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 ................................................................. 2
2. General methods of UV-vis and fluorescence titration experiment ........... 2-3
3. Association constants and fluorescence titration curves of Pd-Q1 with Pd$^{2+}$ .... 3
4. Procedure for the preparation of Pd-Q1 and its Pd$^{2+}$-Complex and their spectroscopic characterization (including $^1$H NMR, $^{13}$C NMR, Mass and IR analysis) ................................................................. 4-6
5. $^1$H NMR (S1) and Mass spectra (S2) of compound 1 ......................... 7
6. $^1$H NMR (S3) and Mass spectra (S4) of compound 2 ......................... 8
7. $^1$H NMR (S5), $^{13}$C NMR (S6) and HRMS spectra (S7) of Pd-Q1 ........ 9-10
8. Mass spectra of the Pd$^{2+}$-Complex (S8) ............................................. 10-11
9. $^1$H NMR (S9), $^{13}$C NMR (S10) and HRMS spectra (S11) of Pd-N1 ....... 11-13
10. Determination of fluorescence quantum yield .................................... 13
11. Fluorescence titration spectra of Pd-Q1 with different guest cations ...... 14-16
12. Fluorescence titration spectra (S13) of Pd-N1 in presence of Pd$^{2+}$ .......... 17
13. Fluorescence titration spectra (S14) of Pd-Q1 in presence of excess S$^{2-}$ .... 17
14. UV-vis titration spectra of Pd-Q1 with different guest metal ions .......... 17-19
15. Table 1: Crystallographic data and structure refinement parameters of Pd$^{2+}$-Complex ................................................................. 20
16. Table 2: Hydrogen-bond parameters (Å, °) of Pd$^{2+}$-Complex ............ 21
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 $\delta$ units and $^1$H–$^1$H and $^1$H–C coupling constants in Hz. UV-vis titration experiments were 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 ($c = 2 \times 10^{-5} \text{ M}^1$) in EtOH-H$_2$O (1:1, v/v, 25 °C). The solution of the guest cations using their chloride salts in the order of $2 \times 10^{-4} \text{ M}^1$ was also prepared in EtOH-H$_2$O (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. $K_a$ was calculated following the equation stated below.

$$1/(A-A_0) = 1/[K(A_{\text{max}}-A_0)[\text{Pd}^{2+}]_n] + 1/[A_{\text{max}}-A_0]$$

Here $A_0$ is the absorbance of receptor in the absence of guest, $A$ is the absorbance recorded in the presence of added guest, $A_{\text{max}}$ is absorbance in presence of added $[\text{Pd}^{2+}]_{\text{max}}$ and $K$ is the association constant $(\text{M}^{-1})$. The association constant $(K)$ could be determined from the slope of the straight line of the plot of $1/(A-A_0)$ against $1/[\text{Pd}^{2+}]_n$. The association constant $(K_a)$ as determined by UV-vis titration method for Pd-Q1 with Pd$^{2+}$ is found to be $4.17 \times 10^4 \text{ M}^{-1}$ (error < 10%).
General procedure for drawing Job plot by UV–vis method:

Stock solution of same concentration of Pd-Q1 and Pd²⁺ were prepared in the order of ≈ 2.0 x 10⁻⁵ mL⁻¹ EtOH-H₂O (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 ∆I.Xₘₚₜ-host vs Xₘₚₜ-host (ΔI = change of intensity of the absorbance spectrum during titration and Xₘₚₜ-host is the mole fraction of the host in each case, respectively).

By fluorescence method:

The binding constant value of Pd²⁺ with Pd-Q1 has been determined from the emission intensity data following the modified Benesi–Hildebrand equation, 1/ΔI = 1/ΔI max + (1/K[C])(1/ΔI 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 Pd²⁺, at an intermediate Pd²⁺ concentration, and at a concentration of complete saturation where K is the binding constant and [C] is the Pd²⁺ 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 (Kₐ) as determined by fluorescence titration method for Pd-Q1 with Pd²⁺ is found to be 4.28 x 10⁴ M⁻¹ (error < 10%).

