Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Highly Sensitive and Selective Pd^{2+} Sensor of Naphthalimide Derivative Based on the Complexation with Alkynes and Thio-heterocycle

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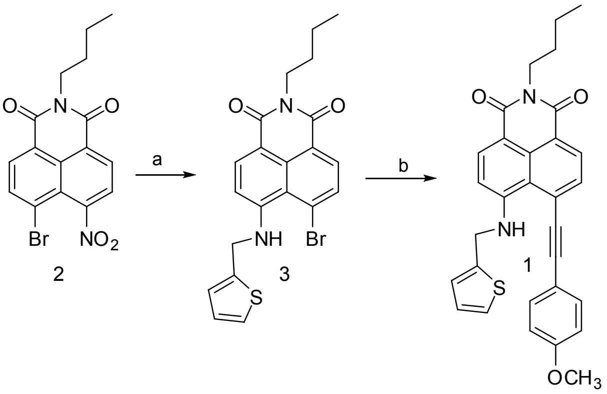
Contents:

1. Materials and general methods

All the solvents were of analytic grade. IR spectra were measured on a Nicolet Enxus 470 FT-IR spectrometer. NMR spectra were measured on a Bruker AM-400 spectrometer with chemical shifts reported in ppm (in DMSO; TMS as internal standard). Mass spectra were measured on a HP 5989A spectrometer. Melting points were determined by using a Büchi Meting Point B-540 apparatus and were uncorrected. Fluorescence spectra were determined on a Varian Cary Eclipse. Absorption spectra were determined on a Varian Cary 100 Spectrophotometer. All absorption spectra and emission spectra were recorded at 24 ± 1°C.

2. Synthesis



N-butyl-4-bromo-5-thiophenemethylamino-1, 8-naphthalimide (3)

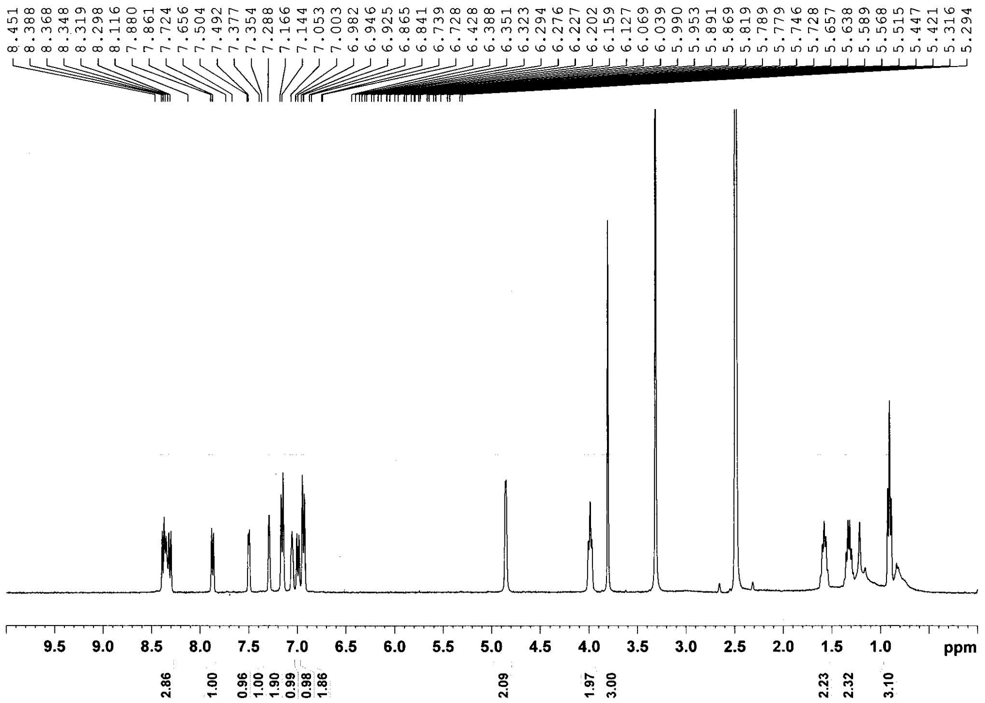
2-Thiophenemethylamine (0.14 ml, 1.41 mM) was added dropwise to a solution of 53 mg (0.141mM) N-Butyl-4-bromo-5-nitro-1, 8-naphthalimide (2) in 2.0 ml DMF at room temperature. After 24 hours, the solution was poured into ice to give yellow needle crystals. The product was filtered, washed with water, and then dried in air. The product was then purified by column chromatography (SiO_2, CH_2Cl_2/CH_3OH, 100:1, v/v) to give **3** as a yellow powder in 65 % yield (40 mg). Mp: 168-169.5 °C[1]

N-butyl-4-(p-methyloxy)phenylethynyl-5-thiophenemethylamino-1,8-naphthalimide (1):

