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PII: S0960-894X(20)30508-4
DOI: https://doi.org/10.1016/j.bmcl.2020.127397
Reference: BMCL 127397

To appear in: *Bioorganic & Medicinal Chemistry Letters*

Received Date: 26 February 2020
Revised Date: 29 June 2020
Accepted Date: 6 July 2020

Please cite this article as: Fang, G., Zhan, D., Wang, R., Bian, Z., Zhang, G., Wu, Z., Yao, Q., A highly selective and sensitive boronic acid-based sensor for detecting Pd^{2+} ion under mild conditions, *Bioorganic & Medicinal Chemistry Letters* (2020), doi: https://doi.org/10.1016/j.bmcl.2020.127397

A highly selective and sensitive boronic acid-based sensor for detecting Pd^{2+} ion under mild conditions

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Herein, a boronic acid-based sensor was reported selectively to recognize Pd^{2+} ion. The fluorescence intensity increased 36-fold after sensor binding with 2.47×10^{-5} M of Pd^{2+} ion. It was carried out in the 99% aqueous solution for binding tests, indicating sensor having good water solubility. In addition, it is discernible that Pd^{2+} ion turned on the blue fluorescence of sensor under a UV–lamp (365 nm), while other ions (Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Cr^{2+}, Cd^{2+}, Co^{2+}, Cs^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, K^+, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+} and Zn^{2+}) did not show the similar change. Furthermore, sensor has a low limit of detection (38 nM) and high selectivity, which exhibits the potential for the development of Pd^{2+} recognition in practical environments.

Keywords: Boronic acid; Fluorescence sensor; Pd^{2+} ion; Mild conditions

Considered to be one of the most important catalysts, palladium is used widely not only in numerous chemical transformations employed for the production of key chemical intermediates, fine chemicals, therapeutic drugs and so on,[1, 2] but also in commercial materials including fuel cells, jewellery, and catalytic converters.[3, 4] In this context, it is difficult to avoid the residual palladium in pharmaceuticals and waste containing palladium accidentally leaking into the environment, and eventually into the body, causing serious impact on the biological system. It is known that palladium species bind to DNA, amino acids, protein, and other biomolecules, which disturb biological processes and cause serious physiological disorders including dizziness, allergies, memory loss, facial paralysis and so on. Therefore, it is significant to develop a simple and effective methodology for the detection of palladium species. Compared to several typical analytical methods, including HPLC coupled with solid-phase microextraction,[5] atomic absorption spectroscopy (AAS)[6] and inductively coupled plasma mass spectrometry (ICP-MS),[7] a solution fluorescence-based sensing method is receiving continued attention due to simple, rapid and sensitive detection of palladium. Consequently, various fluorescent sensors have been designed and synthesized for the detection of Pd^{2+} ion (Table 1). However, these fluorescent sensors still have some drawbacks and limitations such as poor water-soluble,[8] slow response,[9, 10] necessity of heating at high temperature,[9-11] and complex synthetic process of sensor.[12, 13] Therefore, the development of a new fluorescent sensor for detecting Pd^{2+} ion is still increasing interest.

It is well known that Pd can be used as an effective catalyst for the Suzuki-Miyaura coupling, which is the coupling reaction between an arylboronic acid and an aryl halide.[14-16] Currently, there are few boronic acid-based fluorescent sensors for the detection of Pd^{2+} ion. Higashi reported the first boronic acid-based fluorescent sensor for Pd^{2+} ion based on benzofuran-2-boronic acid.[8] However, although there is a lower limit of detection (LOD) and a faster response time, organic solvent acetonitrile is used as sensor buffer solvent, which reflects the poor water solubility and is not conducive to further application of biological experiments. Furthermore, owing to shorter emission wavelengths and the absence of functional groups that can be further modified, it brings much difficult to design Pd^{2+} ion sensors with longer emission wavelengths on this basis. Therefore, it is quite meaningful to find a well water-soluble sensor that can be further modified functional groups on this basis. However, compared to the reported sensors (Table 1), the water-soluble sensor **1** has a low LOD to Pd^{2+} ion, as well as a handle for tethering other functional groups. In addition, the colour of solution changed blue from colourless after Pd^{2+} ion combined with sensor **1** but other ions caused almost unchanged, which was easily recognized by the naked eyes under a UV–lamp (365 nm).

