Pd^{2+} 검출용 고감도 형광화학센서

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Highly Sensitive and Selective Fluorescent Chemosensors Specific for Pd^{2+} Detection

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요　약 : 팔라듐은 치과 및 의료용 기구, 의료용 재료, 보석 및 자동차, 고기능성 점 · 접착제 등을 생산하는데 중요한 역할을 한다. 팔라듐을 이용하는 반응에서의 중요성에도 불구하고 팔라듐은 최종생성물에 잔존할 경우 인체에 해로운 독성을 가지고 있다. 그 중에서도 특히 PdCl$_2$는 독성이 가장 크다. 따라서 Pd^{2+} 이온 검출은 매우 중요한 연구과제인데 그 중에서도 특히 형광분석법은 가장 손쉽고 경제적이면서 감도가 높고 선택성이 높은 방법으로 알려져 있다. 본 연구에서는 알파-카보닐로 치환된 파이렌 유도체인 감마-옥소-1-파이렌부틸산(OPBA)이 수용액에 금속이온으로 감도가 크고 선택성이 우수한 것으로 밝혀졌다.

Abstract: Palladium plays a pivotal role in the production of dental and medicinal devices, medicinal substances, jewellery, automobile and high-performance adhesives. Despite the frequent and fruitful use of such reactions, one major setback is the high level of palladium in the resultant compounds which can harm the human body. Among the palladium species, PdCl$_2$ is the most toxic. As a consequence it is desirable to detect the Pd^{2+} cations by fluorescence spectra because it can provide an operationally simple and cost-effective detection method together with high sensitivity and selectivity. Herein, an α-carbonyl substituted pyrene derivative, γ-oxo-1-pyrenebutyric acid (OPBA), was demonstrated to be a highly sensitive and selective fluorescent probe for Pd^{2+} among the metal cations examined in aqueous solutions.

Keywords: *Pd^{2+} cations, γ-oxo-1-pyrenebutyric acid (OPBA), chemosensor*

1. Introduction

The development of artificial receptors for the sensing and recognition of environmentally and biologically important species has been actively investigated in recent years[1,2]. Palladium is a rare transition metal that plays a pivotal role in the production of dental and medicinal devices, jewellery, automobile, and high-performance adhesives[3-5]. Moreover, organic synthesis that uses palladium as the catalyst is widely applied in the production of medicinal substances. Despite the frequent and fruitful use of such reactions, one major setback is the high level of palladium in the resultant compounds which can harm the human body[6,7]. Among the palladium species, PdCl$_2$ is the most toxic[8]. As a consequence it is desirable to develop efficient methods for detecting the presence of Pd^{2+} cations. Fluorescence spectra stands out because it can provide an operationally simple and cost-effective detection method together with high sensitivity and selectivity[9,10] compared to the other typical analytical methods used for quantification of Pd^{2+} cations.

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The pyrene moiety is one of the most useful fluor-ophores for the construction of fluorogenic chemosensors for a variety of important chemical species as the good photophysical properties[11-13]. Particularly, utilizing the pyrene moiety of monomer versus excimer emission, a variety of heavy and transition metal ions (HTM) recog-nition systems were successfully devised[14-19]. However, less attention was paid to the applications of α-carbonyl substituted pyrene chromophores, a special class of pyr-ene derivatives. To date, only a few studies have reported that employed α-carbonyl substituted pyrene derivatives in sensing systems[20]. Especially, the metal chemo-sensors constructed by α-carbonyl substituted pyrene de-rivatives is rare[21]. Based on these above information, we explored the application of γ-oxo-1-pyrenebutyric acid (OPBA), with a carbonyl group substituted on the α-position of the pyrene chromophore, as a selective and sensitive fluorescent chemosensor specific for Pd^{2+} detection. We hope that the efforts made in this work will contribute to the development of metal chemosensors based on α-car-bonyl substituted pyrene derivatives.

