Supporting Informations

Sequential Detection of Palladium and Chromium oxyanion by Fluorescein based Chemosensor in Mixed Aqueous Media

Aasif Helal*

Center of Research Excellence in Nanotechnology, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

Corresponding authors

Tel: +966 013 860 7532; E-mail address: aasifh@kfupm.edu.sa (A. Helal)

Contents:

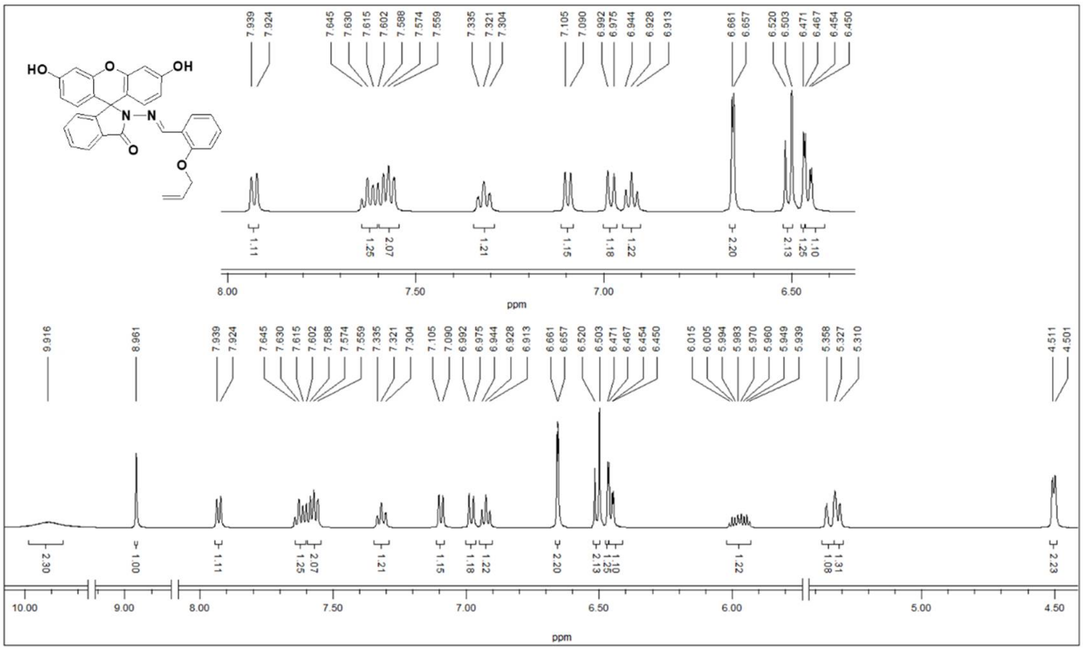

Figure S1. ^{1}H NMR of compound **1.**

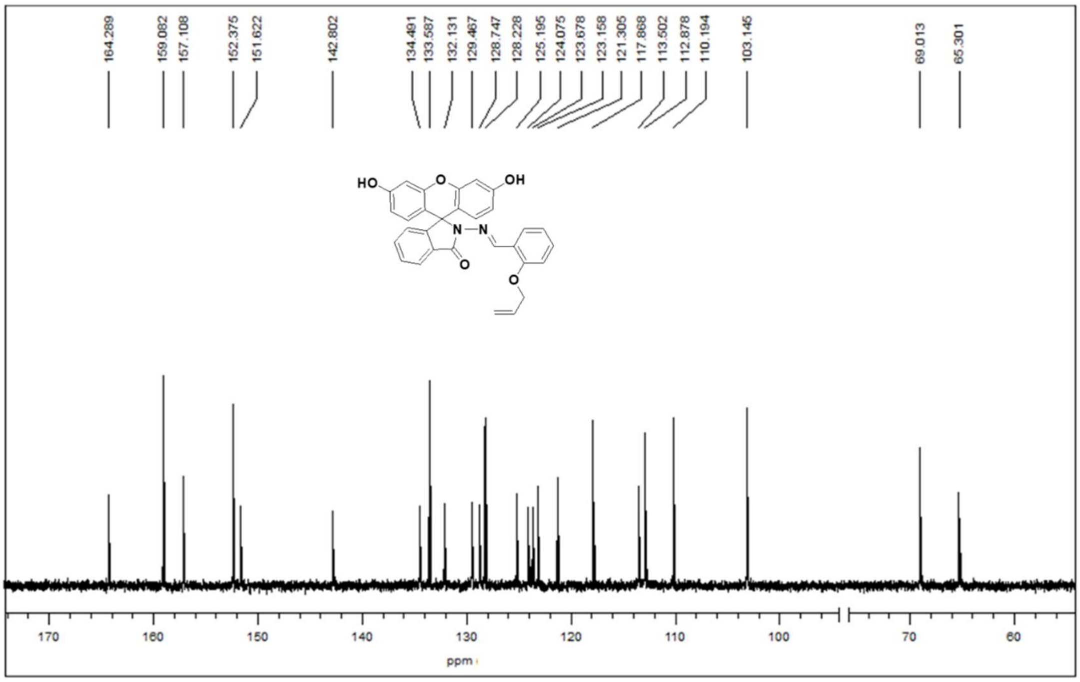

Figure S2. ^{13}C NMR of compound 1.