The UV–vis absorption of the two sensors is shown in the Fig. S1. Sensor **1** has the largest absorption peak at about 337 nm. When the excitation wavelength of sensor **1** was set at 337 nm (slit: 5 nm/5 nm), sensor **1** has the largest emission fluorescence at about 400 nm. However, sensor **1** presents a red-shifted emission peak at 450 nm after adding of Pd^{2+} ion (Fig. 3A). In addition, sensor **2** has strongest emission fluorescence when the excitation wavelength was set at 340 nm for fluorescence tests (slit: 5 nm/5 nm). The quantum yields of sensor **1** and **2** fluorescence were calculated 0.06 and 0.05 respectively using the following equation:[12] $\Phi_D = \Phi_S \times \frac{F_D}{F_S} \times \frac{A_S}{A_D} \times \frac{(n_D)^2}{(n_S)^2}$, where Φ_S is the fluorescence quantum yield of the standard (quinine sulfate in ethanol, Φ =0.55, 25°C); F_D and F_S are the integrated areas of fluorescence intensity at the same excitation wavelength; A_D and A_S are the absorbances at the defined excitation wavelength; n_D and n_S are the refractive indices of the solvents (ethanol) at 25°C.

Fluorescence properties of sensor **1** were investigated toward different cations in DMSO/PBS (pH 8, 0.1M) solution (1:99, v/v), at room temperature. Interestingly, upon addition of Pd^{2+} ion to the solution of sensor **1**, a remarkable fluorescence enhancement appeared at around 450 nm (Fig. 3A). In contrast, upon addition of other metal ions (Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Cr^{2+}, Cd^{2+}, Co^{2+}, Cs^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, K^+, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+} and Zn^{2+}) to the solution of sensor **1**, there were not displaying the similar phenomenon (Fig. 1). These results demonstrated that sensor **1** had remarkably high selectivity toward Pd^{2+} ion.

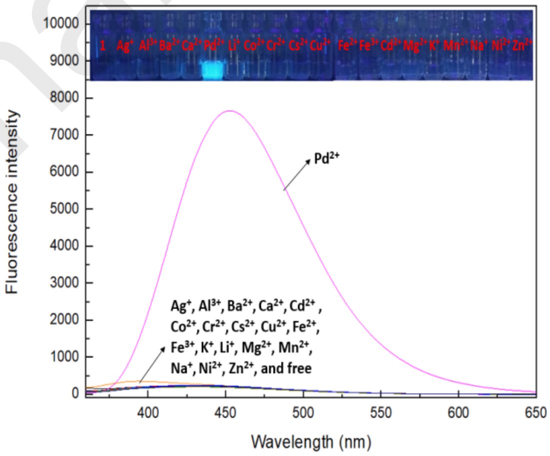


Fig. 1 Fluorescence spectra of sensor **1** (1×10^{-5} M) in the absence and presence of 2.5×10^{-5} M of various metal ions in DMSO/PBS (pH 8, 0.1M) solution (1:99, v/v), at room temperature. **Inset:** Photograph of **1** (1×10^{-5} M) upon adding 2.5×10^{-5} M of various ions, which was observed under a UV–lamp (365 nm).

As an important aspect of a chemical sensor used to practical applications, the sensitivity of sensor **1** toward Pd^{2+} ion was necessary to be evaluated. Therefore, the response time experiments of the reaction system were carried out. Upon addition of 2.5×10^{-5} M of Pd^{2+} ion, the fluorescence of sensor **1** was enhanced at 450 nm and reached the maximum fluorescence emission intensity after 10 min, followed by very weak fluorescence decay (Fig. 2). In addition, sensor **1** recognized Pd^{2+} ion at room temperature (such as 25 °C). These results indicated that sensor **1** had remarkably high sensitivity toward Pd^{2+} ion.

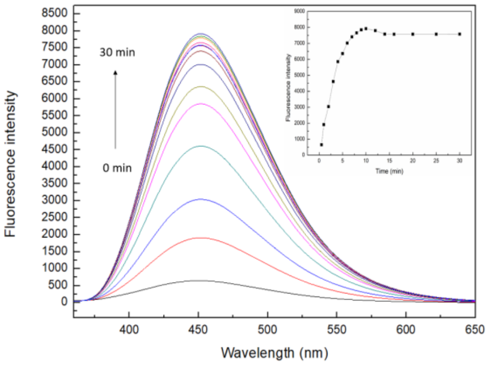


Fig. 2 Fluorescence spectra of sensor **1** (1×10^{-5} M) upon addition of 2.5×10^{-5} M of Pd^{2+} ion from 0 min to 30 min in DMSO/PBS (pH 8, 0.1M) solution (1:99, v/v), at room temperature. **Inset:** Plot of the fluorescence intensities at 450 nm over a period of 30 min.