2. Experimental

2.1. Materials and Instrumentations

All solvents used were of analytical grade. γ-Oxo-1-pyr-enebutyric acid (OPBA), 1-pyrenebutyric acid (PBA) and 1-pyrene-carboxaldehyde (PyCHO) were all purchased from Sigma-Aldrich. The Fourier-Transform Infrared (FTIR) spectra were recorded at room temperature on a JASCO FTIR 460 Plus operated at a resolution 4 cm^{-1}. ^{1}H-NMR spec-tra were recorded on a Varian Gemimi-2000 (300 MHz) spectrometer. The UV-Vis spectra were measured using a Hitachi U-2010 spectrometer. The fluorescence spectra were measured using a Hitachi F-4500 spectrometer. A pH 64 Radiometer (Copenhagen, Denmark) combined with a GK 2401 B electrode was used for the pH measurements.

2.2. Preparation of OPBA Solutions for the Concentration Effect

2.2.1. Studies on the Fluorescence Spectra

12.0 mM solutions of OPBA (0.1825 g, 0.6 mmol) were prepared in dimethylsulfoxide (DMSO) (5 mL), then diluted 2 times with H_2O to get the 6.0 mM stock solutions. The stock solutions of OPBA (6.0 mM) were diluted by using DMSO/H_2O (1/1, v/v) to get the solutions of OPBA ranging from 3.0 mM to 0.5 μM. The fluorescence spectra

of each solution were recorded with excitation at 480 nm.

2.2.2. Studies on the Absorption Spectra

50.0 μM solutions of OPBA (0.76 mg, 2.5 μmol) were prepared in DMSO (5 mL) to get the 50 μM stock solutions. 2 mL of OPBA stock solutions were diluted 50 times by using H_2O to get the 1.0 μM solutions of OPBA in DMSO/H_2O (2/98, v/v). 3.0 mL of OPBA solution at 1.0 μM in DMSO/H_2O (2/98, v/v) was placed in quartz cell (10.0 mm width) and the absorption spectra were recorded.

2.3. Preparation of Solutions for the Fluorescent Detection of Metal Ions by OPBA

0.48 mM solutions of OPBA (0.0073 g, 0.024 mmol), pyrene (0.0049 g, 0.024 mmol), PBA (0.007 g, 0.024 mmol), and PyCHO (0.0055 g, 0.024 mmol) were prepared in DMSO (50 mL), then diluted 240 times with H_2O to get the 2 μM stock solutions. The total volume of DMSO contained in the 2 mM stock solutions was below 0.5%. All of the metal ion stock solutions were prepared at 0.4 mM in H_2O. 1.5 mL of OPBA stock solution was placed in quartz cell (10.0 mm width) and the fluorescence spectra were recorded before and after the addition of 1.5 mL stock solutions of metal ions (200.0 equiv.) to the solution of 1.5 mL OPBA. The metal recognition behavior of OPBA was evaluated from the changes in fluorescence spectra at the emission wavelength of 455 nm upon addi-tion of that sodium salt. The fluorescence spectra of each solution were recorded with excitation at 480 nm.

2.4. Preparation of Solutions for the Sensing of Pd^{2+} by OPBA

A stock solution of OPBA (2.0 μM) was prepared as illustrated in section 2.3. The solution of $PdCl_2$ was in-troduced in portions and the fluorescence intensity changes were recorded at room temperature each time.

