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Water-Soluble Colorimetric and Ratiometric Fluorescent Probe for Selective Imaging of Palladium Species in Living Cells

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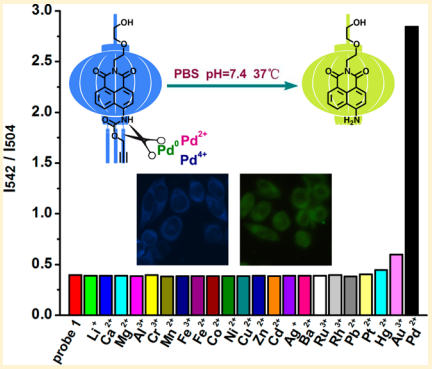
Supporting Information

ABSTRACT: A novel water-soluble colorimetric and ratiometric fluorescent probe was synthesized and applied to imaging palladium species under physiological conditions in phosphate buffered saline (PBS) containing less than 1% organic cosolvent without adding any additional reagents. Based on palladium triggered terminal propargyl ethers cleavage reaction, the probe exhibited a high selectivity and sensitivity for palladium species of all the typical oxidation states (0, +2, +4), with a low detection limit (25 nM, 2.7 μg/L) and an obvious color change. Furthermore, the probe was successfully used for ratiometric fluorescence imaging of palladium in living cells.



INTRODUCTION

Nowadays, palladium species play a very important role in various industrial fields because of their specific chemical and physical properties.[1] As an effective catalyst, they have been widely used in material preparation and medicine synthesis.[2]

As a result of frequent use, however, a large quantity of palladium has been released to the environment, which may cause serious health problems. Palladium can be bound to DNA, thiol-containing amino acids, proteins, and other biomolecules and disturb a variety of cellular processes.[2b] Thus, governmental regulations on the levels of palladium (no more than 5−10 ppm) are fairly strict and the proposed dietary intake is less than 1.5−15 μg per person per day.[3] Consequently, it is necessary to develop convenient and effective methods to detect palladium species in various samples.

Compared with traditional palladium detection methods, including atomic absorption spectrometry, solid-phase micro-extraction−high performance liquid chromatography, plasma emission spectroscopy, and X-ray fluorescence,[4] fluorescent methods are more effective and ideal because they are low cost, simple to operate, nondestructive, and highly sensitive.[5]

Until now, several palladium fluorescent probes have been reported.[1,6,7] Probes based on specific catalytic reactions have attracted tremendous attention because of their excellent selectivity.[7] However, many of the reported Pd probes only work in organic solvents or water with organic cosolvents; some of them need additional reagents. These problems in the detection system will limit their practical application in biological imaging or environmental monitoring. However, so far only a few studies have been reported on sensing palladium in aqueous buffer solution containing less than 1% organic cosolvent.[7i]

Herein, the aim of this work is to develop a water-soluble ratiometric fluorescent and colorimetric probe for palladium species. As shown in Scheme 1, probe **1** was developed with 4-amino-1,8-naphthalimide[8] as the fluorophore and a terminal propargyl ether moiety as the recognition site. Compared with our earlier work,[7j] a key factor was that water solubility was remarkably improved by introducing an alkoxyalcohol group. In this case, the probe can be used to detect Pd (0, +2, +4) under physiological condition (at 37 °C in phosphate buffered saline, pH 7.4, containing less than 1% organic cosolvent) without any additional reagents, and successfully applied for palladium imaging in living cells.

EXPERIMENTAL SECTION

Materials and Instrumentation. All solvents and reagents were commercially available A.R. grade and used without further purification unless otherwise noted. ^{1}H NMR and ^{13}C NMR spectra were obtained using a Bruker DRX400 spectrometer and referenced to the solvent signals. Mass spectrum (ESI) measurements were carried out on a LQC system (Finngan MAT, USA). UV−visible spectra were recorded using a Varian Cary 100 spectrophotometer and fluorescence spectra were measured using a Hitachi F-4500 luminescence spectrometer. Fluorescent quantum yields were determined (to be 0.71 for probe **1** and 0.17 for compound **2**) by an absolute method using an integrating sphere on an Edinburgh Instrument FLS920.

