† Electronic Supplementary Information (ESI)

A colorimetric and fluorometric NBD-based chemosensor for the highly selective recognition of palladium(II) cation

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Materials and General Information

^{1}H and ^{13}C NMR spectra were recorded using TMS as the internal standard in $CDCl_3$ with a Bruker BioSpin GmbH spectrometer at 400 MHz and 100 MHz, respectively. High resolution mass spectra (HRMS) was taken on a Thermo-Fisher LTQ Orbitrap XL instrument. Flash column chromatography was performed with silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co. Ltd. All chemicals were purchased from commercial sources unless otherwise specified. All the solvents were of analytical reagent grade and were used without further purification.

The UV-vis absorption spectra were recorded on a UV-2450 spectrophotometer (Shimadzu, Japan). Fluorescence measurements were performed on an F-4500 fluorescence spectrophotometer (Hitachi, Japan) equipped with quartz cell of 10.0 mm path length. Unless otherwise noted, the spectra were measured in acetonitrile-water solution after the mixtures were equilibrated at room temperature. Confocal fluorescence imaging studies were performed with a Zeiss laser scanning microscope 710 with a 40× oil objective lens with Zen 2009 software (Carl Zeiss, Germany). The excitation wavelength was used a 488 nm Ar laser, and emission collected using a META detector between 500 and 650 nm.

General procedure of spectral Measurements

The stock solution of NBD-PMA (1.0 mM) was prepared by dissolving the required amount in acetonitrile. The stock solution of $PdCl_2$ (1.0 mM) was prepared in 75:25 MeOH-brine. The stock solution of K_2PtCl_4 (10.0 mM) was prepared in DMSO. $Hg(NO_3)_2$ (10.0 mM) was dissolved in methanol. Metal ion (Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Fe^{3+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, Ag^{+}, Ba^{2+}) stock solutions (10.0 mM) were obtained by diluting the standard solutions of the corresponding nitrate salts, respectively. The anions (Cl^{-}, NO_3^{-}, ClO_4^{-}, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{-}$, HCO_3^{-}, SO_3^{2-}, SO_4^{2-}) stock solutions (10.0 mM) were prepared by diluting the standard solutions of the corresponding sodium salts, respectively.

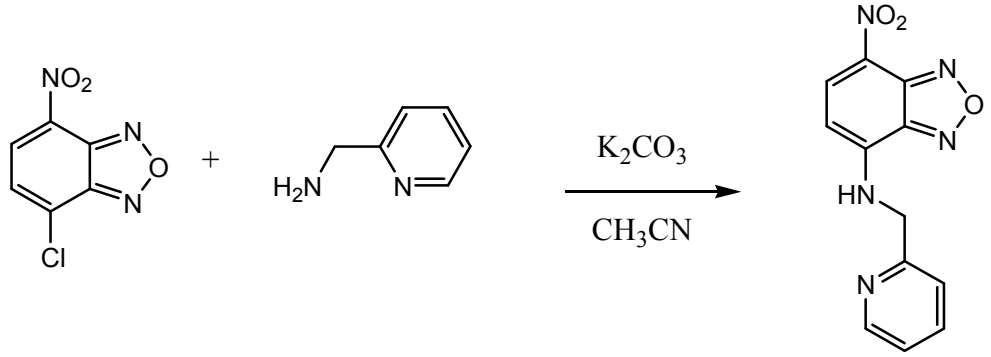
Absorption and fluorescence titrations were performed by adding the small aliquots of NBD-PMA and metal working solutions in a quartz cell (10.0 mm width). The fluorescence intensity was measured at the excitation wavelength of 465 nm with the emission covered over the wavelength range of 480-700 nm.

General procedure of cell imaging

HeLa cells were grown in DMEM media containing 10% fetal bovine serum, 100 U/mL penicillin with 100 μg/mL streptomycin at 37 °C with 5% CO_2 atmosphere. The cells were seeded on a Ø 30 mm glass-bottomed dish at the density of 1×10^5 cells in a culture medium and incubated overnight for living cell imaging by confocal laser scanning microscopy (CLSM). The HeLa cells were treated with 10 μM of Hochest33342 and NBD-PMA, which are prepared by diluting 2.0 μL of stock solution (10 mM in DMSO) with 2 mL of PBS solution and incubated for 30 min at 37 °C and washed with three times with PBS before imaging by CLSM. And the cells were subsequently incubated with $PdCl_2$ (10 μM) for 30 min at 37 °C and washed three times with PBS before imaging by CLSM. The cells were imaged with a 40× objective lens. The excitation wavelengths were 405 nm for Hochest33342 and 488 nm for NBD-PMA, respectively.