2.5. Preparation of Solutions for the ^{1}H NMR and IR Studies

20 μM stock solution of OPBA was prepared similar to the procedures shown in section 2.3. 0.12 mM stock solution of $PdCl_2$ was prepared. The stock solution of OPBA was diluted 2 times by using water and by using the $PdCl_2$ stock solution, respectively. After several minutes, the ^{1}H NMR and IR spectra of samples OPBA (1.0 μM) and OPBA-Pd^{2+} (1.0 μM / 6.0 μM) were recorded.
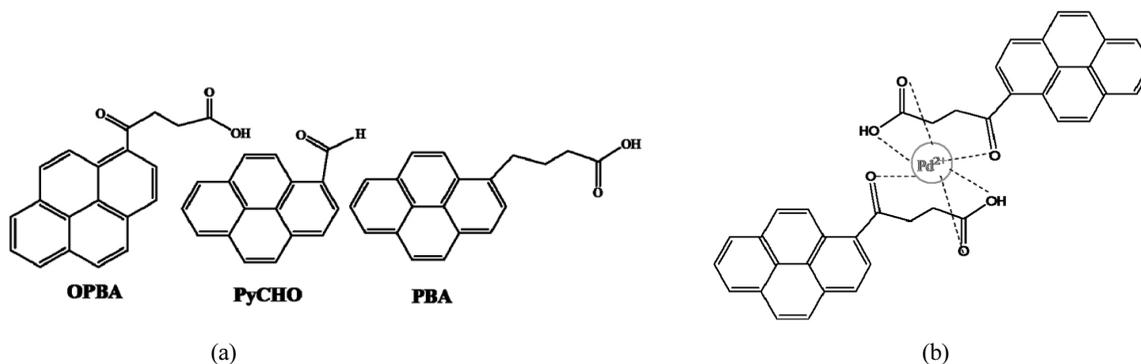
Scheme 1. (a) Chemical structures of γ-oxo-1-pyrenebutyric acid (OPBA), 1-pyrenebutyric acid (PBA) and 1-pyrene-carbox-aldehyde (PyCHO); (b) proposed Pd²⁺ sensing process.
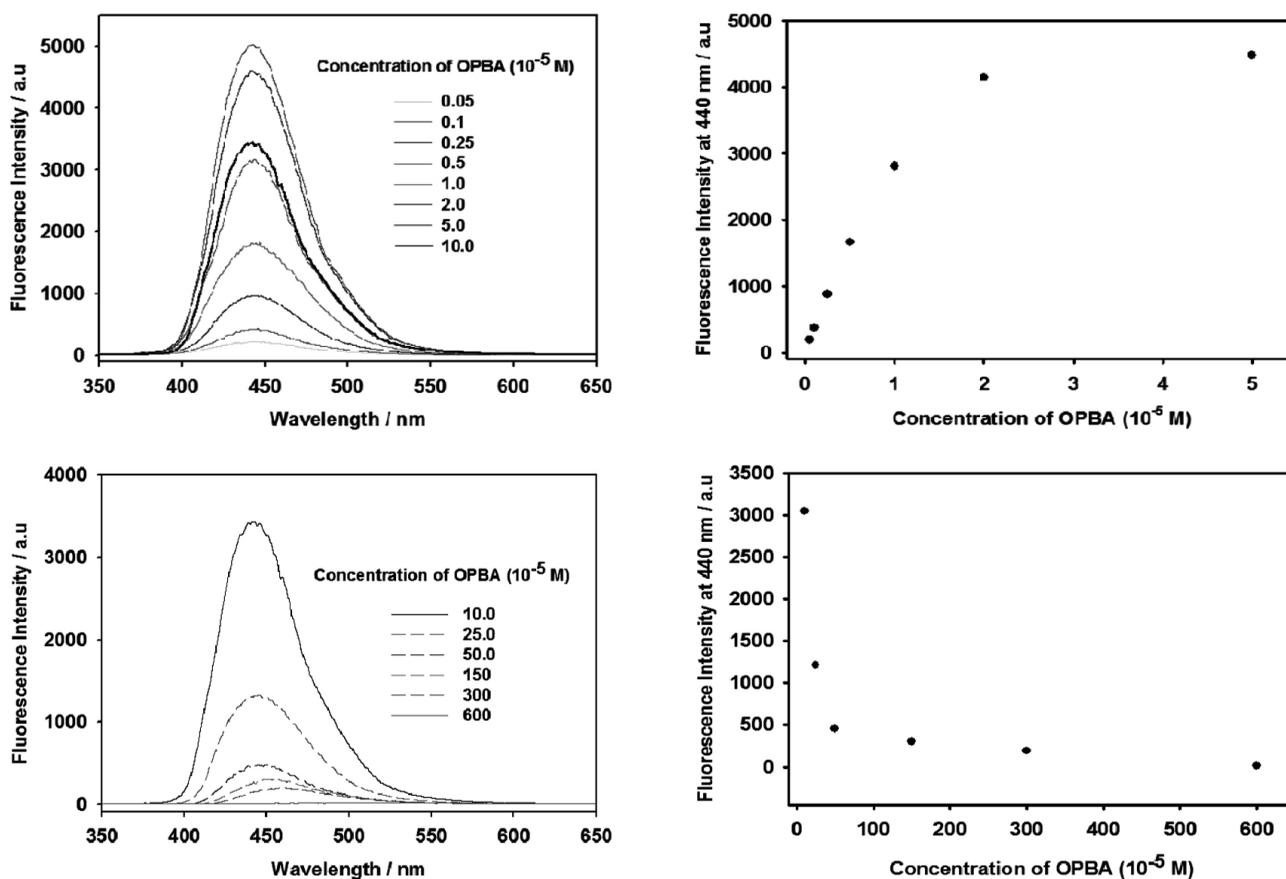
Figure 1. Fluorescence spectra of OPBA with different concentrations (0.6×10^{-3} M) in DMSO/H₂O (1 : 1 (v/v), $\lambda_{ex} = 340$ nm).