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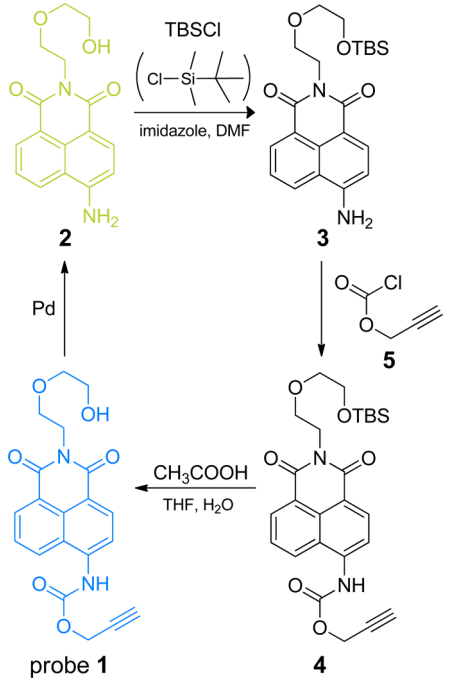
Scheme 1. Synthesis and Proposed Fluorescent Change Strategy of Probe 1



Synthesis of Compounds 2, 3, 5. The naphthalimide derivatives **2**,[9] **3**,[10] and compound **5**[11] (propargyloxycarbonyl chloride) were prepared by adapting published procedures.

Synthesis of Compound 4. To a mixture of compound **5** (593 mg, 5 mmol) and pyridine (1 mL) in 25 mL dry CH_2Cl_2, compound **3** (414 mg, 1 mmol) was added at 0 °C. The mixture was stirred at 0 °C for 2 h under Ar, then warmed to ambient temperature. After another 12 h, the mixture was extracted with dichloromethane. Organic layers were combined and washed with water, dried over anhydrous sodium sulfate, and solvents evaporated. The solid that remained was purified using column chromatography on silica gel (hexane/ethyl acetate = 3/2, v/v) to give compound **4** as a faint yellow powder. Yield: 402 mg, (81%). Mp 106.8−108.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.57 (m, 2H), 8.34 (d, J = 8.2 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.75 (dd, J = 8.5, 7.4 Hz, 1H), 7.59 (s, 1H), 4.89 (d, J = 2.4 Hz, 2H), 4.42 (t, J = 6.1 Hz, 2H), 3.83 (t, J = 6.0 Hz, 2H), 3.74 (t, J = 5.2 Hz, 2H), 3.60 (t, J = 5.2 Hz, 2H), 2.59 (t, J = 2.4 Hz, 1H), 0.82 (s, 9H), −0.01 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 164.01, 163.54, 152.43, 138.75, 132.25, 131.13, 128.60, 126.45, 126.35, 122.99, 122.95, 117.80, 117.10, 77.34, 75.65, 72.33, 68.03, 62.78, 53.46, 39.27, 29.66, 25.87, 18.32, −5.35. MS-ESI m/z [$(M+H)^+$]: 497.2.

Synthesis of Probe 1. Compound **4** (496 mg, 1 mmol) was added to 14 mL of a THF/acetic/H_2O mixture (4:2:1 v/v/v). The mixture was stirred for 24 h at room temperature under Ar. The reaction mixture was extracted with EtOAc. The combined organic layers were washed with sodium bicarbonate solution and water, then dried with anhydrous sodium sulfate, filtered, and concentrated in vacuo. At last, the crude product was chromatographed (hexane/ethyl acetate = 2/3, v/v) to provide probe **1** as a faint yellow powder. Yield: 241 mg, (63%). Mp 156.9−158.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.57−8.61 (m, 2H), 8.34 (d, J = 8.2 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.76 (t, J = 8.0 Hz, 1H), 7.64 (s, 1H), 4.91 (d, J = 2.4 Hz, 2H), 4.45 (t, J = 5.6 Hz, 2H), 3.89 (t, J = 5.6 Hz, 2H), 3.71 (dd, J = 8.4, 2.6 Hz, 4H), 2.60 (t, J = 2.4 Hz, 1H), 2.16 (s, 1H). ^{13}C NMR (100 MHz, DMSO, TMS): δ = 163.41, 162.84, 153.22, 140.37, 131.62, 130.91, 129.23, 128.25, 126.40, 123.85, 122.08, 118.30, 117.18, 78.61, 78.02, 72.09, 66.90, 61.11, 60.17, 52.77. MS-ESI m/z [$(M-H)^+$]: 381.3.