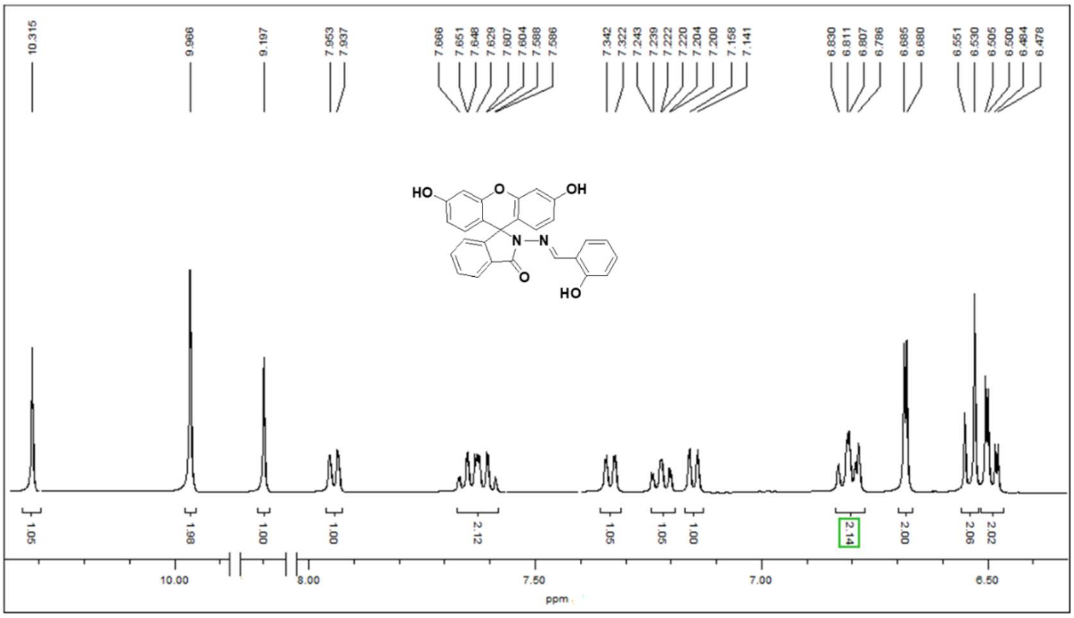

Figure S3. ^{1}H NMR of compound **2.**

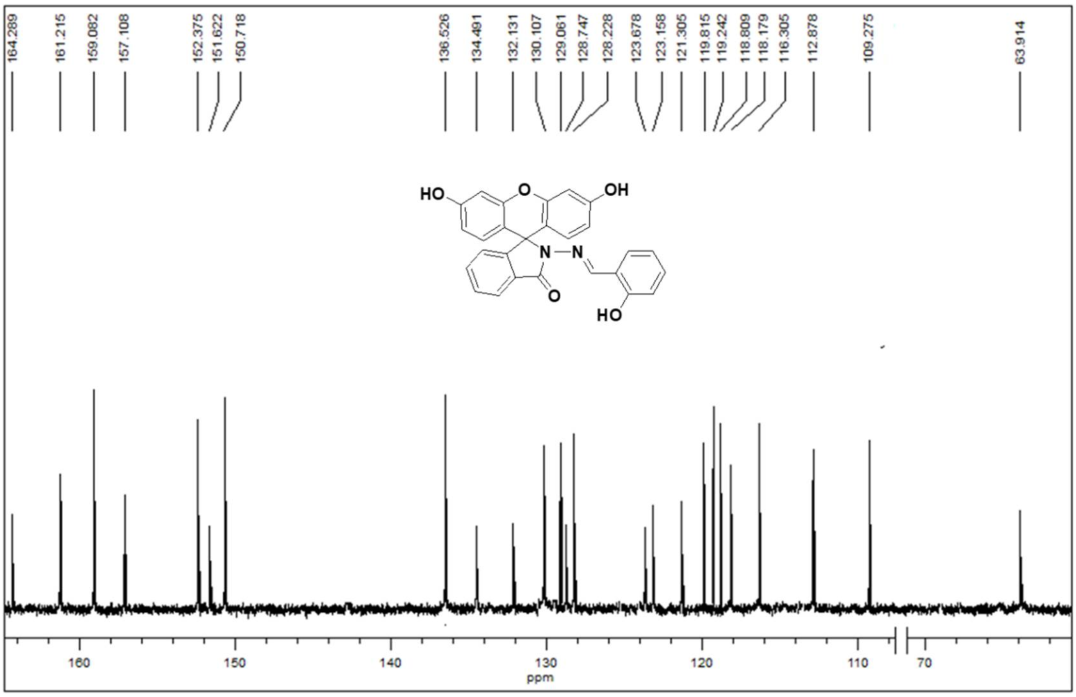

Figure S4. ^{13}C NMR of compound **2.**

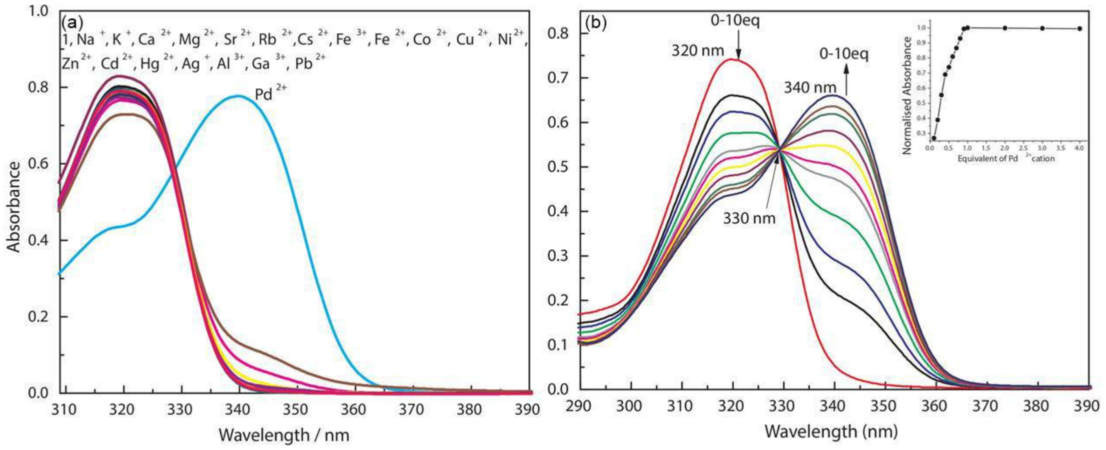

Figure S5. UV-Vis spectra of **1** (10 μM) (a) with different cations (10 equivalents), (b) upon the addition of $PdCl_2$ (100 μM) in H_2O:DMF (9:1) containing HEPES buffer (10 mM, pH 7.4). Inset: Mol ratio plot of absorbance at 340 nm.

