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A ready-to-use fluorescence probe of Pd^{2+} in water: novel tricyclic heterocyclic base on 1,3,4-oxadiazole

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Abstract

A ready-to-use hetero-tricyclic compound, 5,5′-(furan-2,5-diyl) bis (1,3,4- oxadiazol-2-amine) (**5**), was synthesized with a good yield; it has an suitable fluorescence characteristic and research founded that it can respond to trace Pd^{2+} in water at a normal pH range. A fluorescence titration revealed the detection limit for Pd^{2+} was as low as 3.97×10^{-9} M. Density-functional theory calculation using Guassian09 implied that the breakage of conjugation and coplanarity of compound **5** led to fluorescence quenching. Compound **5** could be applied as a chemical probe to detect trace amounts of Pd^{2+} with good accuracy, fast response time, excellent selectivity, and high sensitivity. FT-IR, NMR, and MS were used to characterize the chemical structure of compound **5**.

KEYWORDS
DFT, fluorescent probe, Pd^{2+}, UV–Vis

1 | INTRODUCTION

Along with unceasing economic development, people's living standards are improving, and environmental pollution problems are now increasing producing concerns especially for the pollution from heavy metals.[1] Palladium is a very important metal due to its wide applications in laboratory and industry.[2] Large amounts of residual palladium exist in the environment. Palladium[3] is nonbiodegradable with the characteristics of bioaccumulation and biological concentration along the food chain. It is a serious hazard to animals and plants.[4] Therefore, there is an urgent need to explore a quick, selective, and sensitive method to detect Pd^{2+}.

Traditional methods to detect heavy metal ions such as ICP-MS,[5] ICP-OES, X-ray fluorescence (XRF),[6] and flame atomic absorption spectrometry (FAAS)[7] can detect the target ions with good sensitivity and speed, but most require well trained operators, expensive facilities, and a specific experimental environment.[8] For the reason of low cost, easy operation, speed and sensitivity, a series of colorimetric and fluorimetric methods[9] has been established for determination of trace heavy metal ions. To date, some fluorescent chemical probes for detecting metal ions have been reported involving Fe^{3+},[10] Cu^{2+},[11] Cr^{3+}[[12]] and Zn^{2+}.[13]

Various fluorescent chemical probes have been designed to detect Pd^{2+},[14] unfortunately most of these are derived from traditional fluorescent molecular structures such as coumarin, rhodamine and fluorescein. Moreover, the synthesis of such probes is complex and it is more difficult to further derivatize from those structures. As an important class of heterocyclic compound, there have been many studies on 1,3,4-oxadiazole in virtue of its excellent biological and optical properties,[15] but its strong fluorescence properties have been rarely studied.

Here, a hetero-tricyclic compound 5,5′-(furan-2,5-diyl)bis(1,3,4-oxadiazole-2-amine) (**5**) was synthesized using a one-step-process from the condensation of 2,5-furandicarboxyl hydrazide with bromide cyanogen followed by alkalization. Research shows that compound **5** has very strong fluorescence intensity and that it could react with Pd^{2+} ions in water solvent rapidly, therefore it was designed as a selective chemical probe with speed, sensitivity, and convenient properties.

2 | EXPERIMENTAL

All reagents and raw materials were acquired by commercial procuration.