3. Results and Discussion

3.1. Photophysical Properties of OPBA

The fluorescence spectra of OPBA (Scheme 1(a)) were recorded with different concentrations (0.6×10^{-3} M) in DMSO/H₂O (1 : 1 (v/v), $\lambda_{ex} = 340$ nm). The fluorescence emission intensity of OPBA at 440 nm increased in the concentration range of 0.5×10^{-5} M (Figure 1). Further increasing the concentration above 1×10^{-4} M, the emission of OPBA was red-shifted and significantly decreased, when the concentration of OPBA was at 6×10^{-3} M, the monomer emission at 440 nm completely disappeared and a new emission peak at approximately 518 nm appeared due to the excimer formation of pyrene chromophore on OPBA
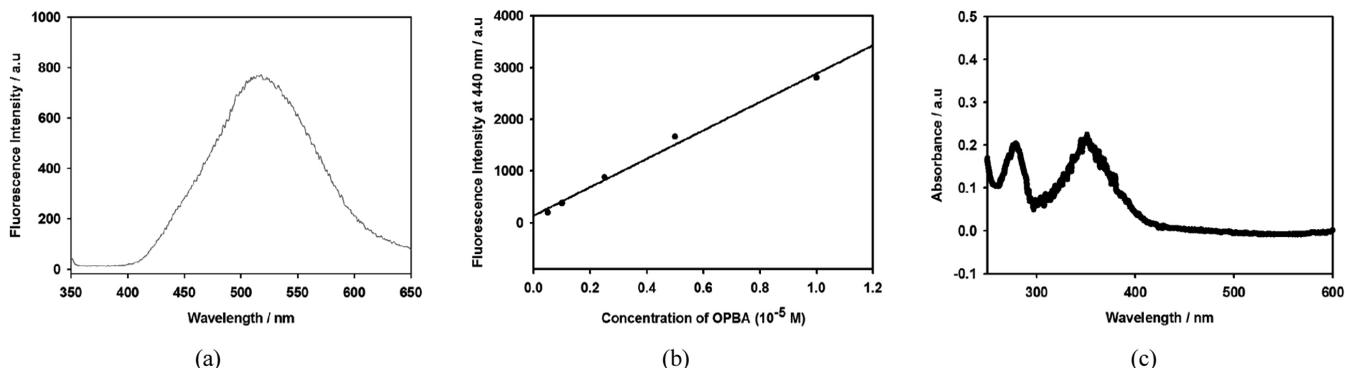
Figure 2. (a) Fluorescence spectra of OPBA (6 × 10^{-3} M) in DMSO/H$_2$O (1 : 1 (v/v), λ_{ex} = 340 nm), (b) the plot of λ_{em} = 455 nm versus the concentration of OPBA (0.1 × 10^{-5} M), (c) UV-Vis absorption spectra of OPBA (1 × 10^{-6} M) in aqueous solutions (DMSO/H$_2$O, 2 : 98 (v/v)).

(Figures 1 and 2(a))[22-25]. In the concentration range of 0.1 × 10^{-5} M (Figure 2(b)), the emission of OPBA at 440 nm versus the concentration of OPBA revealed a linear relationship (R = 0.996). The concentration of OPBA was selected at 1 × 10^{-6} M for all of the following experiments in aqueous solutions (DMSO/H$_2$O (2 : 98, (v/v)).

