Supporting Information (SI)

A new turn-on fluorescent probe for detection of palladium(0) and its application in living cells and zebrafish

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Sample preparation and measurements

Stock solutions of probe 1 and $Pd(PPh_3)_4$ were prepared in DMF with a concentration of 2 mmol/L. Stock solutions of metal ions were prepared in with a concentration of 20 mmol/L. UV-Vis and fluorescence spectra were obtained in Ethanol-PBS buffer solution (2:3, v/v, 10 mM PBS, pH=7.4).

Cells culture and imaging

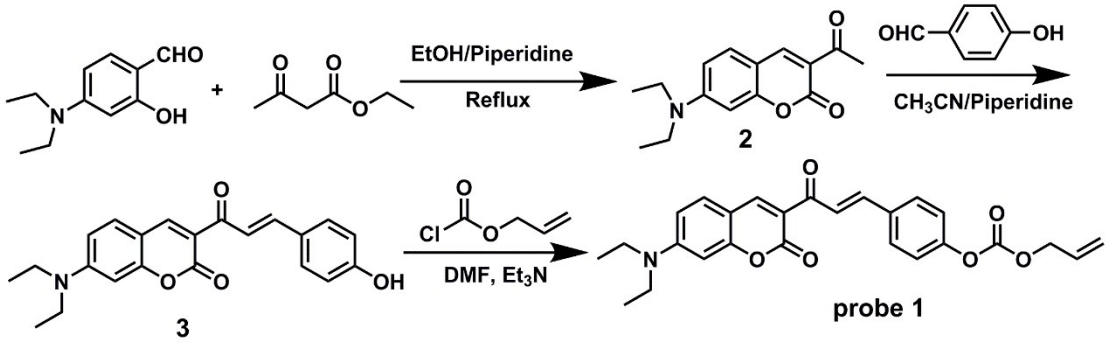
BT-474 cells were cultured in Gibco® RPMI 1640 medium supplemented with 10% FBS in an atmosphere of 5% CO_2 for 24 h at 37°C. BT-474 cells incubated with Pd^0 (10, 40, 100μM) for 0.5h, subsequently incubated with probe (5 μM) for 0.5h at 37°C. Zeiss LSM 880 is used for cell imaging. Emission was collected at 493-591 nm, excited at 458 nm, scale bar: 40 μm.

Zebrafish imaging

TU wild zebrafish were purchased from Nanjing Eze-Rinka Biotechnology Co., Ltd. The 3-day-old zebrafish were used for experiments. Zebrafish were incubated with Pd^0 (10, 40, 100μM) for 0.5h, and then incubated with probe for another 0.5h, the image was obtained using Zeiss LSM 880. Emission was collected at 493-591 nm, excited at 458 nm, scale bar: 500 μm.

