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Highly Selective and Reversible Chemosensor for Pd^{2+} Detected by Fluorescence, Colorimetry, and Test Paper

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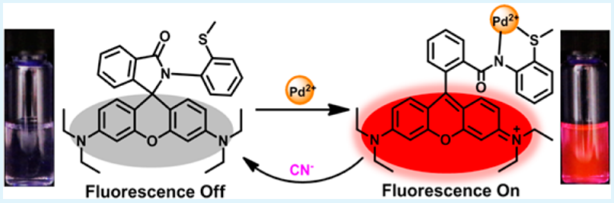
S *Supporting Information*

ABSTRACT: A "turn-on" fluorescent and colorimetric chemosensor (**RBS**) for Pd^{2+} has been designed and synthesized through introduction of sulfur as a ligand atom to Rhodamine B. **RBS** exhibits high selectivity (freedom from the interference of Hg^{2+} in particular) and sensitivity toward Pd^{2+} with a detection limit as low as 2.4 nM. **RBS** is also a reversible sensor, and it can be made into test paper to detect Pd^{2+} in pure water. Compared to the chemosensors that introduced phosphorus to Rhodamine to detect Pd^{2+}, **RBS** can be synthesized more simply and economically.



KEYWORDS: *chemosensor, high selectivity, reversible, palladium, fluorescent, colorimetric*

INTRODUCTION

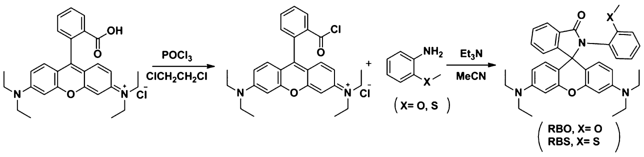
As one of the most important Platinum group elements, palladium was widely used as an effective catalyst for pharmaceutical synthesis.[1,2] Palladium is also an indispensable material in high-tech fields such as aviation, navigation, and the automotive industry. The use of palladium produced residues of palladium in the environment. In addition, palladium can be accumulated in the food chain and may result in potential health danger. For instance, Pd^{2+} can bind to thiol-containing amino acids, proteins, DNA, and other biomolecules and disturb a variety of cellular processes.[3] Therefore, it is very urgent to develop an excellent method to detect residual palladium in drugs and environment.

Among the methods of detecting palladium in the literature, optical (colorimetric and fluorescent) chemosensor gained widespread interest because of its high selectivity, high sensitivity, and convenient operation.[4−9] One popular strategy is to take advantage of Pd-catalyzed reactions to design palladium sensors, such as the Pd-catalyzed cyclization of oxazole,[10] pyrone,[11] and pyrrole,[12] the Pd-catalyzed depropargylation reaction[13−19] and deallylation reaction,[20] the Pd-catalyzed Heck,[21] and the Suzuki−Miyaura coupling reaction.[22] Owing to the fact that Pd^{2+} has a ($4d^8$) electronic configuration, some fluorescent quenching chemosensors for Pd^{2+} were designed based on the PET (photoinduced energy-transfer) or (photoinduced electron-transfer) PeT mechanism.[23−28] Making use of the capacity of coordination between palladium and heteroatoms, some colorimetric chemosensors for Pd^{2+} were reported.[29−33] Among them, the strategy of applying Pd^{2+} to induce spiroring-opening of xanthenes and related derivatives attracted our attention due to the fact that spiroring-opening of xanthenes can cause not only the enhancement of fluorescence, but also significant color change, which can be used to identify analytes with the naked eye. Currently, there have been some reports that introduced O, N, P to rhodamine as ligand atoms to detect Pd^{2+}.[34−40] In fact, as a soft metal ion, Pd^{2+} can easily form stable complexes with sulfur-containing ligands,[3,23] but to the best of our knowledge, there is no precedent that introduces sulfur atoms to rhodamine to detect Pd^{2+}. So we think that introduction of sulfur as a ligand atom to rhodamine may be a good strategy for designing palladium sensor. On the basis of this idea, we designed and synthesized a sulfur-containing rhodamine-based fluorescent chemosensor (**RBS**) for Pd^{2+}, and the experimental results confirmed our idea. **RBS** showed high selectivity toward Pd^{2+}, in particular, freedom from the interference of Hg^{2+}. In addition, it could detect Pd^{2+} sensitively in an aqueous solution with a detection limit as low as 2.4 nM. Furthermore, **RBS** could be easily made into test paper to detect Pd^{2+} in pure water.