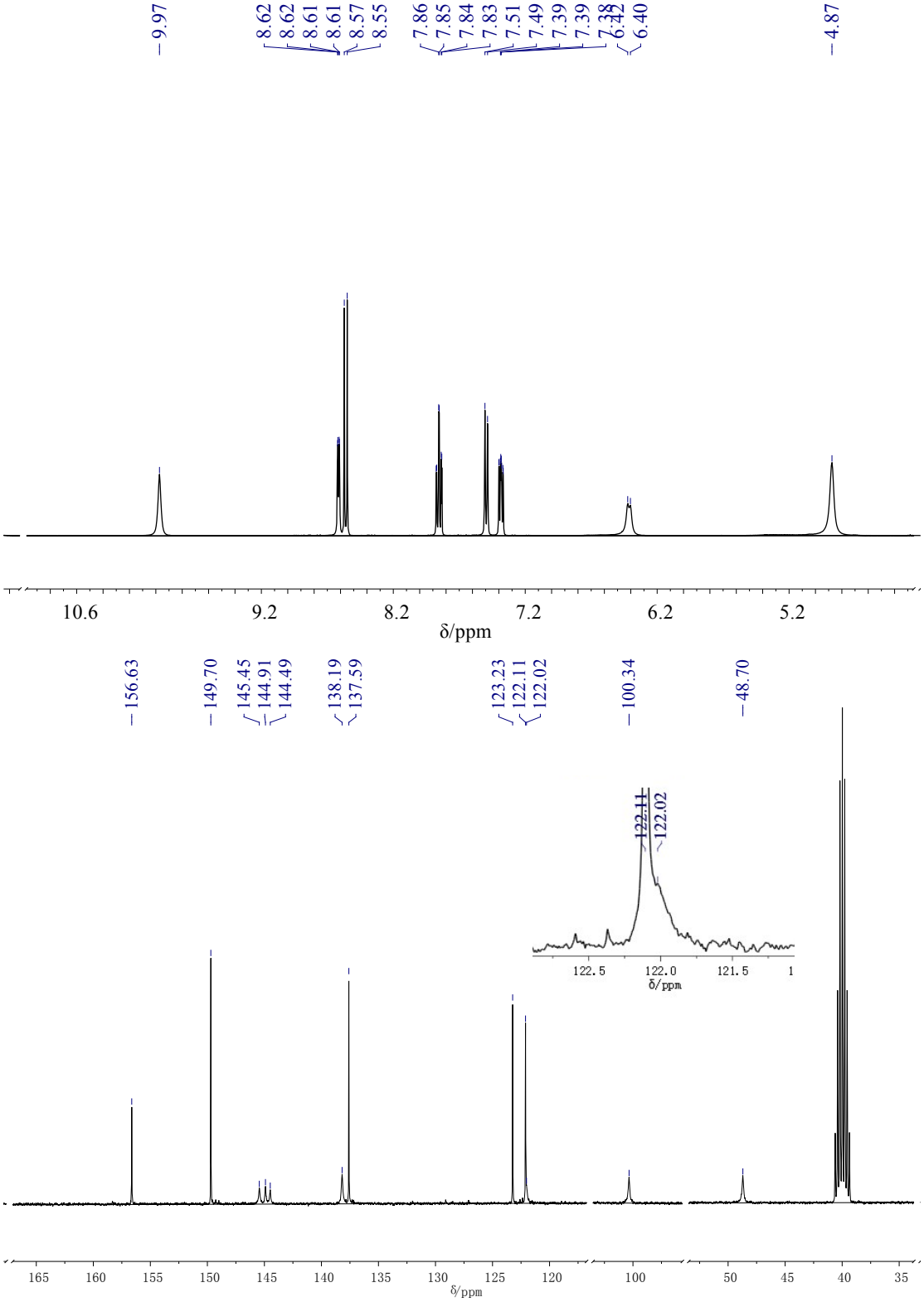
Synthesis and Characterization

Scheme S1. Synthesis of chemosensor NBD-PMA.