Compound **5** was synthesized following the procedures described in Scheme 1. A solution of 0.920 g (5 mmol) dimethyl furan-2,-5-dicarboxylate (**1**) in 30 ml ethanol was added into a flask (50 ml) containing a thermometer and magnetic stirrer. The mixture was heated at 70°C. Then the mixture was added dropwise to 2 ml isothermal hydrazine monohydrate, the reaction mixture was kept at 70°C for 30 min. A large amount of flocculent solids separated out, and the solution was cooled to room temperature. The precipitate was collected using filtration and gave 0.87 g of compound **1** as a white flocculent crystal (compound **2**, furan-2,5 -dicarboxylic acid dihydrazide). Yield: 94.6%; FT-IR spectrum (KBr pellet, cm^{-1}): 3262, 2981, 1669, 1638, 1602, 1554, 1489 and 1298. m.p.178–179°C. Compound **3** (0.552 g, 3 mmol) and potassium bicarbonate (5.544 g, 6.6 mmol) were suspended in methanol (30 ml) at 0°C. Bromine cyanide (0.63 g, 6 mmol) was directly added into the mixture above. Then stirred overnight at 0°C, heated up to room temperature and stirred for another 24 h. TLC under 365 nm ultraviolet irradiation indicated that the target compound was mainly produced, the precipitate was collected and recrystallized from methanol, 0.42 g brown crystals (compound **5**, 59.8% yield) were obtained; m.p. > 300°C, IR (KBr pellet, cm^{-1}): 3440, 2988, 2920, 1649, 1089, and 594. ^{1}H-NMR (600 MHz, DMSO-d_6, ppm): 7.65 (s, 4H), 7.07 (s, 2H). ^{13}C-NMR (125 MHz, DMSO-d_6, ppm): 112.62, 140.42, 149.92, 163.52. MS (ESI): $m/z = 235\ [M + H]^{+}$. m.p. > 300°C.

By directly dissolving compound **5** in ethanol, the stock solutions of compound **5** (1×10^{-2} M) were prepared. Different stock solutions (1×10^{-2} M) of Cu^{2+}, Zn^{2+}, Mg^{2+}, Y^{3+}, Ca^{2+}, Rb^{+}, Ce^{3+}, Ni^{2+}, Pb^{2+}, La^{3+}, and Mn^{2+} were prepared by reverse osmosis (RO) water, in addition, Pd^{2+} (1×10^{-2} M) was placed in dimethyl formamide (DMF). Then to obtain the corresponding concentration value, all the stock solutions were diluted with RO water.

3 | RESULTS AND DISCUSSION

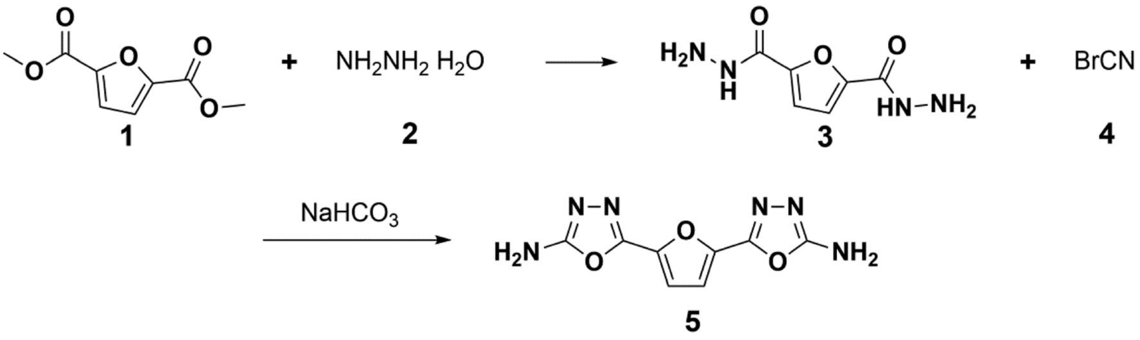
3.1 | Synthesis and characterization

Routinely, it is easy to form an oxadiazole ring using the condensation of cyanogen bromide with amine group compounds promoted using sulfuric acid, hydrochloric acid, phosphoric acid, sodium bicarbonate, or sodium hydroxide at different temperatures under alkalescent conditions. The tricyclic compound, 5,5′-(furan-2,5-diyl)bis(1,3,4-oxadiazole-2-amine) (**5**), has a pair of oxadiazole rings, consequently it was synthesized using one-step-process by condensation of 2,5-furandicarboxyl hydrazide with cyanogen bromide in sodium bicarbonate solution. Caution: cyanogen bromide is toxic, highly irritating, and can cause death; laboratories and personnel must be properly trained. Note: the target compound was formed under acid or base conditions, but the reaction mechanism is not clear.

