Supporting Information

A new rhodamine based colorimetric 'off-on' fluorescence sensor selective for Pd^{2+} along with the first bound X-ray crystal structure

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CONTENTS

1. General:

Unless otherwise mentioned, chemicals and solvents were purchased from Sigma-Aldrich chemicals Private Limited and were used without further purification. Melting points were determined on a hot-plate melting point apparatus in an open-mouth capillary and are uncorrected. ^{1}H-NMR and ^{13}C NMR spectra were recorded on Brucker 300 and 400 MHz instruments respectively. For NMR spectra, $CDCl_3$ was used as solvent using TMS as an internal standard. Chemical shifts are expressed in δ units and ^{1}H–^{1}H and ^{1}H–C coupling constants in Hz. UV-vis titration experiments was performed on a JASCO UV-V530 spectrophotometer and fluorescence experiment was done using PerkinElmer LS 55 fluorescence spectrophotometer using a fluorescence cell of 10 mm path. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer, using KBr discs.

General method of UV-vis and fluorescence titration:

By UV-vis method

For UV-vis and fluorescence titrations, stock solution of **Pd-Q1** was prepared (c = 2 x 10^{-5} ML^{-1}) in EtOH-H_2O (1:1, v/v, 25 °C). The solution of the guest cations using their chloride salts in the order of 2 x 10^{-4} ML^{-1} was also prepared in EtOH-H_2O (1:1, v/v, 25 °C). pH of the solution is adjusted at 7.2 by using 50 mM HEPES buffer. Solutions of various concentrations containing **Pd-Q1** and increasing concentrations of cations were prepared separately. The spectra of these solutions were recorded by means of UV-vis methods. Binding constant was calculated according to the Benesi-Hildebrand equation. *Ka* was calculated following the equation stated below.

$$1/(A\text{-}Ao) = 1/\{K(Amax–Ao)\,[Pd^{2+}]_n\} + 1/[Amax\text{-}Ao]$$

Here Ao is the absorbance of receptor in the absence of guest, A is the absorbance recorded in the presence of added guest, Amax is absorbance in presence of added $[Pd^{2+}]$max and K is the association constant (M^{-1}). The association constant (K) could be determined from the slope of the straight line of the plot of 1/(A-Ao) against $1/[Pd^{2+}]_n$. The association constant (K_a) as determined by UV-vis titration method for **Pd-Q1** with Pd^{2+} is found to be 4.17 x 10^4 M^{-1} (error < 10%).

General procedure for drawing Job plot by UV–vis method:

Stock solution of same concentration of **Pd-Q1** and Pd^{2+} were prepared in the order of ≈ 2.0 x 10^{-5} mL^{-1} EtOH-H_2O (1:1, v/v, 25 °C) at pH 7.2 using 50 mM HEPES buffer. The absorbance in each case with different *host–guest* ratio but equal in volume was recorded. Job plots were drawn by plotting $\Delta I.X_{host}$ *vs* X_{host} (ΔI = change of intensity of the absorbance spectrum during titration and X_{host} is the mole fraction of the host in each case, respectively).

By fluorescence method:

The binding constant value of Pd^{2+} with **Pd-Q1** has been determined from the emission intensity data following the modified Benesi–Hildebrand equation, $1/\Delta I = 1/\Delta I$ max $+(1/K[C])(1/\Delta I$ max). Here ΔI = I-Imin and ΔI max = Imax-Imin, where Imin, I, and Imax are the emission intensities of **Pd-Q1** considered in the absence of Pd^{2+}, at an intermediate Pd^{2+} concentration, and at a concentration of complete saturation where K is the binding constant and [C] is the Pd^{2+}concentration respectively. From the plot of (Imax-Imin)/(I-Imin) against $[C]^{-1}$ for **Pd-Q1**, the value of K has been determined from the slope. The association constant (K_a) as determined by fluorescence titration method for **Pd-Q1** with Pd^{2+} is found to be 4.28 x 10^4 M^{-1} (error < 10%).

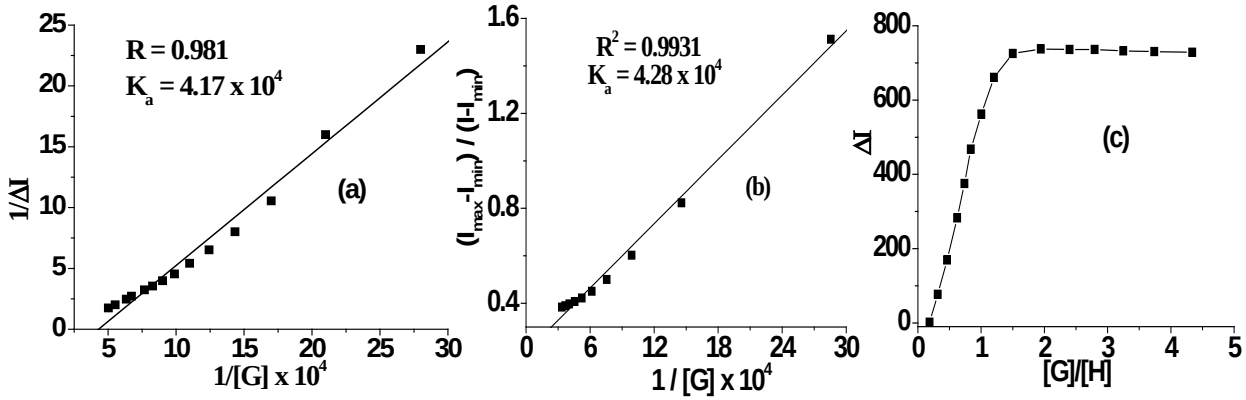


Figure 1: Association constant curve of **Pd-Q1** for Pd^{2+} determined by UV-vis method (a). By fluorescence method (b). Fluorescence titration curve of **Pd-Q1** with Pd^{2+}, where ΔI is the change of emission intensity and G, H represents the concentration of Pd^{2+} and **Pd-Q1** respectively (c).

Stock solution of the **Pd-Q1** ($c = 2 \times 10^{-5}$ ML^{-1}) and the guest cations ($c = 2 \times 10^{-4}$ ML^{-1}) were prepared in EtOH-H_2O (1:1, v/v, 25 °C) at pH 7.2 using 50 mM HEPES buffer. Fluorescence spectra were initially recorded taking 2 mL portions of **Pd-Q1** solution and adding increasing amount of guest Pd^{2+} solution to it.

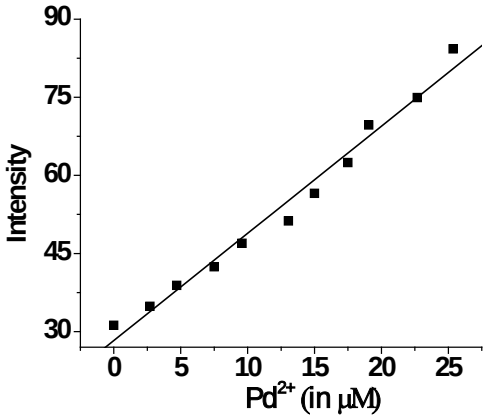


Figure 2: Emission intensity of **Pd-Q1** (10 μM) at 562 nm upon addition of Pd^{2+} (0-25 μM).

References:

1. *(a)* H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc*., 1949, **71**, 2703; *(b)* K. A. Conners, Binding Constants, The Measurement of Molecular Complex Stability; Wiley: New York, 1987.

Synthetic procedures for the preparation of Pd-Q1:

Compound 1: 1, [2-(Quinolin-8ylcarbamoyl)-ethyl]-carbamic acid *tert*butylester:

N-tert-Boc β-alanine (500 mg, 2.65 mmol) and DMAP (50 mg, 0.41 mmol), were added to the 8-Aminoquinoline (400 mg, 2.8 mmol). The mixture was dissolved in dry methylenechloride (20 mL) and chilled at 0 ^{0}C followed by the addition of a solution of DCC (800 mg, 3.9 mmol) in dry methylenechloride. The reaction mixture was stirred under nitrogen atmosphere at 0 ^{0}C for 15 minutes and then at r.t. for 20 h. The precipitated urea was removed by filtration and the filtrate was concentrated in high vacuum to give an oily residue. This residue was purified by column chromatography

using silica gel (100-200 mesh) and 20% ethylacetate in pet ether as eluent to afford compound **1** as a white solid (667 mg, 80 %).

Mp. 130-132 °C.

FT-IR (KBr): 3302, 3062, 2971, 2928, 1685, 1531, 1487, 1323, 1283, 1249, 1167, 1065, 759 cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 9.83 (bs, 1H), 8.8 (dd, 1H, *J* = 1.4 Hz, 1.4 Hz), 8.74 (d, 1H, *J* = 5.2 Hz), 8.18 (d, 1H, *J* = 7.4 Hz), 7.56-7.45 (m, 3H), 5.3 (bs, 1H), 3.58 (t, 2H, *J* = 5.6 Hz), 2.81 (t, 2H, *J* = 5.4 Hz), 1.43 (s, 9H).

Mass (ESI-MS): (m/z, %): 338.25 (M+Na).

Compound 2: [3-Amino-N-quinolin-8yl-propionamide]:

Compound **2** was obtained simply by the deprotection of the *N-tert*-Boc group of compound **1** using mild acidic reagent. Compound **1** (600 mg, 1.9 mmol) was dissolved in dichloromethane. Trifluoroacetic acid (0.4 mL) was added to it and the stirring was continued at r.t. for 30 minutes. Solvent and excess TFA were removed under high vacuum and then the whole mass was neutralized by saturated sodium bicarbonate solution followed by addition of dichloromethane. The organic layer was then extracted and finally dried over anhydrous $MgSO_4$. Compound **2** was isolated by a short column using silica gel (60-100 mesh) and 8% methanol in dichloromethane as eluent to give a white solid (370 mg, 90 %).