As shown in Figure 2(c), the absorption spectra of OPBA (1 × 10^{-6} M) shows an intense band centered at 351 nm, while in the emission spectra the monomer emission maxima of OPBA (1 × 10^{-6} M) was about 455 nm (Figure 3(a))[26]. The Stokes'shift was calculated from the difference in the absorption and the emission maxima to be 104 nm. Moreover, with increasing the water content, we observed strong red shift of the fluorescence emission band from 440 nm (DMSO/H$_2$O (1 : 1 (v/v)), Figure 1) to 455 nm (DMSO/H$_2$O (2 : 98 (v/v)), Figure 3) which can be attributed to the fact that hydrogen bonding raises the energy of the triplet ^{3}n-π^* (which was found in the vicinity of lowest singlet $^1\pi$-π^* excited states) above the lowest singlet $^1\pi$-π^* excited states thereby reducing the efficiency of the intersystem crossing[24,26].

3.2. Fluorescence Detection of Pd^{2+} Cations

Upon titration with Pd^{2+} (0.2 × 10^{-5} M), the fluorescence intensity of the monomer emission maximum at 455 nm decreased gradually with the increase of Pd^{2+} concentration (Figure 3(a)). The fluorescence intensities at 455 nm are linearly proportional to the amount of Pd^{2+} in the range of 0.2 × 10^{-5} M (Figure 3(b)) which demonstrated that the Pd^{2+} ions can be detected quantitatively in the concentration range of 0.2 × 10^{-5} M. This curve (Figure 3(b)) can also be served as the calibration curve for the detection of Pd^{2+}, the detection limit of Pd^{2+} was calculated
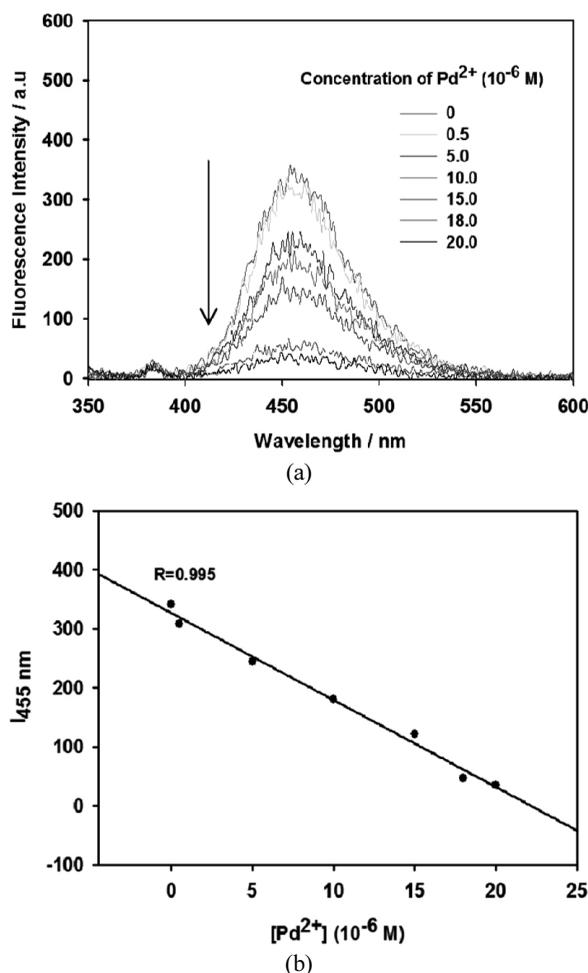
Figure 3. (a) Fluorescence emission spectra of OPBA (1 × 10^{-6} M) in the presence of different amounts of Pd^{2+} cations (0.2 × 10^{-5} M); (b) fluorescence emission of OPBA at 455 nm versus the concentration of the added Pd^{2+} cations.

to be approximately 0.14 μm[12]. It was assumed that the FL changes was induced by the 2 : 1 complex for-