Compound **5** was characterized (Figure S1–S4). Detailed data analysis is provided as follows.

3.1.1 | Spectra date

To evaluate the effects of different ions on the optical response of compound **5**, UV–Vis spectra of compound **5** with or without different metal ions in water were recorded (Figure 1). According to the UV–Vis absorbance data (Figure 1), the λ_{max} of compound **5** was



SCHEME 1 Synthesis of 5,5′-(furan-2,5-diyl)bis(1,3,4-oxadiazole-2-amine) (**5**)

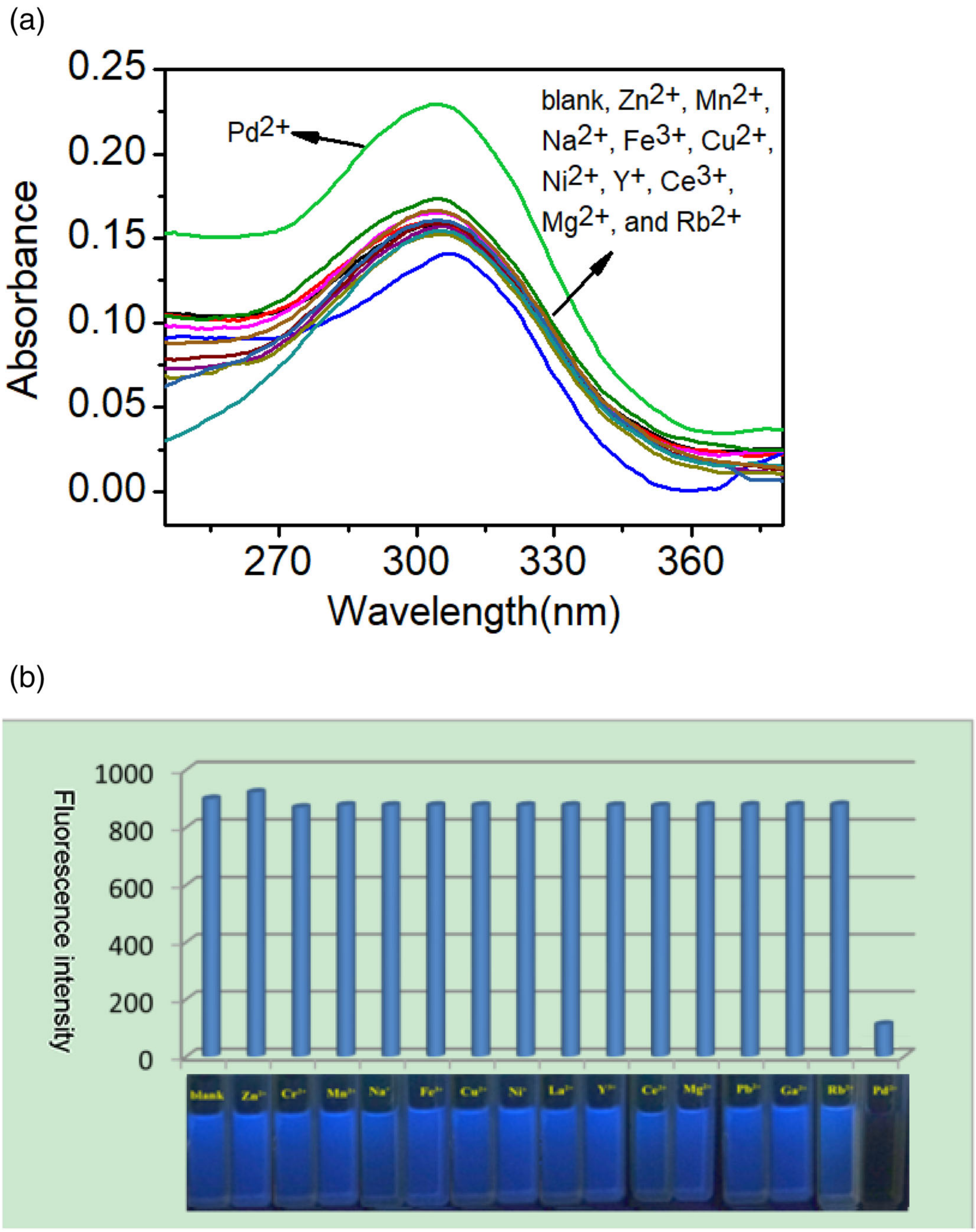


FIGURE 1 (a) UV–vis absorptions of compound **5** (1×10^{-3} M) with or without different metal ions (1 eq). (b) Maximum fluorescence emission intensity of compound **5** (1×10^{-6} M) with or without different metal ions

305 nm, and metal ions were affected little by both wavelength and intensity of compound **5** except for Pd^{2+}. This was because supramolecular interaction only took place between reaction sites of compound **5** and metal ions with a complementary structure. For Pd^{2+}, the absorption spectrum of compound **5** showed a red shift accompanied by an absorbance increase, meaning that the coordination reaction between compound **5** and Pd^{2+} weakened the conjugation and resulted in a red shift. Correspondingly, the fluorescence emission spectra of compound **5** determined with or without different metal ions in water were recorded, and the maximum fluorescence emission intensity is shown in a histogram (Figure 1b). Interestingly, compared with Pd^{2+}, other metal ions such as Fe^{3+}, Cu^{2+}, and Mn^{2+}, hardly affected the fluorescence of compound **5**, one equivalent Pd^{2+} could almost totally quench the fluorescence. Probably, this is also because the coordination reaction could form a nonfluorescent or low-fluorescent complex. This unique feature indicated that compound **5** could be further developed as a selective photochemical probe for Pd^{2+}.

For further exploration of the effect of Pd^{2+} on the UV–Vis absorption spectrum of compound **5**, UV–Vis titrations of compound

