L** for Pd^{2+} met the WHO specified threshold limit for palladium content in drug chemicals [4.7×10^{-5} M (5 ppm) to 9.4×10^{-5} M (10 ppm)].[17] In fact, over 34-fold and 68-fold fluorescence enhancement was observed in the presence of 5 ppm and 10 ppm of Pd^{2+} ions, respectively (Fig. S5, ESI†). Reversible binding of **L** with Pd^{2+} was also carried out. The addition of Na_2S to a mixture of **L** and Pd^{2+} resulted in diminution of the fluorescence intensity at 587 nm, which indicated the regeneration of the free chemosensor **L**. The fluorescence was recovered by the addition of Pd^{2+} again (Fig. S6, ESI†). Such reversibility and regeneration are important for the fabrication of devices to sense the Pd^{2+} ion. In the presence of one equivalent of commonly found palladium catalysts, such as $PdCl_2$(cod), $Pd(PhCN)_2Cl_2$, $Pd_2(dba)_3$, $Pd(PPh_3)_4$, K_2PdCl_4, **L** showed significant fluorescence enhancement and prominent colour changes (Fig. S7, ESI†), indicating that **L** could be a promising potential selective fluorescent chemosensor for the direct detection of residual palladium including Pd(II) and Pd(0) species in drug chemicals. Thus, the fact that **L** responded not only to Pd^{2+} compounds but also to Pd^0 species indicated that the selectivities were determined by ligand exchange between **L** and the ligand of palladium species.

In the presence of palladium species, both absorption and fluorescence spectra present a prominent OFF–ON signal, indicating that palladium induced the structural conversion of the chemosensor from spirolactam to the ring-opened xanthene form of the rhodamine moiety. Upon adding 2 equiv. of Pd^{2+}, the maximum absorbance at 566 nm produced immediately, and then it was gradually converted to a new one at 550 nm within 30 min. During the conversion process, the appearance of an isosbestic point at 555 nm indicated that the chelating mode of **L**·Pd^{2+} converted from one to another (Fig. S8, ESI†). In the presence of Pd^{2+}, the time-dependent fluorescence response was also observed to be maximum after 20 min (Fig. S9, ESI†). Accordingly we hypothesized that the interaction of **L** with Pd^{2+} to form the final five-membered ring N^P–Pd^{2+} complex occurs *via* a seven-membered intermediate O^P–Pd^{2+} as depicted in Scheme 2. High-resolution mass spectra (HRMS) provided additional evidence for the formation of a 1 : 1 complex of **L**·Pd^{2+} (Fig. S10, ESI†).

Subsequently, various metal ions were used to evaluate the metal ion binding properties and the selectivity of **L** (1 μM) by means of fluorescence spectra in EtOH–H_2O (4 : 1, v/v). Among the metal ions examined, **L** showed a selective fluorescence increase only with Pd^{2+} (Fig. S11, ESI†). The addition of 2 equiv. of Pd^{2+} resulted in a significant enhancement of the emission intensity (22-fold) positioned at 587 nm. However, the addition of other ions has no obvious effect on the fluorescence emission. Thus, **L** can function as a highly selective fluorescent chemosensor for Pd^{2+} ions.



Scheme 2 Reversible binding of **L** with Pd^{2+}.

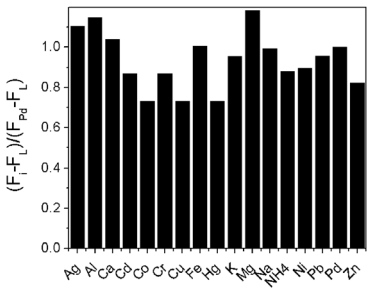


Fig. 3 Change in the ratio $((F_i - F_L)/(F_{Pd}^{2+} - F_L))$ of fluorescence intensity of **L** at 587 nm upon the addition of 2 equiv. of Pd^{2+} in the presence of 2 equiv. of background metal ions in EtOH–H_2O (4 : 1, v/v). λ_{ex} = 530 nm. Slit: 5.0 nm; 10.0 nm.

To explore the possibility of using **L** as a practical ion-selective fluorophore for Pd^{2+}, competition experiments were carried out, in which **L** (1 μM) was firstly mixed with 2 equiv. of various metal ions including Ag^+, Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, K^+, Fe^{3+}, Hg^{2+}, Mg^{2+}, Na^+, NH_4^+, Ni^{2+}, Pb^{2+}, and Zn^{2+}, followed by addition of 2 equiv. of Pd^{2+}. Emission spectroscopy was used to monitor the competition events. As shown in Fig. 3, in the presence of the above-mentioned ions, it still has an excellent turn-on ratio for the detection of Pd^{2+}. Similar fluorescence enhancement was observed for **L** after the addition of Pd^{2+} salts with different counteranions, such as ClO_4^-, NO_2^-, PF_6^-, AcO^-, and BF_4^-, *etc.* (Fig. S12, ESI†). The fluorescence responses of **L** and **L** + Pd^{2+} in acidic and basic regions of the pH range were examined, which showed that **L** can be used within a wide pH span of 5.3–10 (Fig. S13, ESI†). The investigation of **L** for the detection of the Pd^{2+} ions in tap water (T-water) and earth-soaked water (ES-water) from the campus of this university indicated that **L** could have potential application in the Pd^{2+} ions detection in the environmental milieu (Fig. S14, ESI†). Therefore, **L** was shown to be a promising selective fluorescent chemosensor for Pd^{2+} in the presence of most competing metal ions.

In summary, we have described the synthesis and properties of **L**, an excellent organophosphorus fluorescent chemosensor for Pd^{2+} ions. The chemosensor exhibited very high selectivity for Pd^{2+} ions over other relevant metal ions and anions with a very low detection limit of 1.49×10^{-9} M. Furthermore, the chemosensor was shown to be a promising potential selective fluorescent chemosensor for the direct qualitative determination of a wide range of residual palladium species in drug chemicals. We anticipate that this work provides a new approach to design metal ion chemosensors that take full advantage of the selective affinity and chelating properties of phosphorus ligands.

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