Mp. 125-127 °C.

FT-IR (KBr): 3252, 3211, 2998, 2927, 2800, 2176, 1689, 1623, 1538, 1493, 1405, 1323, 1219, 1023, 778 cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 10.07 (bs, 1H), 8.8 (dd, 1H, *J* = 1.6 Hz, 1.6 Hz), 8.69 (d, 1H, *J* = 5.5 Hz), 8.15 (d, 1H, *J* = 8.4 Hz), 7.54-7.45 (m, 3H), 5.97 (bs, 2H), 3.28 (t, 2H, *J* = 6.0 Hz), 2.88 (t, 2H, *J* = 6.0 Hz),

Mass (ESI-MS): (m/z, %): 216.05 $(M+H)^+$

Synthesis of Pd-Q1:

Finally the chemosensor **Pd-Q1** was synthesized by the condensation of compound **2** (400 mg, 1.86 mmol) with rhodamine-6G (900 mg, 1.9 mmol). The whole mixture was

dissolved in dry ethanol (10 mL) containing dry triethylamine (1 mL) and refluxed for 24 h. After ensuring that there was no excess amine left the solvent was distilled out and the crude product obtained was purified by column chromatography using silica gel (100-200 mesh) and 40% ethylacetate in pet ether as eluent to afford a light pink solid compound (455 mg, 40 %).

Mp. 238-240 °C.

FT-IR (KBr): 3422, 3389, 3372, 2967, 2927, 1692, 1679, 1622, 1521, 1465, 1159, 1137, 953 cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 9.53 (bs, 1H), 8.72 (dd, 1H, *J* = 1.6 Hz, 1.6 Hz), 8.6 (q, 1H, *J* = 6.0 Hz), 8.12 (d, 1H, *J* = 7.8 Hz), 7.93 (d, 1H, *J* = 6.6 Hz), 7.47-7.40 (m, 5H), 7.04 (d, 1H, *J* = 7.2 Hz), 6.33 (s, 2H), 6.27 (s, 2H), 3.62 (t, 2H, *J* = 7.35 Hz), 3.35 (bs, 2H), 3.12 (m, 4H,), 2.54 (t, 2H, *J* = 7.4 Hz), 1.8 (s, 6H), 1.26 (t, 6H, *J* = 6.64 Hz).

^{13}C NMR (CDCl3, 100 MHz): δc (ppm): 169.3, 168.5, 154.1, 151.8, 148.9, 147.4, 138.2, 136.2, 134.5, 132.5, 130.9, 128.3, 127.9, 127.8, 127.3, 123.8, 122.8, 121.5, 121.1, 117.91, 116.37, 105.7, 96.8, 65.2, 60.4, 38.3, 36.4, 36.3, 16.7, 14.7.

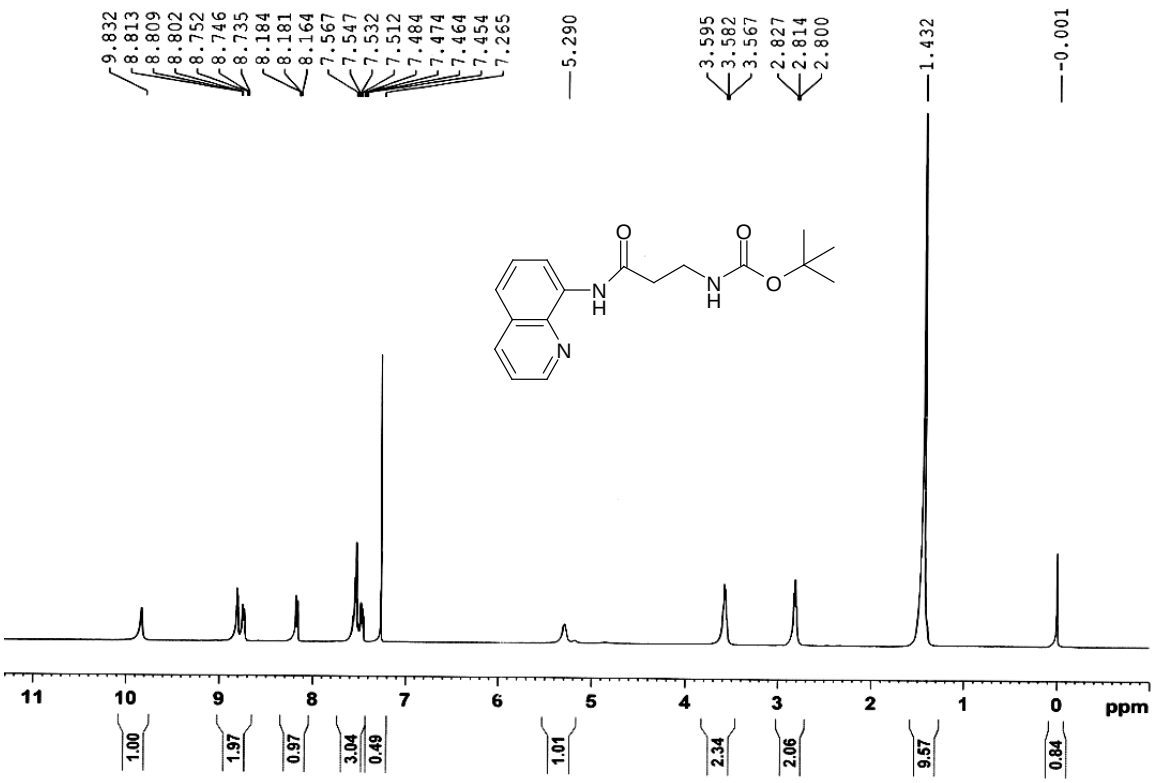
HRMS (ESI-TOF): (m/z, %): Calculated for $C_{38}H_{37}N_5O_3$ is 612.2975 $(M+H)^+$; Found: 612.2935 $(M+H)^+$.

Synthesis of the Pd^{2+}-complex of Pd-Q1:

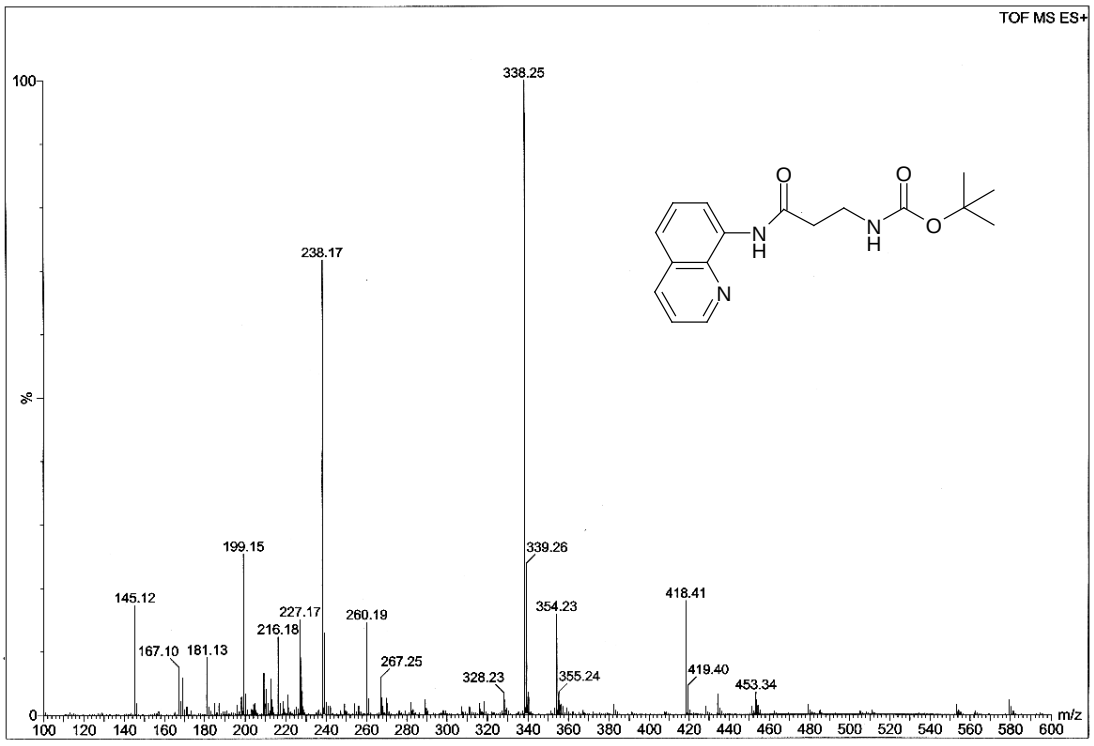
Pd^{2+} complex of the chemosensor **Pd-Q1** was synthesized by adding the chemosensor (100 mg, 0.16 mmol) into a refluxing solution of $PdCl_2$ (30 mg, 0.17 mmol) and the whole mixture was stirred for 30 minutes. The solvent was removed under vacuum and the whole mass was washed with diethyl ether in several times. Finally a deep pink colored solid was obtained (82 mg, 70 %) which was characterized by HRMS (ESI-TOF).

HRMS (ESI-TOF): (m/z, %): Calculated for $C_{38}H_{37}N_5O_3$.Pd is 717.1931 $(M + Pd^{2+})^+$; Found: 717.1981 $(M + Pd^{2+})^+$.