RESULTS AND DISCUSSION

Compared to most of the O-, N-, or P-containing rhodamine-based chemosensors for Pd^{2+}, **RBS** has been synthesized more easily and economically according to Scheme 1. The structure of RBS was confirmed by ^1H NMR, ^{13}C NMR, and HRMS (Supporting Information, SI, Figure S11). A comparative compound (**RBO**) has also been synthesized and characterized.

Scheme 1. Synthetic Route and Structures of RBS and RBO



Received: October 28, 2014
Accepted: December 22, 2014
Published: December 22, 2014

DOI: 10.1021/am507479m
ACS Appl. Mater. Interfaces 2015, 7, 1284−1289

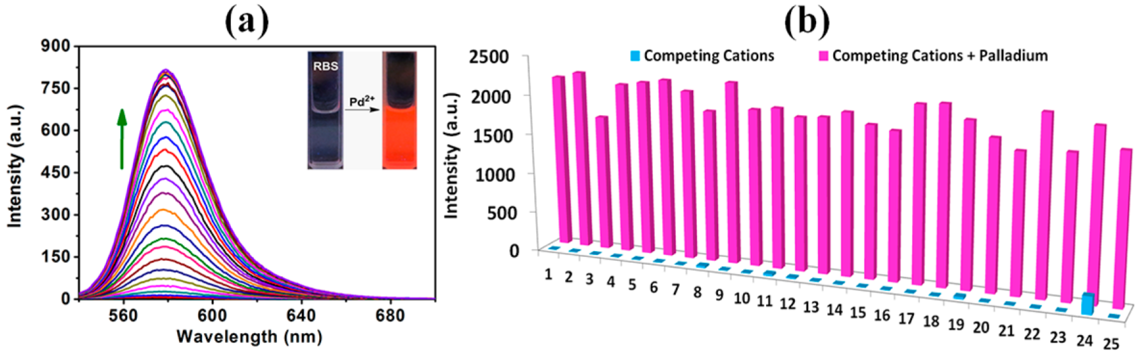


Figure 1. (a) Fluorescence spectra of **RBS** (5.0 μM) in 80:20 (v/v) MeCN−H_2O solution in response to the presence of Pd^{2+} (0.0 to 2.5 equiv), λ_{ex} = 530 nm. Inset: fluorescence images of **RBS** and **RBS** + Pd^{2+}. (b) Fluorescence intensity of **RBS** (10 μM) in 80:20 (v/v) MeCN−H_2O solution at 578 nm after addition of 1.0 equiv of various cations (blue bars) and those after further addition of 1.0 equiv of Pd^{2+} (pink bars). 1, Free; 2, Ag^+; 3, Au^{3+}; 4, Ba^{2+}; 5, Ca^{2+}; 6, Cd^{2+}; 7, Co^{2+}; 8, Cr^{3+}; 9, Cu^{2+}; 10, Fe^{2+}; 11, Fe^{3+}; 12, Hg^{2+}; 13, K^+; 14, Li^+; 15, Mg^{2+}; 16, Mn^{2+}; 17, Na^+; 18, Ni^+; 19, Pb^{2+}; 20, Pt^{2+}; 21, Rh^{3+}; 22, Zn^{2+}; 23, Zr^{4+}; 24, a mixture of 1.0 equiv of Cu^{2+}, Fe^{3+}, Hg^{2+}, Pb^{2+} and Zn^{2+}; and 25, a mixture of 1.0 equiv of Au^{3+}, Pt^{2+} and Rh^{3+}. λ_{ex} = 530 nm.