5 upon addition of Pd^{2+} were carried out. As displayed in Figure 2, after the addition of Pd^{2+}, λ_{max} of compound **5** experienced a slight red shift, at the same time a small absorbance enhancement occurred. In addition, a Job's plot (inset of Figure 2) showed that the molar ratio of coordination between compound **5** and Pd^{2+} was 1:1. What is even more interesting is that the quantum yield of compound **5** was 0.5149, which was calculated using the equation $Y_u = (Y_s \times F_u \times A_s)/(F_s \times A_u)$, where Y_u is the quantum yield of compound **5**, Y_s is the reference compound (quinine sulfate, 0.55), F_u is the fluorescence intensity integral of compound **5**, F_s refers to the fluorescence intensity integral of quinine sulfate, Au indicates the absorbance of compound **5**, and A_s is the absorbance of quinine sulfate, indicating that compound **5** had good luminescence efficiency.

Apart from metal ions, cations in solution could influence the fluorescence properties of a fluorophore and the pH of the solution could interfere with the normal proper working of fluorescent probes. To understand how pH affected the detection of palladium ions using compound **5**, a further study in water was investigated. The fluorescence intensities of compound **5**, in addition at pH range 7.0–5.0, greatly changed. Moreover, the adjunction of one eq Pd^{2+} could almost quench the fluorescence intensity of compound **5** over a wide pH range (shown in Figure 3), suggesting that compound **5** could only be used to detect Pd^{2+} at the pH range from 5 to 7. To meet potential applications in an internal environment for animals and plants, here further fluorescence research was carried out using phosphate-buffered saline (PBS) at pH 7.4.

To further investigate the fluorescence properties of compound **5** and Pd^{2+}, compound **5** was fluorescently titrated with Pd^{2+}. As shown in Figure 4, the maximum emission wavelength for compound **5** was 425 nm, corresponding to visible blue fluorescence.