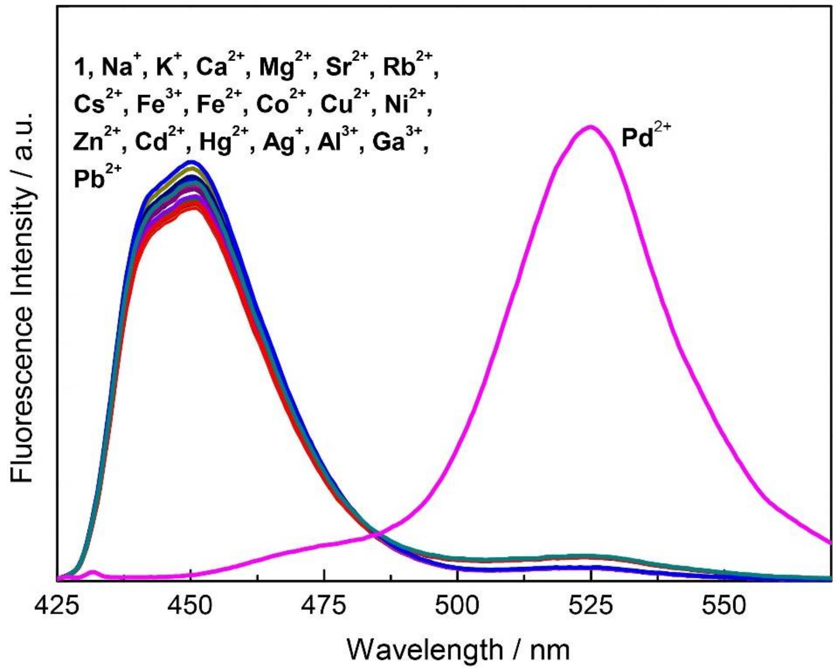

Figure S6. Fluorescence spectra of **1** (1.0μM) with different cations (10 μM) in H_2O:DMF (9:1) containing HEPES buffer (10 mM, pH 7.4). (λ_{ex} = 330 nm).

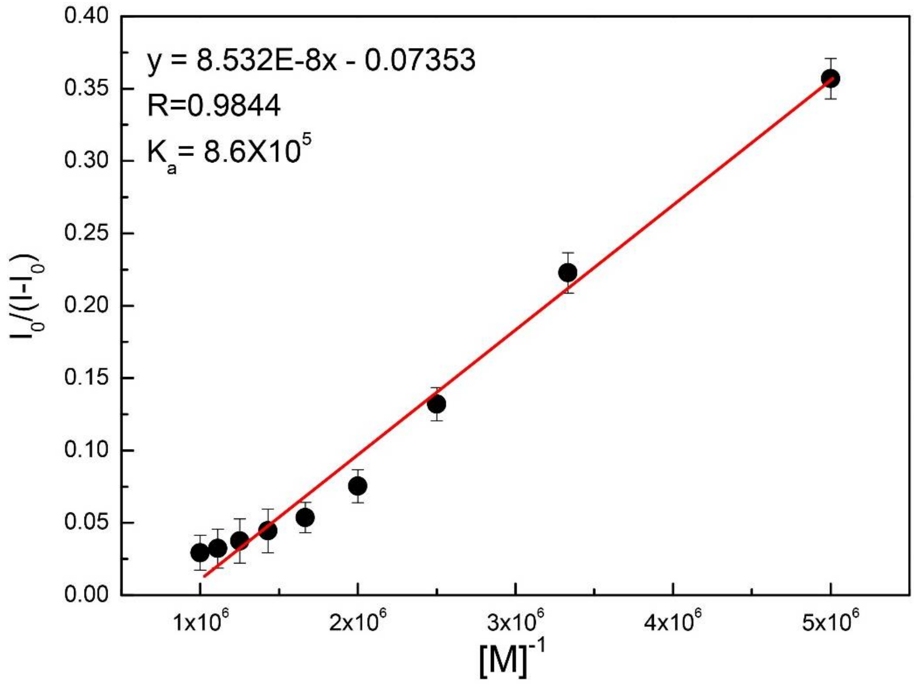

Figure S7. Linear regression curve of **1** obtained by plotting $I_0/(I-I_0)$ as a function of $1/[Pd^{2+}]$ in H_2O:DMF (9:1) containing HEPES buffer (10 mM, pH 7.4). (λ_{ex} = 330 nm).

Limit of detection was calculated according to the procedure given in the literature.[1]