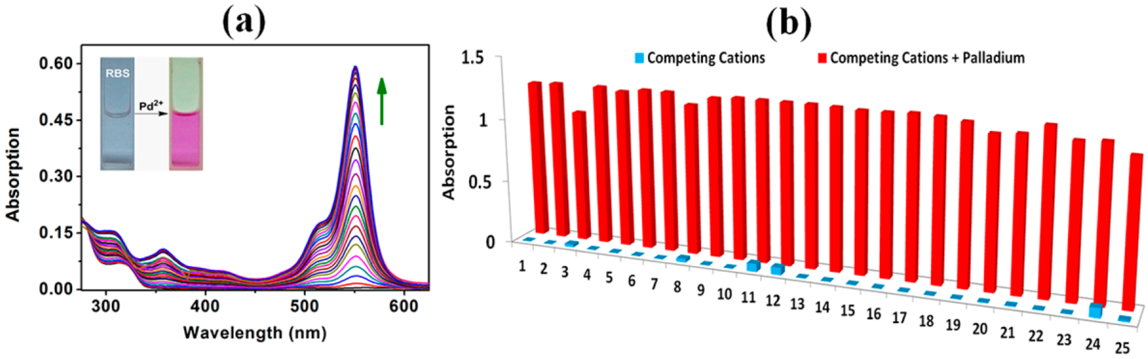


Figure 2. (a) UV−vis spectra of **RBS** (5.0 μM) in response to Pd^{2+} (0.0 to 2.5 equiv) in 40:60 (v/v) EtOH−H_2O solution. Inset: color images of **RBS**, **RBS** + Pd^{2+}. (b) Absorption of **RBS** (10.0 μM) at 550 nm in 40:60 (v/v) EtOH−H_2O solution after addition of 5.0 equiv of various cations (blue bars) and those after further addition of 2.0 equiv of Pd^{2+} (red bars). 1, Free; 2, Ag^+; 3, Au^{3+}; 4, Ba^{2+}; 5, Ca^{2+}; 6, Cd^{2+}; 7, Co^{2+}; 8, Cr^{3+}; 9, Cu^{2+}; 10, Fe^{2+}; 11, Fe^{3+}; 12, Hg^{2+}; 13, K^+; 14, Li^+; 15, Mg^{2+}; 16, Mn^{2+}; 17, Na^+; 18, Ni^+; 19, Pb^{2+}; 20, Pt^{2+}; 21, Rh^{3+}; 22, Zn^{2+}; 23, Zr^{4+}; 24, a mixture of 2.0 equiv of Cu^{2+}, Fe^{3+}, Hg^{2+}, Pb^{2+} and Zn^{2+}; 25, a mixture of 2.0 equiv of Au^{3+}, Pt^{2+} and Rh^{3+}.

To examine the sensitivity of **RBS** toward Pd^{2+}, fluorescence titration of Pd^{2+} was carried out using 5.0 μM of **RBS** in 80:20 (v/v) MeCN/H_2O solution. As shown in Figure 1a, without Pd^{2+}, it had almost no fluorescence, while the significant increase of the fluorescence intensity of the solution was observed at 578 nm upon gradual addition of Pd^{2+}. This is attributed to the formation of the ring-opened Rhodamine derivative. The fluorescence response of **RBS** toward Pd^{2+} was calculated to cover a linear range from 0.6 equiv to 1.9 equiv (R^2 = 0.9974) of Pd^{2+}(SI Figure S1), with a detection limit as low as 2.4 nM.