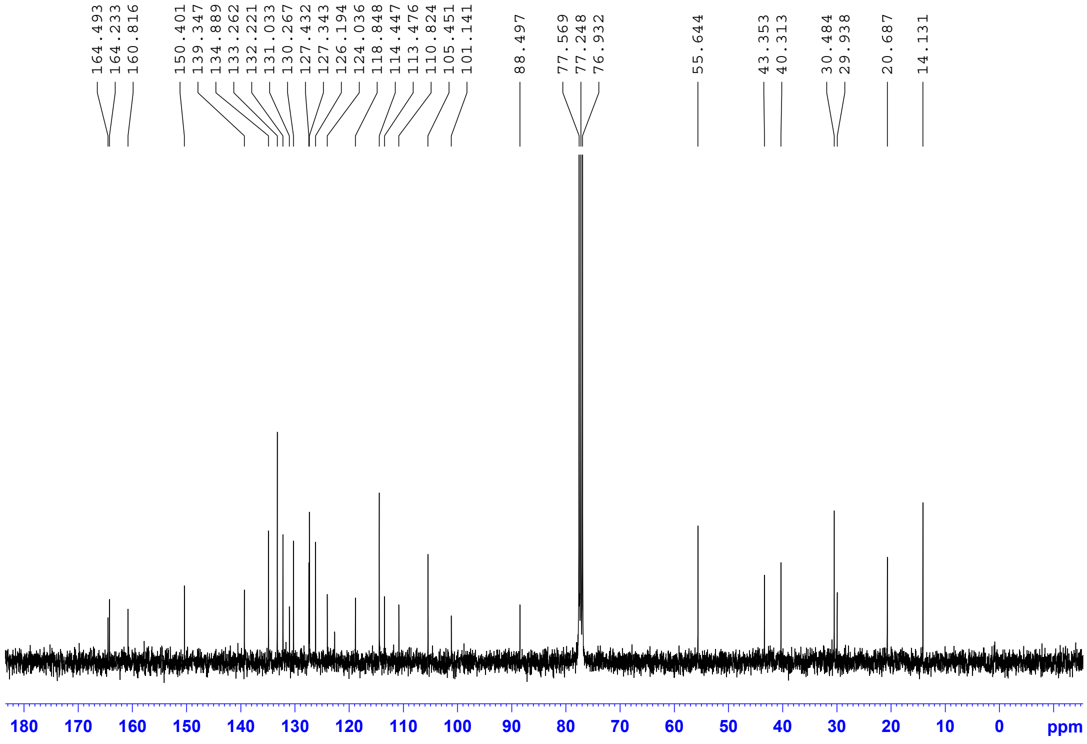
To the solution of 3 (44 mg, 1mmol) and triethylamine, under N_2 protection, CuI (2 mg, 0.01mmol), $Pd(PPh_3)_4$ (4.6 mg, 0.04 mmol) and 4-methyoxyphenylethyne were added. The reaction mixture was stirred at reflux temperature for 4 h. The suspension was filtered and washed with chloroform. The organic layer was washed with water, dried over anhydrous $MgSO_4$ and the solvent was removed in vacuo. The residual material was purified by column chromatography (SiO_2, CH_2Cl_2/CH_3OH, 20:1, v/v) to give **1** as a red solid in 85 % yield (42 mg). Mp: 161-162 °C. IR (KBr) v: 3444, 3318, 2185, 1669, 1621, 1573. ^1H NMR (DMSO, 400 MHz) δ 0.985 (t, J=7.2Hz, 3H), 1.42-1.47 (m, 2H), 1.69-1.75 (m, 2H), 3.80(s, 3H), 4.16 (t, J=7.2Hz, 2H), 4.85(s, 2H), 6.93 (d, J=8.4Hz, 2H), 6.98(s, 1H), 7.00(s, 1H), 7.15 (d, J=8.0Hz, 2H), 7.28(s, 1H), 7.49(s, 7.49), 7.87(d, J=8.0Hz, 1H), 8.34(m, 3H). ^{13}C NMR (CDCl3, 100 MHz) δ 14.13, 20.68, 29.93, 30.48, 40.31, 43.35, 55.64, 88.49, 88.50, 101.14, 105.45, 110.82, 113.47, 114.44, 118.84, 124.03, 126.19, 127.34, 127.43, 130.26, 131.03, 132.22, 133.26, 134.88, 139.34, 150.401, 160.81, 164.23, 164.49. (ESI) $C_{30}H_{26}N_2O_3S$ [$M+Na^+$]: calculated: 517.1559, found: 517.1559.

