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A new ratiometric ESIPT sensor for detection of palladium species in aqueous solution†

Bin Liu, Hu Wang, Taisheng Wang, Yinyin Bao, Fanfan Du, Jiao Tian, Qianbiao Li and Ruke Bai*

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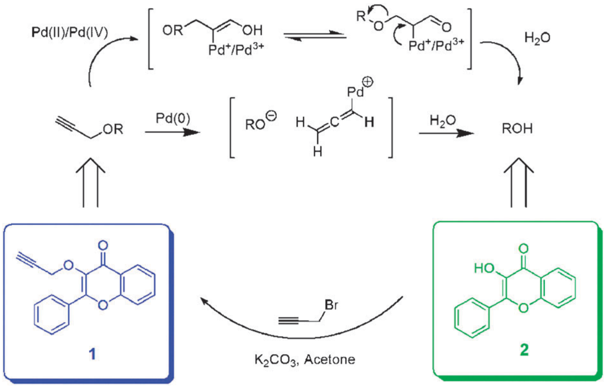
An aqueous ratiometric ESIPT sensor with a 87 nM (15.4 ppb) detection limit was successfully synthesized and applied for detection of all oxidation states of palladium species.

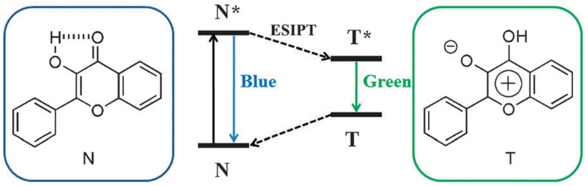
In view of extensive applications of palladium species in fuel cells and catalyst industry,[1] it is possible that food, medicine and water may be contaminated with palladium species. Palladium may cause a serious health problem owing to the formation of complexes between Pd and some biomacromolecules such as proteins, DNA and RNA.[2] Thus, government restrictions on the levels of residual heavy metals in end products are very strict, and its threshold for palladium is 5–10 ppm.[3] Therefore, it is necessary and important to urgently develop an effective and convenient method for detecting palladium species. Conventional analytical methods can be used for the detection of palladium in biological and environmental samples, including atomic absorption spectrometry, plasma emission spectroscopy, solid-phase microextraction-high performance liquid chromatography, X-ray fluorescence and inductively coupled plasma mass spectrometry (ICP-MS).[4] However, these methods often require sophisticated and time-consuming sample preparation procedures or expensive equipments. Thus, recently significant effort has gone into developing fluorescent methods, because of their low cost, simplicity and sensitivity for palladium species.[5]

Very recently, we have also reported some conjugated fluorescent sensors based on aggregation-induced fluorescent quenching mechanism for palladium detection.[6] However, we noticed most of the sensors based on a coordination mechanism suffered varying degrees of interference from other transitional metal ions, in contrast, sensors based on a catalytic mechanism usually show excellent selectivity. Also, most of the fluorescent sensors for palladium possess a small Stokes' shift, which is an extremely serious limitation in quantitative determination and bioimaging because of the excitation interference.[7] Thus, catalytic mechanism-based sensors are highly desired for detection of palladium species with a large Stokes' shift.

Here we present a new aqueous ratiometric sensor 3-(prop-2-ynyloxy)hydroxyflavone (**1**) based on excited-state intramolecular photon-transfer (ESIPT) as a probe for Pd species. The experimental results show that this new sensor has excellent properties for detection of Pd species. The proposed sensing mechanism is shown in Scheme 1 *via* depropargylation of **1** catalyzed by Pd species. In order to design a new sensor, we chose 3-hydroxylflavone (**2**) as the fluorophore which has a large Stokes' shift (> 150 nm) because 3-hydroxylflavone can undergo an excited-state intramolecular photon-transfer (ESIPT) process upon photoexcitation whereby rapid photo-induced proton transfer results in tautomerization, as shown in Scheme 2. Excitation of **2**, which exists as a normal isomer (N) in the ground state, leads to an adiabatic ESIPT reaction and results in the formation of the tautomer (**T***). Blue fluorescence occurs from **N***, whereas green fluorescence



Scheme 1 Proposed depropargylation process of **1** *via* Pd species catalytic reaction.