An important feature of **RBS** is its high selectivity toward Pd^{2+} over other competitive cations (Figure 1b). The fluorescence intensity showed little or almost no change when Ag^+, Au^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^+, Li^+, Mg^{2+}, Mn^{2+}, Ni^{2+}, Na^+, Pb^{2+}, Pt^{2+}, Rh^{3+}, Zn^{2+}, or Zr^{4+} was added separately to the solution of **RBS** (10 μM) in 80:20 (v/v) MeCN/H_2O. While the fluorescence intensity enhanced 774 times at 578 nm when 1.0 equiv of Pd^{2+} was added to the same solution. Even in the presence of Pd^{2+} and the respective above-described competitive cations, the fluorescence change is similar to that in the presence of only Pd^{2+}. In the next experiment, We have investigated the selectivity of RBS toward Pd^{2+} in the mixture of many interfering ions. As shown in Figure 1b (bar 24 and 25), RBS also exhibited high selectivity toward Pd^{2+} in a mixture of five common heavy metal ions (Cu^{2+}, Fe^{3+}, Hg^{2+}, Pb^{2+}, and Zn^{2+}) and a mixture of three common noble metal ions (Au^{3+}, Pt^{2+}, and Rh^{3+}). These results indicate that RBS is a highly selective Pd^{2+} sensor and has good antijamming capability.

For practical applicability, the fluorescence spectra of the solution of **RBS** at different pH in the absence and presence of Pd^{2+} were recorded (SI Figure S2). Without Pd^{2+}, the fluorescence of the solution of **RBS**(10 μM) had no obvious change in the pH range 5−9. It showed almost the same fluorescence intensity upon addition of the same amount of Pd^{2+} in this range. These results indicated that **RBS** could detect Pd^{2+} under complicated conditions within a wide pH span of 5−9.

In order to examine if **RBS** can detect Pd^{2+} with the naked eye, the UV−vis absorption spectra of **RBS** for sensing Pd^{2+} was conducted. The results indicated that among the above-described 22 kinds of cations, only Pd^{2+} could cause a sharp rise of the absorption of **RBS** at 550 nm in 40:60 (v/v) EtOH−H_2O solution (SI Figure S3), accompanied by a color change from colorless to pink (SI Figure S4). In addition, whether the interfering cations exist or not, Pd^{2+} could cause the same change (Figure 2b). Furthermore, **RBS** can detect Pd^{2+} within the wide pH span of 4−10 (SI Figure S5). Finally, the UV−vis absorption spectrum of **RBS** upon titration with Pd^{2+} was recorded, with gradual addition of Pd^{2+}, the absorption of the solution of **RBS** (5.0 μM) at 550 nm rose gradually and stabilized when 2.0 equiv of Pd^{2+} was added (Figure 2a). There is a good linear relationship between the absorption and the concentration of Pd^{2+} from 0.2 to 2.0 equiv ($R^2 = 0.9978$), and the detection limit was measured to be 6.3 nM (SI Figure S6), which is close to the result by fluorescence experiments (2.3 nM). Reasons responsible for such differences may be as follows: the sensitivity of the different instruments is not the same; deviation exists in every instrument; or the solvent is not the same, which leads to different results. So **RBS** is a highly selective, highly sensitive, and colorimetric sensor for Pd^{2+} and can recognize Pd^{2+} with the naked eye.

Practical application is one of most important criteria of an excellent chemosensor, however, most of the O-, N-, or P-containing rhodamine based chemosensors for Pd^{2+} were operated in the solvent, which may not be convenient for on-site assay. In order to investigate the practical application of RBS, test paper experiments were conducted in pure water. As shown in Figure 3, with the increase of Pd^{2+}, the color of **RBS** test paper changed from light to deep, even in the presence of 2.5 μM of Pd^{2+}, **RBS** test paper had an obvious color change from white to pink. According to the WHO specified threshold limit for palladium content in drug chemicals [5.0 ppm to 10.0 ppm (47.0 μM to 94.0 μM)],[41] the sensitivity of **RBS** test paper can satisfy the demands of WHO for palladium detection. These results exhibit the practical application value of RBS and its potential to be used for on-site assay in the future.