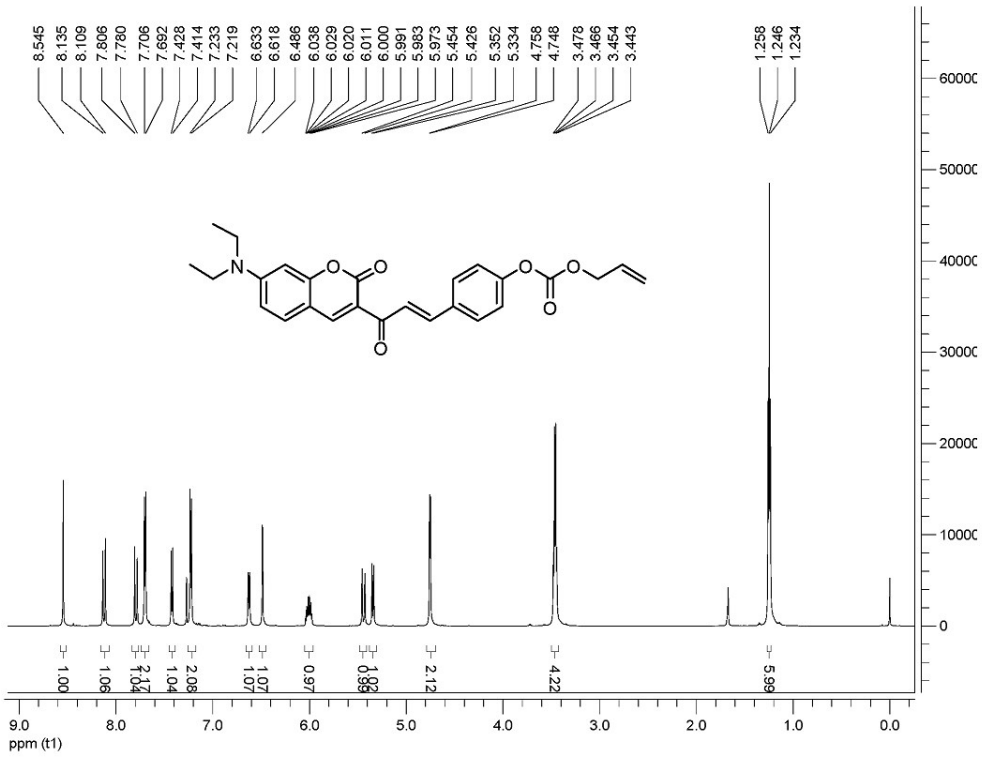
Figure S1: Synthesis, ^{1}H NMR, ^{13}C NMR, ESI-MS of the probe 1, the reaction product of probe 1 with Pd^0.

Synthesis of probe

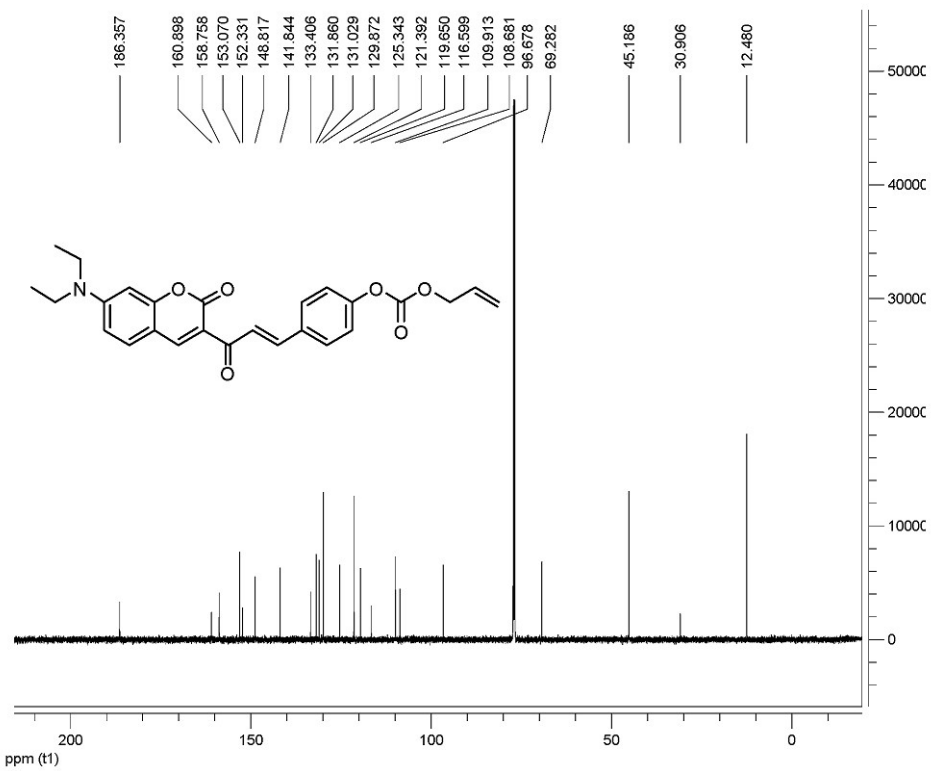


The synthetic methods of probe were summarized in **Scheme 1**. Probe was synthesized according to the published procedure[1]. Allyl chloroformate (0.14g, 1.1 mmol) was added to a solution of compound 3 (0.36 g, 1.0 mmol) and triethylamine (0.11 g, 1.1 mmol) in DMF (10 mL). The reaction mixture was stirred for 12h at 25°C, and the resulting solution was treated with water and CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4 and then concentrated. The crude product was purified by column chromatography (DCM:PE=1:1) to afford probe **1**