Scheme 2 General mechanism of ESIPT process and chemical structures of normal isomer (**N**) and tautomer (**T**) in the ESIPT process of **2**.

CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, P. R. China 230026. E-mail: bairk@ustc.edu.cn; Fax: 0086-551-3631760; Tel: 0086-551-3600722

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originates from **T***.[8] Modification of the hydroxyl group of **2** can block the ESIPT process and result in quenching of the **T** emission. Conversely, regeneration of the free hydroxyl group can restore the dual emission associated with **N–T** tautomerism. In view of their large Stokes' shift and dual emission, ESIPT compounds have been successfully applied to sensors[9] for fluoride and cysteine. However, to the best of our knowledge, no report has been published on sensors for palladium detection based on ESIPT signal transduction mechanism.

The synthetic approach for sensor **1** is shown in ESI†. First, the reaction between benzaldehyde and 2′-hydroxyacetophenone in MeOH afforded **3** in a yield of 67% and then **3** was oxidized with H_2O_2 to obtain **2** in 43% yield. Finally, propargylation of the hydroxyl group of **2** was achieved with 3-bromo-1-propyne to give sensor **1** in a yield of 53%. The chemical structure of compound **1** was verified by HRMS, ^{1}H NMR and ^{13}C NMR spectroscopy (see ESI†). UV-Vis absorption and fluorescence spectra of **1** and **2** were measured in $CH_3CN–H_2O$ (1 : 4, v/v) solution buffered at pH 7.0 (HEPES, 10 mM) at room temperature (Fig. S1 and S2, ESI†). Fluorescence spectra shows that compound **2** can emit dual emission maximum at 412 nm (**N** form) and 517 nm (**T** form), while compound **1** only emits the **N** form emission at 412 nm, as expected.

The fluorescence sensing behavior of **1** toward palladium was investigated using a 10 μM solution of **1** in $CH_3CN–H_2O$ (1 : 4, v/v) buffered at pH 7.0 (HEPES, 10 mM). $PdCl_2$ was selected as the representative palladium species in the following titration experiments since it is among the most toxic of palladium compounds. As shown in Fig. 1a, upon addition of 0.1 mM $PdCl_2$, the emission at λ = 412 nm initially decreases. This may be attributed to that a Pd^{2+} addition-induced intermediate product with a carbon–carbon double bond (Scheme 2) leads to fluorescence quenching through a photoinduced electron-transfer (PET) process.[10,11] After 30 min, the emission band slowly increases and gradually levels off. This is because the PET-induced fluorescence quenching terminates along with the completion of depropargylation. Meanwhile deprotection of the hydroxyl group of **1** results in the formation of **2**, which exhibits ESIPT process, and the **T**-form emission band at λ = 517 nm gradually grows. It takes about 3 h to reach the relative saturation point, as can be seen from the plot of the time-dependent intensity change (Fig. 1b). The mechanism of the palladium catalyzed depropargylation was verified by LC-MS. The peak at *m/z* 239.0700 $[M - H]^+$ corresponding to compound **2** was observed in the LC-MS spectra of the product mixture (Fig. S3 ESI†). Therefore, the fluorescence change is due to the formation of compound **2** by the palladium-catalyzed depropargylation reaction.

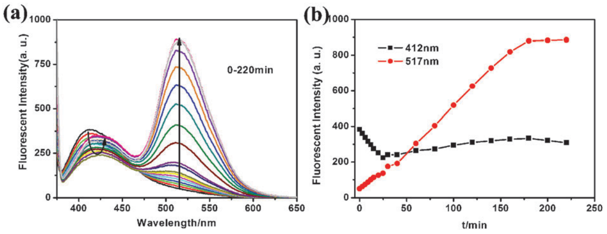

Fig. 1 Time-dependent fluorescence spectral changes (a) and intensity changes (b) of **1** (10 μM) in the presence of 0.1 mM $PdCl_2$ in $CH_3CN–H_2O$ (1 : 4, v/v) solution with HEPES buffer (10 mM).