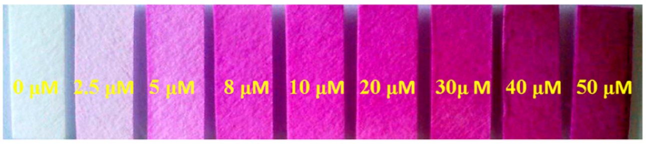
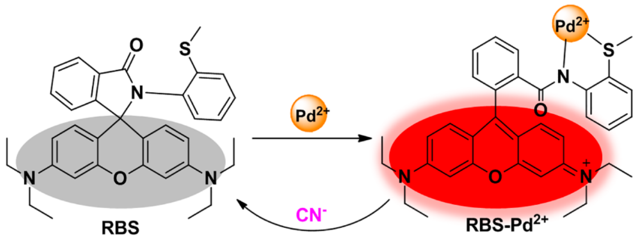


Figure 3. Colorimetric detection of Pd^{2+} by **RBS** test paper.

For better understanding the interaction between **RBS** and Pd^{2+}, a reversible experiment was performed. When 10.0 equiv of CN^- was added into the solution of **RBS**-Pd^{2+} (10 μM **RBS** + 10 μM Pd^{2+}) in 80:20 (v/v) MeCN/H_2O, the fluorescence intensity of the solution at 578 nm decreased by 95.5%, accompanied by the color change from deep to light (Figure 4a). A reasonable explanation for this phenomenon is that CN^- and Pd^{2+} can form more stable compounds, such as $Pd(CN)_2$ and $Pd(CN)_4^{2+}$,[42] so when CN^- was added, it snatched Pd^{2+} from the RBS−Pd^{2+} complex and RBS reclosed to its spiro ring (the proposed mechanism of CN^- closing the ring of RBS shown in SI Figure S8). These results indicated that Pd^{2+} induced the ring opening of **RBS** and formed a complex with **RBS**, rather than inducing the hydrolysis of **RBS** to generate acid (rhodamine B) and amine (2-methylthio-aniline). In order to quantify the complexation ratio between compound **RBS** and Pd^{2+}, a job-plot measurement was carried out (SI Figure S7), and the molar fraction of $[Pd^{2+}]/[\mathbf{RBS} + Pd^{2+}]$ was found to be 0.509, which indicates that the coordinated ratio between Pd^{2+} and **RBS** is about 1:1. Finally, high resolution mass spectra (HRMS) provided additional evidence for the formation of a 1:1complex of **RBS**-Pd^{2+} (Figure 4b). On the basis of the results discussed above, we proposed the possible mechanism shown in Scheme 2.

Scheme 2. Proposed Mechanism for the Identification of Pd^{2+} by RBS



In order to study whether the coordination ability of S plays a key role in the detection system, a comparative compound (**RBO**) has been synthesized. **RBS** and **RBO** have a very similar structure, the only difference is that **RBS** introduces S, while **RBO** introduces O as a ligand atom. But this small difference leads **RBS** and **RBO** to exhibit great differences in the recognition of Pd^{2+}: upon addition of Pd^{2+}, the fluorescence intensity rises to 15.1 times that of **RBS** at 578 nm, and the UV−vis absorption at 550 nm rises 17.4 times that of **RBO** (Figure 5), which indicates that the coordination ability between **RBS** and Pd^{2+} is much stronger than that of **RBO** and Pd^{2+}.

