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Journal Name

COMMUNICATION

Highly Selective Fluorescent Detection for Pd$^{2+/4+}$ Species Based on the Catalyzed Aromatic Claisen Rearrangement

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A highly selective chemodosimeter based on 1,8-naphthalimide for Pd$^{2+/4+}$ species via Claisen rearrangement was developed, which not only discriminated Pd from competing Pt species, but also distinguished Pd in an oxidation state without altering its oxidation states from Pd^{0}. Under the optimized reaction conditions, the detection limit can reach 1.4 µM for Pd^{2+}.

As one of the rare transition metals, palladium plays an important role in many fields, such as electronics, dentistry, medicine, jewelry, and the catalyst in synthetic chemistry or automotive catalytic converters.[1] And such increasing industrial use has raised great concern on its emission in biosphere and the further toxicological effects on human health.[2] Consequently, the detection of palladium is of great interest and importance to many chemists, biologists and environmentalists. In the past few years, many analytic methods, including inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS), plasma emission spectroscopy (ICP-AES), X-ray fluorescence (XRF), etc, have been developed for the detection of palladium.[3] However, these methods often require the complicated sample pretreatment, sophisticated instrumentation, and highly skilled individuals. Meanwhile, the development of fluorescence methods based on chemodosimeters for qualitatively and quantitatively detecting palladium species has blossomed in recent years due to its low cost, convenient operation, and high accuracy.[4]

Up to now, the fluorescent-sensing systems for palladium species reported were mostly based on the following three mechanisms: Pd-coordination reaction,[5] Pd-triggered cleavage reaction[1,6-13] and Pd-catalyzed Claisen rearrangement reaction.[14] In the first case, the fluorescent probes provide well-organized coordination geometry for palladium ion.

Because the coordination capability of ligands for palladium ion is significantly influenced by the solvent condition such as the change in pH value, its selectivity may be a major issue for such coordination based sensing systems. In the second case, Koide et al. developed a chemodosimeter based on Pd-triggered Tsuji-trost reaction. In this system, an allylated fluorescein, which is nonfluorescent, undergoes the catalytic deallylation or depropargylation reaction with Pd^{0} generated in situ from Pd^{2+} species to regenerate the fluorescein. However, most of this type of chemodosimeters require initial conversion of Pd$^{2+/4+}$ to Pd^{0} using a reducing agent such as PPh$_3$, TFP(tri-2-furyiphosphine) or TFP-NaBH$_4$. To overcome the above limitation, in 2008, Koide et al.[14] further presented the third type of Pittsburgh Green based chemodosimeter by using Claisen rearrangement reaction, in which Pd species in an oxidation state-specific manner without altering oxidation states could be detected. Although there were some improvements on the detection of Pd$^{2+/4+}$, this method couldn't discriminate Pd$^{2+/4+}$ from Pt^{4+} species. As one of the platinum-group elements, palladium shows a similar catalytic effect as platinum and is usually used in automotive catalytic converters with platinum together,[14] which indicates that any interference from platinum is a disadvantage from the viewpoint of selective detection. Therefore, the search for selective chemodosimeters for Pd species in an oxidation state is still a challenging task.

On the other hand, 1,8-naphthalimide with an electron donor and an acceptor group is characteristic of an internal charge transfer (ICT) chromophore, and its fluorescent property is highly sensitive to the polarity of the local environment. So far, the naphthalimide derivatives have been widely used as fluorescent chemodosimeters.[15] Inspired by the success application of the Claisen rearrangement reaction in Pittsburgh Green based chemodosimeter, we hope to further investigate the feasibility of this strategy on the design of one based on naphthalimide.

Based on the above considerations, probe **1** was synthesized in four steps from commercially available 4-bromo-1,8-naphthalic anhydride in a satisfactory yield (Scheme 1,

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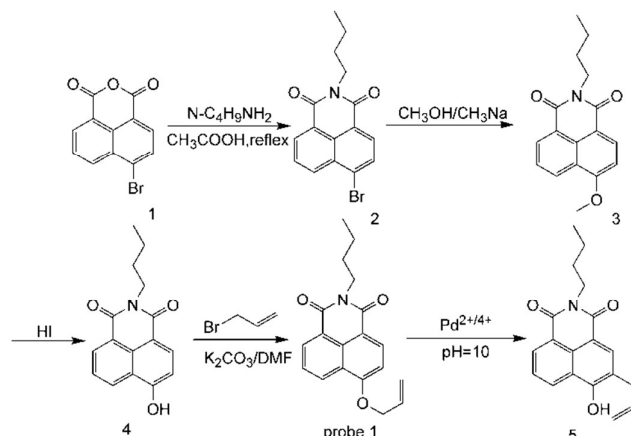
Scheme 1 Synthetic Route to naphthalimide-based probe **1** for $Pd^{2+/4+}$ species.