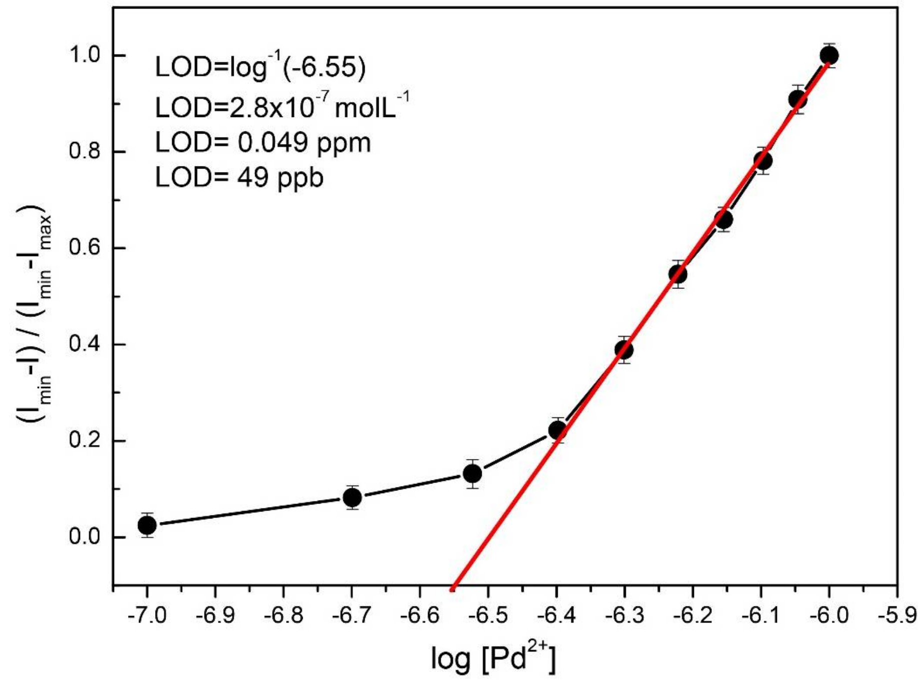

Figure S8. Plot of normalized fluorescence intensity of **1** as a function of $\log[Pd^{2+}]$ in H_2O:DMF (9:1) containing HEPES buffer (10 mM). (λ_{ex} = 330 nm).

Determination of quantum yield

The fluorescence quantum yields were determined using fluorescein as a reference, with a known Φ value of 0.89 in EtOH.[2] The quantum yield was calculated according to the following equation (1):

$$\Phi_S/\Phi_R = (A_S/A_R) \times (Abs_R/Abs_S) \times (\eta^2_S/\eta^2_R) \quad (1)$$

where Φ is the fluorescence quantum yield; A is the integral of fluorescence spectrum; Abs is the corresponding absorbance at the excitation wavelength; η is refractive index; and the subscripted letters S and R denote sample and reference, respectively.

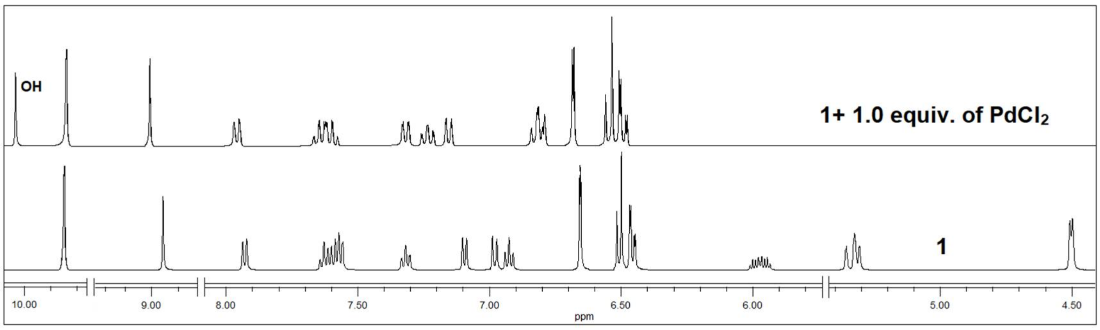

Figure S9. Partial ^{1}H NMR spectra of **1** and **1** with $PdCl_2$ in DMSO-d_6.

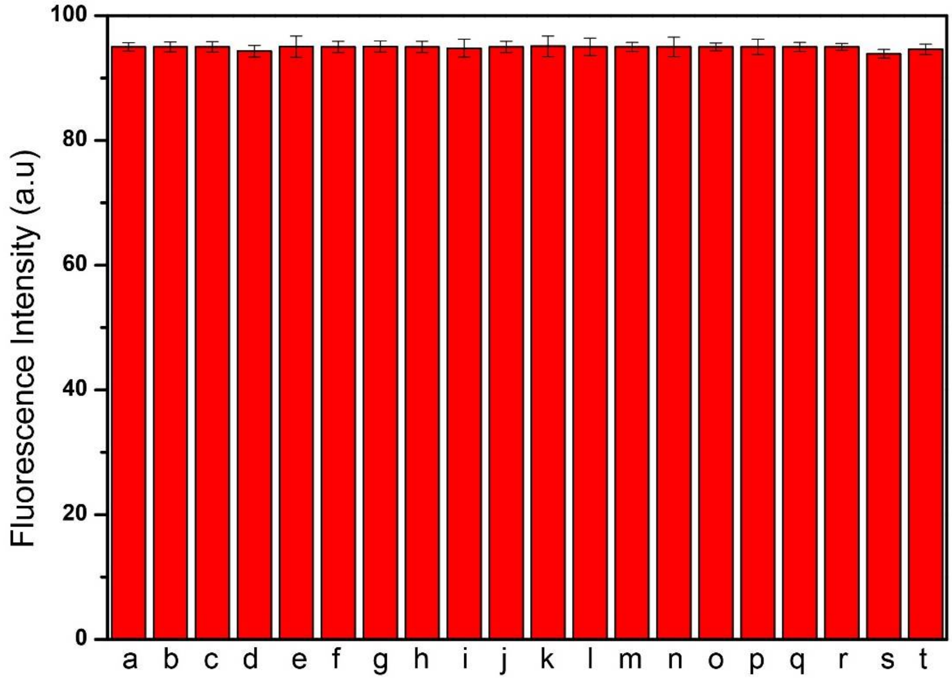

Figure S10. Competitive metal ion selectivity of **1**: Bars indicate the fluorescence intensity (330 nm excitation, 525 nm emission). Salts of various metal ions (100 equivalent) were added to **1** and Pd^{2+} (a) **1** and Pd^{2+}, (b) Ag^{+} + Pd^{2+}, (c) Pb^{2+} + Pd^{2+}, (d) Zn^{2+} + Pd^{2+}, (e) Mg^{2+} + Pd^{2+}, (f) Fe^{3+} + Pd^{2+}, (g) K^{+} + Pd^{2+}, (h) Co^{2+} + Pd^{2+}, (i) Al^{3+} + Pd^{2+}, (j) Fe^{2+} + Pd^{2+}, (k) Na^{+} + Pd^{2+}, (l) Cd^{2+} + Pd^{2+}, (m) Sr^{2+} + Pd^{2+}, (n) Rb^{+} + Pd^{2+}, (o) Cu^{2+}+ Pd^{2+} (p) Ni^{2+} + Pd^{2+}, (q) Hg^{2+} + Pd^{2+}, (r) Ga^{3+} + Pd^{2+}, (s) Cs^{+} + Pd^{2+} (t) Ca^{2+} + Pd^{2+} in H_2O:DMF (9:1) containing HEPES buffer (10 mM).