In order to get more insight on the binding ability of sensor **1** toward Pd^{2+} ion, fluorescence spectrum titrations were performed. Upon the addition of increasing concentrations of Pd^{2+} ion, the fluorescence intensity of sensor **1** increased 36-fold at 450 nm (Fig. 3A). In order to investigate the function of boronic acids groups recognizing Pd^{2+} ion, sensor **2** without boronic acids groups was also used in the fluorescence spectrum titration study.[17] Interestingly, as the concentration of Pd^{2+} ion increased, the fluorescence intensity of sensor **2** was almost unchanged (Fig. 3B). This study indicates that boronic acids group plays a key role in the recognition of Pd^{2+} ion. Moreover, the formed structure of sensor **1** and Pd^{2+} ion has been discussed according to mass spectrometry. It showed that the sensing mechanism of sensor combined with 2 equivalents of Pd^{2+} ion (Fig. S10).[18, 19] After sensor **1** combined with catechol, the fluorescence of sensor **1**-catechol is quenched owing to photoinduced electron transfer (PET) mechanism.[17] Interestingly, after sensor **1** combined with 2 equivalents of Pd^{2+} ion, however, the fluorescence of sensor **1**-2Pd^{2+} is enhanced. Therefore, we speculate that sensor **1** has a certain action of PET, the formed sensor **1**-catechol enhanced it while the formed sensor **1**-2Pd^{2+} may inhibit it, thereby Pd^{2+} turning on the fluorescence sensor **1**. In addition, Tharmaraj reported similar compound structure which has inhibition of PET mechanism.[20] Nevertheless, all these results indicated that sensor **1** could be used as a fluorescent response sensor for rapid detection of Pd^{2+} ion in aqueous solutions under mild conditions.

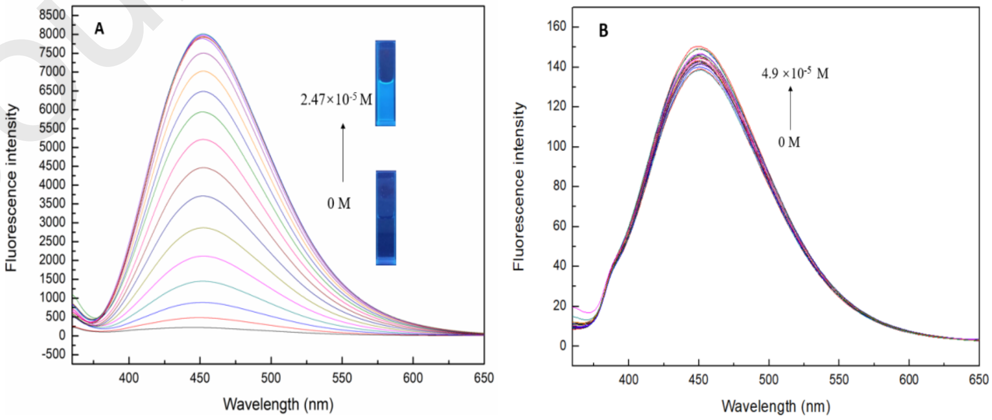
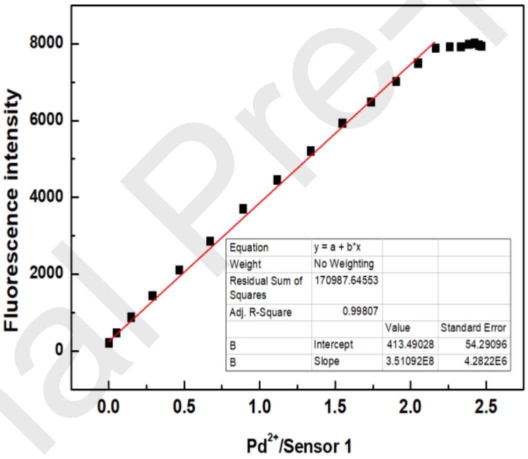


Fig. 3 A) Fluorescence spectra of **1** (1×10^{-5} M) in the presence of different concentrations of Pd^{2+} ion in DMSO/PBS (pH 8, 0.1M) solution (1:99, v/v), at room temperature, measured after addition of Pd^{2+} ion for 30 min. **Inset:** Photograph of **1** (1×10^{-5} M) upon adding $2.47\times10^{-}$

^{5} M of Pd^{2+} ion, which was observed under a UV–lamp (365 nm); B) Fluorescence spectra of **2** (1×10^{-5} M) in the presence of different concentrations of Pd^{2+} ion in DMSO/PBS (pH 8, 0.1M) solution (1:99, v/v), at room temperature, measured after addition of Pd^{2+} ion for 30 min.