Supporting information Fig. S1-S4). After being treated with $Pd^{2+/4+}$ species under mild condition, probe **1** is expected to be converted to compound **5** by Claisen rearrangement reaction.

We firstly studied the spectroscopic properties of probe **1** in $Na_2CO_3/NaHCO_3$ buffer (pH=10) solution. As shown in Fig. 1, in the absence of Pd^{2+}, probe **1** (12.5 µM) showed a relatively short emission wavelength with a maximum at 461 nm (blue), as a result of the electron-withdrawing effect of the amide group. After being treated with Na_2PdCl_4 (25 µM) at 50 °C for 4 h, the fluorescence intensity of probe **1** at 461 nm decreased dramatically, and a new weak emission band appeared at 552 nm. From the inset in Fig. 1, such colour change in the solutions, ranging from colourless to yellow, even could be distinguished by the naked eyes which is also verified by the change on the corresponding adsorption spectra (Fig. S6). To disclose the sensing mechanism of probe **1** toward palladium species, after the separation and purification, the reaction product of probe **1** with Pd^{2+}, which was the product of typical Claisen rearrangement reaction, was confirmed by ^{1}H NMR and ^{13}C NMR (Fig. S5). In addition, the characteristic fluorescence spectrum of a standard pure compound **5** also supports this consideration (Fig. S9). Similar to the mono allyl ether Pittsburgh Green,[14] Claisen rearrangement of probe **1** with Pd^{2+} may proceed through the mechanism shown in Scheme S1.

As we know, Claisen rearrangement reaction is generally influenced by various factors,[16] such as temperature, pH and reaction time. To achieve an optimal analytical performance, the experiment conditions for the fluorescence emission were further optimized through adjusting temperature from 30 to 70 °C, pH from 4 to 14, and the reaction time from 0 to 5 h. As shown in Fig. S10, the fluorescence intensity at 461 nm just decreased considerably when the temperature was higher than 50 °C, which indicates that 50 °C was the critical temperature for Claisen rearrangement reaction. For the effect of pH on the fluorescence emission (Fig. S11), it can be clearly seen that the reaction just occurred at pH 7-14 and the corresponding fluorescence intensity obviously decreased in this range. Fig. S12 gave the fluorescence intensity at 461 nm
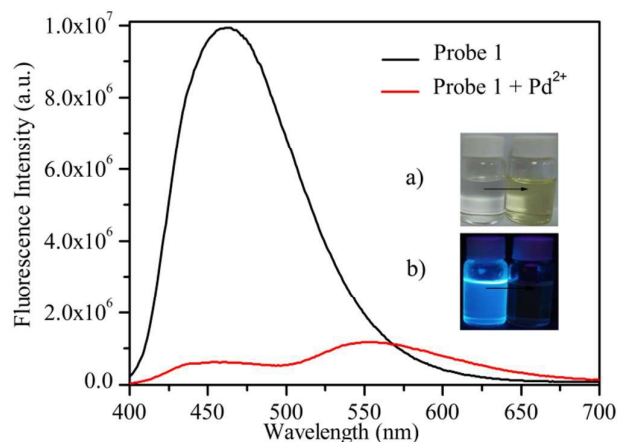