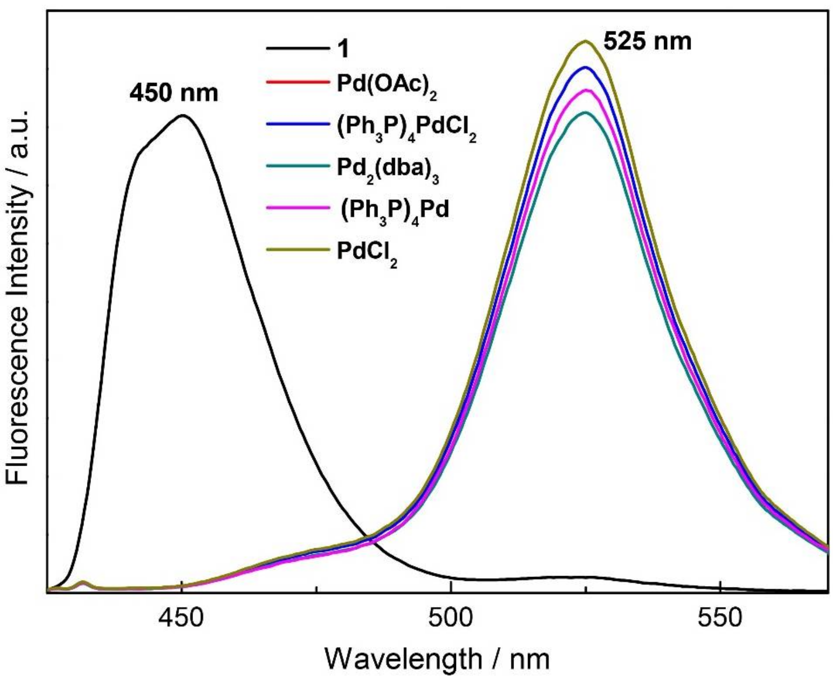

Figure S11. Change in the fluorescence emission spectrum with different palladium complexes, measured for an equimolar mixture of probe **1**(1.0μM) and the palladium species in H_2O:DMF (9:1) containing HEPES buffer (10 mM, pH 7.4). (λ_{ex} = 330 nm).

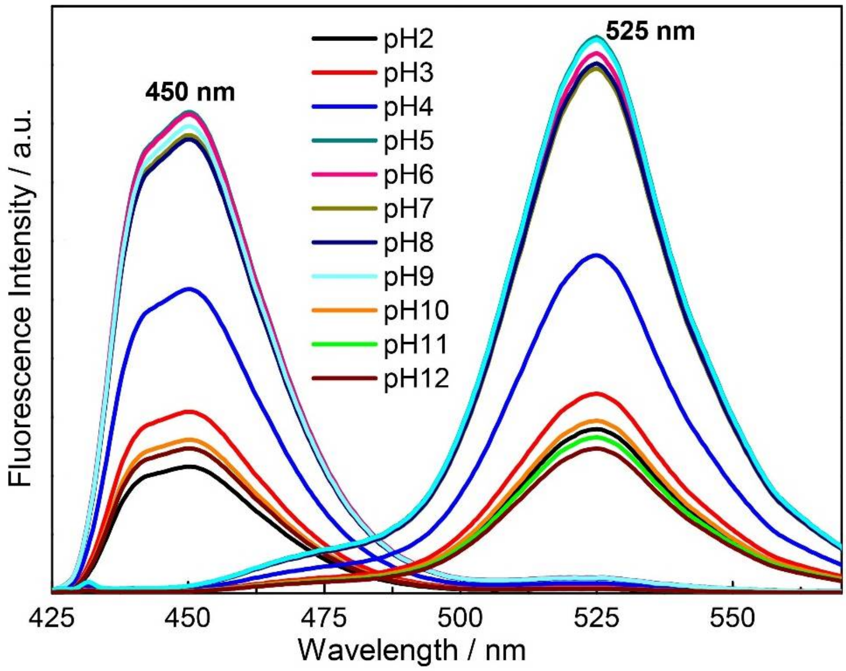

Figure S12. Effect of pH on the emission spectrum of **1** (390 nm) and **2** (540 nm) in H_2O:DMF (9:1) containing HEPES buffer (10 mM, pH 7.4). (λ_{ex} = 330 nm).