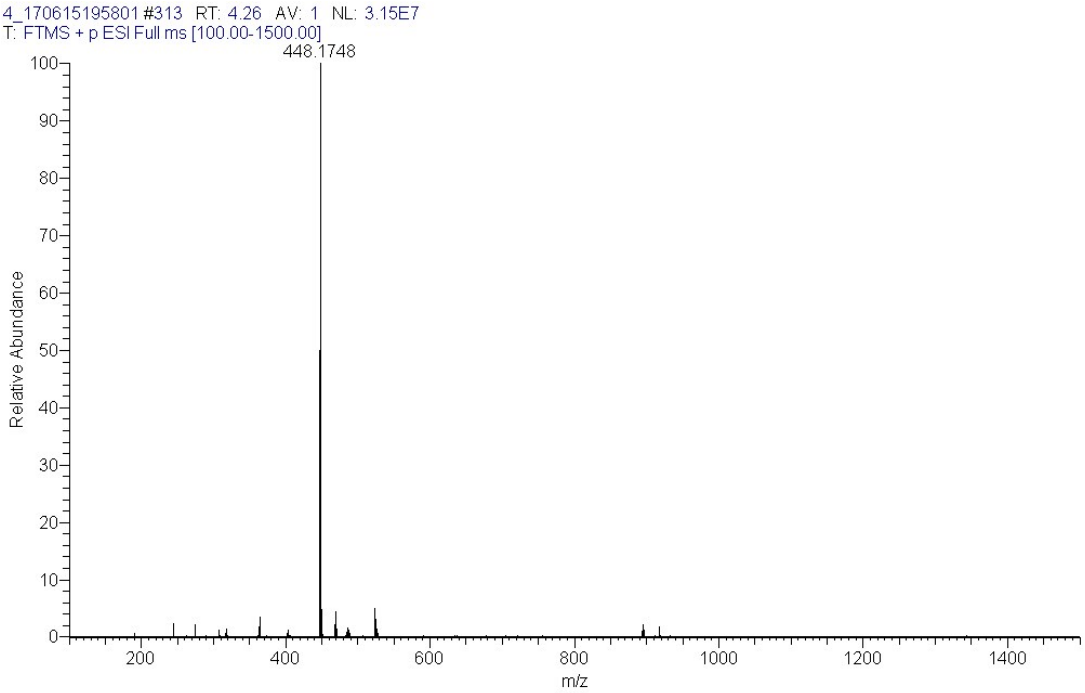
(0.24g, 53%). M.p. 158.8～159.6℃. ^{1}H NMR (600MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.12 (d, *J*=15.6Hz, 1H), 7.79 (d, *J*=15.6Hz, 1H), 7.70 (d, *J*=9.6Hz, 1H), 7.42 (d, *J*=8.4Hz, 1H), 7.23 (d, *J*=8.4Hz, 2H), 6.63(d, *J*=9.0Hz, 1H), 6.49(s, 1H), 5.97-6.04(m, 1H), 5.44(d, *J*=16.8Hz, 1H), 5.34(d, *J*=10.8Hz, 1H), 4.75(d, *J*=6.0Hz, 1H), 3.44-3.48(m, 4H), 1.25(t, *J*=14.4Hz, 3H); ^{13}C NMR (150MHz, $CDCl_3$) δ 186.4, 160.9, 158.8, 153.1, 152.3, 148.8, 141.8, 133.4, 131.9, 131.0,129.9, 125.3, 121.4, 119.7, 116.6, 109.9, 108.7, 96.7, 45.2, 30.9, 12.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}NO_6$ 448.1754, Found 448.1748.



The ^{1}H NMR (600MHz) spectra of probe 1 in $CDCl_3$.