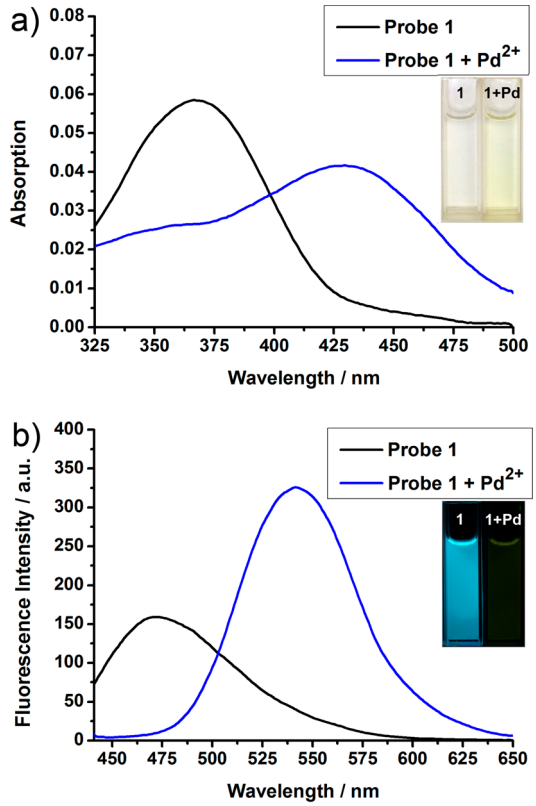
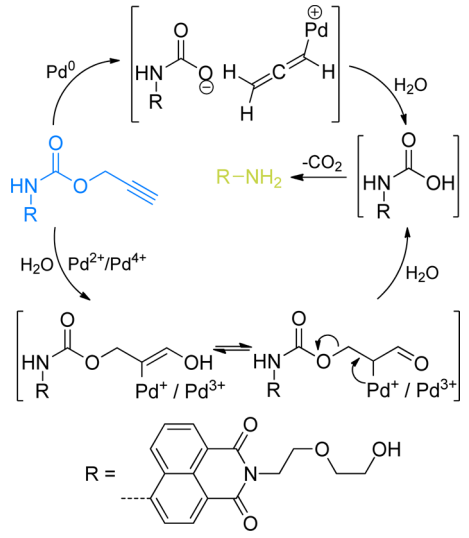


Figure 1. (a) UV−vis absorption spectra of probe **1** (5.0 μM) in the absence and presence of Pd^{2+} (25.0 μM). Inset: Color changes in probe **1** upon addition of Pd^{2+}. (b) Fluorescence spectra of probe **1** (5.0 μM) in the absence and presence of Pd^{2+} (25.0 μM). Inset: Fluorescence changes excited by UV lamp (365 nm) in probe **1** upon addition of Pd^{2+}. All spectra were acquired 2 h after Pd^{2+} addition at 37 °C in PBS buffer solutions (10 mM, pH = 7.4, containing 0.5% EtOH). Ex = 430 nm. Slit: 5.0 nm/5.0 nm.

Scheme 2. Mechanism for Selective Recognition of Palladium (0, +2, +4)



RESULTS AND DISCUSSION

The synthetic route of probe **1** is outlined in Scheme 1. The complete characterization is shown in the Experimental Section and Supporting Information. Initial spectroscopic properties of