3. The characterization data of sensor 1

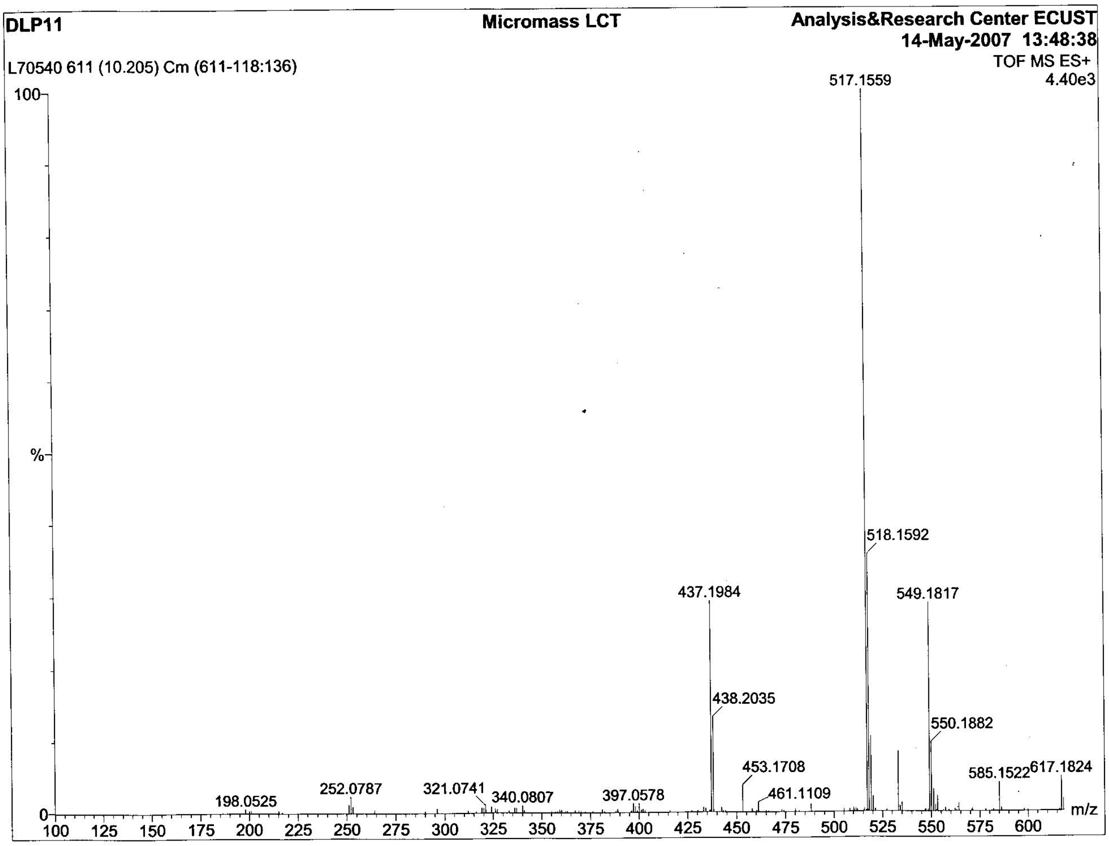
^{1}H NMR spectra of **1**



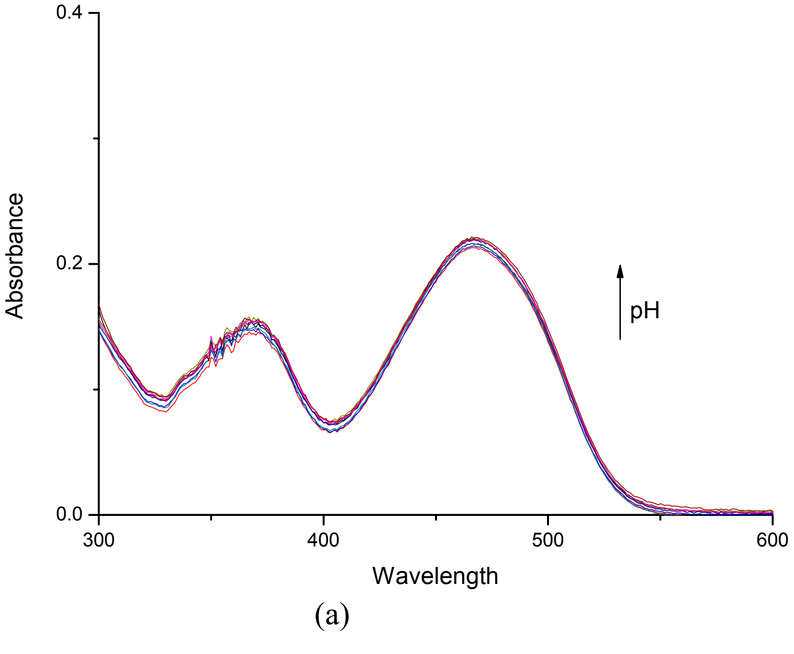
^{13}C NMR spectra of **1**



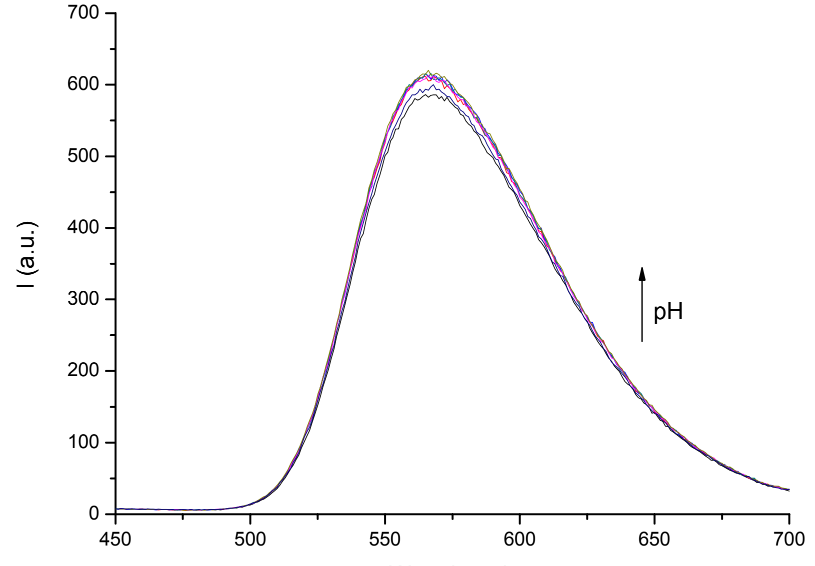
HRMS of **1**



4. pKa value determination



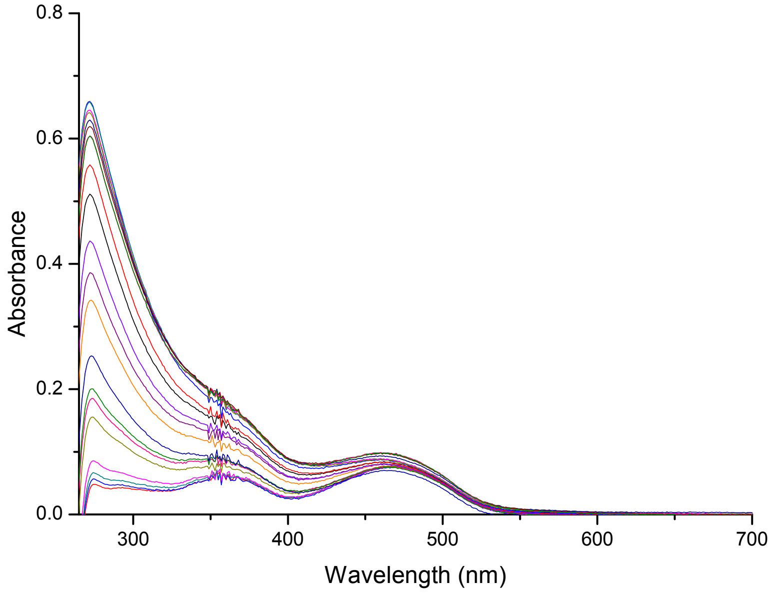
(a)