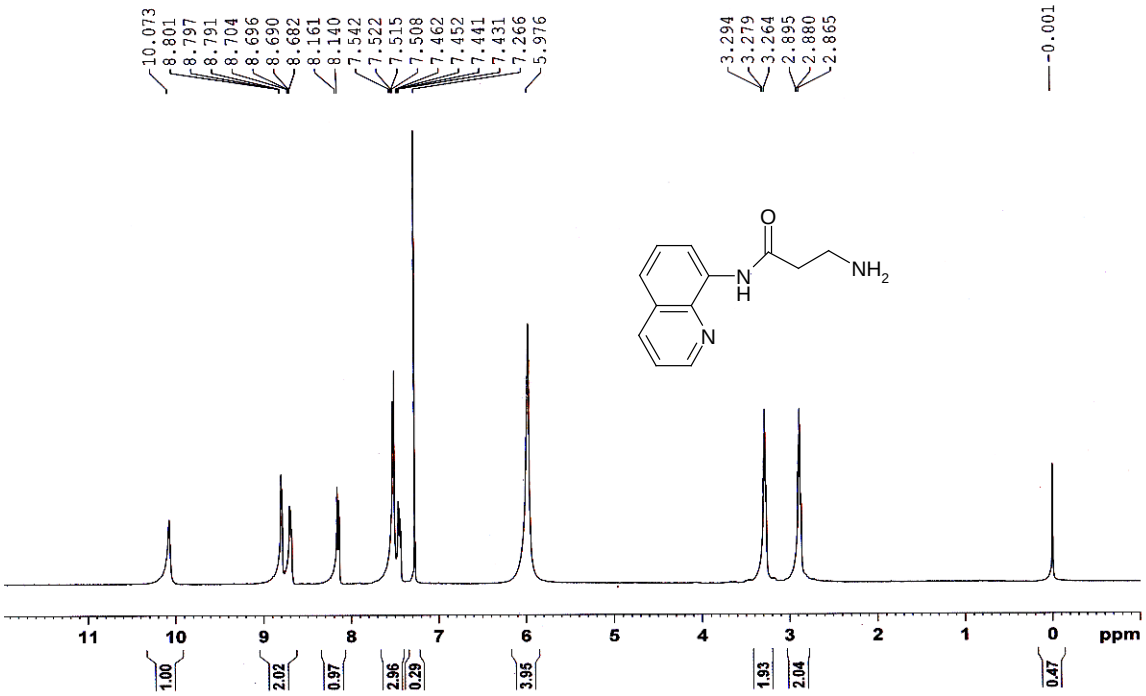
^{1}H NMR spectrum (S1) of Compound 1:



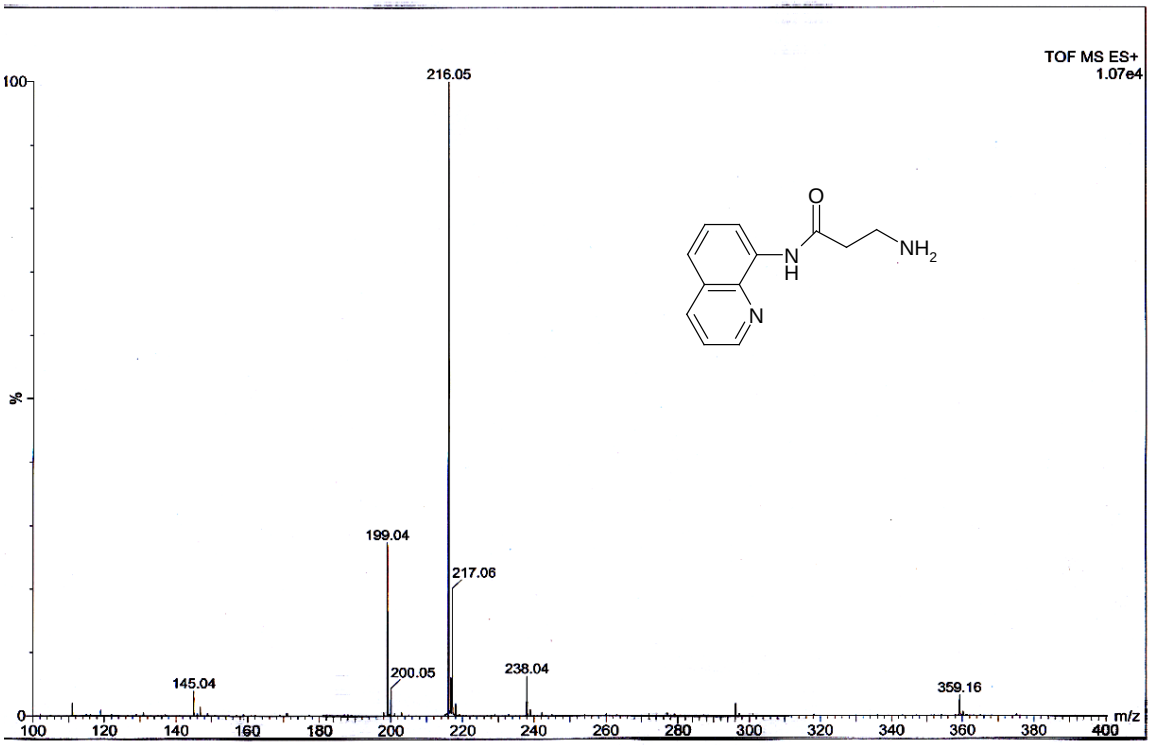
Mass (ESI-TOF) spectrum (S2) of Compound 1:



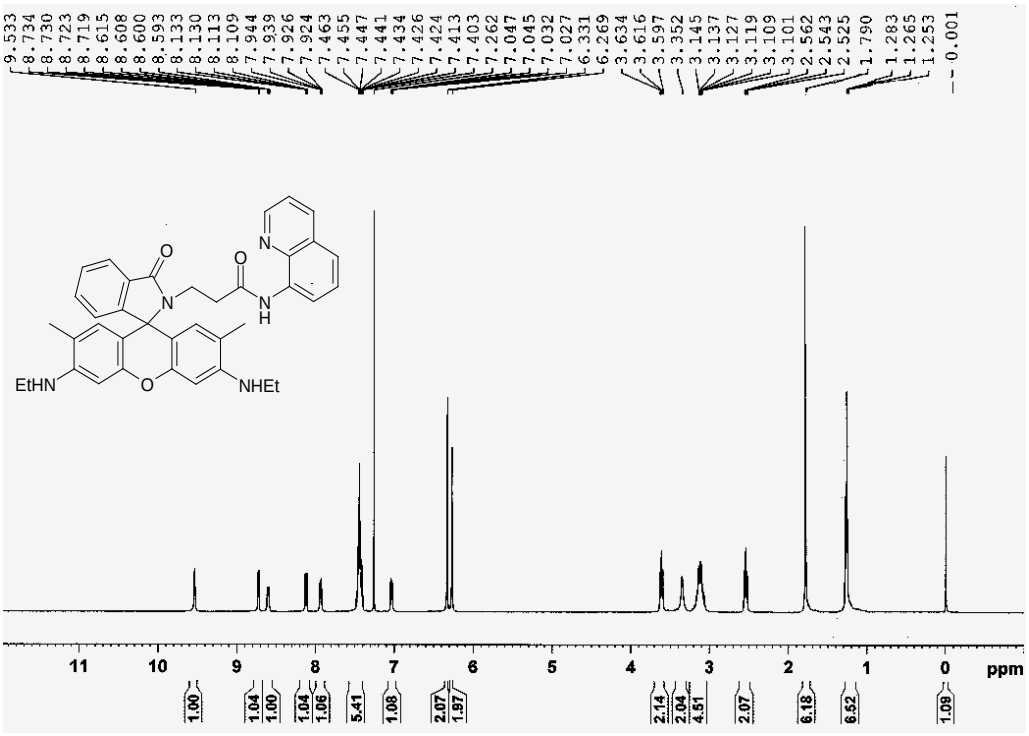
^{1}H NMR spectrum (S3) of Compound 2:



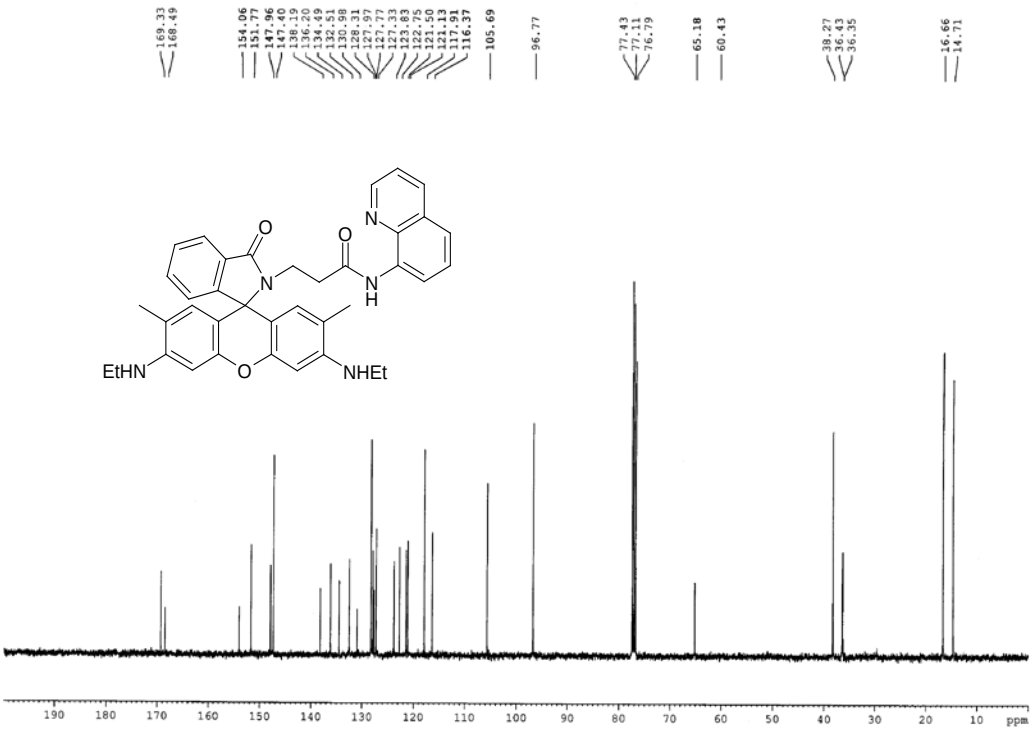
(ESI-TOF) spectrum (S4) of Compound 2:



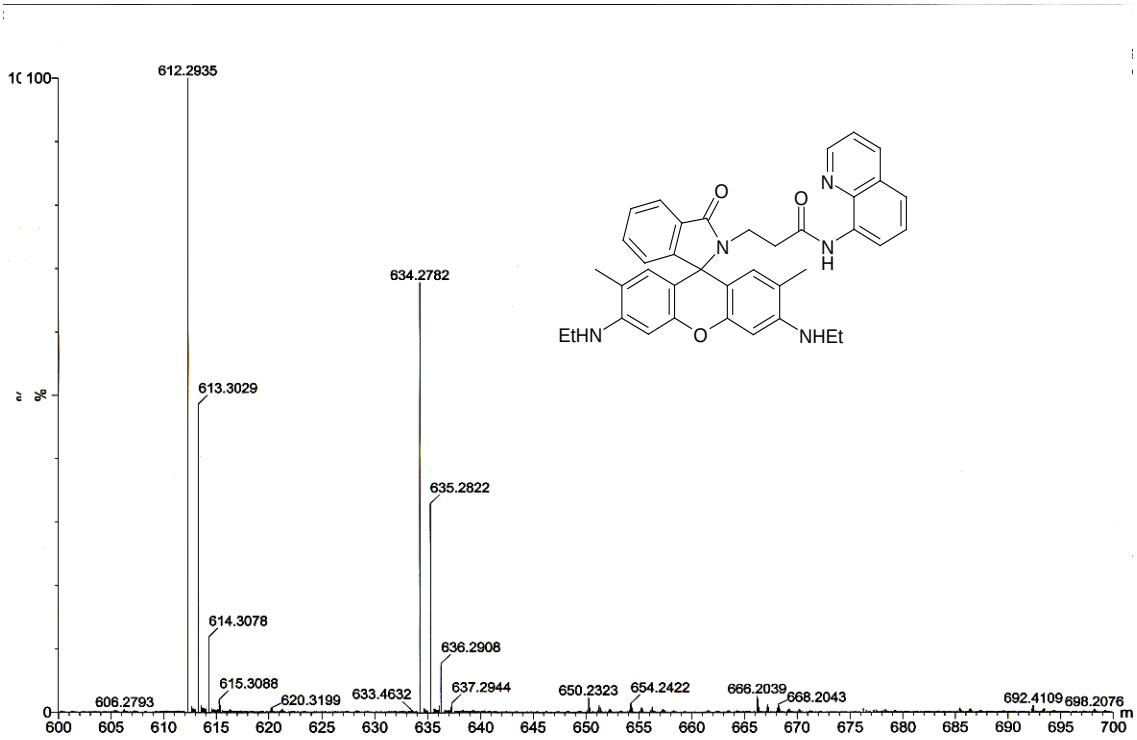
^{1}H NMR spectrum (S5) of Pd-Q1:



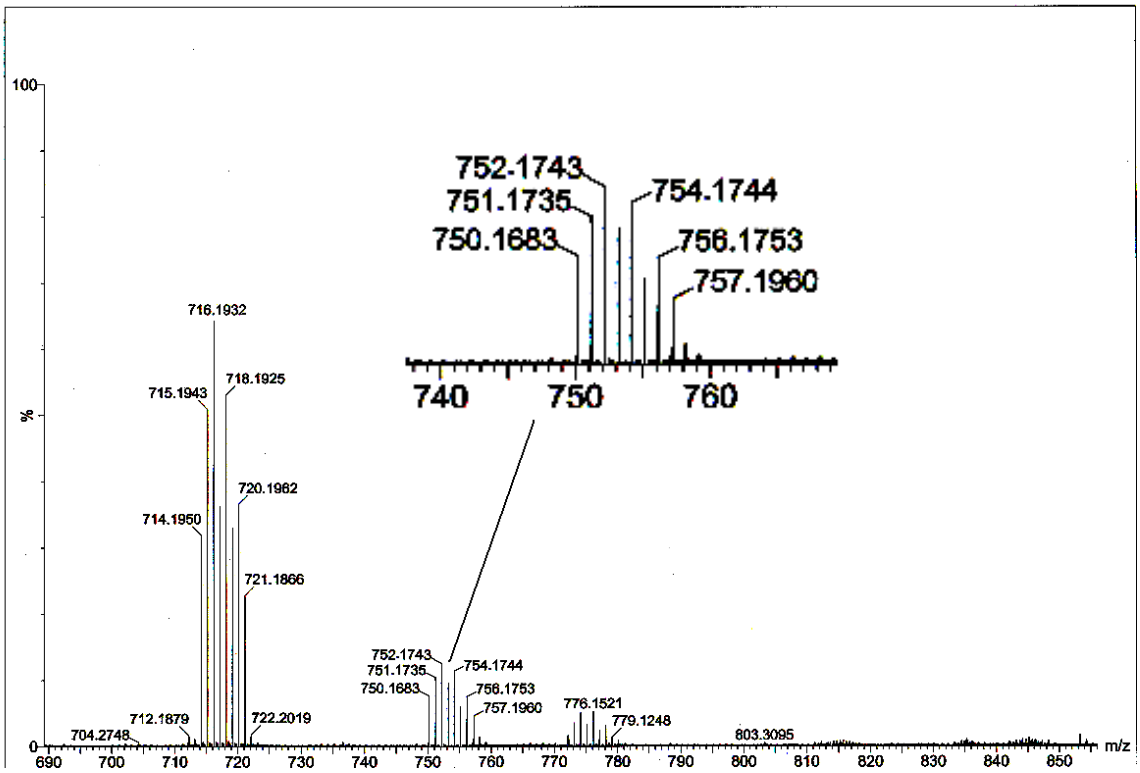
^{13}C NMR spectrum (S6) of Pd-Q1:



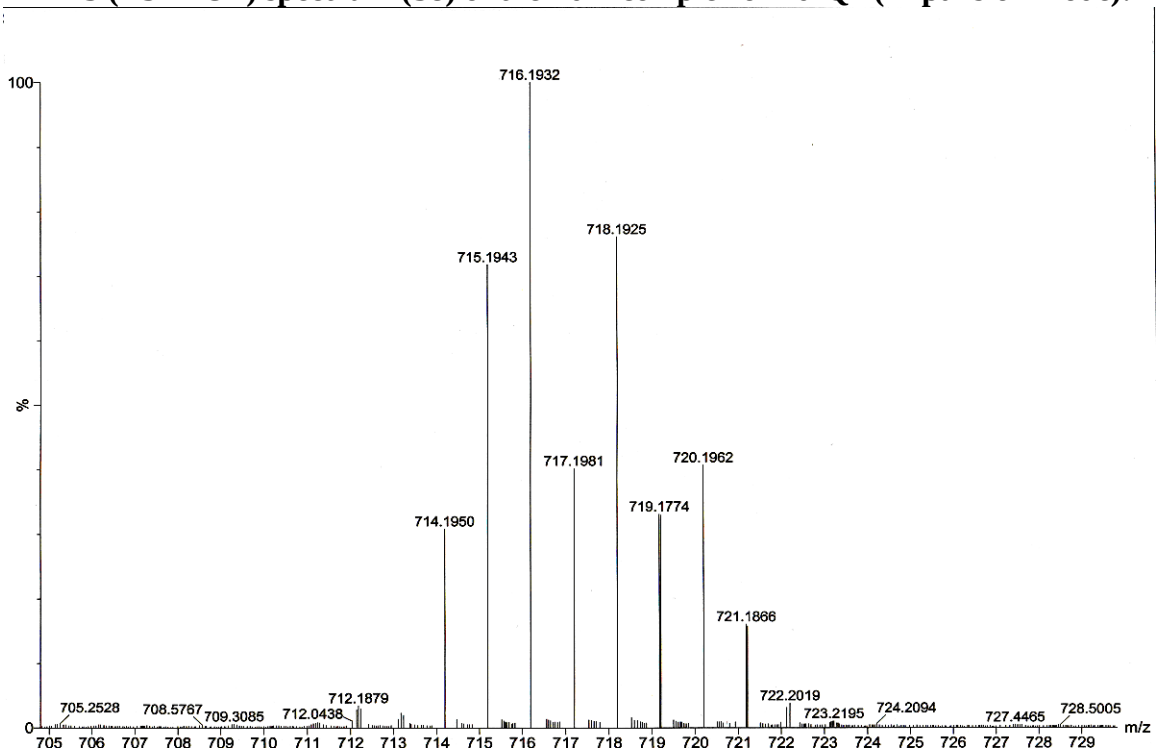
HRMS (ESI-TOF) spectrum (S7) of Pd-Q1:



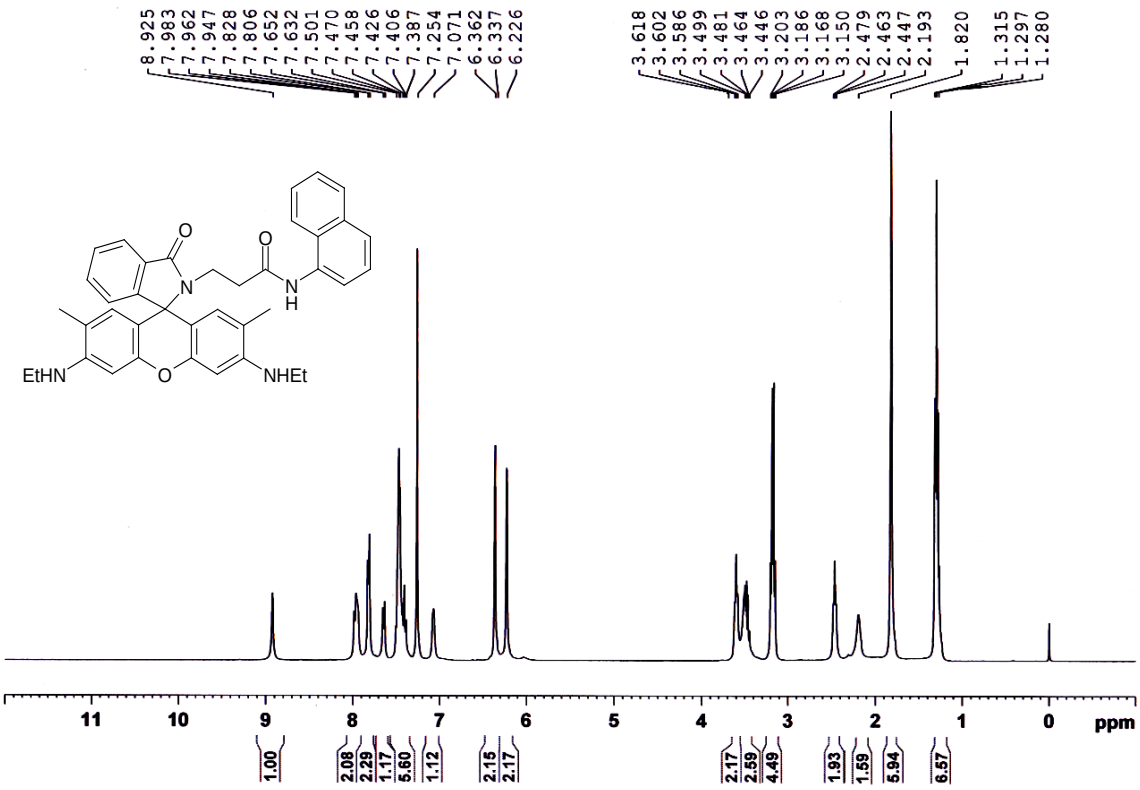
HRMS (ESI-TOF) spectrum (S8) of the Pd^{2+}-complex of Pd-Q1:



HRMS (ESI-TOF) spectrum (S8) of the Pd^{2+}-complex of Pd-Q1 (Expansion mode):

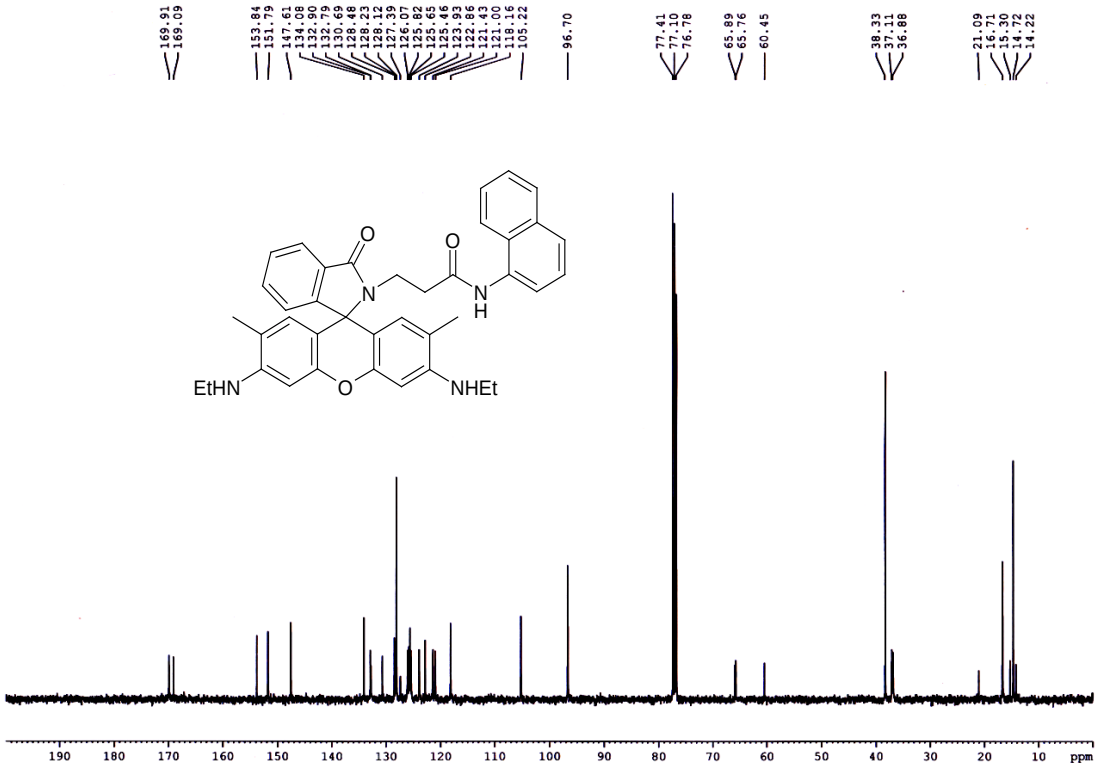


^{1}H NMR spectrum (S9) of Pd-N1:



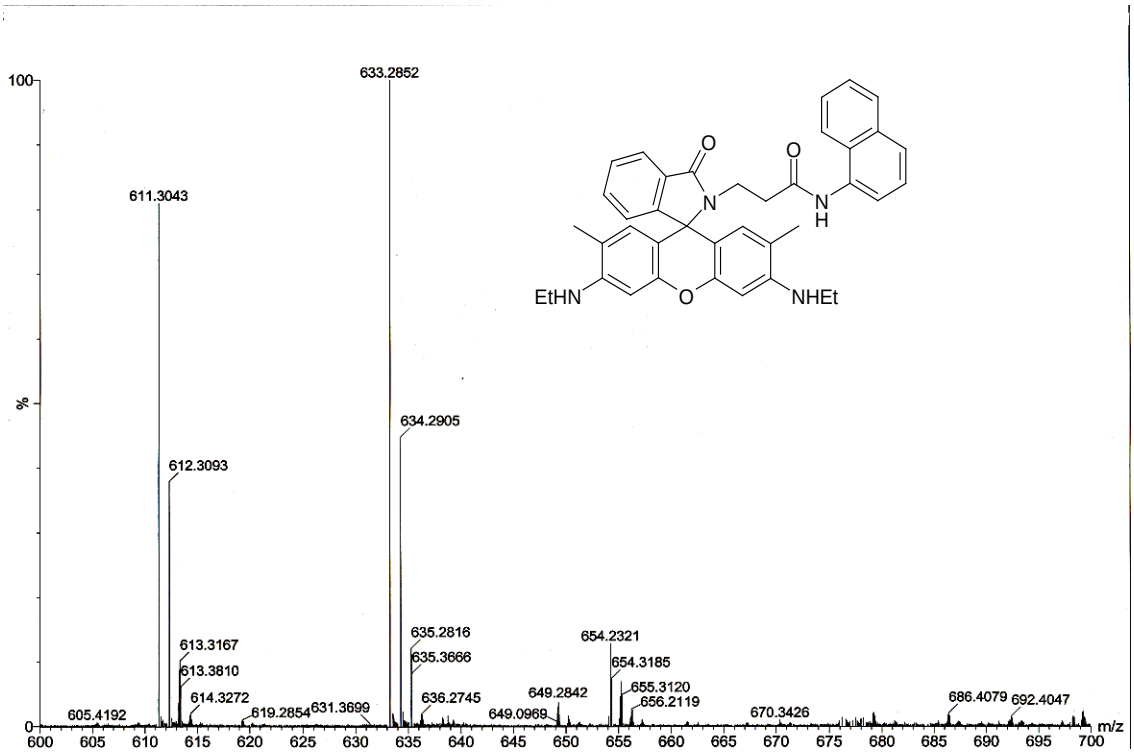
^{1}H NMR ($CDCl_3$, 400 MHz) data of Pd-N1: δ (ppm): 8.93 (bs, 1H), 7.96 (t, 2H, *J* = 7.2 Hz), 7.82 (d, 2H, *J* = 8.0 Hz), 7.64 (d, 1H, *J* = Hz, 8.0 Hz), 7.47-7.39 (m, 5H), 7.04 (d, 1H, *J* = 7.6 Hz), 6.36 (s, 2H), 6.26 (s, 2H), 3.6 (t, 2H, *J* = 6.5 Hz), 3.5-3.45 (m, 2H), 3.18 (q, 4H, *J* = 4.25 Hz), 2.46 (t, 2H, *J* = 6.4 Hz), 2.04 (bs, 1H), 1.82 (s, 6H), 1.23 (t, 6H, *J* = 7.0 Hz).