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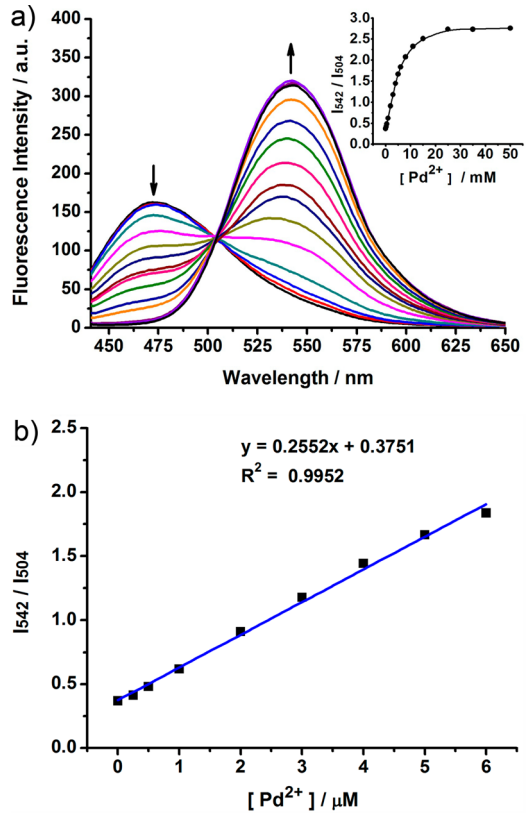

Figure 2. (a) Fluorescence responses of probe **1** (5 μM) toward different concentrations of Pd^{2+} (0−50 μM). Inset: Ratiometric calibration curve I_{542} nm/I_{504} nm as a function of Pd^{2+}. (b) Fluorescence intensity ratio (I_{542} nm/I_{504} nm) of probe **1** versus increasing concentrations of Pd^{2+}. All spectra were acquired 2 h after Pd^{2+} addition at 37 °C in PBS buffer solutions (10 mM, pH = 7.4, containing 0.5% EtOH). Ex = 430 nm. Slit: 5.0 nm/5.0 nm.

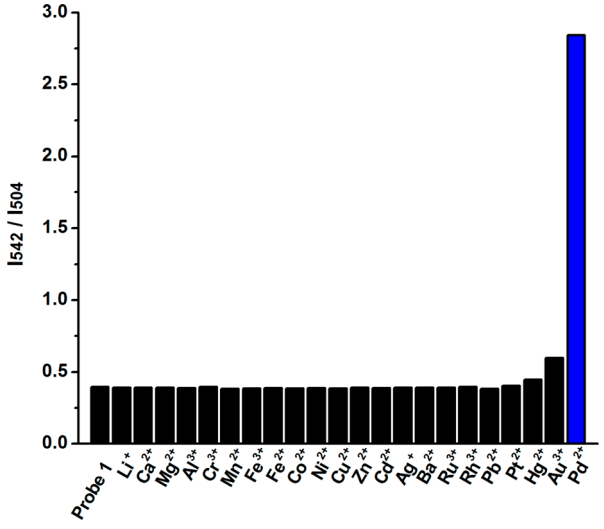

Figure 3. Metal ion selectivity of probe **1** (I_{542} nm/I_{504} nm).

the probe **1** were rated in PBS (10 mM, pH = 7.4, containing 0.5% EtOH).

As shown in Figure 1, probe **1** (5 μM) showed the maximum absorption and emission peaks at 367 and 472 nm, respectively. Upon the addition of Pd^{2+} (25 μM), the maximum absorption peak underwent a red-shift to 430 nm while the maximum emission peak showed up at 542 nm. Additionally, the marked

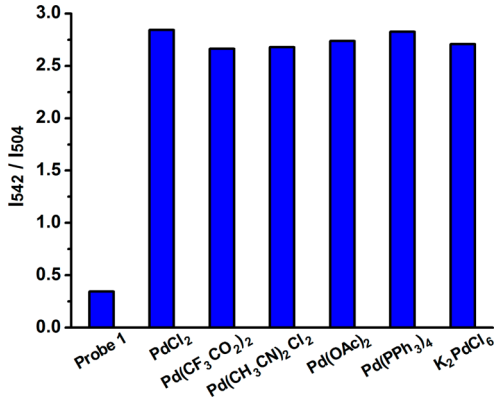

Figure 4. Fluorescence responses of probe **1** (5 μM) to palladium sources (25 μM). ($Pd(PPh_3)_4$ reacted with probe **1** at the Ar atmosphere.)

color changes were also noticed. The obvious changes in both the absorption and fluorescence spectra indicated that a free amino compound **2** was generated by the palladium-triggered cleavage reaction.