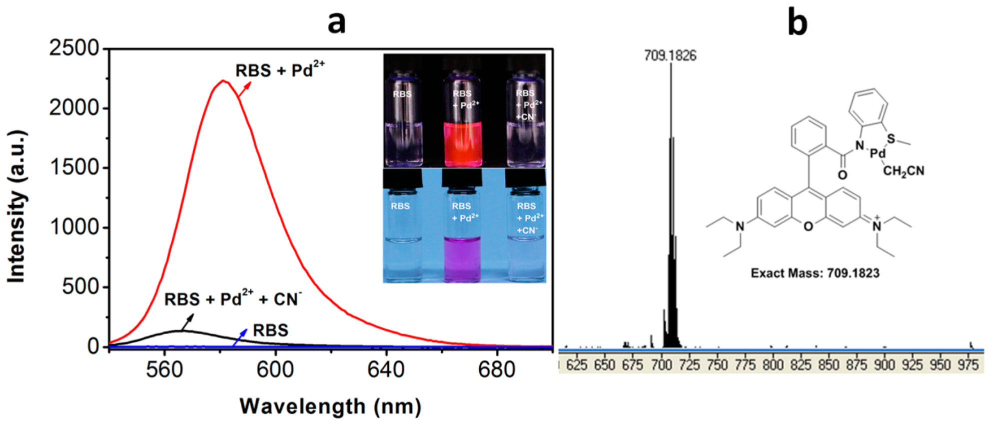


Figure 4. (a) Fluorescence spectra of **RBS** (10 μM) in 80:20 (v/v) MeCN−H_2O solution after addition of 1.0 equiv of Pd^{2+} and further addition of 10.0 equiv of CN^-, λ_{ex} = 530 nm. Inset: fluorescence and color images of **RBS**, **RBS** + Pd^{2+}, and **RBS** + Pd^{2+} + CN^- in 80:20 (v/v) MeCN−H_2O solution. (b) High resolution mass spectrum of **RBS**-Pd^{2+}.

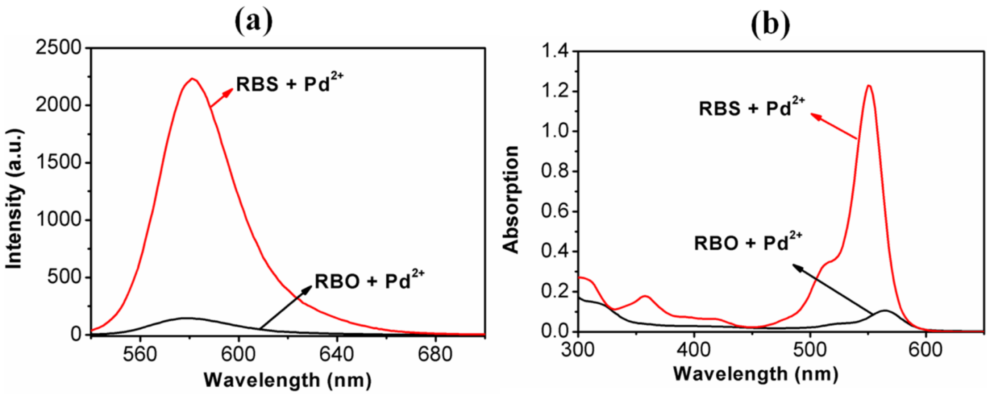


Figure 5. (a) Fluorescence spectra of **RBS** (10 μM) and **RBO** (10 μM) in 80:20 (v/v) MeCN–H_2O solution after addition of 1.0 equiv of Pd^{2+}, λ_{ex} = 530 nm. (b) UV–vis spectra of **RBS** (10 μM) and **RBO** (10 μM) in 40:60 (v/v) EtOH–H_2O solution after addition of 2.0 equiv of Pd^{2+}.

In addition, the quantum calculations are also consistent with this explaination (S9 and S10). The local difference between RBS (c) and RBO (d) in the optimized geometries was compared. Although the whole conformation of RBS was similar to RBO, the orientation of the aromatic six-ring connected with the S atom (in RBS) was changed compared with O atom (in RBO). The dihedral angle between S—C—N—O (in RBS) was 103.56° while that of O—C—N—O (in RBO) was 108°. The distance between S and O (in RBS) was 3.401 Å, while that between O and O (in RBO) was 2.941 Å. The sulfur atom charge in RBS (a) was 0.255, while the oxygen atom charge in RBO (b) was −0.742. It was shown that the local spatial conformation and Mulliken atomic charge distribution of sulfur atom in RBS were better and more suitable as ligands to Pd^{2+} than that of the oxygen atom in RBO. So the introduction of sulfur as a ligand atom to **RBS** was critical to the detection system for sensing Pd^{2+}.