During the fluorescence titration, the fluorescence intensity of compound **5** decreased gradually. When the molar ratio between Pd^{2+} and compound **5** reached 1:1, the fluorescence emission intensity was eventually reduced to 91.2%, confirming that the coordination ratio of the complex formed between Pd^{2+} and compound **5** was 1:1, consistent with the results of the Job's equation. Exploiting the data from the fluorescence titration (11 groups in parallel experiments), the lowest detection limit (3S/slope) of compound **5** for Pd^{2+} (where S is standard deviation) was estimated to be 3.97×10^{-9} M.

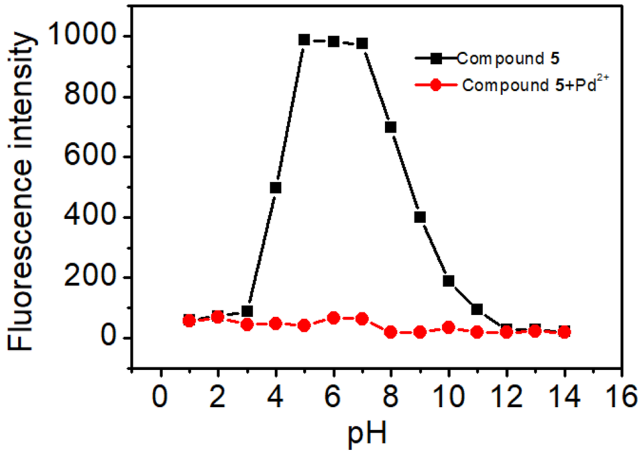


FIGURE 3 pH effects on the Pd^{2+} recognition of compound **5**

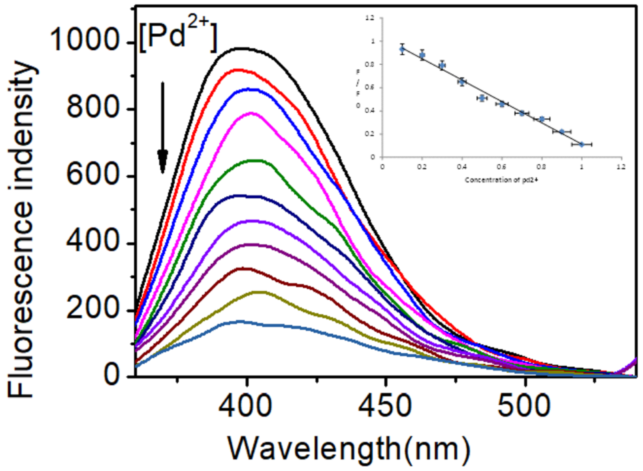


FIGURE 4 Fluorescence emission titration spectra of compound **5** (10^{-6} M) with Pd^{2+} at room temperature (RT) in PBS buffer, embedded as plot of F/F0 versus $[Pd^{2+}]$

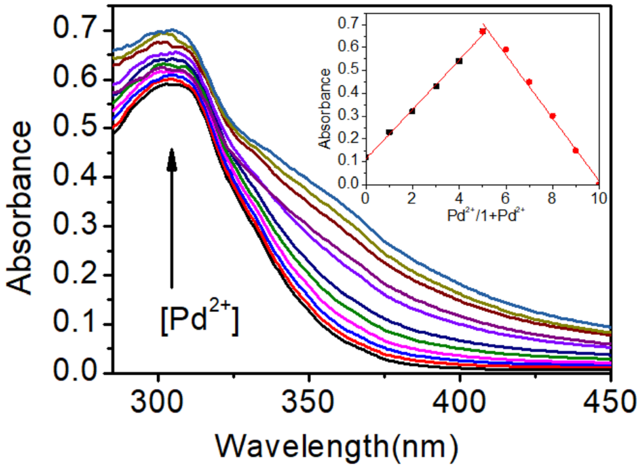


FIGURE 2 UV–vis titration of compound **5** (5×10^{-3} M) with Pd^{2+}. Inset: Job's plot of compound 5 and Pd^{2+}; total concentration of compound **5** and Pd^{2+} was kept constant at 5×10^{-3} M