Owing to the specific reactivity of the palladium-catalyzed chemical reaction,[7m,12] probe **1** displayed a high sensitivity and selectivity toward palladium species. A feasible mechanism of the cleavage reaction is shown in Scheme 2. The terminal propargyl ether moiety could be cleaved readily by palladium (0, +2, +4) to yield the carbamate, and then decarboxylation of the carbamate product compound **2**. Moreover, a peak at m/z 301.3, corresponding to compound **2**, was predominantly detected in mass spectrum (Supporting Information, Figure S8), which further confirmed this mechanism.

Since $PdCl_2$ is the most toxic among the palladium species, it was selected as the representative palladium species in the following experiments. To determine the response time of probe **1** for Pd, the time-dependent experiment was tested. As shown in Supporting Information Figure S1, the response time of the reaction system is about 2.5 h at 37 °C.

Upon addition of different concentrations of Pd^{2+} (0−25 μM), the fluorescence intensity at 472 nm decreased progressively, while a new red-shifted emission peak was observed around 542 nm with an isoemission point at 504 nm. Importantly, the ratio of emission intensities (I_{542} nm/I_{504} nm) increased by nearly 7-fold and exhibited good linear correlation with the amount of Pd^{2+} (0−6 μM, R^2 = 0.995) (Figure 2, inset). The detection limit of probe **1** for Pd^{2+} was determined as 25 nM (Pd^{2+} content =2.7 μg/L), which was below the governmental threshold in drugs (5−10 ppm).[3] The results indicated that probe **1** can be a sensitive ratiometric fluorescent sensor for quantitative detection of Pd^{2+}.

Next, fluorescence responses of probe **1** (5 μM) to various other common metal ions were investigated. After addition of 5.0 equiv of metal ions such as Li^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+, Ba^{2+}, Ru^{3+}, Rh^{3+}, Pb^{2+}, Pt^{2+}, Hg^{2+}, and Au^{3+} under the established conditions, however, discernible changes in both color and the emission ratio (I_{542} nm/I_{504} nm) occurred only in the prescene of the Pd^{2+} (Figure 3). Gratifyingly, other metal ions showed little or no interference to probe **1**. Au^{3+} displayed a slight response on account of its high p-electrophilicity.[7f]

To further examine the sensing selectivity of probe **1** toward Pd^{2+}, we carried out competitive experiments. As shown in

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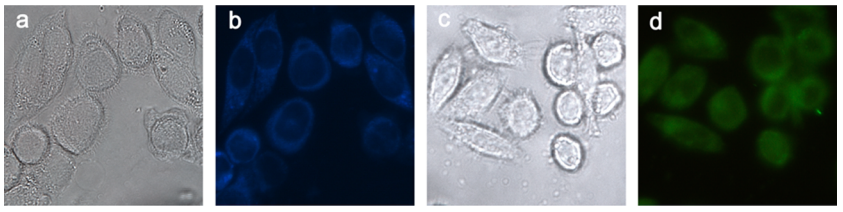

Figure 5. Bright-field and fluorescence imaging of Hep G2 cells incubated with probe **1** (10 μM) for 1 h (b) and then further incubated with $PdCl_2$ (50 μM) for 2 h (d). (a,c) Bright-field image of Hep G2 cells in (b) and (d).