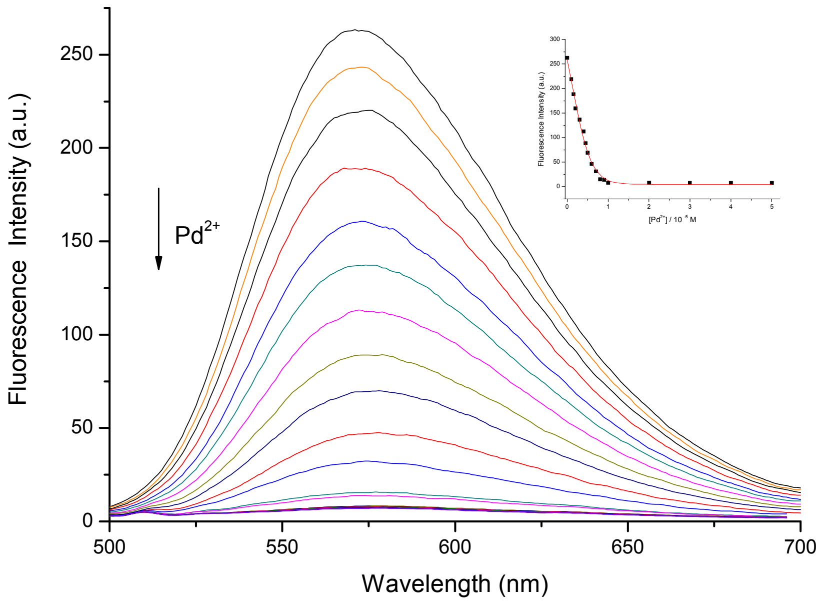
(b)

Figure S1 (a) UV spectra of **1** (10 μM) in ethanol-water (60:40, v/v) solutions after the different pH at 25 ^{o}C. (b) Fluorescence spectra of **1** (10 μM) in ethanol-water (60:40, v/v) solution with different pH values at 25 ^{o}C.

5. Absorption and Emission Spectra

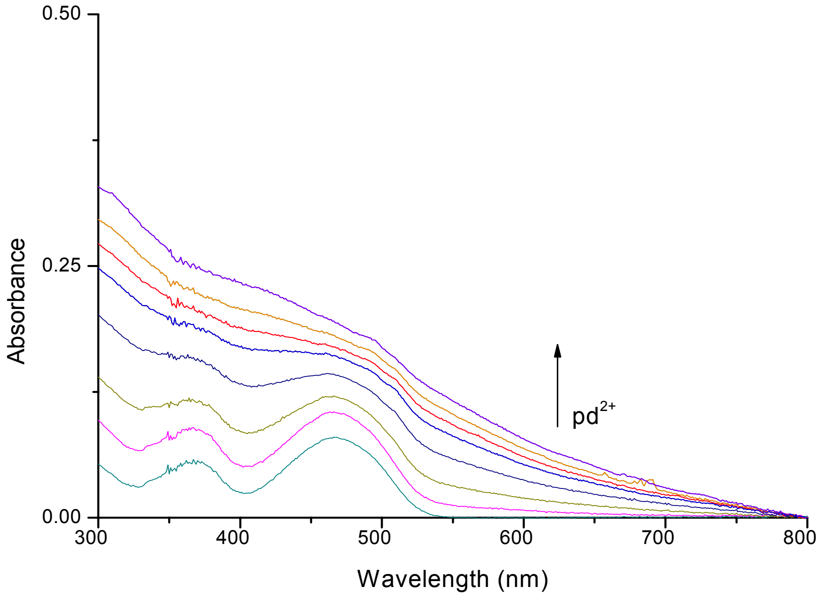


(c)

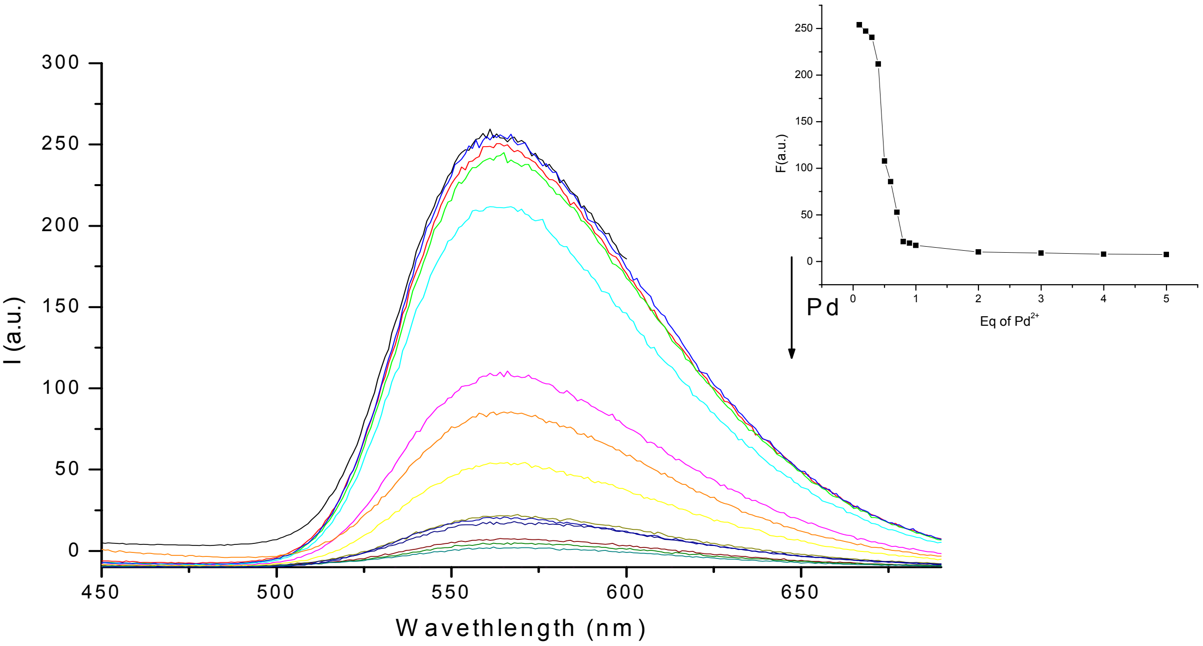


(d)