For the reasons of simplicity, speed and convenience in the process of practical application, and requiring no complex and expensive equipment, a test paper plays an important role in practical application. By impregnating a filter paper with compound **5**, a portable test strip can be easily prepared to detect Pd^{2+}. The test strips (s5) prepared above had bright blue fluorescence under ultraviolet light and completely disappeared when Pd^{2+} was added. This visible phenomenon allowed quick and easy detection of Pd^{2+} in the natural environment. In addition, other ions could not affect the fluorescence of test strips under ultraviolet light. For the effect on the fluorescence of the phosphor, apart from the interference of cations, anions should also be given attention. The influence of anions on the method for compound **5** to detect Pd^{2+} was studied (Figure S6), one equivalent of Pd^{2+} salt with Br^-, Cl^- or AcO^- ions for fluorescence of compound **5** was identically quenched after it was added and could quench the fluorescence of compound **5**.

The practical application of measurement is of vital importance, therefore a standard curve of compound **5** to detect known $[Pd^{2+}]$ in five samples was drawn, the samples were prepared with DMF and diluted to corresponding concentrations with water (Figure 5). Another five samples were diluted with filtered water from the Fujiang river. The analysis results showed that, after the addition of Pd^{2+} in the samples, considerable accuracy (relative error approximately is 6.64%) could be obtained, and testified that compound **5** was able to be used to detect Pd^{2+} in real water samples system.

The results of the experiment above suggested that the coordination molar ratio between Pd^{2+} and compound **5** was 1:1. A mixture of compound **5** and $Pd(CH_3CHO)_2$ solution in methanol was prepared uniformly, after a full reaction it was then evaporated in a vacuum to prepare complex **6**. The possible process that Pd^{2+} and compound **5** experienced is shown (Scheme 2). Interestingly, the mass-to-charge ratio of complex **6** was found through the measurement of mass spectrometry (Figure S7) at m/z 459.56.

The FT-IR spectra of complex **6** and compound **5** are given in Figure 6. As the IR data shows, between 1800 cm^{-1} and 900 cm^{-1}, compound **5** and complex **6** were quite different. The adsorption bands *c*. 1652 cm^{-1} of complex **6** were slightly increased compared with compound **5** accompanied by the disappearance of a slightly structured vibration peak, showing that, after introducing acetate ions, the skeleton structure of the heterocyclic ring was certain influenced. The bands at *c*. 1381 cm^{-1} and 1090 cm^{-1} were the skeleton vibrations of heterocyclic rings, after complexation the intensity decreased considerably, and revealed that the N and O atoms in the furan and oxadiazole rings are probably sites where compound **5** participates in the coordination.

Therefore, the optimized structures of compound **5** with or without palladium metal ions are given in Figure 7 using DFT calculations and the Guassian09 software (attention: basis set of C, H, O, N and S is 6–31+G, LANL2DZ for Pd). As we can see in the Figure 7, 3′-N atoms in the oxazole ring and O atoms in the furan ring of compound **5** played the role of donors, while Pd^{2+} ion is a recipient, then the coordination bonds were formed. The addition of Pd^{2+} broke the coplanarity of compound **5**, and conjugation was also weakened, therefore fluorescence was quenched totally.

To search for the detailed mechanism of optical changes before and after complexation, the molecular orbitals of compound **5** with or without palladium metal were also studied. As shown in Figure 8, the clouds of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) implied that the electrons in compound **5** were well distributed, but that those in complex **4** locate were disordered.