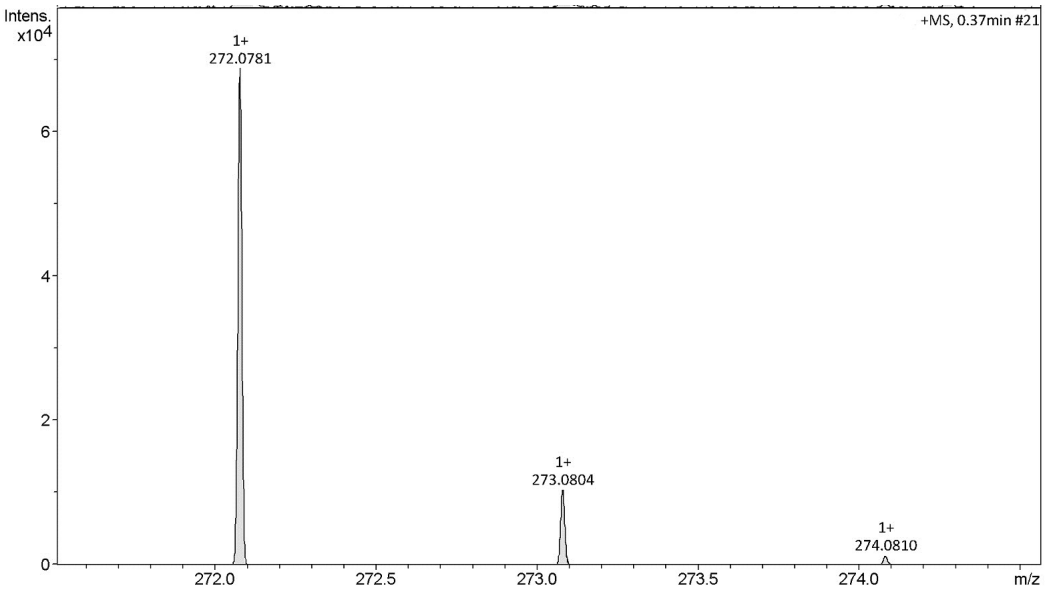


The chemosensor NBD-PMA was synthesized according to the literature[1] except for the replacement of THF with CH_3CN to afford NBD-PMA in 65% yield as brown crystal. Melting point: 191-192 °C. ESI-HRMS (m/z): $[M+H]^+$ calcd: 272.0778, found: 272.0781. ^{1}H-NMR (400 MHz, d_6-DMSO) δ 9.91 (s, 1H), 8.55 (dd, J = 4.8, 0.7 Hz, 1H), 8.50 (d, J = 8.3 Hz, 1H), 7.79 (m, 1H), 7.43 (d, J = 7.9 Hz, 1H), 7.32 (m, 1H), 6.35 (d, J = 8.2 Hz, 1H), 4.81 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 156.63, 149.70, 145.45, 144.91, 144.49, 138.19, 137.59, 123.23, 122.11, 122.02, 100.34, 48.75. The results are consistent with the literature.

