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A new rhodamine based colorimetric '*off–on*' fluorescence sensor selective for Pd^{2+} along with the first bound X-ray crystal structure†

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A new fluorescence rhodamine derivative bearing an 8-aminoquinoline moiety has been designed and synthesized for selective sensing of Pd^{2+} in the presence of other competing metal ions in aqueous media. Pd^{2+} induced spirolactam ring opening of rhodamine is confirmed for the first time by the X-ray crystal structure of the bound Pd^{2+}-complex.

Development of colorimetric fluorescence receptors for monitoring heavy and transition metal cations (HTM) of biological importance has received continuous attention because of their widespread use in agriculture, chemical and industrial processes that are causing serious threats to living organisms.[1]

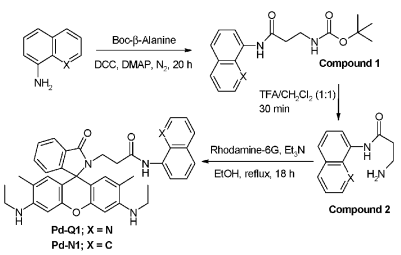
Among the metal ions, palladium is an important platinum-group element (PGEs) and is extensively being used in numerous materials such as alloys, jewellery, dental crowns, fuel cells and catalysts.[2] Palladium(II) salts are predominantly used as oxidizing reagents and pre-catalysts for many cross-coupling reactions.[3] A large number of organic reactions, namely Buchwald–Hartwig, Heck, Sonogashira and Suzuki–Miyaura are facilitated by palladium catalysis,[4] many of which involve carbon–carbon bond formation and therefore have a significant role in medicinal chemistry.[5] However, the largest use of palladium today is in catalytic converters of automobiles, that frequently release a large quantity of palladium to the environment,[6] that may cause a serious health problem.[7] Hence, considerable efforts have been paid for the development of methods for selective sensing of palladium. Conventional methods for its selective detection include atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), solid-phase microextraction high-performance liquid chromatography (SPME-HPLC) *etc*., all of which are associated with high cost of instrumentation.[8] Colorimetric and fluorimetric methods for the quick detection of Pd^{2+} are very popular in recent years because they are inexpensive and nondestructive in nature.[9] Being a paramagnetic species, most of the reported fluorescence sensors of Pd^{2+} readily undergo fluorescence quenching.[10] Unfortunately, there are only few reports of fluorescence enhanced probes for Pd^{2+}, which are either reaction based[11a–d] or reversible[11e–h] in nature. In this regard the rhodamine architecture, provides an ideal mode for the construction of new '*off–on*' type fluorescence enhanced probes for metal ions which is based on spirolactam (colorless, nonfluorescence) to ring-open amide (pink colored, fluorescence) equilibrium.[12]

Herein, we report a new rhodamine based colorimetric '*off-on*' fluorescence probe containing an 8-aminoquinoline moiety (**Pd-Q1**) that can selectively detect Pd^{2+} (0–25 μM) over other examined metal ions studied in aqueous solution. Though there is a number of literature reports of rhodamine based palladium sensors, this is the first report of the X-ray crystal structure of a rhodamine-Pd^{2+} complex.

The detailed synthetic methods for the preparation of the chemosensors are shown in Scheme 1. Initially coupling of 8-aminoquinoline with *N-tert*-Boc protected β-alanine in the presence of DCC gives **1** which on de-amidation of the *N-tert*-Boc group affords **2**. Finally the chemosensors are obtained by condensation of **2** with rhodamine-6G in presence of Et_3N in ethanolic solution.

The recognition event of **Pd-Q1** is based on the Pd^{2+} induced opening of the spirolactam ring which is associated with a brilliant pink coloration and remarkable fluorescence enhancement of the rhodamine dye (Scheme 2).

Interestingly, the introduction of a carboxamido group is of extra advantage to the deprotonation of the 8-aminoquinoline moiety after binding with the metal ion. The deprotonation process strengthens the electron-donating ability from the nitrogen atom of 8-amino group to the quinoline ring, and



Scheme 1 Synthesis of **Pd-Q1** and **Pd-N1**.

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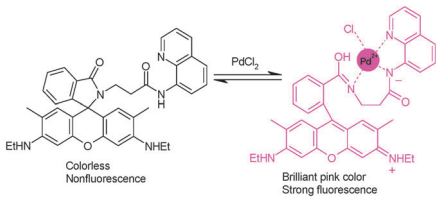

Scheme 2 Proposed Pd^{2+} sensing process.

thus electron transfer from the nitrogen atom of the heterocycle to the metal ion, possibly further enhances the charge transfer (CT) process. The X-ray crystal structure of the Pd^{2+}-complex also confirms the above and clearly reveals that the complex prefers to exist in the enol form (Fig. 3). Although the pink coloration is presumably due to spirolactam ring opening, the role of the quinoline nitrogen seems to be very crucial. This reasoning is proved when we compare the naphthalene analogue. Only a very faint pink coloration and small CHEF effect are observed for **Pd-N1** in the presence of excess Pd^{2+}.