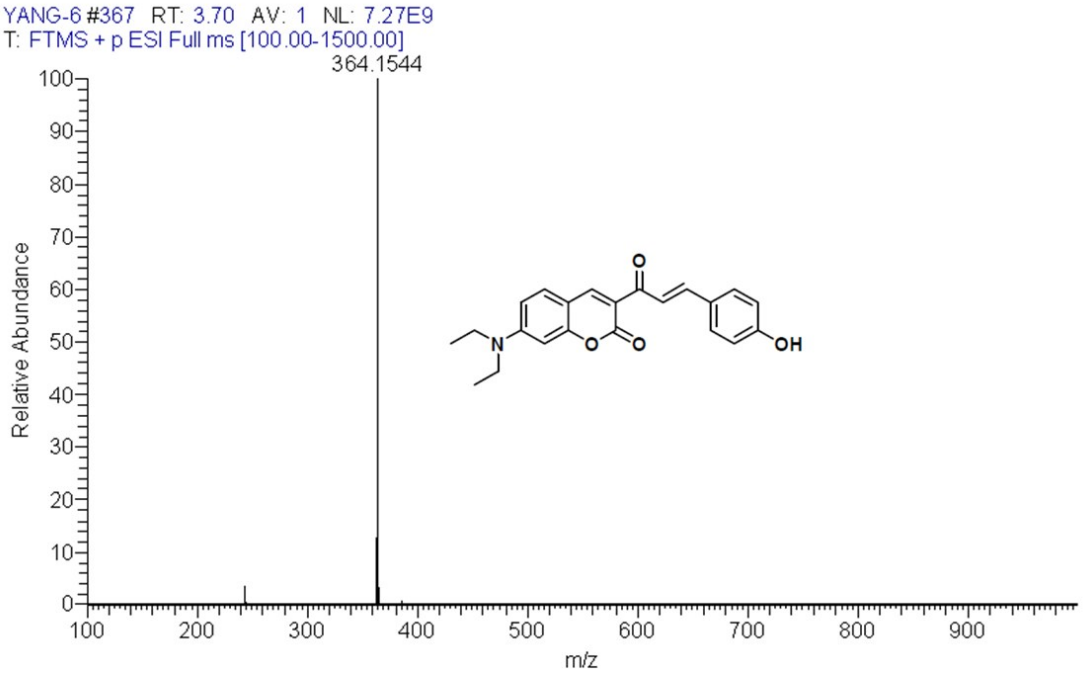


The ^{13}C NMR (150MHz) spectra of probe 1 in $CDCl_3$

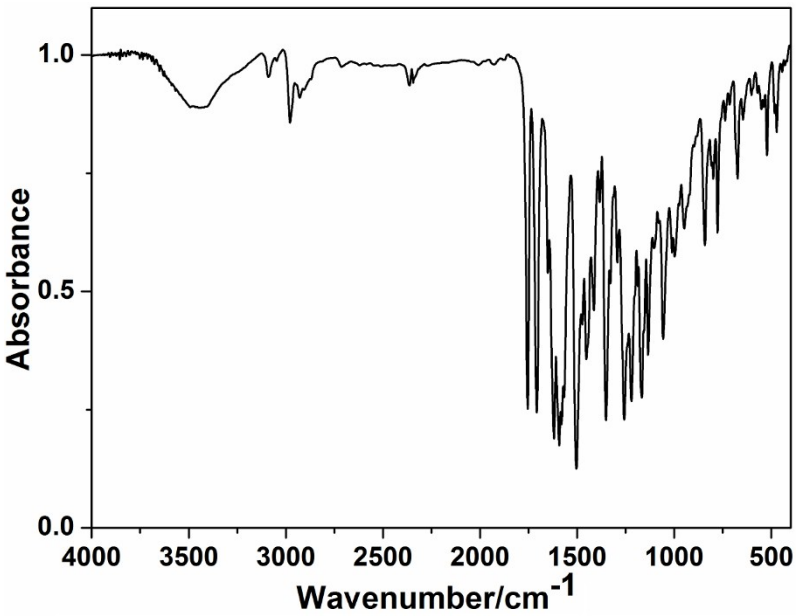


ESI-MS of probe 1

The ^{1}H NMR (600MHz) spectra of reaction product of probe 1 with Pd^{0} in DMSO-d_6



ESI-MS of the reaction product of probe 1 with Pd^{0}



IR spectra of the probe 1

Figure S2: The detection limits of Pd^0.