Figure S2 (c) UV spectra of compound **1** upon addition of Pd^{2+}. (d) Fluorescence spectra of compound **1** upon addition of Pd^{2+}. (Condition: **1** (1×10^{-5} M) in ethanol-water (60:40, v/v) solution at pH 7.2 maintained with HEPES buffer (50 mM) after the addition of 0, 0.1, 0.15, 0.2, 0.3, 0.4, 0.45, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 2, 3, 4 and 5 equivalents of Pd^{2+}).



(e)

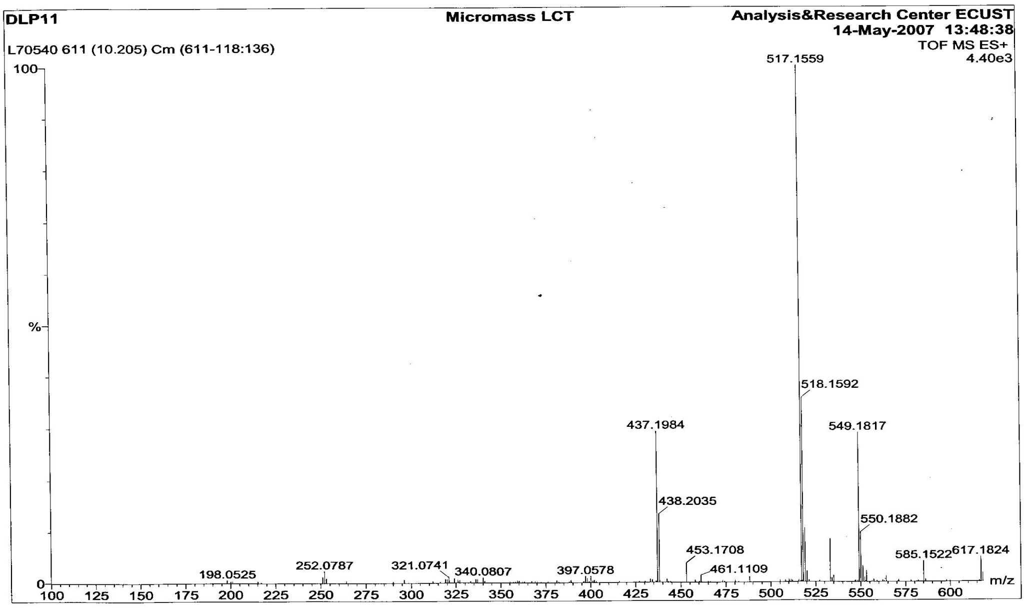


(f)

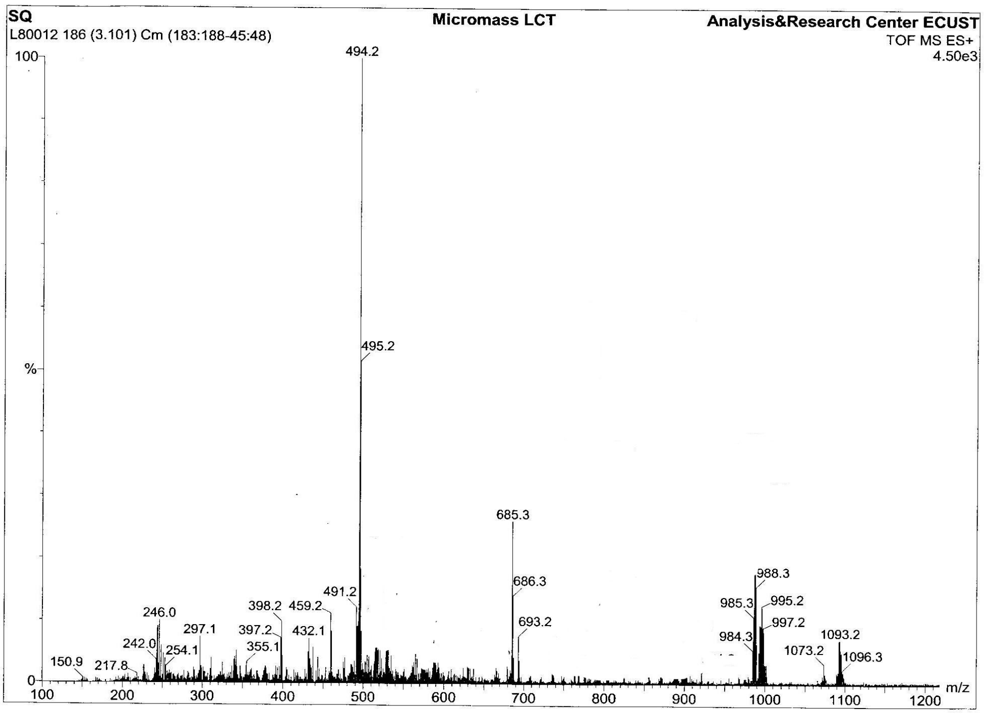
Figure S3 (e) UV spectra of compound **1** upon addition of Pd^{2+}. (f) Fluorescence spectra of compound 1 upon addition of Pd^{2+}. (Condition: **1** (1×10^{-5} M) in DMSO solution after the addition of 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 2, 3, 4 and 5 equivalents of Pd^{2+} ion.