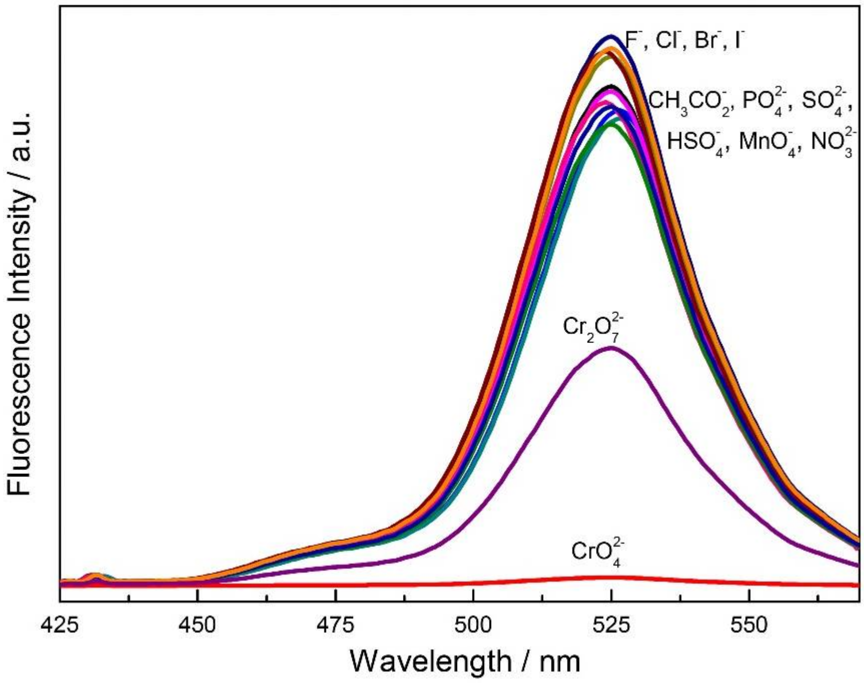

Figure S13. Fluorescence spectra of **2** (1.0μM) with different anions (10 μM) in H_2O:DMF (9:1) containing HEPES buffer (10 mM, pH 7.4). (λ_{ex} = 330 nm).

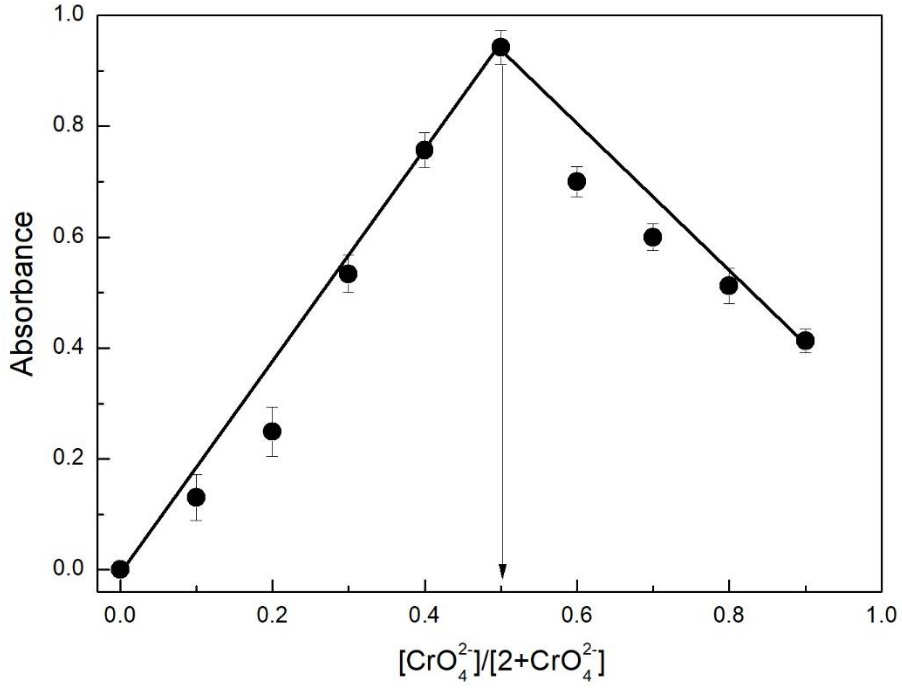

Figure S14. Job's plot for **2** with K_2CrO_4 in H_2O:DMF (9:1) containing HEPES buffer (10 mM, pH 7.4). (λ_{ex} = 330 nm).

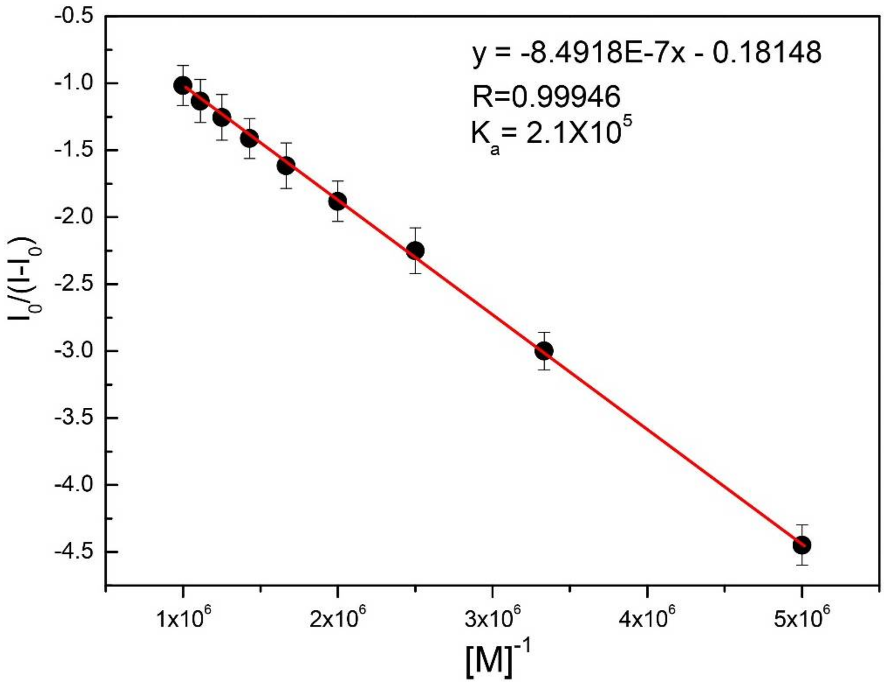

Figure S15. Linear regression curve of **2** obtained by plotting $I_0/(I-I_0)$ as a function of $1/[CrO_4^{2-}]$ in H_2O:DMF (9:1) containing HEPES buffer (10 mM, pH 7.4). (λ_{ex} = 330 nm).