^{1}H NMR spectra and ^{13}C NMR spectra



ESI-HRMS spectra



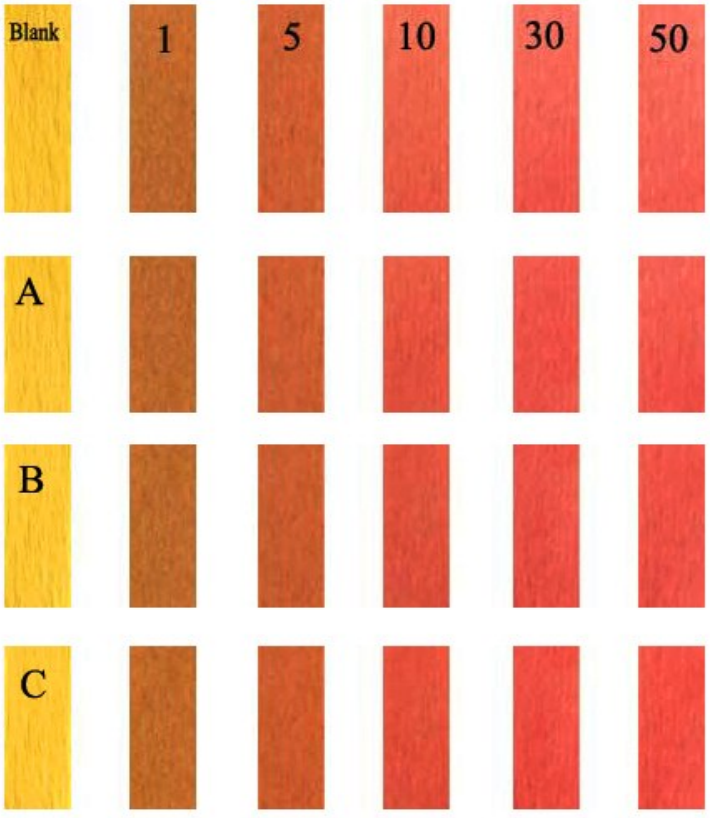


Fig. S1. The colorimetric Pd^{2+} ion chemosensor: test paper socked with NBD-PMA, dried, then immersed in different concentration of Pd^{2+} ion. (A = Washing water, B = River water, C =Tap water)

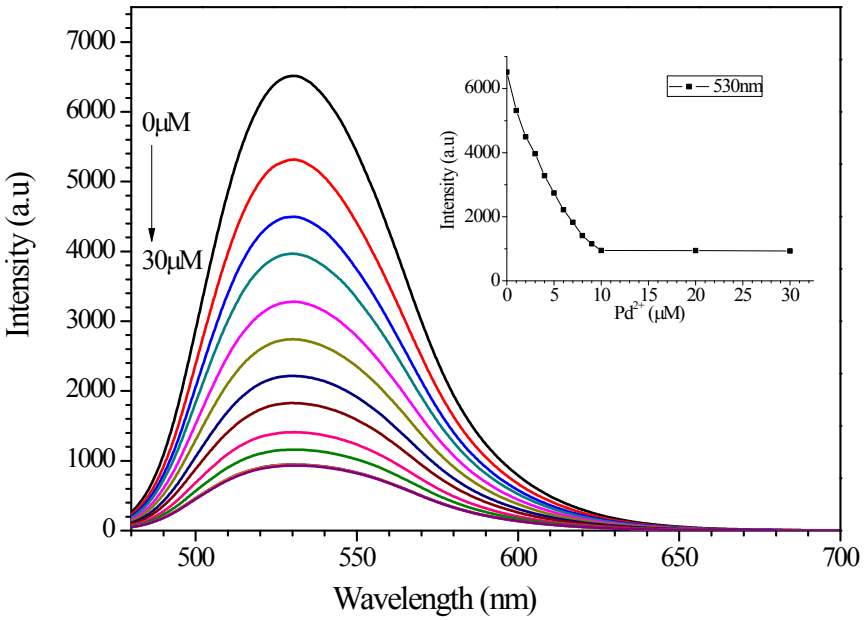


Fig. S2. Fluorescence spectra of NBD-PMA (10 μM) upon the addition of Pd^{2+} cation (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30 μM) in acetonitrile-water (4:1) solutions. Inset: fluorescence intensity at 530 nm versus Pd^{2+} concentration.