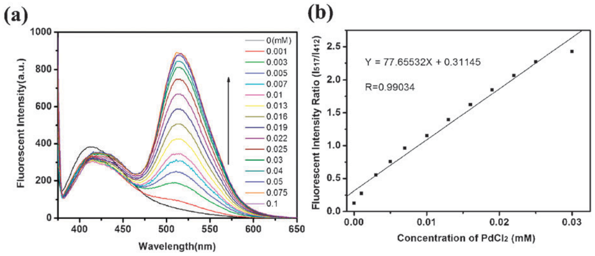

Fig. 2 Fluorescence spectra changes (a) and fluorescence intensities ratio (I_{517}/I_{412}) (b) of **1** (10 μM) in the presence of increasing concentrations of $PdCl_2$ (concentrations: 0, 0.001, 0.003, 0.005, 0.007, 0.01, 0.013, 0.016, 0.019, 0.022, 0.025, 0.03, 0.04, 0.05, 0.075, 0.1 mM) in $CH_3CN–H_2O$ (1 : 4, v/v) solution with HEPES buffer (10 mM).

Fig. 2a shows the fluorescence changes with various amounts of $PdCl_2$ in $CH_3CN–H_2O$ (1 : 4, v/v) solution with HEPES buffer (10 mM) after 3 h. When the concentration of $PdCl_2$ is gradually increased, the fluorescence peak at λ = 412 nm shows a 10–15 nm red shift with a slow decrease. At the same time, a new fluorescence peak occurred at λ = 517 nm and then becomes the maximum peak. It is observed that the ratios of fluorescence intensities (I_{517}/I_{412}) change from 0.13 to 2.43 (R = 18.7-fold) (Fig. 2b). More importantly, the ratios of the fluorescent intensities are linearly proportional to the amount of $PdCl_2$ from 0 to 30 μM. The ratiometric fluorescent measurement which is based on the ratio of two fluorescent bands instead of the absolute intensity of one band, makes it possible to measure the analyte more accurately and sensitively with minimization of the background signal.[12] If we arbitrarily define the detection limit as the Pd concentration at which a 10% increase in fluorescence emission intensity ratio (I_{517}/I_{412}) can be measured by employing 10 μM sensor **1** in $CH_3CN–H_2O$ (1 : 4, v/v) solution with HEPES buffer (10 mM), the detection limit of $PdCl_2$ is calculated to be 87 nM (15.4 ppb, Pd content = 9.2 ppb), which is far below the allowable level of palladium ions (5–10 ppm) from the European Agency for the Evaluation of Medicinal Products (EMEA).[13] The sensitivity of sensor **1** was also measured in pure water which is particularly important for detection in drinking water (Fig. S4 and Fig. S5 ESI†). Such sensitivity readily satisfies the requirement of medical and environmental monitoring.

To demonstrate the potential application of this palladium-specific method, we tested whether it could detect all the oxidation states of palladium [Pd(0): $Pd(PPh_3)_4$; Pd(II): $PdCl_2$, $PdCl_2(PPh_3)_2$, $PdCl_2(dppf)_2$; Pd(IV): K_2PdCl_6]. According to the intensity ratios (I_{517}/I_{412}), sensitivities of sensor **1** to palladium species was in the order: $PdCl_2$ > $Pd(PPh_3)_2Cl_2$ > K_2PdCl_6 > $Pd(PPh_3)_4$ > $PdCl_2(dppf)_2$, as shown in Fig. 3. The results reveal that chemosensor **1** remarkably responds to all the oxidation states of palladium with significant fluorescence changes. These results prove once again that the depropargylation reaction can occur not only *via* Pd(IV)/Pd(II)-catalyzed hydration intermediates, but also *via* allenylpalladium resulting from the oxidative addition of Pd(0) without additional reagents, as shown in Scheme 1.[14] On the other hand, $PdCl_2$ and K_2PdCl_6 induce the largest enhancement of the fluorescent intensity at λ = 517 nm. Due to the wide use of the aqueous solutions of these two palladium ions in plating baths, chemosensor **1** is particularly important for detection in environmental water.