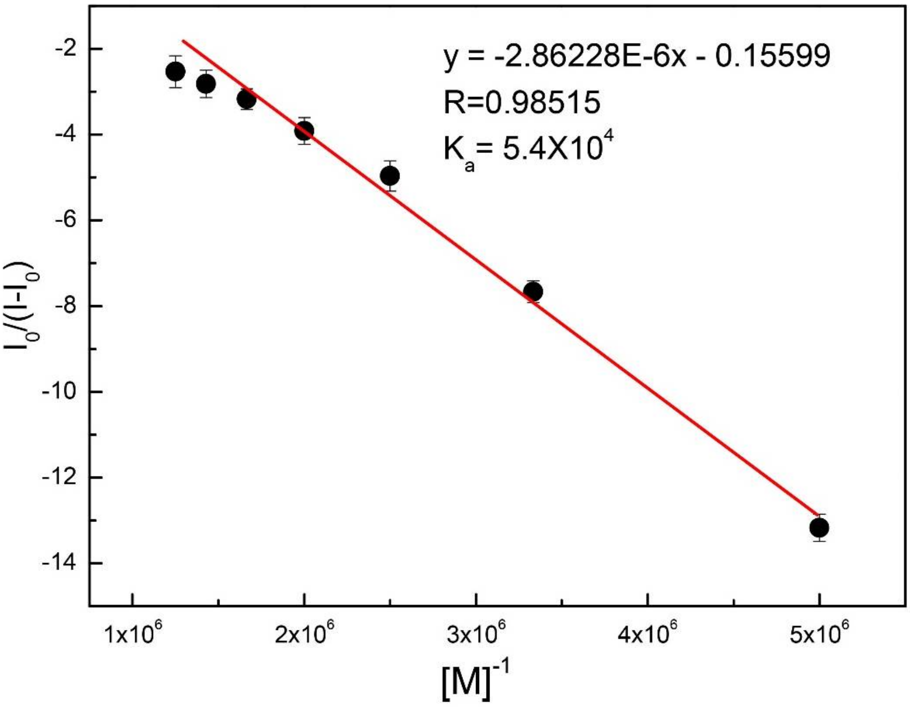

Figure S16. Linear regression curve of **2** obtained by plotting $I_0/(I-I_0)$ as a function of $1/[Cr_2O_7^{2-}]$ in H_2O:DMF (9:1) containing HEPES buffer (10 mM, pH 7.4). (λ_{ex} = 330 nm).

Limit of detection was calculated according to the procedure given in the literature.[1]

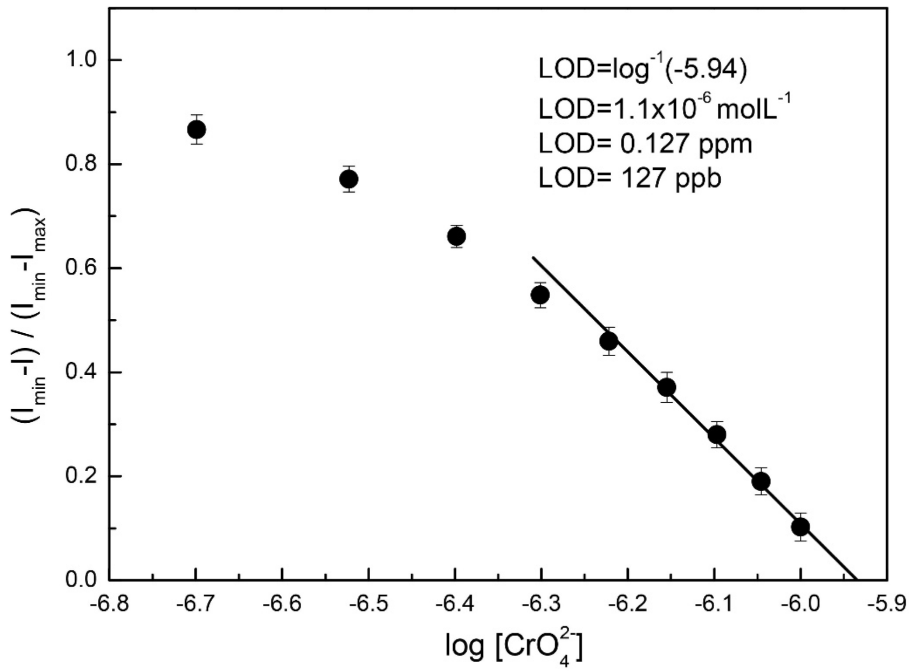

Figure S17. Plot of normalized fluorescence intensity of **2** as a function of $\log[CrO_4^{2-}]$ in H_2O:DMF (9:1) containing HEPES buffer (10 mM). (λ_{ex} = 330 nm).

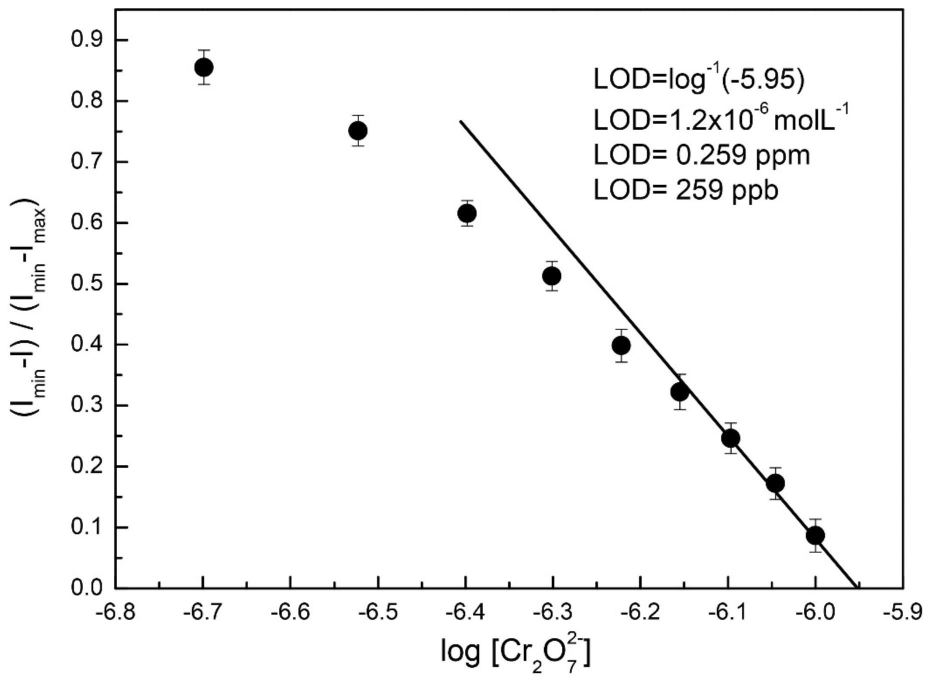

Figure S18. Plot of normalized fluorescence intensity of **2** as a function of log[$Cr_2\ O_7^{2-}$] in H_2O:DMF (9:1) containing HEPES buffer (10 mM). (λ_{ex} = 330 nm).