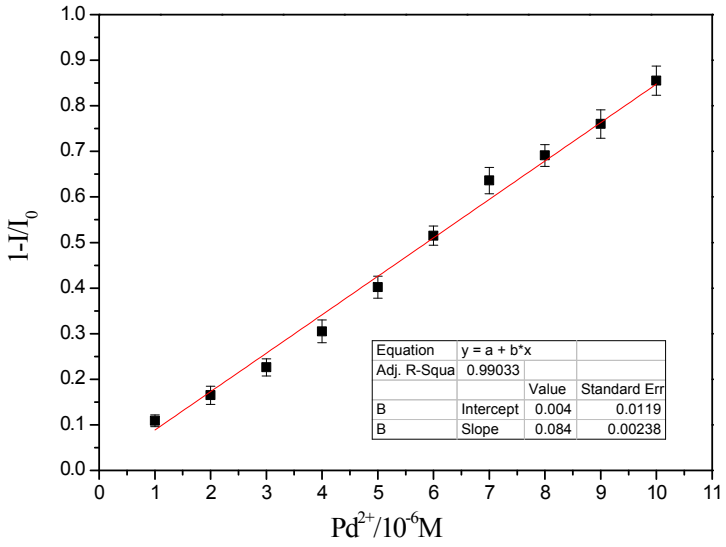


Fig S3. Detection limit of NBD-PMA (10 μM) for Pd^{2+} through fluorescence intensity in acetonitrile-water (4:1) solutions. The excitation wavelength was 465nm and the emission wavelength was 530 nm. The detection limit of Pd^{2+} ions using chemosensor NBD-PMA was determined from the following equation: DL = K × SD/S, where K=3; SD is the standard deviation of the blank solution; S is the slope of the calibration curve. D.L = K × SD/S = 3 × 0.0115 / 0.0867 × 10^{-6} M= 0.39 × 10^{-6} M.

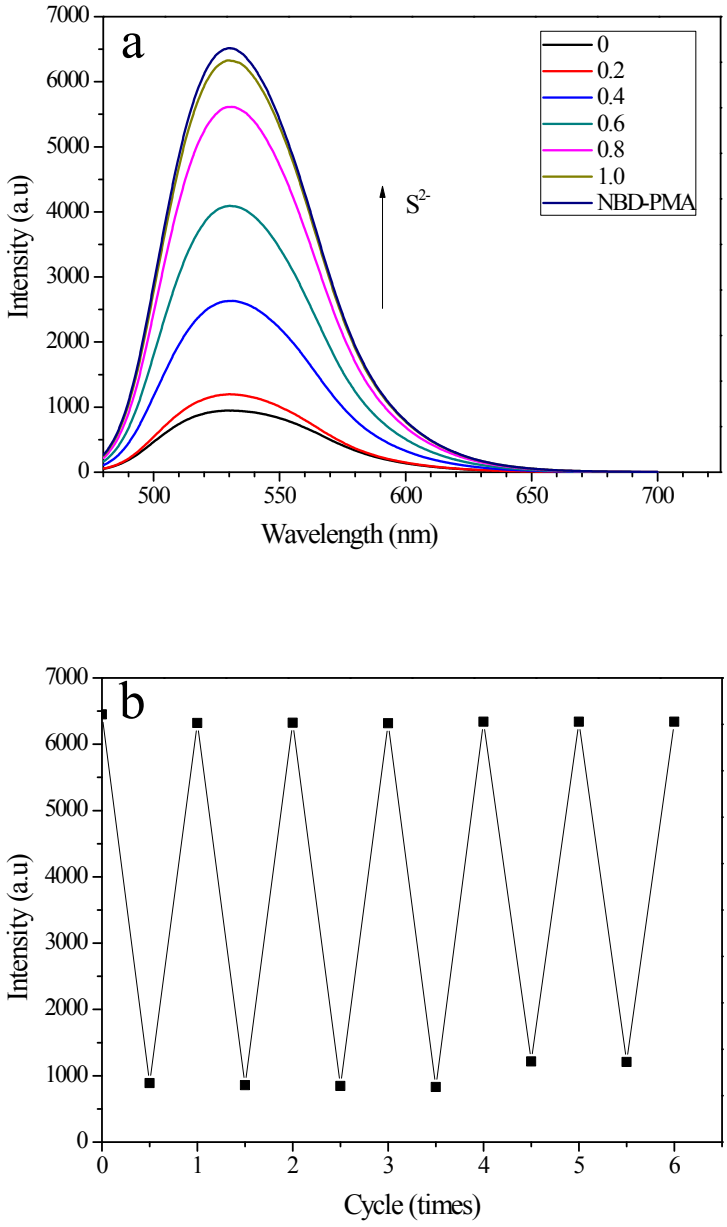


Fig. S4. Fluorescent spectra of NBD-PMA-Pd upon the addition of S^{2-} anion; b) the reversible study. The test conditions: NBD-PMA: 10 μM, Pd^{2+}: 10 μM, S^{2-}:10 μM in acetonitrile-water (4:1) solutions.