Moreover, a significant fluorescence increase at 450 nm was observed with 36-fold emission enhancements when nearly 2 equiv. Pd^{2+} ion was added to the solution of sensor **1** (Fig.4). Pd^{2+} ion exhibited the dependence of the intensity of emission at 450 nm, which indicated the formation of a sensor **1**/ Pd^{2+} adduct of 1 : 2 stoichiometry.[21, 22] Then the LOD was calculated to 38 nM with the following equation (Fig. S2): $\mathrm{LOD} = 3\delta/S$, where δ is the standard deviation of the 8 times blank signal of sensor, and S is the slope of the calibration curve. Sensor **1** has a low LOD and good linear relationship in the range of 1.48 μM to 21.7 μM. As a "turn on" type sensor, sensor **1** is more sensitive than "turn off" type sensors. In addition, the fluorescence tests of sensor **1** under the 99% aqueous solution is more advantageous than the sensors with a larger proportion of organic solvent [19]. Furthermore, the sensitivity of sensor **1** can satisfy the requirement which the WHO specified threshold limit for palladium content in drug chemicals (47.0 μM to 94.0 μM) [19]. The enhancement efficiency was quantitatively explained by the Stern–Volmer (SV) equation:[23] $I_0/I = 1 + K_{SV} \times [M]$, where I_0 and I are the maximum fluorescence intensity of **1** before and after the addition of Pd^{2+} ion, respectively, and $[M]$ is the molar concentration of Pd^{2+} ion. Pd^{2+} ion has a significant effect on the fluorescence enhancement of the sensor **1** with a large K_{SV} of -3.9×10^{-4} M^{-1}. The SV plot for Pd^{2+} was nearly linear at low concentrations, as shown in Fig. S3.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	170987.64553		
Adj. R-Square	0.99807		
		Value	Standard Error
B	Intercept	413.49028	54.29096
B	Slope	3.51092E8	4.2822E6

Fig. 4 Photograph of sensor **1** linear relationship.

To further evaluate the selectivity of sensor **1** for Pd^{2+} ion, the interference experiments of sensor **1** for Pd^{2+} ion were carried out in the presence of various ions under the same conditions, as shown in Fig. 5. It was found that competitive ions had litter interference to sensor **1** responding to Pd^{2+} ion. Sensor **1** and **2** had neglectable fluorescence change in the presence of 2.5×10^{-5} M of the ions Ag^{+}, Al^{3+}, Ba^{2+}, Ca^{2+}, Cr^{2+}, Cd^{2+}, Co^{2+}, Cs^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Li^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+} and Zn^{2+}. However, after addition of Pd^{2+} ion, sensor **1** had remarkable fluorescence enhancement.

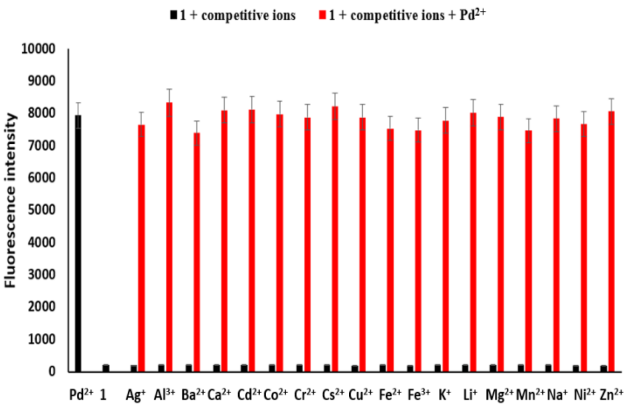


Fig. 5 Fluorescence intensities of **1** (1×10^{-5} M) in DMSO/PBS (pH 8, 0.1M) solution (1:99, v/v), at room temperature, measured after addition various metal ions for 30 min. Black bars represent the fluorescence intensity (450 nm) of **1** in the presence of 2.5×10^{-5} M of the ions Pd^{2+}, Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Cr^{2+}, Cd^{2+}, Co^{2+}, Cs^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, K^+, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+} and Zn^{2+}. Red bars represent the fluorescence intensity (450 nm) of **1** in the presence of various metal ions after the addition of Pd^{2+} ion.