^{13}C NMR spectrum (S10) of Pd-N1:



^{13}C NMR ($CDCl_3$, 100 MHz) data of Pd-N1: δc (ppm): 169.9, 169.1, 153.8, 151.8, 148.9, 147.6, 134.1, 132.9, 132.8, 130.7, 128.5, 128.2, 127.4, 126.1, 125.8, 125.6, 125.5, 123.9, 122.9, 121.43, 121.0, 118.2, 105.2, 96.7, 65.9, 65.8, 60.4, 38.3, 37.1, 36.9, 21.1, 16.71, 15.3, 14.7, 14.2.

HRMS (ESI-TOF) spectrum (S11) of Pd-N1:



HRMS (ESI-TOF): (m/z, %): Calculated for $C_{39}H_{38}N_4O_3$ is 611.3023 $(M+H)^+$; Found: 611.3043 $(M+H)^+$.

Determination of fluorescence quantum yield (Φ) of the chemosensor itself and after complexation with Pd^{2+}:

The fluorescence quantum yield of the chemosensor and the metal-complex were obtained by the following equation given below. [1-2]

$\Phi_u = \Phi_s\ (FA_u/FA_s)(A_s/A_u)(\eta_u^2/\ \eta_s^2)(\lambda_{exs}/\lambda_{exu})$

Where, Φ is the fluorescence quantum yield; FA is the integrated area under the corrected emission spectra; A is the absorbance at the excitation wavelength; η is the refractive index of the solution; λ_{ex} is the excitation wavelength; and the subscript u and s refer to the unknown and standard respectively. We have taken rhodamine B as standard that has a fluorescence quantum yield of 0.49 in ethanol.

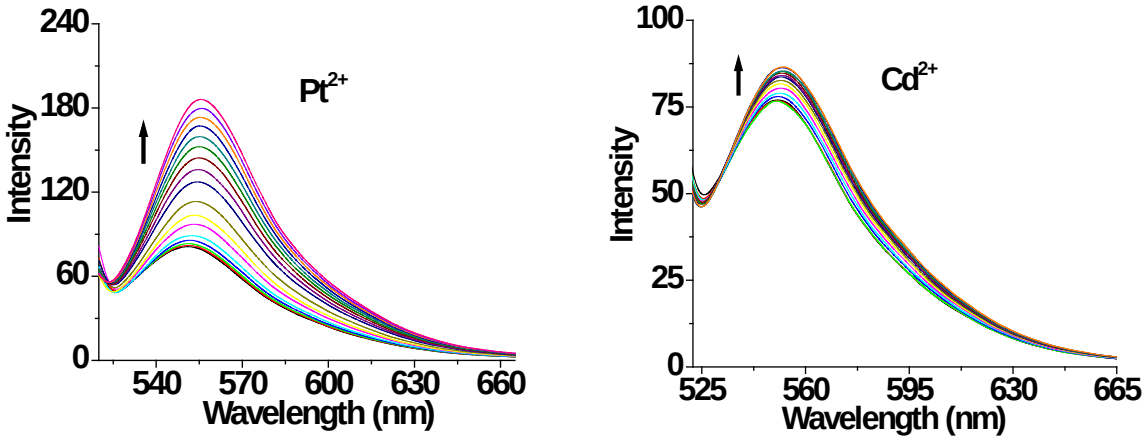
Following the above equation, the quantum yield value obtained for the chemosensor itself is 0.021 and after chelation with Pd^{2+} the quantum yield value for Pd^{2+}-complex is 0.125. Therefore, fluorescence quantum yield increases as a result of metal complexation.

References:

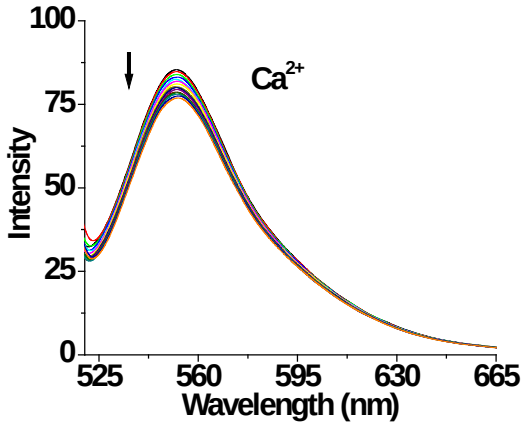
1. (a) K. G. Casey and E. L. Quitevis, *J. Phys. Chem*. 1988, **92**, 6590. (b) J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Kluwer Academic/Plenum Press, NewYork, 1999, Second Edition. (c) K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, NewYork, 1992.

2. (a) Li, H. L.; Fan, J. L.; Song, F. L.; Zhu, H. ; Du, J. J. ; Sun, S. G.; Liu, X. J.; Peng, X. J. *Chem. Eur. J*. 2010, **16**, 12349. (b) Li, H. L.; Fan, J. L.; Du, J. J.; Guo, K. X.; Sun, S. G.; Liu, X. J.; Peng, X. J. *Chem. Commun*. 2010, 46, 1079.

Fluorescence emission spectra of Pd-Q1 (S12) with different cations in EtOH-H_2O (1:1, v/v, 25 °C):



(a) **(b)**



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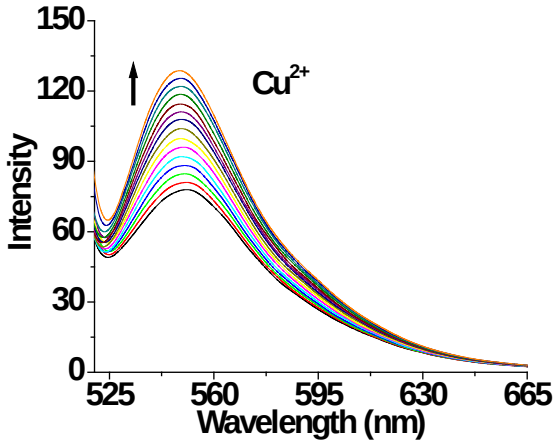

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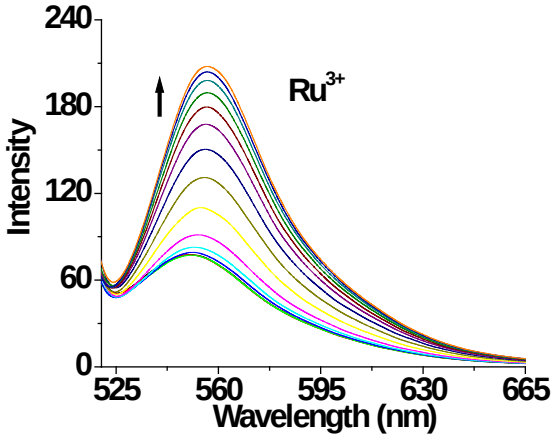

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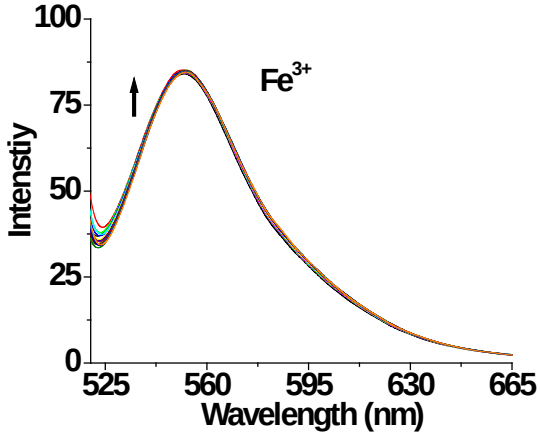

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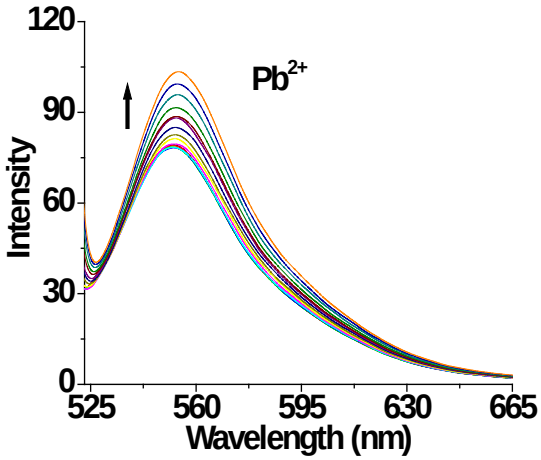

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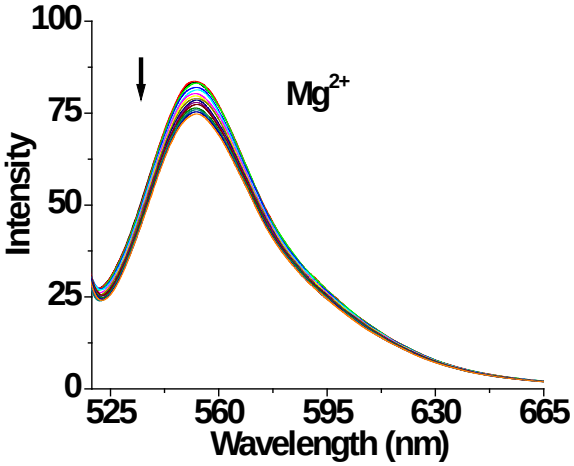