(a)　　　　　　　　(b)　　　　　　　　(c)
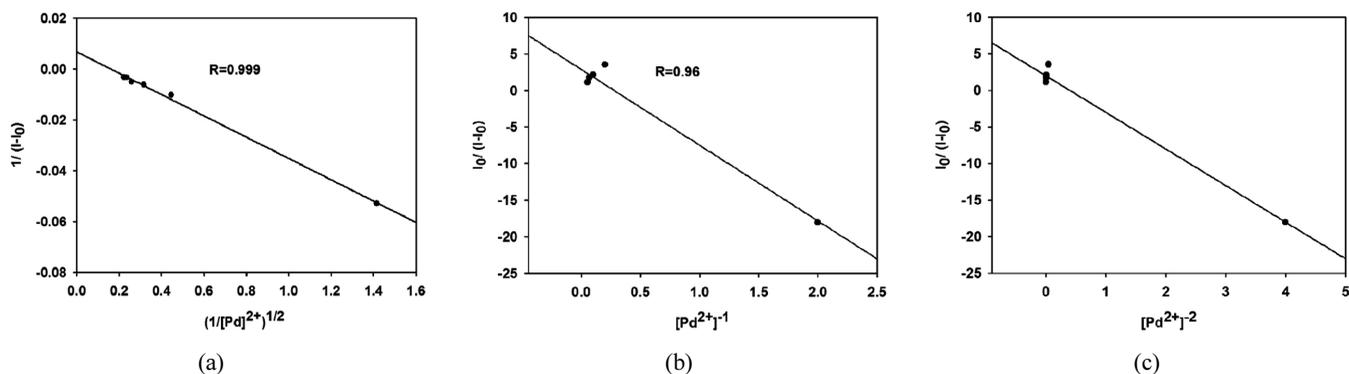
Figure 4. (a) Plot of $1/(I-I_0)$ versus $(1/[Pd]^{2+})^{1/2}$ based on 2 : 1 binding stoichiometry between OPBA and Pd^{2+}, (b) Plot of $I_0/(I-I_0)$ versus $[Pd^{2+}]^{-1}$ based on 1 : 1 binding stoichiometry, and (c) plot of $I_0/(I-I_0)$ versus $[Pd^{2+}]^{-2}$ based on 1 : 2 stoichiometry (bottom) between OPBA and Pd^{2+}. I_0 and I are the fluorescence intensity of OPBA at 455 nm in the absence and presence of Pd^{2+}.
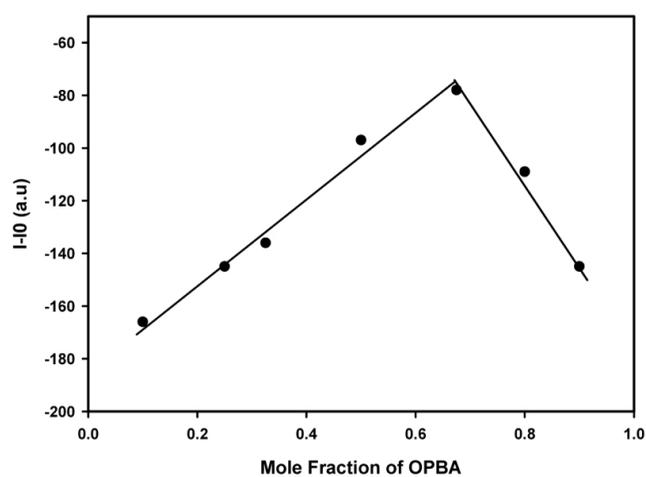
Figure 5. Job's plot of OPBA with Pd^{2+}. I and I_0 are the fluorescence intensity of OPBA in the presence and absence of Pd^{2+}, respectively; the total concentration of OPBA and Pd^{2+} is 10 μM.

mation between OPBA and Pd^{2+}, the association constant was calculated to be 1.6×10^3 M^2 (Figure 4)[27a]. Moreover,

The approximate Job's plot[27b] also suggests that OPBA forms a 2 : 1 complex with Pd^{2+} (Figure 5). There was no pyrene excimer emission in the 2 : 1 complex formed between OPBA and Pd^{2+} which suggested that the two pyrene chromophores are in the divergent position[11-21].

^{1}H-NMR experiments were carried out to confirm the coordination sites of OPBA with Pd^{2+}. As shown in Figure 6, the proton (OH) signal at 11.4 ppm completely disappeared in the presence of Pd^{2+} which indicated the binding of Pd^{2+} with an oxygen atom on OH of the carboxyl group. This was due to Pd^{2+}-induced deprotonation of the carboxyl group in OPBA during Pd^{2+} binding[28]. The peaks of protons in both of the pyrene-CO-CH$_2$- unit and CH$_2$-COO- unit were shifted to down-field which attributed to the deshielding effect arising from the decrease of the electron density caused by oxygen atoms-Pd^{2+} complexation in both of carbonyl group next to the pyrene chromophore and carbonyl group present in the carboxyl group. The chemical shifts of the aromatic protons in the pyrene moiety did not show any significant changes