As Lewis acids, boronic acids can be affected by acidic and alkaline environments.[24] Therefore, it is necessarily to investigated a suitable pH condition for the interesting process of sensor **1** recognizing Pd^{2+} ion. As shown in the Fig. 6, sensor **1** has a large fluorescence response in the range of pH 7 to 10 under the same condition. These fluorescence intensity data come from strongest emission wavelength (450nm). Interestingly, boronic acid exists in the form of trivalent plane *sp*^{2} (neutral) under acidic conditions and turns into tetravalent tetrahedral *sp*^{3} (anionic) under basic conditions.[25] Due to the electrostatic attraction, the anionic form of boronic acid can interact with the cationic Pd^{2+} under slightly alkaline condition, inducing fluorescence enhancement. However, OH^- can interact with Pd^{2+} when the alkaline condition is too strong, weakening this induction effect. Therefore, the bell-shaped pH *vs* fluorescence intensity plot is obtained.

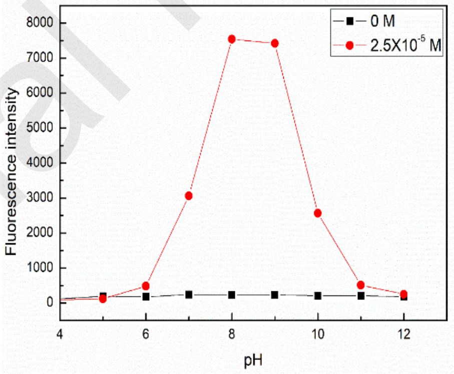
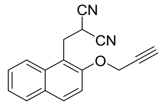
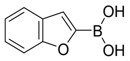
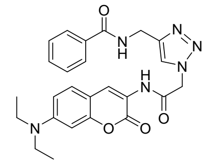
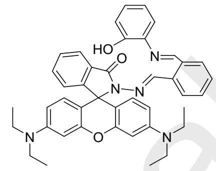
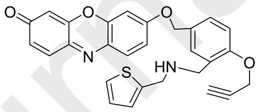
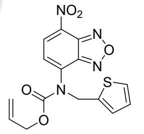
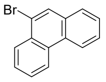
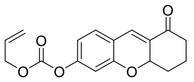
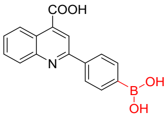


Fig. 6 Fluorescence responses of sensor **1** (1×10^{-5} M) to Pd^{2+} ion in DMSO/PBS (1:99, v/v, 0.1 M) at different pH values, at room temperature.

Many sensors were reported earlier selectively recognize Pd^{2+} ion, however, there still had some drawbacks. Although some of the reported sensors have superior optical properties, there are some aspects that require further improvement. For example, as an important parameter, the LOD of many reported sensors has reached the nM level, which plays a significant role in the trace detection of real samples. However, these tests were performed under non-ideal conditions, such as long binding time, high binding temperature and high proportion of organic solvent used in the buffer.[8-11] Interestingly, we found that the mother nucleus (sensor **1**) designed previously into diboronic acid sensors by us had a significant fluorescence enhancement with Pd^{2+} ion but did not show the similar phenomenon with other ions. We have reported the recognition of Fe^{3+} ion by diboronic acid sensor mentioning sensor **1** having a fluorescence quenching response to Fe^{3+}, Cr^{+} and Al^{3+}, but it does not affect the response of sensor **1** to Pd^{2+} ion.[18] Owing to the difference of turning on and off in responding mode, it is easier to use sensor **1** to recognize the Pd^{2+} ion among various ions. The biggest advantage of sensor **1** over the reported sensors is water-soluble and mild detection conditions (room temperature, 30 min response time, *etc.*). In addition, as a known and commercially available compound, sensor **1** is more suitable to be further researched. The LOD of sensor **1** was measured at 38nM indicated high sensitivity to Pd^{2+} ion. Moreover, it is discernible that Pd^{2+} ion turned on the blue fluorescence of sensor **1** under a UV–lamp (365 nm), while other ions did not show the similar change.

Table 1 key information of the reported sensor for Pd^{2+} ion.