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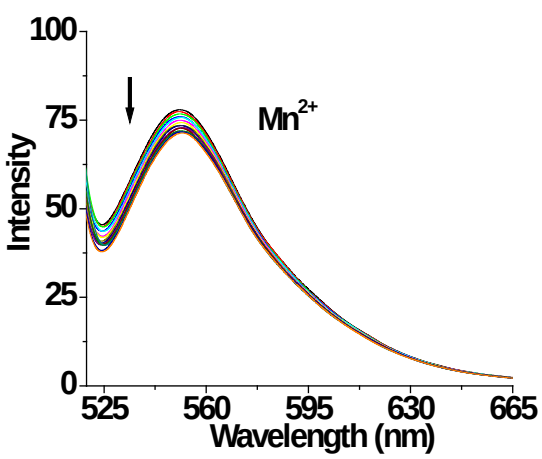
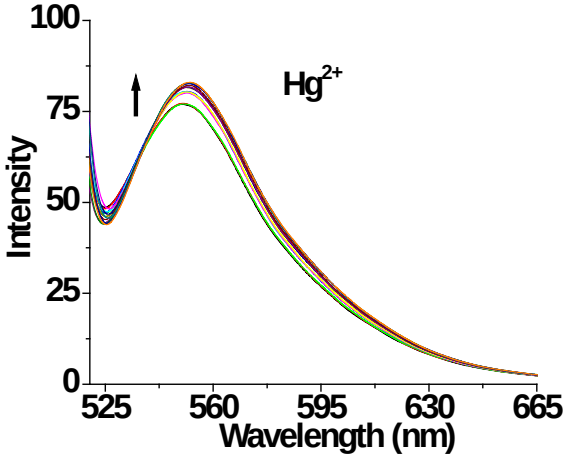


(i)



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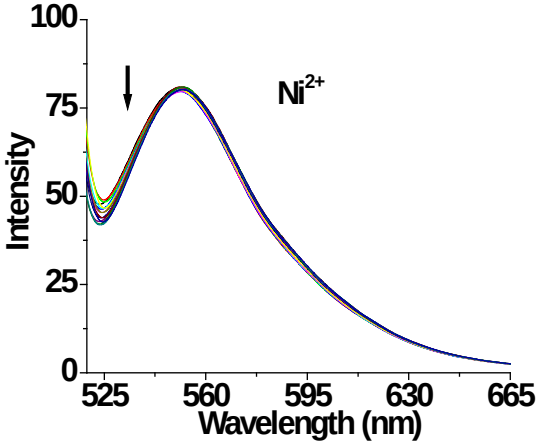

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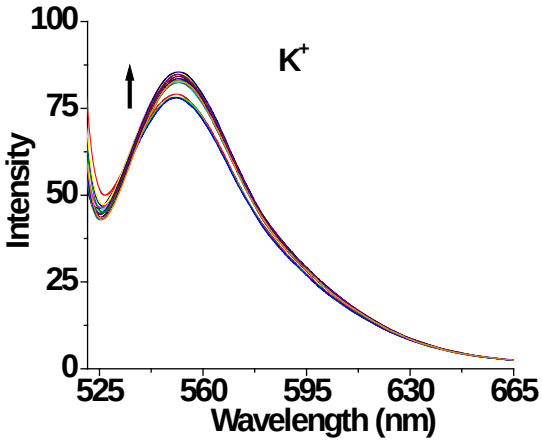

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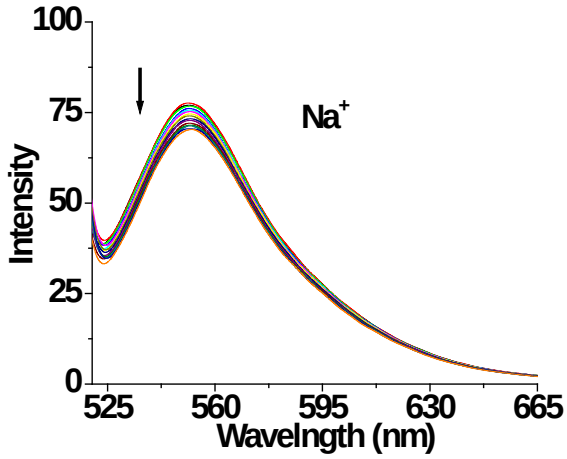

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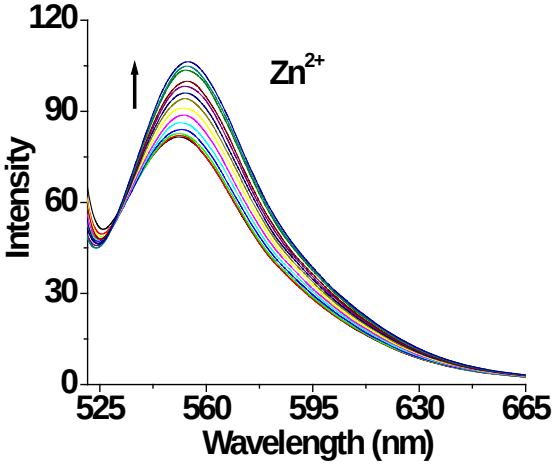
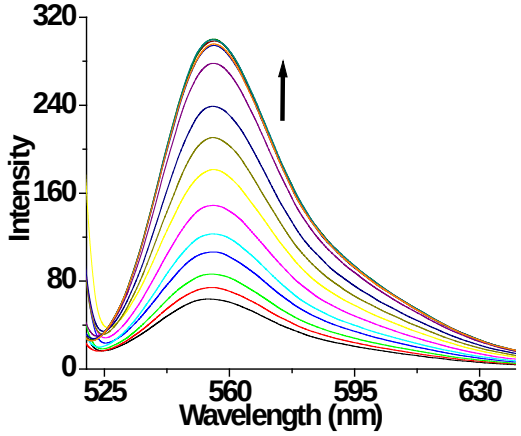
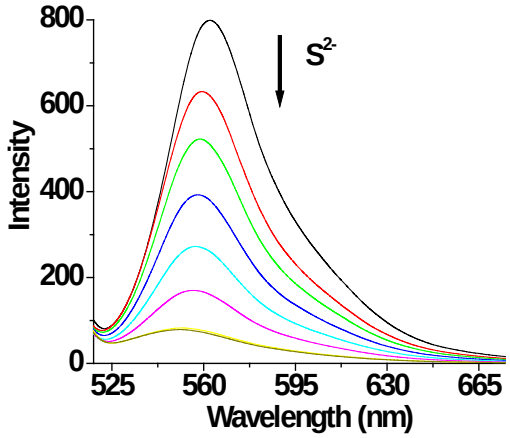


(n)

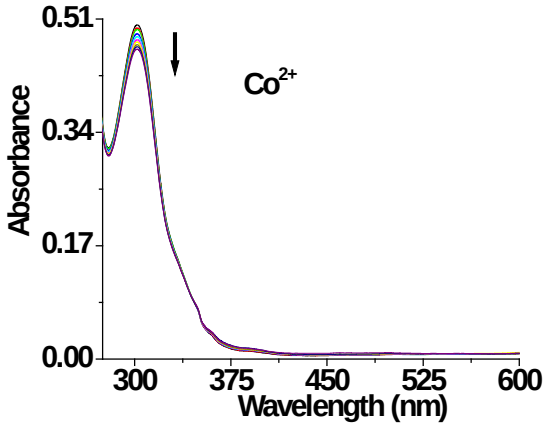
Emission spectra (S13) of Pd-N1 (c = 2.0 x 10^{-5} M) in presence of increasing amount of Pd^{2+} (c = 2.0 x 10^{-4} M).



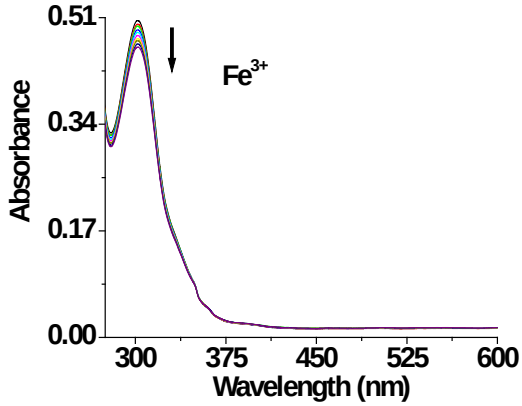
Emission spectra (S14)of Pd-Q1 (c = 2.0 x 10^{-5} M) upon addition of S^{2-} (c = 5.0 x 10^{-3} M) in EtOH-H_2O (1:1, v/v, 25 °C).