The cation binding properties of the chemosensors are studied by employing the chloride salts of K^+, Na^+, Mg^{2+}, Mn^{2+}, Ca^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Cu^{2+}, Pd^{2+}, Pt^{2+} and Ru^{3+} ions in EtOH–H_2O (1 : 1, v/v, 25 °C) at pH 7.2 (50 mM HEPES buffer). Upon addition of Pd^{2+} to a colorless solution of **Pd-Q1**, a low-energy strong absorption band centered at 540 nm is observed. The intensity of the band increases regularly as the amount of Pd^{2+} is added progressively (up to 5.0 equiv.) (Fig. 1a) resulting in a brilliant pink coloration of the solution accompanying the spirolactam ring opening of the rhodamine dye (Scheme 2). Most importantly, neither pink coloration nor large CHEF effect is observed (S14, ESI†) in the presence of excess $Pd(PPh_3)_4$, which implies that **Pd-Q1** is inert towards Pd^0 (Fig. 1b). This observation is indeed helpful for the selective detection of Pd^{2+} in the presence of Pd^0.

The titration experiment fits nicely a 1 : 1 (host : guest) binding model as suggested by the Job plot diagram (Fig. 2a) and the association constant determined for the metal complexation process is 4.17×10^4 M^{-1} (error < 10%). The HRMS (TOF-MS) spectrum of the Pd^{2+}-complex shows peaks at m/z 717.1981 and 752.1743 possibly for [**Pd-Q1** + Pd^{2+}]$^+$ and [**Pd-Q1** + Pd^{2+} + Cl^-]$^+$ ions, respectively, which also proves a single mononuclear complex between **Pd-Q1** and Pd^{2+} (S8, ESI†). Thus we assume a four-coordinated square planar geometry for Pd^{2+}.

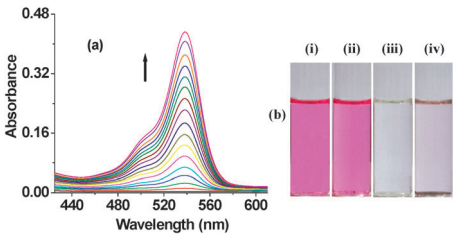

Fig. 1 (a) UV-vis absorption titration spectra of **Pd-Q1** ($c = 2.0 \times 10^{-5}$ M) in the presence of Pd^{2+} ($c = 2.0 \times 10^{-4}$ M) at pH 7.2. (b) Color changes in the presence of (i) **Pd-Q1** + $PdCl_2$ (5.0 equiv.); (ii) **Pd-Q1** + $Pd(OAc)_2$ (5.0 equiv.); (iii) **Pd-Q1** + $Pd(PPh_3)_4$ (10.0 equiv.); (iv) **Pd-N1** + $PdCl_2$ (50.0 equiv.).

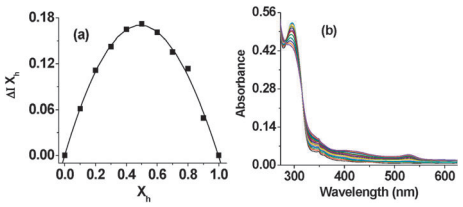

Fig. 2 (a) Job plot diagram of **Pd-Q1** for Pd^{2+} determined by UV-vis method (X_h is the mole fraction of **Pd-Q1** and ΔI indicates the change of absorbance). (b) UV-vis absorption spectra of **Pd-N1** ($c = 2.0 \times 10^{-5}$ M) in presence of Pd^{2+}.

The X-ray crystal structure of the Pd^{2+}-complex of **Pd-Q1** shows the mode of binding of **Pd-Q1** with $PdCl_2$ (Fig. 3). The complex crystallizes in the monoclinic crystal system in space group $C2/c$ from hot aqueous methanol (Tables 1 and 2, ESI†). Pd^{2+} is coordinated by two nitrogen atoms of the 8-aminoquinoline moiety (Pd–N 2.003(10) and 2.038(11) Å) and one nitrogen atom of the 3-aminopropionamide moiety (Pd–N 1.993(8) Å), along with one chlorine atom (Pd–Cl 2.309(4) Å) to furnish a distorted square planar geometry.

No pink coloration is observed initially when Pd^{2+} (5.0 equiv.) is added gradually to **Pd-N1** ($c = 2.0 \times 10^{-5}$ M) solution (Fig. 2b). Hence, **Pd-N1** is quite innocent towards Pd^{2+}. However, a very faint pink coloration is noticed (Fig. 1b) only on prolonged standing when excess Pd^{2+} (50.0 equiv.) is added. These results suggest that for **Pd-Q1**, the aminoquinoline moiety is effectively adjusted in terms of electron density and coordinating properties which lead to better selectivity of **Pd-Q1** toward Pd^{2+} over **Pd-N1**.

The acid–base titration experiment reveals that **Pd-Q1** does not undergo any significant fluorescence enhancement within the pH range from 5–10 which suggests that the molecule prefers the spirocyclic form. But in strong acidic conditions (pH < 3) protonation causes the coloration due to opening of the spirolactam ring (inset, Fig. 4). Thus **Pd-Q1** may be employed for the detection of Pd^{2+} in near-neutral pH range.