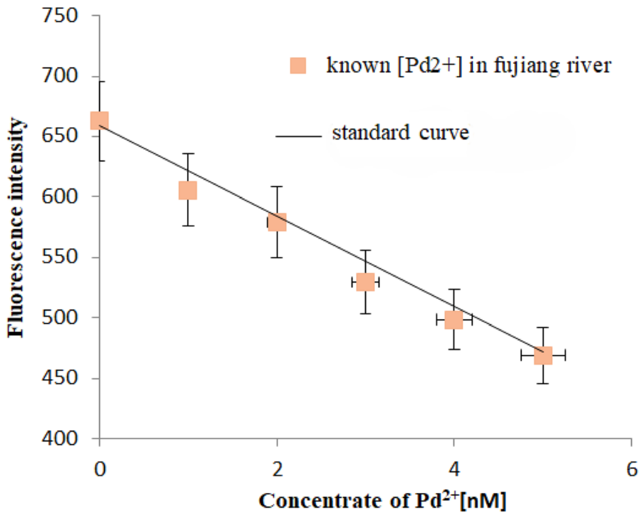


FIGURE 5 Standard curve of compound **5**, red dots means the known $[Pd^{2+}]$ in Fujiang river

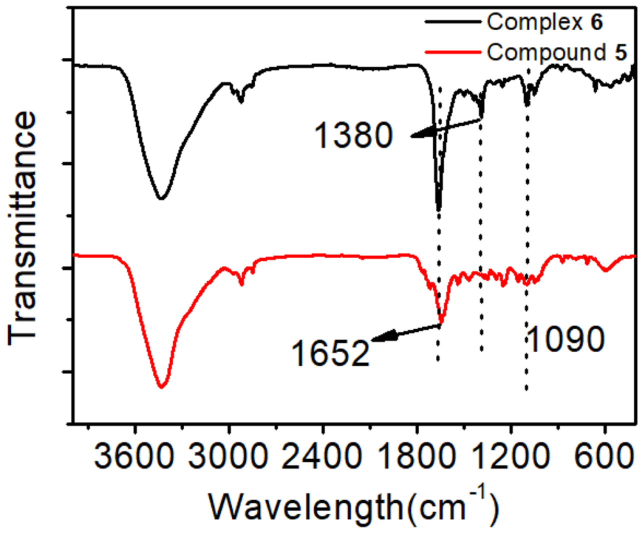
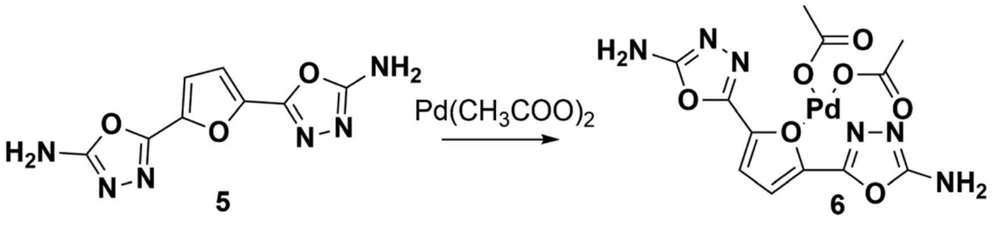