■ CONCLUSIONS

In summary, the rhodamine based colorimetric chemosensor **RBS** has been designed and synthesized simply. **RBS** exhibited high sensitivity and high selectivity toward Pd^{2+}over 22 other kinds of interference metal ions. The detection limit is as low as 2.4 nM. Furthermore, **RBS** can detect Pd^{2+} with a wide pH range from 5 to 9. More importantly, **RBS** test paper can detect Pd^{2+} semiquantitatively in pure water, which could be potentially used in the detection of Pd^{2+} in real samples. Finally, the introduction of sulfur as a ligand atom to **RBS** was critical to the detection system for Pd^{2+}, and we hope that these results will contribute to the rational design of a more excellent chemosensor for Pd^{2+} in the future.

■ EXPERIMENTAL SECTION

Materials and Instrumentations. All reagents and solvents were purchased from commercial sources and were of analytic grade. All reactions were magnetically stirred and monitored by thin-layer chromatography (TLC). Flash chromatography (FC) was performed using silica gel (200−300 mesh). UV−vis absorption spectra were recorded on a PerkinElmer Lambda-25 spectrometer. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance AVII-300 MHz spectrometer ($CDCl_3$ as solvent and $SiMe_4$ as internal standards). High Resolution Mass Spectra were recorded on a Bruker ESI-Q-TOF mass spectrometer.

Preparation of RBS Stock Solutions. **RBS** stock solution was prepared at the concentration of 1.0×10^{-3} M in 10.0 mL of CH_3CN or EtOH and then diluted to a desired concentration.

Preparation of Various Ions Stock Solutions. Unless otherwise noted, each ion was prepared at the concentration of 1.0×10^{-3} M in 10.0 mL distilled water and then diluted to a desired concentration. Au^{3+} and Zr^{4+} was prepared from $AuCl_3(HCl)(H_2O)_4$ and $ZrCl_4$, respectively: $AuCl_3(HCl)(H_2O)_4$ or $ZrCl_4$ was dissolved in distilled water and then carefully adjusted to neutral with ammonia−water. Cr^{3+} was prepared from $CrCl_3(H_2O)_6$. Pd^{2+}, Pt^{2+}, and Rh^{3+} was prepared from $PdCl_2$, $PtCl_2$, and $RuCl_3$, respectively: the metal chlorides were dissolved in dilute hydrochloric acid and then carefully adjusted to neutral with ammonia−water. Ag^+, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^+, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, and Zn^{2+} were prepared from their perchlorates, CN^- was prepared from NaCN.

UV−vis and Fluorescence Titration Experiments. Unless otherwise noted, all the UV−vis titration experiments were operated in 40:60 (v/v) EtOH−H_2O solution, all the fluorescence titration experiments were operated in 80:20 (v/v) MeCN-H_2O solution (λ_{ex} = 530 nm, scan speed = 240 nm/min, excitation slit = 5.0 nm, emission slit = 5.0 nm, and PMT voltage = 700 V). The pH value of the solution was adjusted by $HClO_4$ or NaOH.

Test Paper Experiments. **RBS** test papers were prepared by immersing filter papers into a THF solution of **RBS** (0.01 M) and then drying them in air. Then, the **RBS** test papers were immersed separately in a solution of pure water with 0, 2.5, 5.0, 8.0, 10, 20, 30, 40, and 50 μM of Pd^{2+}, taken out, and dried.