(a)　　　　　　　　(b)　　　　　　　　(c)
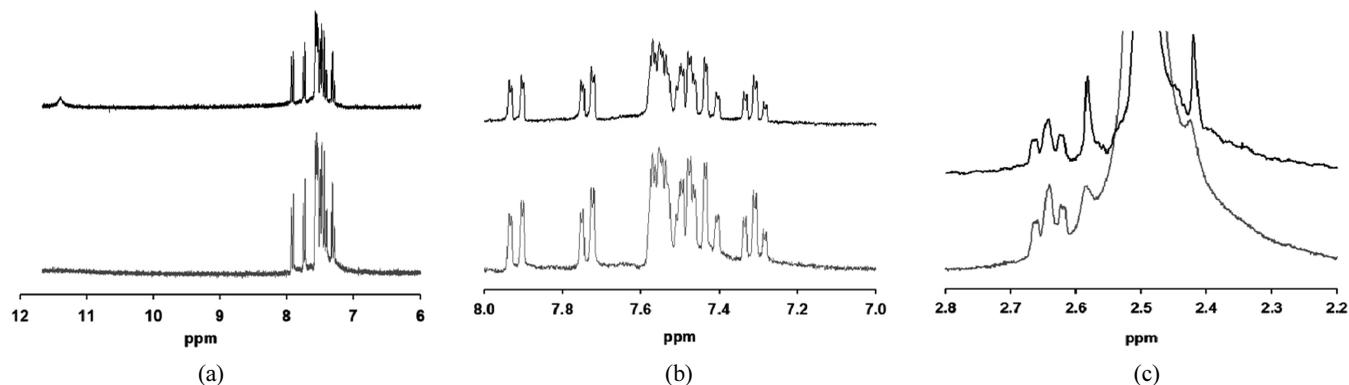
Figure 6. ^{1}H NMR spectra of OPBA (1×10^{-5} M) in the absence (black lines) and presence (red lines) of Pd^{2+} (6×10^{-5} M).

Figure 8. FTIR spectra of OPBA (1×10^{-5} M) in the absence (a, black line) and presence (b, pink line) of Pd^{2+} (6×10^{-5} M).

Figure 7. Fluorescence emission of PBA (a) and PyCHO, (b) in the absence (red lines) and presence (black lines) of 20.0 equiv. of Pd^{2+} cations.

in the ^{1}H-NMR spectra, therefore, we were able to exclude the interaction of pyrene ring with Pd^{2+}.

At the same time, to further confirm the role of coordination sites during the sensing of OPBA to Pd^{2+}, we tested a pair of model compounds, 1-pyrene-carboxaldehyde (PyCHO) and 1-pyrene-butyric acid (PBA) (Scheme 1(a)). As shown in Figure 7, no spectral changes of PBA and PyCHO were induced by Pd^{2+} ions, implies that both of carbonyl and carboxyl groups on OPBA took part in chelating with Pd^{2+}. All of the three oxygen atoms in the ligating moiety OPBA play important roles in the combination of Pd^{2+}. The binding mode was suggested in Scheme 1(b).

In addition, the IR spectra of OPBA (1×10^{-5} M) before and after Pd^{2+} (6×10^{-5} M) exposure were investigated. As shown in Figure 8, not much difference was observed before and after Pd^{2+} binding. The reason may be explained as follows: in the IR spectra of OPBA, the characteristic vibrations of the C=O group and COOH group cannot be observed in water which may be due to the hydrogen bonding between OPBA and water, and the hydrogen bonded complex may be formed[26].