FIGURE 6 IR absorption of compound **5** and complex **6**



SCHEME 2 Synthesis of complex **6**

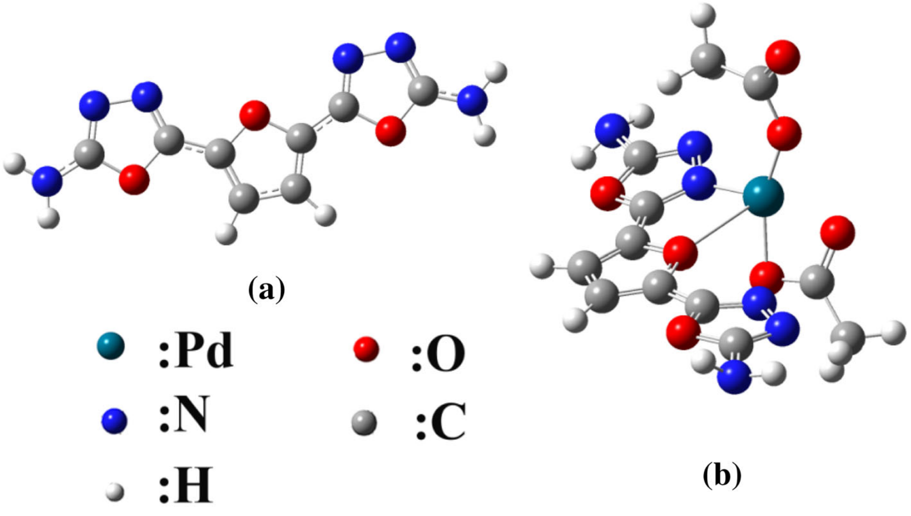


FIGURE 7 Optimized conformations of compounds **5(a)** and complex **6(b)**

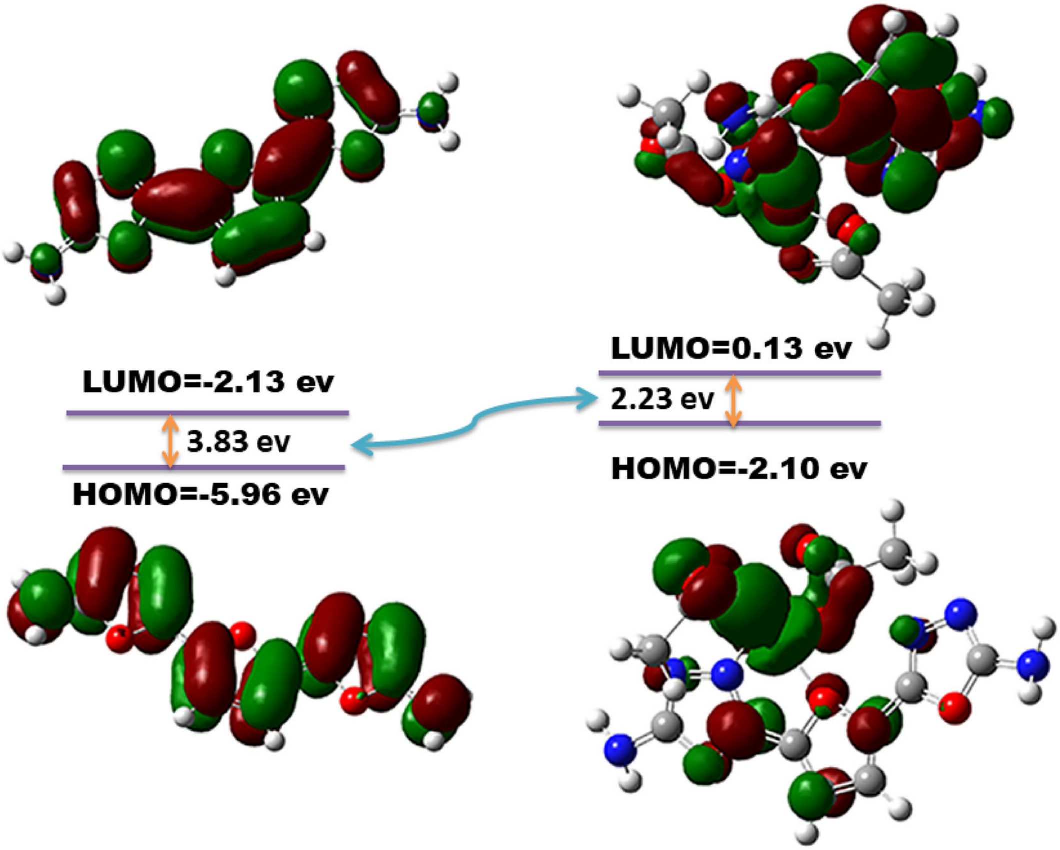


FIGURE 8 HOMO–LUMO energy and the interfacial gap of the orbitals for compound **5** and complex **6**

This indicates that the fluorescence quenching of compound **5** was due to the introduction of Pd^{2+}, which inhibits intramolecular charge transfer. What is more interesting, after coordination, the orbital energy gap between the HOMO and LUMO of complex **6** was slightly lower compared with compound **5**, which coordinates with the tiny red shift existing in the UV–vis spectra and fluorescence emission compound **5** with Pd^{2+}.

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SUPPORTING INFORMATION

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