The fluorescence spectra of **Pd-Q1** ($\phi_f = 0.021$) are recorded by excitation of the rhodamine fluorophore at 505 nm. Addition of Pd^{2+} to the **Pd-Q1** solution leads to a large fluorescence enhancement ($\phi_f = 0.125$) and the emission intensity increases very sharply at 562 nm that is accompanied by spirolactam ring opening of **Pd-Q1** (Fig. 4).

Addition of other examined metal ions, even in excess amount to **Pd-Q1**, causes no significant absorption and emission changes. For Pt^{2+} and Ru^{3+}, a slight increase in emission intensity is observed. This is possibly because of their similar chemical properties. Fig. 5(a) shows a comparative view of emission intensity of the rhodamine fluorophore **Pd-Q1** after adding 5.0 equiv. of each of the guest cations.

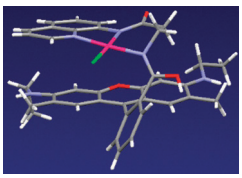

Fig. 3 View of the X-ray crystal structure of the Pd^{2+}-complex of **Pd-Q1** (water and disordered $PdCl_2$ are omitted for clarity).

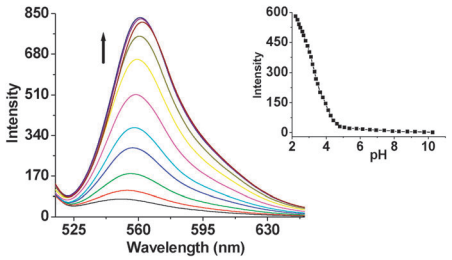

Fig. 4 Fluorescence titration spectra of **Pd-Q1** ($c = 2.0 \times 10^{-5}$ M) in the presence of Pd^{2+} ($c = 2.0 \times 10^{-4}$ M) at pH 7.2. Inset: Fluorescence response of **Pd-Q1** ($c = 1.0 \times 10^{-5}$ M, $\lambda_{ex} = 505$ nm) as a function of pH in EtOH-H_2O (1 : 1, v/v, 25 °C), pH is adjusted by using aqueous solutions of 1 M HCl or 1 M NaOH.

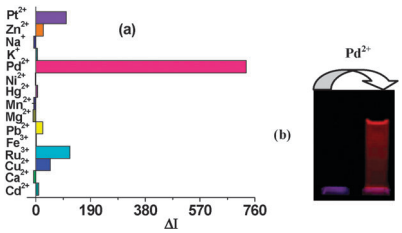

Fig. 5 (a): Change of emission intensity of **Pd-Q1** after adding 5.0 equiv. of each of the guest cations in EtOH–H_2O (1 : 1, v/v, 25 °C) at 562 nm. (b) Colored emission observed for **Pd-Q1** during titration with Pd^{2+}.

To further explore the selectivity of **Pd-Q1** for Pd^{2+}, competition experiments are performed in the presence of Pd^{2+} mixed with 6.0 equiv. of each of the guest cations *viz.* Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Cu^{2+}, Pt^{2+} and Ru^{3+} respectively. While some metal ions, especially Cu^{2+}, Pt^{2+} and Ru^{3+} bound to **Pd-Q1**, the addition of 1.5 equiv. of Pd^{2+} displaces most of them (Fig. 6). Thus these free cations would have very little influence towards **Pd-Q1** and do not hamper the fluorogenic detection of Pd^{2+}.

Although for **Pd-N1** a similar increase in emission intensity is observed, the fluorescence enhancement is less compared to **Pd-Q1** during addition of Pd^{2+} (S13, ESI†). This again proves the 8-aminoquinoline mediated amplification of the fluorescence signal of **Pd-Q1**. Hence, a smaller CHEF effect is observed for **Pd-N1** compared to **Pd-Q1** in the presence of Pd^{2+}.

The reversibility of the Pd^{2+} complexation process as proposed in Scheme 2 is confirmed after adding an excess amount of S^{2-} to the colored solution of the metal–ligand complex. The pink colored solution turns colorless and the fluorescence is quenched, indicating that S^{2-} sequesters Pd^{2+} from the metal–ligand complex, liberating free **Pd-Q1** (S14, ESI†). Thus **Pd-Q1** may be classified as a reversible chemosensor for Pd^{2+}.

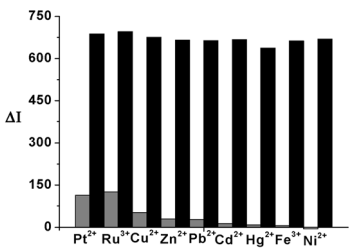

Fig. 6 M^{n+}-selectivity profile of **Pd-Q1**: (grey bars) change of emission intensity of **Pd-Q1** + 6 equiv. M^{n+}; (black bars) change of emission intensity of **Pd-Q1** + 6 equiv. M^{n+}, followed by 1.5 equiv. Pd^{2+}.

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