6. MS analysis

(g)



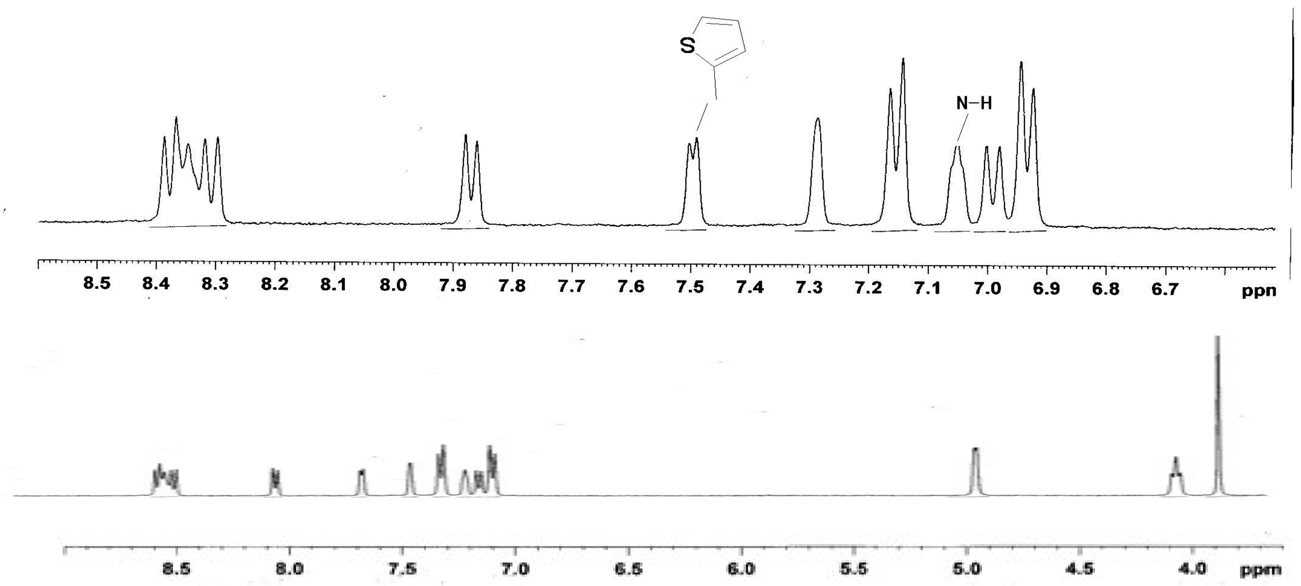
(h)



Figur eS4 MALDI-TOF-MS spectra of free ligand **1** (g), and in the presence of Pd^{2+} (h)

7.1H NMR studies

(i)



(j)

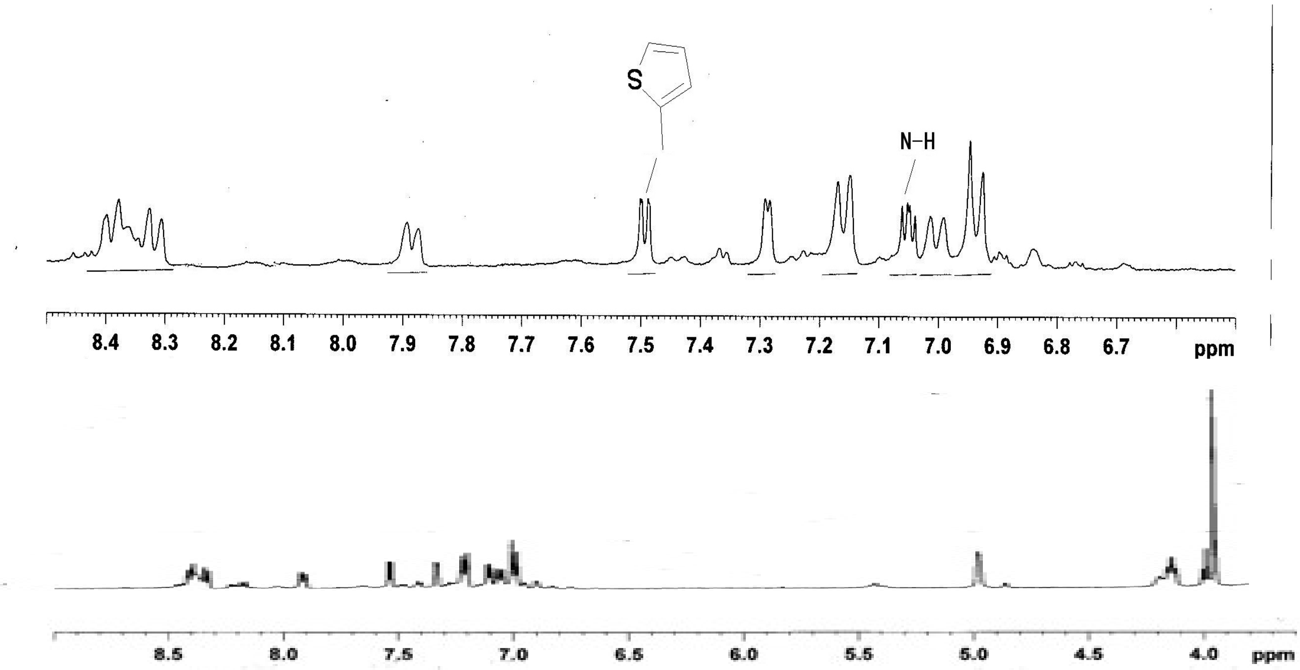


Figure S5. ^{1}H NMR spectra of i): ligand **1**, j): after the addition of 1.0 equivalent of Pd^{2+}.