3.3. Effect of pH

The study performed pH titration of OPBA to investigate a suitable pH range for Pd^{2+} sensing. As depicted in Figure 9, after mixing OPBA with Pd^{2+}, the emission intensity at 455 nm decreased between pH 2.5 and pH 4.5 and reached a minimum in the pH range of 4.5∼7.0. When the pH is higher than 7.0, the emission intensity increased. For pH < 4, the emission intensity is higher due to the protonation of the carboxyl groups that partially prevents the formation of OPBA-Pd^{2+} complexes. While the change in pH value does not disturb the detection of Pd^{2+} in the pH range of 5.0∼7.0. On the other hand, when pH was 8.0, Pd^{2+} was easy to bind with OH^- anion and form $Pd(OH)_2$ precipitation in high pH solution, which would reduce its complexation with OPBA[29]. These results demonstrated that OPBA can work in the pH range of 5.0∼7.0 for Pd^{2+} detection. Moreover, the emission of OPBA was almost constant in the pH range of 6∼10.5[30]. Therefore, all of the detections of metal cations were operated at pH 6.5 in aqueous solutions.
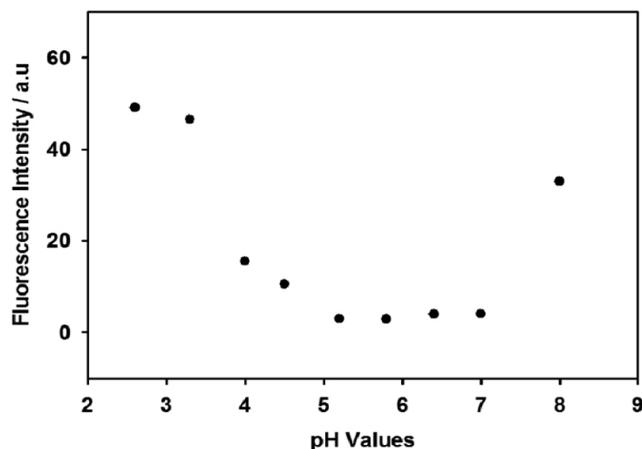
Figure 9. Influence of pH on the fluorescence of OPBA (1×10^{-6} M) at 455 nm in the presence of Pd²⁺ (2×10^{-5} M) in aqueous solutions, λ_{ex} = 340 nm. The pH of solution was adjusted by aqueous solution of NaOH (1 M) or HCl (1 M).

3.4. Selectivity of OPBA Toward Pd²⁺ Cations

An important feature of the sensor is its high selectivity towards the target analyte over other competitive species. As shown in Figure 10, upon addition of various metal cations (200 equiv.), the monomer emission of OPBA at 455 nm decreased greatly in the presence of Pd²⁺, and quenched slightly by Cu²⁺ and Pb²⁺, while minimal changes were observed for the other investigated metals. However, even 100 equiv. of Cu²⁺ and Pb²⁺ did not induce the changes on the fluorescence emission of OPBA at 455 nm[30], thus, OPBA cannot be used as the probes for the detection of metal cations of Cu²⁺ and Pb²⁺. To further investigate the selectivity for Pd²⁺ ions over other metal ions, interferences to the selective response of receptor OPBA to Pd²⁺ by coexisting ions were evaluated; no significant interference in detection of Pd²⁺ was observed in the presence of other competitive cations. These results suggested that OPBA can be used as a potential chemosensor for the Pd²⁺ ions.

3. Conclusions

In conclusion, γ-oxo-1-pyrenebutyric acid (OPBA) showed highly selective on-off fluorescence changes for Pd²⁺ among the other investigated metal cations. The binding stoichiometry was established to be 2 : 1 between OPBA and Pd²⁺ ions, with a binding constant of 1.6×10^3 M^{-2}. Moreover, the Pd²⁺ ions can be detected quantitatively in the concentration range of 0.2×10^{-5} M by OPBA.
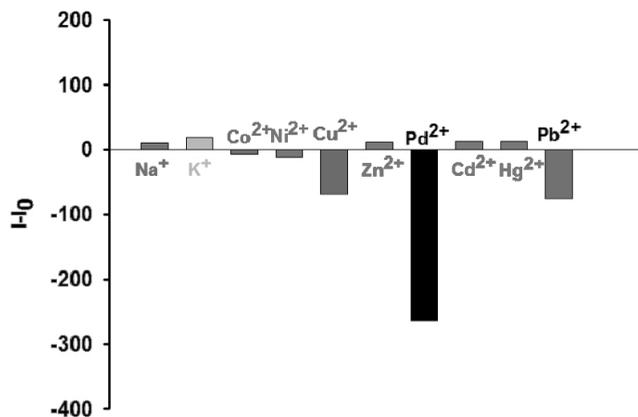
Figure 10. Fluorescent emission changes of OPBA (1×10^{-6} M) at 455 nm in the presence of 200.0 equiv. of metal cations in aqueous solutions. Excitation wavelength was set at 340 nm.

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