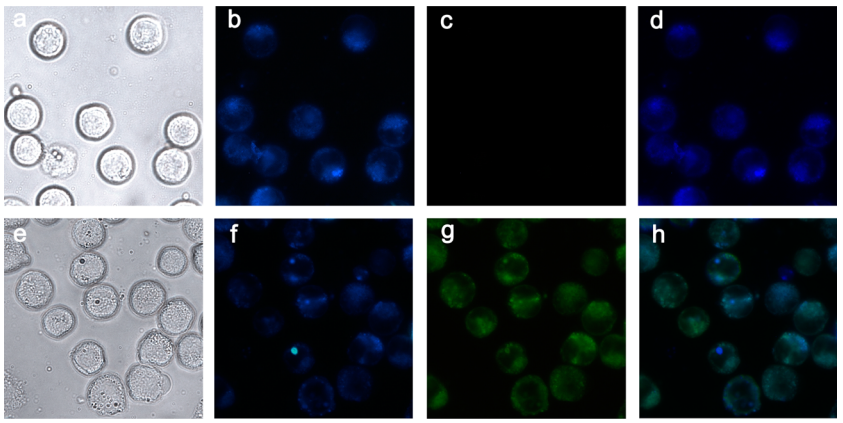

Figure 6. Bright-field and fluorescence images of HL60 cells with probe **1**. (a–d) Cells only incubated with probe **1** (10 μM) for 1 h: (a) bright-field image, (b) blue channel, (c) green channel, (d) overlay of the blue and green channels. (e–h) Cells incubated with probe **1** (10 μM) for 1 h, and then addition of $PdCl_2$ (50 μM) for another 30 min: (e) bright-field image, (f) blue channel, (g) green channel, (h) overlay of the blue and green channels.

Supporting Information Figure S2, the sensing behavior for Pd^{2+} was hardly disturbed by the presence of other metal ions.

In order to investigate the sensing behavior of probe **1** to other palladium metal sources in different oxidation states of 0, +2, and +4, different species of palladium such as $Pd(CF_3CO_2)_2$, $Pd(CH_3CN)_2Cl_2$, $Pd(OAc)_2$, $Pd(PPh_3)_4$, and K_2PdCl_6 were examined. Interestingly, similar fluorescence changes as $PdCl_2$ were observed (Figure 4). Probe **1** can recognize palladium species in all the typical oxidation states (0, +2, +4).

The pH effects on the fluorescence responses of probe **1** to Pd^{2+} were also investigated. As seen in Supporting Information Figure S3, probe **1** was stable between pH 3 and 11 in the absence of Pd^{2+}, whereas the probe **1**-Pd system showed a noticeable emission ratio (I_{542} nm/I_{504} nm) change within the pH range 3–11. Thus, within the biologically relevant pH range (5–10), probe **1** could be used to detect palladium species in living cells without interference.

The research on intracellular image detection of palladium was very important.[13] Then, the potential application of probe **1** in living systems was studied. We chose two different types of living cells (Hep G2 cells and HL60 cells) for fluorescence imaging of Pd^{2+}. Hep G2 cells were incubated with probe **1** (10 μM) for 1 h at 37 °C and washed with PBS buffer. An intense intracellular blue fluorescence could be seen (Figure 5). The cells with probe **1** (10 μM) were incubated with Pd^{2+} (50 μM) at the same condition. As expected, the cells exhibited yellow fluorescence (Figure 5). Moreover, probe **1** (10 mM) was treated with HL60 cells at 37 °C for 1 h, and then washed with PBS buffer. We could observe a clear blue fluorescence through the blue channel and almost no fluorescence at the green channel (Figure 6). After incubation with Pd^{2+} (50 μM) for another 30 min, a probe **1** significant ratiometric fluorescence response was noticed through the blue channel and green channel (Figure 6). Furthermore, the control experiments (Supporting Information Figure S9) were carried out to prove that probe **1** exhibited a good selectivity for Pd^{2+} in cells and the recognition process was not affected by the complex intracellular environment. The obvious changes suggest that probe **1** has a good cell membrane permeability and can be applied in ratiometric imaging of Pd^{2+} in living cells.

CONCLUSION

In summary, we have rationally developed a new water-soluble fluorescent ratiometric and colorimetric probe for palladium species. Based on the palladium triggered cleavage reaction, the probe exhibited a specific and ratiometric fluorescent response toward palladium species of all the typical oxidation states (0, +2, +4) under physiological conditions in neutral PBS containing less than 1% organic cosolvent without any additional reagents. Also, the probe exhibited a high selectivity and sensitivity for Pd^{2+}, with a noticeable color change and a low detection limit (25 nM, 2.7 μg/L). Gratifyingly, the probe was used for the fluorescent imaging of Pd^{2+} in living cells. The above results indicated that the probe may be favorable for biological and environmental applications.

ASSOCIATED CONTENT

Supporting Information

Preparation of stock solutions; additional fluorescence spectral data; ^1H NMR, ^{13}C NMR, and ESI-MS spectra; determination of the detection limit; cell culture and imaging. 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.

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