8. Determination of quantum yields

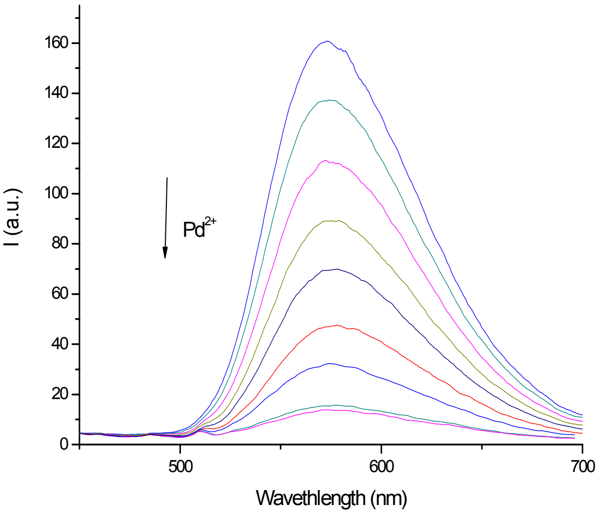
The quantum yield of sensor **1** and Pd^{2+}-**1** were determined according to the literature.[2]

$$\phi_1 = \frac{\phi_B I_1 A_B \lambda_{exB} \eta_1}{I_B A_1 \lambda_{ex1} \eta_B}$$

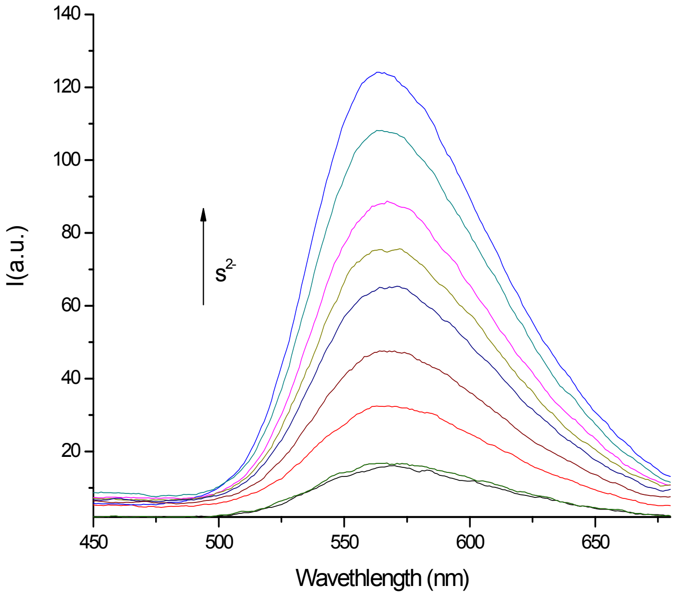
Where φ is quantum yield; I is integrated area under the corrected emission spectra; A is absorbance at the excitation wavelength; λ_{ex} is the excitation wavelength; η is the refractive index of the solution; the subscripts 1 and B refer to the unknown and the standard, respectively. We chose Rhodamine B with trifluoroacetic acid as standard, which has the quantum yield of 0.49. The quantum yields of 1 and Pd^{2+}-1 complex were calculated as 0.24 and 0.03, respectively.

9. Reversibility of Pd^{2+}-Induced Fluorescence

Figure 6 displays the reversible binding of Pd^{2+} to 1 upon addition of the chelating agent S^{2-} with excitation at 365nm. Recycle: [1] = 5μM; (k): fluorescence decrease upon addition of 1 equiv Pd^{2+}; (l): increase in fluorescence resulting from addition of 1 equiv NaS.



(k)

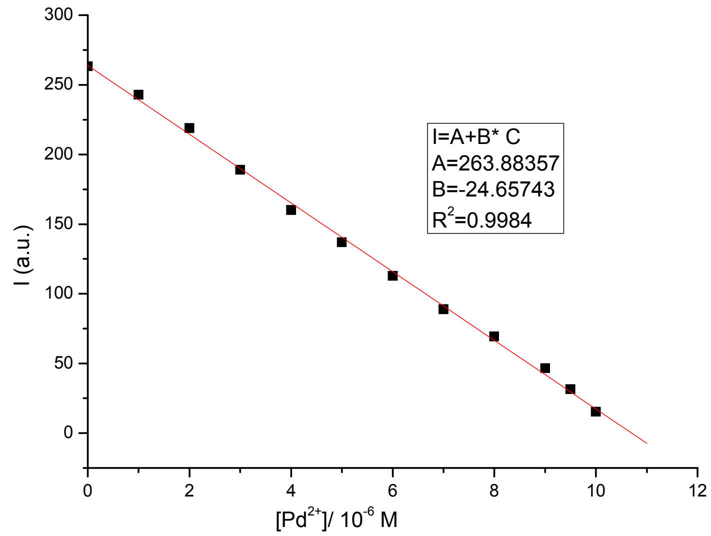


(l)

Figure S6 Reversibility of Pd^{2+} binding to **1** upon addition of NaS. Excitation wavelength was 365 nm. (k) Fluorescence spectra of compound **1**upon addition of 0, 0.2, 0.4, 0.6, 0.8, 1.0 equivalents of Pd^{2+}. (l) Fluorescence spectra of complex **1** and Pd^{2+} upon addition of 0, 0.2, 0.4, 0.6, 0.8, 1.0 equivalents of S^{2-} ion.The suspension was filtered and washed with chloroform. The organic layer was washed with water, dried over anhydrous $MgSO_4$ and the solvent was removed in vacuo. Then these compounds were dissolved in ethanol-water (60:40, v/v) solution at pH 7.2 maintained with HEPES buffer (50 mM).