	Sensor	Buffer	Time； Temperature	λ_{ex}; λ_{em}	LOD
Chen *et al.* reported [11]		PBS buffer/EtOH (99:1, v/v)	60 min; 37 °C	395 nm; 457 nm↑	53 nM
Higashi *et al.* reported [8]		acetonitrile	5 min; 25 °C	315 nm; 360 nm↑	9.8 nM
Hou *et al.* reported [26]		PBS buffer/DMF (200:1, v/v)	5 min; -	410 nm; 491 nm↓	260 nM
Long *et al.* reported [27]		EtOH/HEPES buffer (4/6, v/v)	1 min; -	540 nm; 583 nm↑	3490 nM
Ren *et al.* reported [28]		MeOH/PBS buffer (8:2, v:v)	30 min; 25 °C	550 nm; 586 nm↑	50 nM
Xu *et al.* reported [9]		PEG400 solutions	120 min; 55°C	480 nm; 526 nm↑	1.13 nM
Qin *et al.* reported [10]		EtOH/H_2O (3:7, v:v)	120 min; 70°C	240 nm; 359 nm↑	50 nM
Wang *et al.* reported [29]		MeOH/PBS buffer (1:1, v:v)	6 min; 25°C	405 nm; 511 nm↑	690 nM

Our sensor		DMSO/PBS buffer (1:99, v:v)	10 min; 25°C	337 nm; 450 nm↑	38 nM

↑: turn on; ↓: turn off

Sensor **1** is an interesting compound because the quinoline ring has a handle (carboxylic acid functional group) for tethering other functional groups. A very striking example is the structural modification of sensor **1** by Chen *et al.*, which synthesized PBAQA-PGMA fluorescent composite nano-microsphere biosensor.[30] It showed good detection sensitivity and selectivity to 5-hydroxymethylcytosine in genomic DNA. Compared to the fluorescence tests of none boronic acid-based sensor **2** to Pd^{2+} ion, it is determined that the boronic acid group of sensor **1** is a key site for interaction with Pd^{2+} ion. There are some excellent features in sensor **1**. The connection of phenylboronic acid to the quinoline ring provides the possibility of electron transfer between the quinoline ring and the benzene ring after the combination of boronic acid and the analyte. In addition, both the boronic acid group and N on the quinoline are hydrophilic, which offer a water-soluble feature. Furthermore, the quinoline ring has a large conjugated structure which provides potential for its derivatives to have long emission wavelengths. The long wavelength and water solubility may be increased when the carboxylic acid on sensor **1** is further modified to a larger conjugated compound or linked to new materials. Thus, these studies indicate that sensor **1** has the potential to be modified for the detection of other meaningful analytes, including Pd^{2+} ion.

In summary, a highly selective and sensitive boronic acid-based sensor was reported selectively recognizing Pd^{2+} ion under mild conditions. Interestingly, Pd^{2+} ion turned on the fluorescence of sensor **1** while other ions did not show the similar change. In addition, the conditions of tests are quite mild, which were carried out under the 99% aqueous solution, at room temperature. Moreover, sensor **1** not only has high selectivity and sensitivity toward Pd^{2+} ion, but also provides further modified functional group, which bring great potential for designing higher binding affinity and longer emission wavelength sensors on this basis. These studies indicate that sensor **1** has potential for Pd^{2+} ion recognition in practical environments.

Acknowledgements

The authors would like to thank Shiyanjia Lab (www.shiyanjia.com) for analysis molecular weight of the sensor **1**-2$Pd^{2+}$and the Innovation Project of Shandong Academy of Medical Sciences for financial support. This work was supported by National Natural Science Foundation of China (Grant No. 21801158), Shandong Academy of Medical Sciences Foundation (Grant No. 2018-17), Graduate Instructor Guidance Ability Improvement Project of University of Jinan (Grant No. JDYY1804), Academic Promotion Programme of Shandong First Medical University (nos. 2019LJ003).

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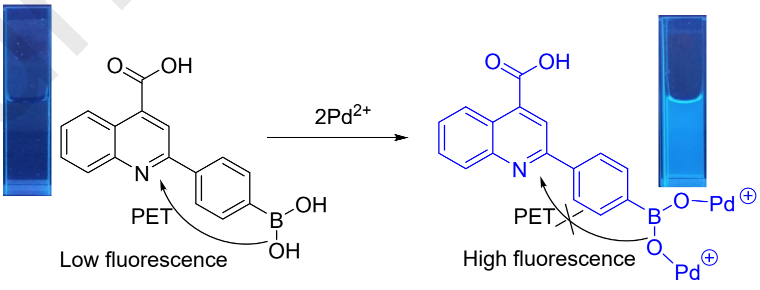
Graphical Abstract



A boronic acid-based sensor was reported selectively to recognize Pd^{2+} ion, which has a low limit of detection (38 nM) and exhibits the potential for the development of Pd^{2+} recognition in practical environments.