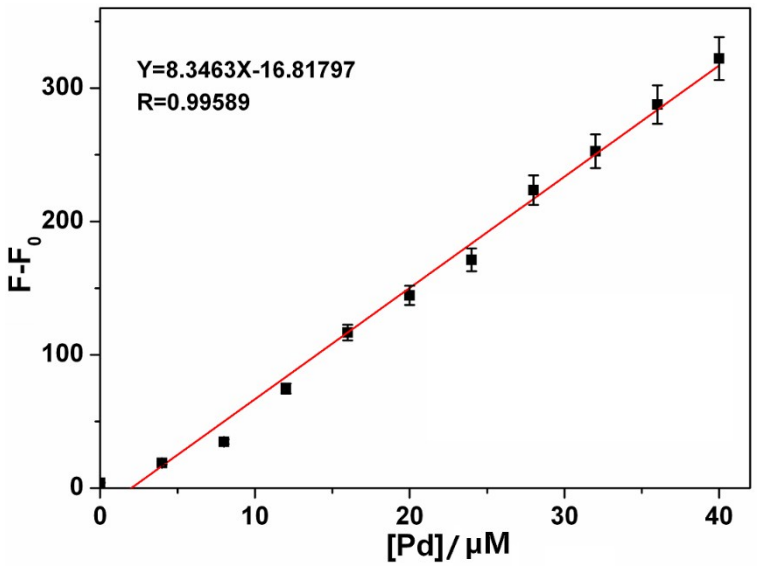
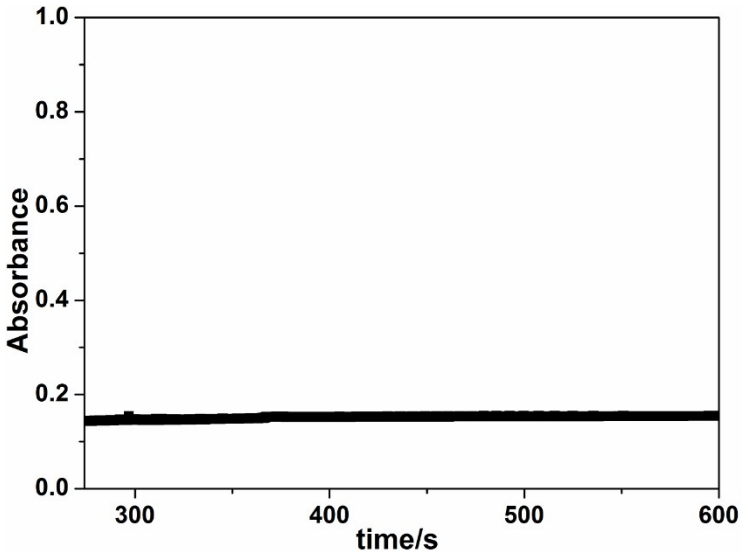
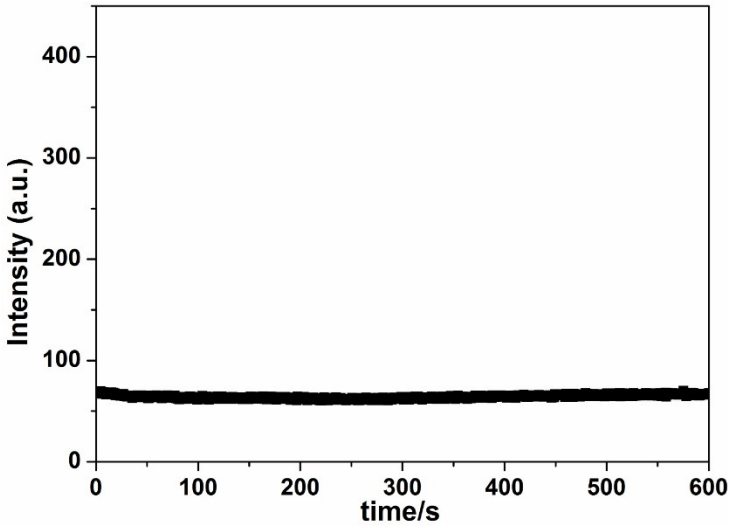


Figure S2: Emission intensity at 560 nm of probe 1 (5 μM) as a function of the concentration of Pd^0 (0- 40μM) in Ethanol-PBS buffer solution (2:3, v/v, 10 mM PBS, pH=7.4(λ_{ex} = 450 nm, slits: 5nm /5 nm).