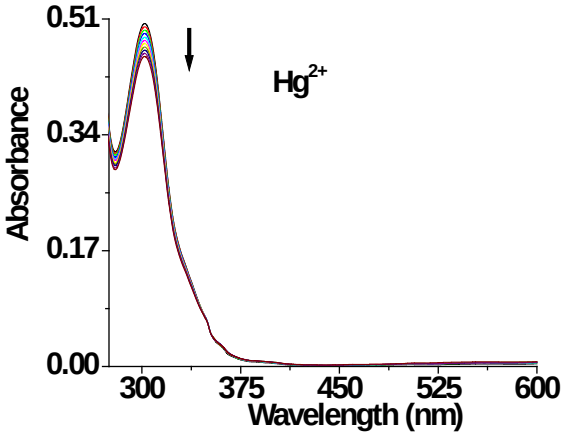
UV-vis absorption spectra of Pd-Q1 (S15) with different cations in EtOH-H_2O (1:1, v/v, 25 °C):



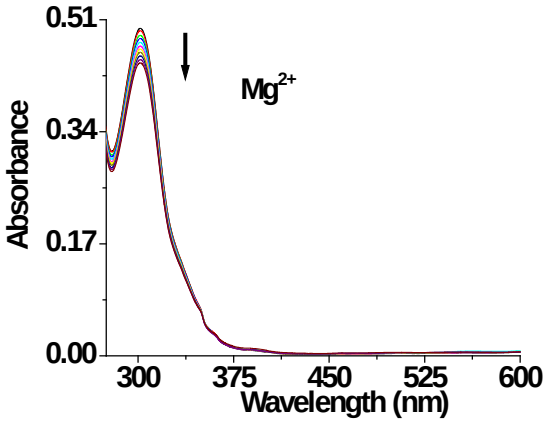
(a)



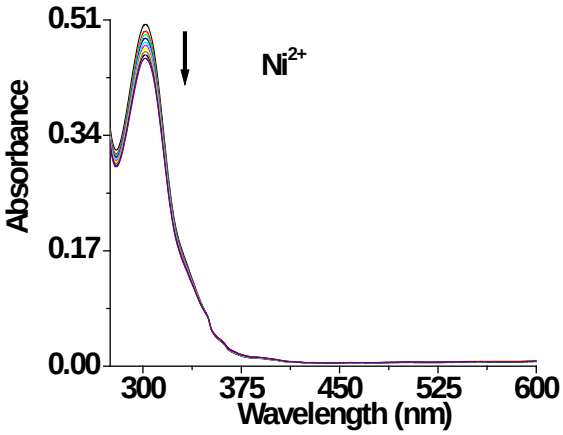
(b)



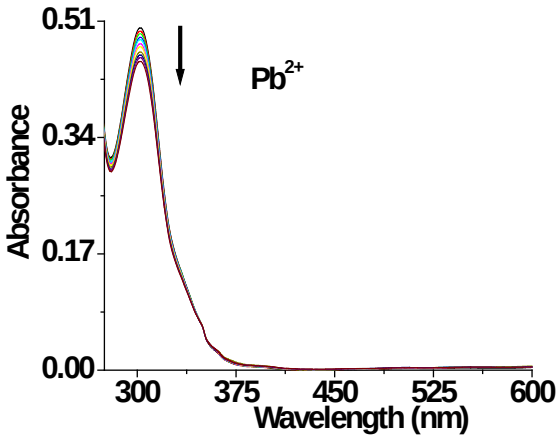
(c)



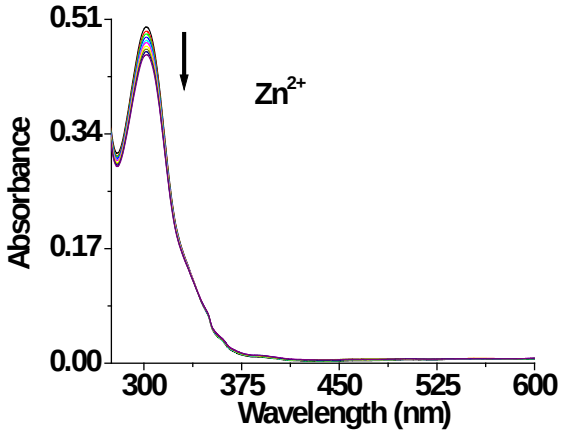
(d)



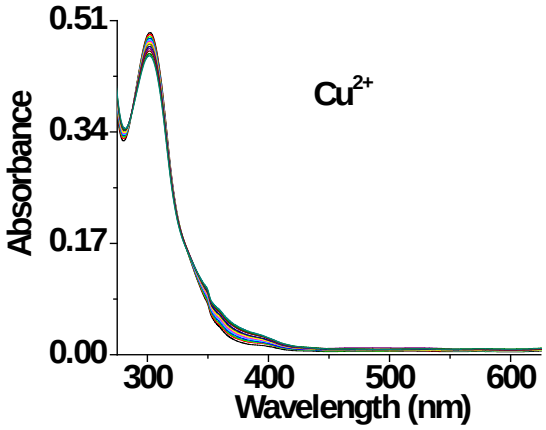
(e)



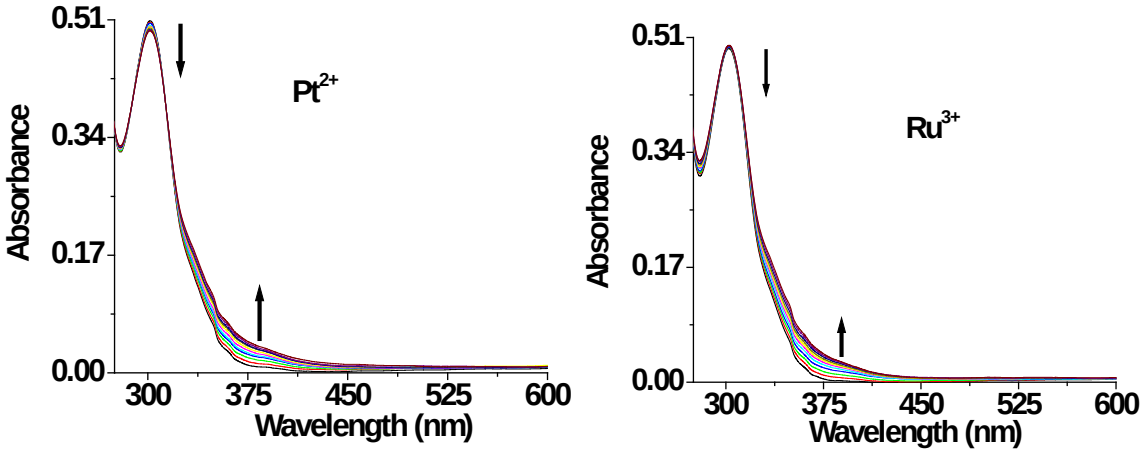
(f)



(g)



(h)



(i) **(j)**

UV-vis absorption spectra (a) and emission spectra (b) of Pd-Q1 (S16) upon gradual addition of $Pd(PPh_3)_4$ in EtOH-H_2O (1:1, v/v, 25 °C):

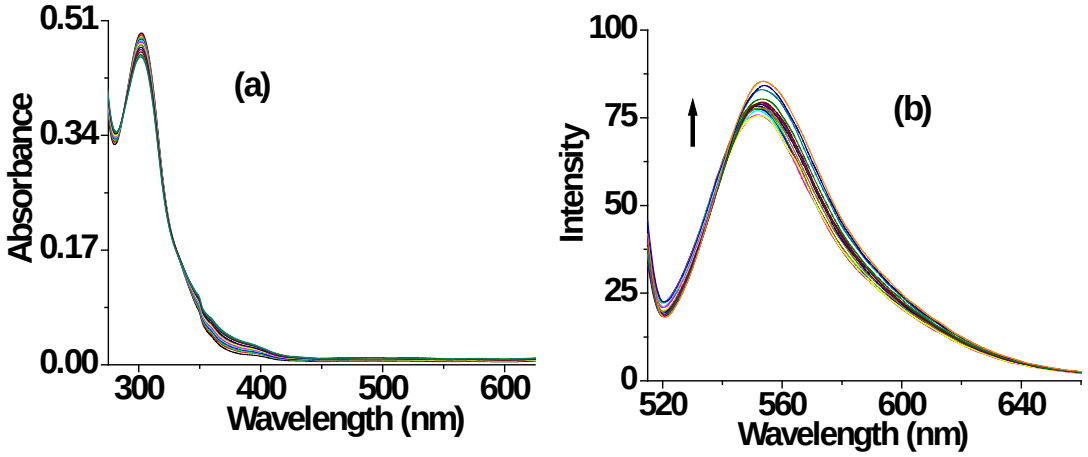


Table 1: Crystallographic data and structure refinement parameters of Pd^{2+}-complex of Pd-Q1:

Compound	Pd^{2+}-complex
CCDC No.	824877
Empirical Formula	$C_{38}H_{37}ClN_5O_3Pd \cdot 0.5(Cl_4Pd) \cdot 0.44(Cl_2Pd) \cdot H_2O$
Formula weight	973.88
Crystal system	Monoclinic
Space group	C2/c (No. 15)
T [K]	100
a [Å]	21.8033(4)
b [Å]	16.4269(3)
c [Å]	22.7565(5)
α [deg]	90
β [deg]	103.155(1)
γ [deg]	90
Z	8
V [Å^3]	7936.6(3)
Ï [Å]	0.71073
D_{calc} [g/cm^3]	1.630
F [000]	3914
Crystal size [mm]	0.11x 0.13x 0.34
Theta min-max [deg]	1.6, 27.5
μ [mm^{-1}]	1.188
Index ranges	-19≤ h ≤28 -21≤ k ≤21 -29≤ l ≤27
Reflections collected	34522
Unique reflections	9119
Observed reflections [I > 2.0 sigma(I)]	4803
R_1 [$I > 2\sigma(I)$]	0.1176
wR2	0.3417
GOF	1.03

Table 2: Hydrogen-bond parameters (Å, °) of Pd^{2+}-complex of Pd-Q1:

D-H….A	D-H	H….A	D….A	D-H….A
Intra O2-H2....O1W	0.84	1.75	2.538(12)	156
O1W-H2W1....O3^{i}	0.74	1.90	2.630(15)	171
N5-H5B....Cl1^{ii}	0.88	2.77	3.563(15)	151
C38-H38C....Cl1^{ii}	0.98	2.81	3.577(16)	136

Symmetry codes: (i) = 1/2-x,-1/2+y,1/2-z; (ii) = x,1-y,1/2+z