Figure 1: Association constant curve of Pd-Q1 for Pd²⁺ determined by UV-vis method (a). By fluorescence method (b). Fluorescence titration curve of Pd-Q1 with Pd²⁺, where ΔI is the change of emission intensity and G, H represents the concentration of Pd²⁺ and Pd-Q1 respectively (c).
Stock solution of the Pd-Q1 (c = 2 x 10^{-5} ML^{-1}) and the guest cations (c = 2 x 10^{-4} ML^{-1}) were prepared in EtOH-H2O (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:

Synthetic procedures for the preparation of Pd-Q1:

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

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 °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 °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

**¹H NMR (CDCl₃, 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 MgSO₄. 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

**¹H NMR (CDCl₃, 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

**¹H NMR (CDCl₃, 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).

**¹³C 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 C₃₈H₃₇N₅O₃ is 612.2975 (M+H)⁺; Found: 612.2935 (M+H)⁺.

**Synthesis of the Pd²⁺-complex of Pd-Q1:**
Pd²⁺ complex of the chemosensor **Pd-Q1** was synthesized by adding the chemosensor (100 mg, 0.16 mmol) into a refluxing solution of PdCl₂ (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 C₃₈H₃₇N₅O₃.Pd is 717.1931 (M + Pd²⁺)⁺; Found: 717.1981 (M + Pd²⁺)⁺.
$^1$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: $\delta$ (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: $\delta$ c (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_{4}O_{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: \(^{(1-2)}\)

\[
\Phi_u = \Phi_s \left( \frac{F_{A_u}}{F_{A_s}} \right) \left( \frac{A_{s}/A_{u}}{\eta_u^2/\eta_s^2} \right) \left( \frac{\lambda_{exs}/\lambda_{exu}}{\lambda_{exs}/\lambda_{exu}} \right)
\]

Where, \(\Phi\) is the fluorescence quantum yield; \(FA\) is the integrated area under the corrected emission spectra; \(A\) is the absorbance at the excitation wavelength; \(\eta\) is the refractive index of the solution; \(\lambda_{ex}\) 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:**


**Fluorescence emission spectra of Pd-Q1 (S12) with different cations in EtOH-H\(_2\)O (1:1, v/v, 25 °C):**

(a) [Fluorescence emission spectrum of Pt\(^{2+}\) with Pd-Q1 (S12) in EtOH-H\(_2\)O (1:1, v/v, 25 °C)].

(b) [Fluorescence emission spectrum of Cd\(^{2+}\) with Pd-Q1 (S12) in EtOH-H\(_2\)O (1:1, v/v, 25 °C)].
Emission spectra (S13) of Pd-N1 \((c = 2.0 \times 10^{-5} \text{ M})\) in presence of increasing amount of Pd\(^{2+}\) \((c = 2.0 \times 10^{-4} \text{ M})\).

Emission spectra (S14) of Pd-Q1 \((c = 2.0 \times 10^{-5} \text{ M})\) upon addition of S\(^2-\) \((c = 5.0 \times 10^{-3} \text{ M})\) in EtOH-H\(_2\)O \((1:1, \text{ v/v, 25 }^\circ\text{C})\).

UV-vis absorption spectra of Pd-Q1 (S15) with different cations in EtOH-H\(_2\)O \((1:1, \text{ v/v, 25 }^\circ\text{C})\):
UV-vis absorption spectra (a) and emission spectra (b) of Pd-Q1 (S16) upon gradual addition of Pd(PPh₃)₄ in EtOH-H₂O (1:1, v/v, 25 °C):
Table 1: Crystallographic data and structure refinement parameters of Pd$^{2+}$-complex of Pd-Q1:

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<th>Compound</th>
<th>Pd$^{2+}$-complex</th>
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Symmetry codes: (i) = 1/2-x,-1/2+y,1/2-z; (ii) = x,1-y,1/2+z