Figure S3: The kinetic study of the probe.



(a)



(b)

Figure S3: The kinetic study of the probe in absorption and fluorescence spectra.

Figure S4: Selectivity in absorbance spectra.

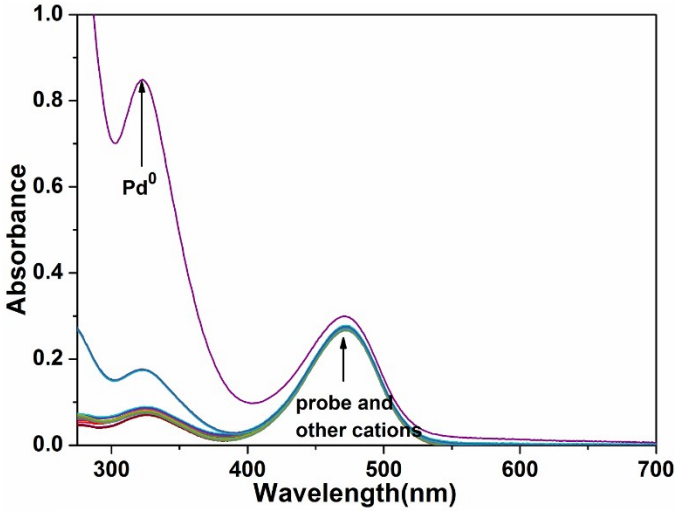
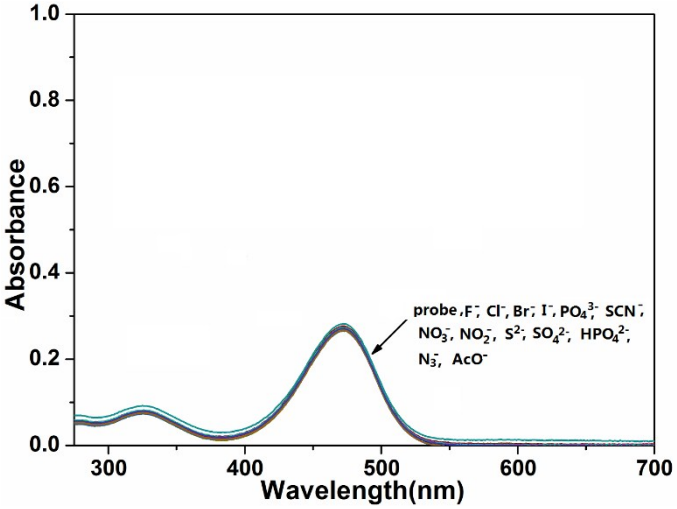
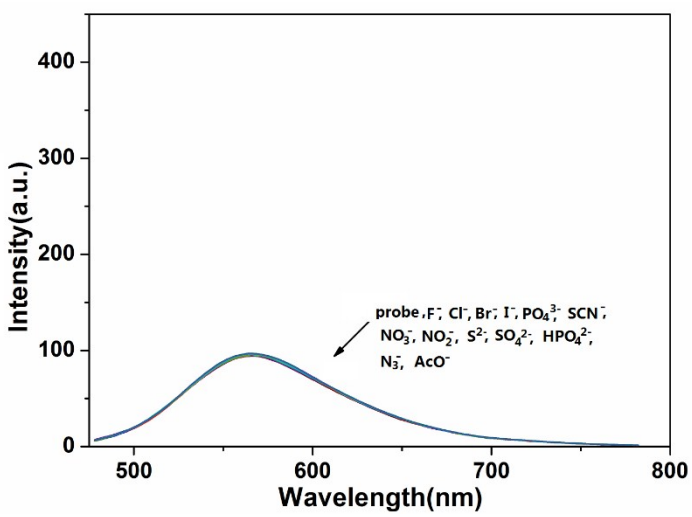