10. The detection limit of the assay

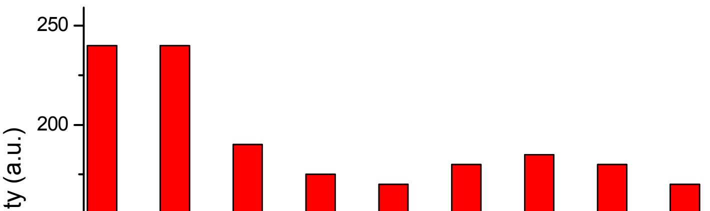
According to the proposed procedure, the calibration curve for the determination of Pd^{2+} by **1** was constructed under the optimized condition, which was: (10 μM) in ethanol-water (60:40, v/v) solution at pH 7.2 maintained with HEPES buffer (50 mM) in the presence of different metal ions (5×10^{-5} M) at 25°C. The relationship between excitation at 575 nm and Pd^{2+} concentration was: $I = -24.65743C+263.88357$, where I was fluorescence intensity under the emission at 575nm and C was the concentration of Pd^{2+}. The linear range of the method was found to be at least 1–10μM Pd^{2+} with a correlation coefficient of $R^2 = 0.9984$ (n = 12). The detection limit, based on the definition by IUPAC (CDL =3Sb/m)[3] was found to be 0.2μM from 10 blank solutions. The relative standard deviation (R.S.D.) for five repeated measurements of 5 μM Pd^{2+} was 1.7%.



(m)

Figure S7 The relationship between excitation at 575 nm and Pd^{2+} concentration was: $I = -24.65743C+263.88357$, where I was fluorescence intensity under the emission at 575nm and C was the concentration of Pd^{2+}.

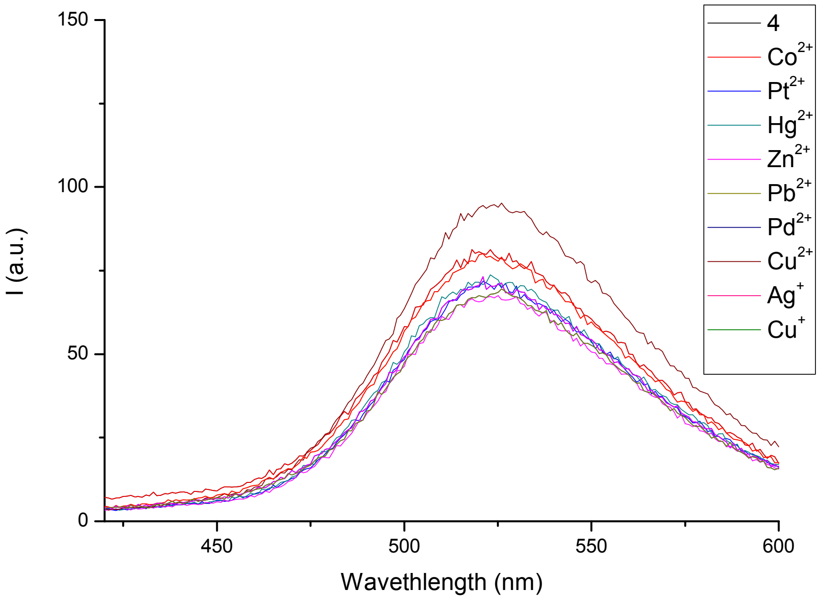
11. Competition experiments



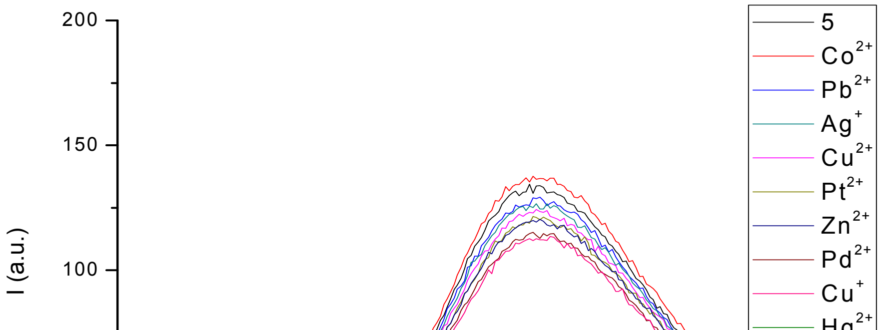
(n)

Figure S8 In ethanol-water (60:40, v/v) solution at pH 7.2 maintained with HEPES buffer (50 mM), the competitive experiments were tested in the presence of Pd^{2+}, as well as in a mixture of 5-fold other metal ion , respectively. No significant variation in fluorescent intensity was found by comparison with that only containing Pd^{2+}.

12. Emission Spectroscopies of model compounds



(o)



(p)

FigureS 9 (o) The fluorescence responses of **4** (10 μM) in ethanol-water (60:40, v/v) solution at pH 7.2 maintained with HEPES buffer (50 mM) in the presence of different metal ions (5×10^{-5} M) at 25 °C. (p) The fluorescence responses of **5** (10 μM) in ethanol-water (60:40, v/v) solution at pH 7.2 maintained with HEPES buffer (50 mM) in the presence of different metal ions (5×10^{-5} M) at 25 °C.

13. References

[1] Z. Xu, Y. Xiao, X. Qian, J. Cui,and D. Cui, *Org. Lett.*, 2005, **7,** 889.
[2] K. G. Casey, E. L.Quitevis, *J. Phys. Chem.* 1988, **92,** 6590-6594
[3] H.M.N.H. Irving, H. Freiser, T.S. West, IUPAC Compendium of Analytical Nomenclature, Definitive Rules, Pergamon Press, Oxford, 1981.