Synthesis of RBS. 1.0 g of Rhodamine B (2.1 m mol) was dissolved in 20.0 mL of dichloroethane, 2.0 mL of phosphorus oxychloride (21.8 m mol) was added dropwise at room temperature, and then the mixture was refluxed for 4 h. After the solvent and the excess phosphorus oxychloride was removed under reduced pressure, Rhodamine B chloride was obtained as a purple sticky solid, which was used in the next step without any characterization and purification.The Rhodamine B chloride obtained from 1.0 g of Rhodamine B (2.1 m mol) was dissolved in 20 mL of anhydrous acetonitrile and cooled to 0 °C, 5.0 mL anhydrous acetonitrile solution of triethylamine (2.0 g, 19.8 m mol) and 2-(methylthio)aniline (0.42 g, 3.0 m mol) was added dropwise. The mixture was refluxed for 0.5 h and cooled to room temperature, and then the mixture was poured into 50 mL of ice water. After being extracted with ethyl acetate and dried over anhydrous Na_2SO_4, the organic layer was evaporated, and the crude residue was purified by flash chromatography using CH_2Cl_2 as an eluent to give 0.8 g of **RBS** as white solid in 67.9% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14−8.06 (m, 1H), 7.65−7.53 (m, 2H), 7.34−7.24 (m, 2H), 7.16 (td, J = 7.7, 1.4 Hz, 1H), 6.96−6.85 (m, 2H), 6.67 (d, J = 8.8 Hz, 1H), 6.42 (dd, J = 8.8, 2.6 Hz, 1H), 6.36 (d, J = 2.5 Hz, 1H), 6.26 (dd, J = 8.9, 2.6 Hz, 1H), 6.21 (dd, J = 8.0, 1.3 Hz, 1H), 6.18 (d, J = 2.6 Hz, 1H), 3.51−3.20 (m, 8H), 2.14 (s, 3H), 1.23 (t, J = 7.0 Hz, 6H), 1.14 (t, J = 7.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.00, 153.96, 153.42, 152.00, 148.63, 148.34, 139.14, 134.72, 132.21, 131.74, 130.67, 129.06, 128.66, 127.90, 127.71, 127.62, 125.25, 123.93, 123.26,108.03, 107.71, 106.78, 105.23, 97.64, 97.04, 67.96, 44.11, 43.99, 17.55, 12.26, 12.20. HRMS calcd for $C_{35}H_{37}N_3O_2S$: [M + H^+] 564.2679, found 564.2677.

Synthesis of RBO. **RBO** was synthesized according to the synthesis method of **RBS**, which was obtained as white solid in 70.6% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05−7.98 (m, 1H), 7.54−7.47 (m, 2H), 7.24−7.17 (m, 1H), 7.15−7.08 (m, 1H), 6.71−6.59 (m, 4H), 6.30 (dd, J = 8.9, 2.5 Hz, 2H), 6.25 (dd, J = 7.8, 1.7 Hz, 1H), 6.19 (d, J = 2.5 Hz, 2H), 3.43 (s, 3H), 3.30 (q, J = 7.0 Hz, 8H), 1.13 (t, J = 7.0 Hz, 12H).^{13}C NMR (75 MHz, $CDCl_3$) δ 166.38, 155.76, 153.32, 152.39, 148.33, 131.99, 131.96, 129.56, 129.17, 128.71, 127.73, 124.38, 123.88, 123.05, 119.65, 111.17, 107.21, 106.39, 97.25, 67.34, 54.92, 44.03, 12.25. HRMS calcd for $C_{35}H_{37}N_3O_3$: [M + H^+] 548.2908, found 548.2913.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR and high resolution mass spectra of **RBS** and **RBO**, fluorescence and UV−Vis studies, Job's plot of **RBS** with Pd^{2+}, the optimized structures of **RBS** and **RBO**, and the Mulliken atomic charge distribution of **RBS** and **RBO**.This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China and the Chinese University scientific fund.

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