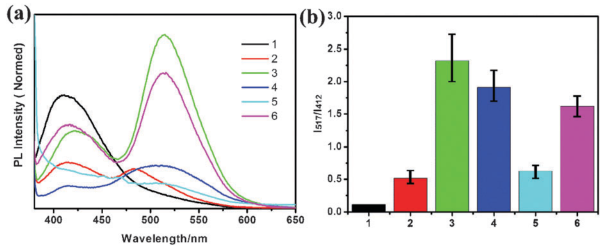

Fig. 3 Comparison of the fluorescence spectra changes (a) and intensity ratio (I_{517}/I_{412}) changes on different palladium complexes, measured for a mixture of sensor **1** (10 μM) and the palladium species (100 μM) in $CH_3CN–H_2O$ (1 : 4, v/v) solution with HEPES buffer (10 mM): 1, sensor **1** only; 2, $Pd(PPh_3)_4$; 3, $PdCl_2$; 4, $Pd(PPh_3)_2Cl_2$; 5, $PdCl_2(dppf)_2$; 6, K_2PdCl_6.

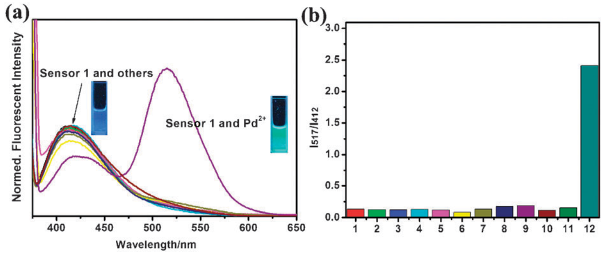

Fig. 4 Fluorescence spectral changes (a) and fluorescence intensities ratio (I_{517}/I_{412}) (b) of **1** upon addition of different metal cations in $CH_3CN–H_2O$ (1 : 4, v/v) solution with 10 mM of HEPES buffer. (1, sensor **1** only; 2, Ag^+; 3, Ca^{2+}; 4, Cd^{2+}; 5, Co^{2+}; 6, Cu^{2+}; 7, Fe^{3+}; 8, Hg^{2+}; 9, Mg^{2+}; 10, Ni^{2+}; 11, Zn^{2+}; 12, Pd^{2+}): [**1**] 10 μM, [metal ion] = 0.5 mM.

An exceptional feature of this sensor is its very high selectivity towards the target analyte over other competitive species. The selectivity of chemosensor **1** toward different metal ions was investigated and results are shown in Fig. 4. The results indicate that the sensor **1** displays a selective fluorophores behavior toward palladium ion with a fluorescence change from blue to green, which can be easily seen by the naked eye (Fig. 4a inset). Under the same conditions, nearly no ratiometric response changes are observed in the presence of 0.5 mM of Ag^+, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Ni^{2+}, Zn^{2+} in $CH_3CN–H_2O$ (1 : 4, v/v) solution with HEPES buffer (10 mM). These results demonstrate that chemosensor **1** possesses excellent selectivity towards palladium species.

In conclusion, we have developed a chemical reaction-based ratiometric ESIPT fluorescent sensor **1** specific for palladium species with a large Stokes' shift of more than 150 nm. The results demonstrate that sensor **1** exhibits a high sensitivity and an excellent selectivity for Pd^{2+} detection in aqueous solution, with detection limit down to ~87 nM (15.4 ppb). Moreover, obvious ratiometric responses are observed towards all the oxidation states of palladium among other transition metal ions without additional reagents. This work provides a new mild and promising strategy for the detection of Pd species in biological and environmental systems.

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