Fig. 1 Fluorescence spectral changes of probe **1** (12.5 µM) upon treatment with Na_2PdCl_4 (45 µM) in $Na_2CO_3/NaHCO_3$ buffer (pH=10) solution at 50 °C. Ex=379 nm. Slit: 5.0 nm/5.0 nm. Inset: Photos further show corresponding changes in colour (a) and fluorescence colour (b) upon the addition of Na_2PdCl_4.
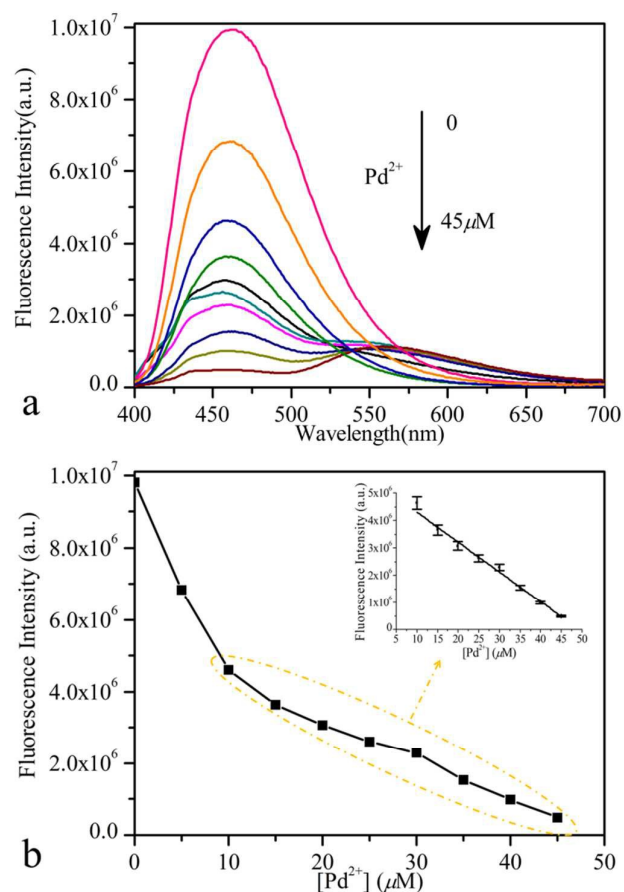

Fig. 2 Fluorescence emission spectrum of probe **1** (12.5 µM) toward different concentrations of Na_2PdCl_4 in $Na_2CO_3/NaHCO_3$ buffer (pH=10) solution. (a) Fluorescence spectra of probe in the presence of increasing concentrations of Na_2PdCl_4 (final concentration: 0, 5, 10, 15, 20, 25, 30, 35, 40, 45 µM); (b) Plot of fluorescence intensity at 461 nm depending on $[Pd^{2+}]$ in the 0-45 µM. Inset: Correlation between fluorescence intensity and $[Pd^{2+}]$ in the 10-45 µM.

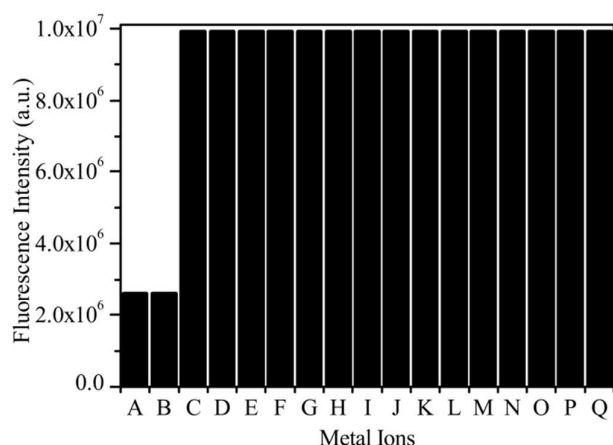**Fig. 3** Metal ion selectivity of probe **1** (12.5 μM) in Na$_2$CO$_3$/NaHCO$_3$ buffer (pH=10) towards various metal cations (25 μM)[A, Pd^{2+}; B, Pd^{4+} ; C, Pd^0; D, Pt^0; E, Pt^{2+}; F, Pt^{4+}; G, N^{a+}; H, Ca^{2+}; I, Mn^{2+}; J, Co^{2+}; K, Cu^{2+}; L, Zn^{2+}; M, Cd^{2+}; N, Ni^{2+}; O, Au^{3+}; P, Ag$^+$; Q, Fe^{3+}]. Each spectrum was acquired at 4 h after metal ions addition at 50 ^{o}C. Ex=379 nm. Slit: 5.0 nm/5.0 nm.

in the presence of Pd^{2+} at 50 ^{o}C as a function of incubation time, and it can be found that the fluorescence intensity decreased quickly in 2 h and reached the minimum after 4 h reaction. According to the above results, in the following reactions, the detection of Pd$^{2+/4+}$ was performed in Na$_2$CO$_3$/NaHCO$_3$ buffer (pH=10) at 50 ^{o}C with 4 h incubation.