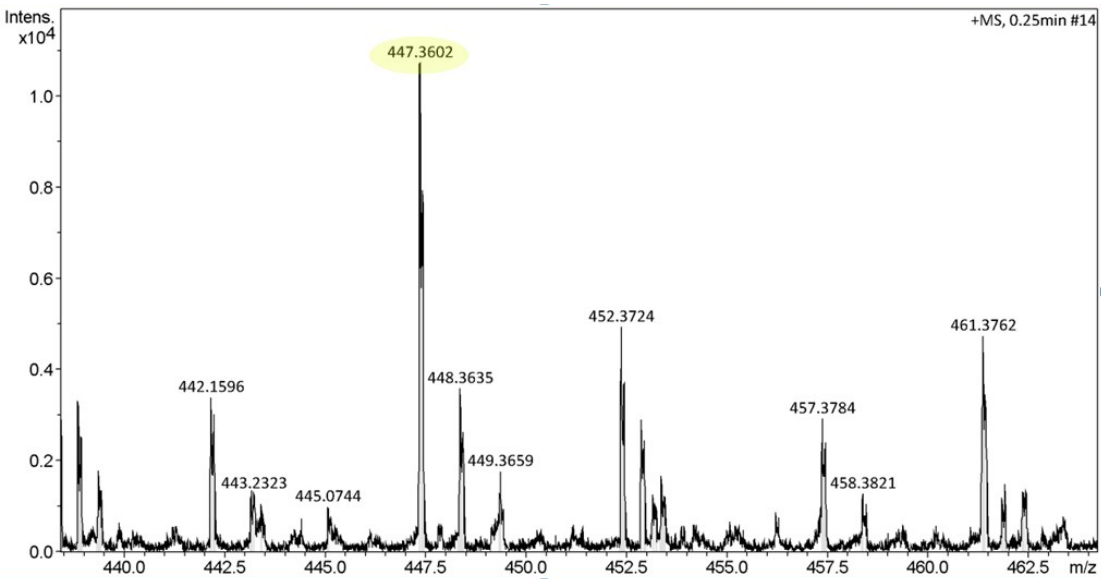


Fig. S5. The mass spectra of NBD-PMA with addition of $PdCl_2$.

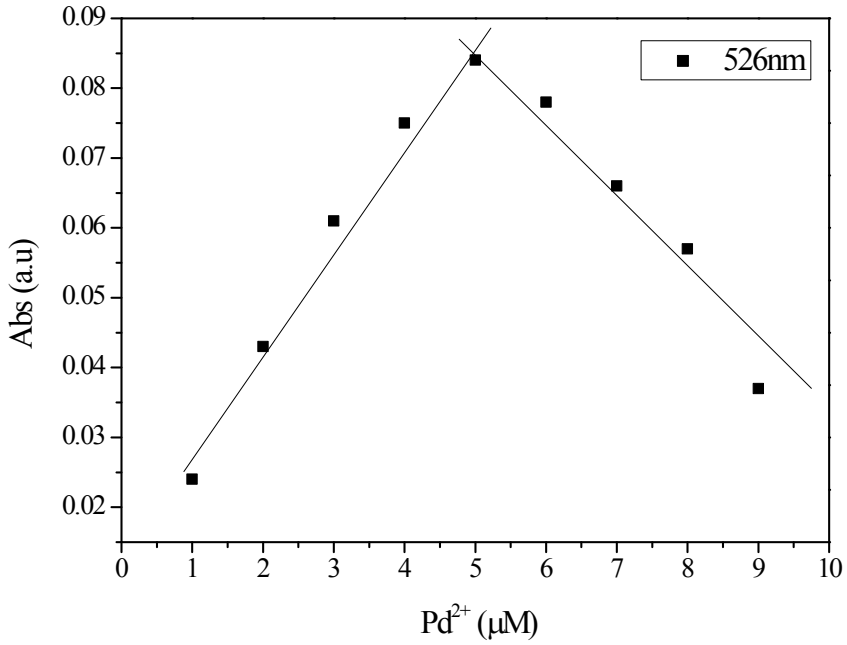


Fig. S6. Job's plot for the binding of NBD-PMA with Pd^{2+} cation.

1. F. Qian, C. L. Zhang, Y. M. Zhang, W. J. He, X. Gao, P. Hu, Z. J. Guo, J. Am. Chem. Soc., 2009, **131**, 1460-1468.