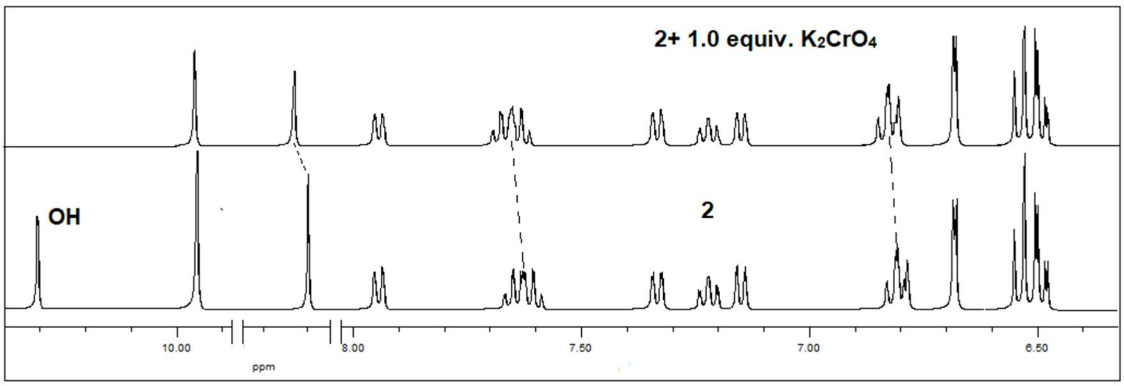

Figure S19. Partial ^{1}H NMR spectra of **2** and **2** with K_2CrO_4 in DMSO-d_6.

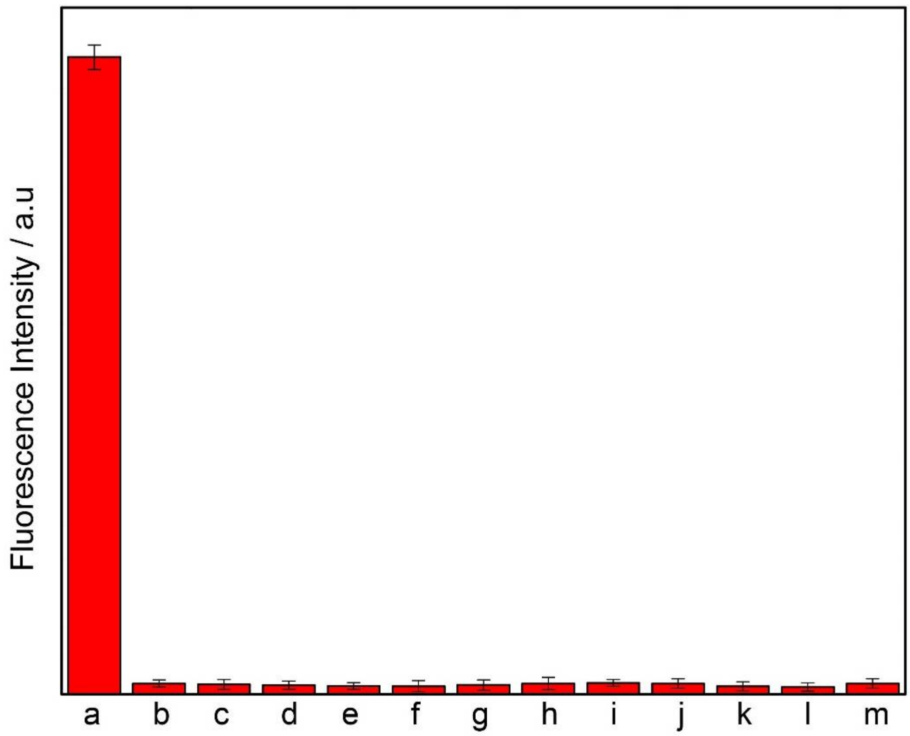

Figure S20. Competitive anion selectivity of **2**: Bars indicate the fluorescence intensity (330 nm excitation, 525 nm emission). Salts of various metal ions (100 equivalent) were added to **2** and CrO_4^{2-} (a) **2**, (b) $CH_3CO_2^-$ + CrO_4^{2-}, (c) PO_4^{2-} + CrO_4^{2-}, (d) SO_4^{2-} + CrO_4^{2-}, (e) $Cr_2O_7^{2-}$ + CrO_4^{2-}, (f) F^- + CrO_4^{2-}, (g) Cl^- + CrO_4^{2-}, (h) Br^- + CrO_4^{2-}, (i) I^- + CrO_4^{2-}, (j) HSO_4^- + CrO_4^{2-}, (k) MnO_4^- + CrO_4^{2-}, (l) NO_3^- + CrO_4^{2-}, (m) CrO_4^{2-} in H_2O:DMF (9:1) containing HEPES buffer (10 mM).

References:

1. Shortreed, M.; Kopelman, R.; Kuhn, M.; Hoyland, B. Fluorescent Fiber-Optic Calcium Sensor for Physiological Measurements. *Anal. Chem.* **1996**, *68*, 1414-1418.
2. Magde, D.; Wong, R.; Seybold, P. G. Fluorescence quantum yields and their relation to lifetimes of rhodamine 6G and fluorescein in nine solvents: improved absolute standards for quantum yields. *Photochem. Photobiol.* **2002**, *75*, 327-334.