Variation of fluorescence spectra of probe **1** as a function of Pd^{2+} concentration were measured to evaluate its sensing behaviour, as shown in Fig. 2a. As expected, upon the increase of Pd^{2+} concentration (0-45 μM), a gradual decrease in fluorescence intensity at 461 nm was observed (Fig. 2b). In Fig. 2b inset, the sensor exhibited a linear response toward Pd^{2+} at the concentration range from 10 to 45 μM. The linear equation was y=5387520-109106x, and the linear relative coefficient was R^2=0.995. The detection limit under these conditions was determined as 1.4 μM with a signal-to-background ratio (S/B) of 3, which was slightly higher than the result reported by Koide et al. by using the similar detection mechanism.[14]

The selectivity of probe **1** was further examined by the fluorescence responses of the probe toward different metal ions. As shown in Fig. 3, the fluorescence at 461 nm of the probe **1** decreased only in the cases of Pd^{2+} and Pd^{4+}; other metal ions such as Pd^0, Pt^0, Pt^{2+}, Pt^{4+}, N^{a+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Au^{3+}, Ag$^+$ and Fe^{3+} had no effect on the emission of probe **1**. This results clearly demonstrated that probe **1** had a high selectivity and could discriminate Pd$^{2+/4+}$ species from both Pd^0 and Pt$^{0/2+/4+}$ species, which was better than the result reported by Koide et al,[14] in which Pittsburgh Green based chemodosimeter couldn't discriminate Pd$^{2+/4+}$ from Pt^{4+} via the similar Claisen rearrangement reaction. Considering the fact that the catalysis of Claisen rearrangement is complex and greatly depends on the substance and reaction parameters,[16] the above result is understandable. In our system, 1,8-naphthalimide was used as the chromophore instead of xanthene moiety. To the best of our knowledge, it is the first report that the resulting

chemodosimeter for Pd$^{2+/4+}$ species has such the high selectivity.

To demonstrate the practical application of probe **1**, we conducted experiments to detect residual Pd ion in a typical Heck reaction. The cross coupling of acrylic acid with iodobenzene catalyzed by Pd^0 was performed according to the reported method.[17] Many studies had indicated that the activity of Pd^0 that decreased in re-use was probably due to the leaching of palladium into the solution in the state of Pd^0 or Pd^{2+}. To verify the above speculation, probe **1** was added into the solution after the separation of Pd^0 and product. After being treated at 50 ^{o}C for 4 h, the fluorescence intensity of the resulting solution decreased significantly. According to the decrement in fluorescence intensity, the concentration of Pd^{2+} was about 33.5 μM. Therefore, it can be concluded that the leaching of Pd into the solution in an oxidation state was one of the causes that leads to the decrease of the activity of catalyst Pd^0 in the Heck reaction.

Due to our successful detection for Pd$^{2+/4+}$ with no Pt-interference, we next performed the test for three-way catalyst (TWC) sample. TWC was used in this case because it contains both palladium and platinum simultaneously.[18] After initial treatment of TWC with 5% HNO$_3$, the concentrations of Pd^{n+} and Pt^{n+} were about 15 μM and 25 μM, respectively. As shown in Fig. S13, the fluorescence intensity at 461 nm of TWC corresponded to 15.5 μM of Pd^{2+}, which further supported the above result that any interference from Pt^{n+} had no effect on the detection of Pd$^{2+/4+}$ by using probe **1**.

Conclusions

In conclusion, we have synthesized a highly selective chemodosimeter based on 1,8-naphthalimide for Pd$^{2+/4+}$ species. The recognition mechanism is via the Claisen rearrangement reaction. The resulting fluorescent probe not only discriminated Pd from competing Pt species, but also distinguished Pd in an oxidation state without altering its oxidation states from Pd^0. With the experiment condition optimized, the probe exhibits a liner response for Pd^{2+} from 10 to 45 μM, with a detection limit of 1.4 μM.

Acknowledge

Notes and references

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Table of contents entry

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Claisen Rearrangement

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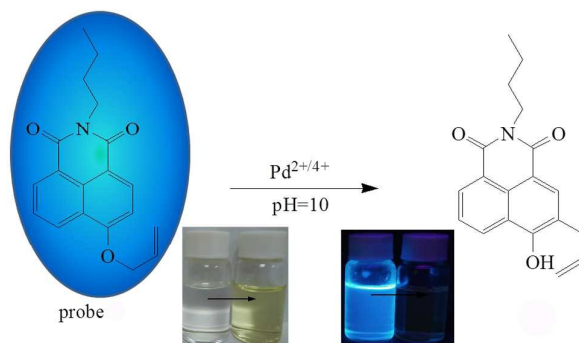
A highly selective chemodosimeter via based on 1,8-naphthalimide for Pd$^{2+/4+}$ species via Claisen rearrangement was developed with the detection limit of 1.4 μM.