Figure S4: Absorption spectra of probe 1 (5 μM) in the present of Pd0 (40 μM) and other metal ions (Ag^{+}, Ce^{3+}, K^{+}, Ni^{2+}, Na^{+}, Mn^{2+}, Mg^{2+}, Ca^{2+}, Hg^{2+}, pb^{2+}, Fe^{3+}, Cd^{2+}, Zn^{2+}, Cr^{3+}, Al^{3+}, Cu^{2+} and Co^{2+}) (200 μM) in Ethanol-PBS buffer solution (2:3, v/v, 10 mM PBS, pH=7.4).

Figure S5: The effect of anion.



(a)



(b)

Figure S5: The effect of anion in absorption and fluorescence spectra.

Figure S6: MTT assay.

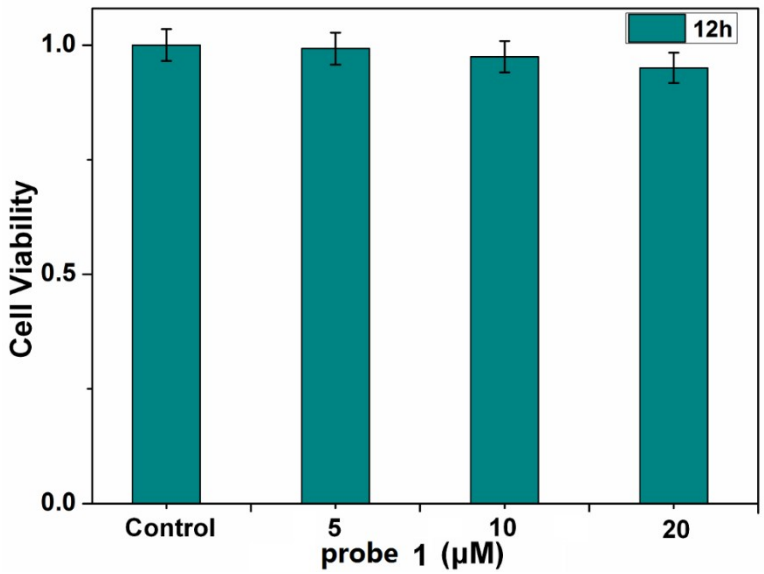


Table S1: A comparison table about the detection limit.

Ref.	analyte	signal output	solvent	detection limit
1	Pd^0	fluorescence	DMSO/PBS	1.7×10^{-8} M
2	Pd^0	fluorescence	Methanol/PBS	6.9×10^{-7} M
3	Pd^0	fluorescence	DMF/HEPES	2.5×10^{-8} M
4	Pd^{2+}	Chemiluminescence	DMSO–H_2O	8.8×10^{-5} M
5	Pd^{2+}	fluorescence	Ethanol/PBS	2.2×10^{-7} M
this work	Pd^0	fluorescence	HEPES	4.2×10^{-6} M

References

1. K. Wang, G.Q. Lai, Z.F. Li, M.M. Liu, Y.J. Shen and C.Y. Wang, Tetrahedron, 2015, 71, 7874.
2. J.Y. Wang, Z.R. Liu, M.G. Ren, B.B. Deng and W.Y. Lin, J. Photoch. Photobio. A, 2016, 317, 108.
3. W. Liu, J. Jiang, C.Y. Chen, X.L. Tang, J.M. Shi, P. Zhang, K.M. Zhang, Z.Q. Li, W. Dou, L.Z. Yang, and W.S. Liu, Inorg. Chem., 2014, 53, 12590.
4. W. Su, B. Gu, X.J. Hu, X.L. Duan, Y.Y. Zhang, H.T. Li and S.Z. Yao, Dyes Pigments, 2017, 137, 293.
5. H.J. Cui, H. Chen, Y. Pan and W.Y. Lin, Sens. Actuators, B, 2015, 219, 232.