Electronic Supplementary Material (ESI) for Analyst.

Turn-On fluorescence chemosensor based on a tripodal amine [tris(pyrrolyl-α-methyl)amine]-rhodamine conjugate for the selective detection of zinc ions

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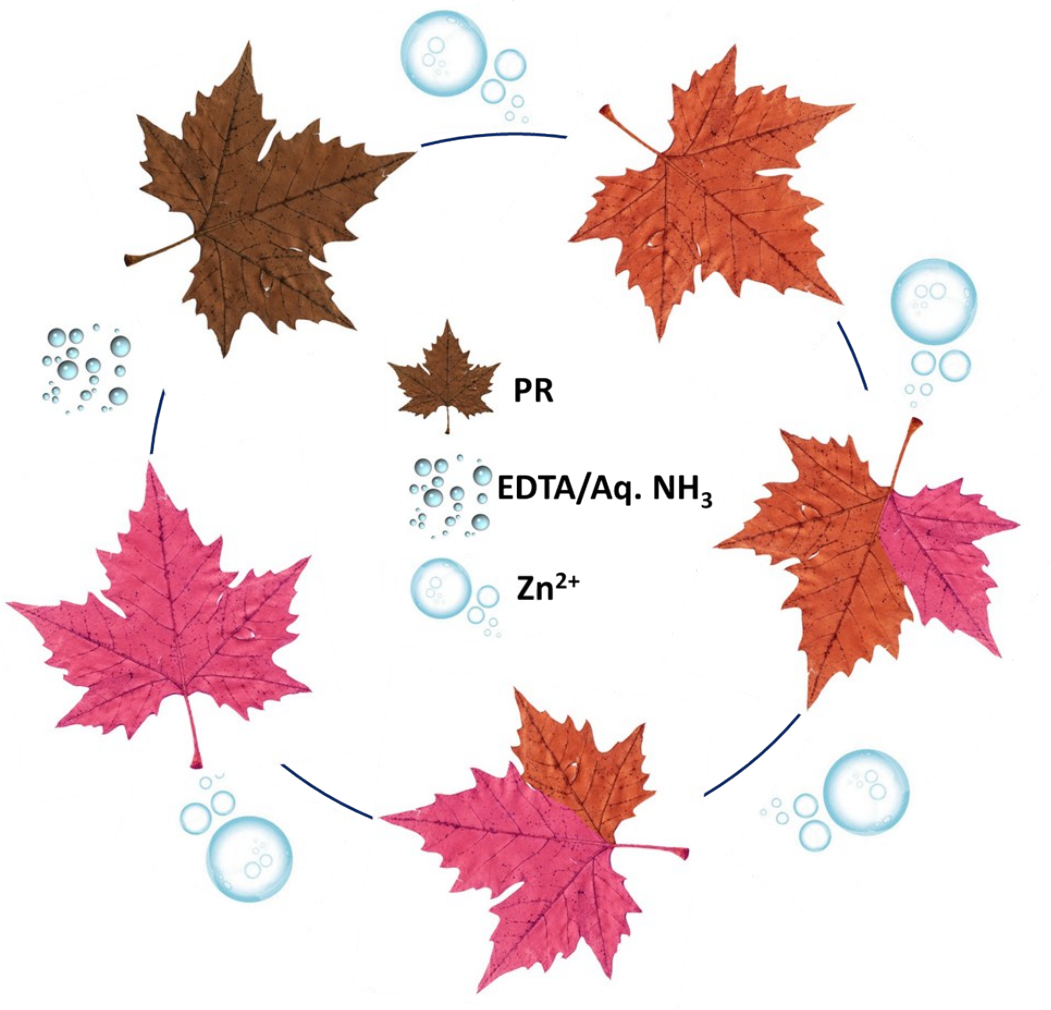

Graphical picture of PR and response with Zn^{2+}

Determination of fluorescence quantum yield

The quantum yield can be calculated as follows:

$$\Phi_D = \Phi_S X \frac{F_D}{F_S} X \frac{A_S}{A_D} X \frac{(n_D)^2}{(n_S)^2}$$

Where Φs is the fluorescence quantum yield of the standard (rhodamine B in ethanol, 0.49, 25°C), F_D and F_S are the integral areas of fluorescence intensity of the chromophore and the standard at the same excitation wavelength, respectively, A_D and A_S are the absorbances of the chromophore and the standard at the defined excitation wavelength, respectively, and n_S and n_D are the refractive indices at 25°C of the solvents of the standard (ethanol) and of the chromophore, respectively.

Synthesis of precursors and the probe

Synthetic routes of precursors and the probe are shown in Scheme 3-1 to 3-3. The following details the experimental conditions and steps.

Synthesis of RhB1

The intermediate **2** was synthesized by refluxing rhodamine B (4.8 g, 10 mmol) with excess ethylenediamine (5 mL) in ethanol until the solution lost its red color. After completion of the reaction, the solvent was removed by rotary evaporator. The resultant solid was extracted with dichloromethane and washed with water several times. The organic layer was separated and dried over anhydrous $MgSO_4$, and then the solvent was removed thoroughly. The resultant solid was washed with hot hexane (10 mL) and dried. Finally, the crude solid was purified by column chromatography (eluent, EA: Hexane = 1:3, R_f = 0.45) [13a,b].

Yield= 80%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.88–7.90 (d, 1H, ArH), 7.42–7.45 (m, 2H, ArH), 7.07–7.09 (d, 1H, ArH), 6.26–6.43 (m, 6H, ArH), 3.20–3.35 (q, 8H, $NC\underline{H_2}CH_3$), 3.17–3.18 (t, 2H, $NC\underline{H_2}CH_2N$), 2.41–2.43 (t, 2H, $NCH_2C\underline{H_2}N$), 0.85–1.55 (t, 12H, $NCH_2C\underline{H_3}$).
Molecular formula: $C_{30}H_{32}N_4O_2$ (484 g/mol).

Synthesis of Tris(pyrrolyl-α-methyl)amine (H_3tpa) (3)

Compound **3** was synthesized by following reported procedures[14]. Pyrrole (18 g), 37% aqueous formaldehyde (20 mL), NH_4Cl (4.78 g), ethanol (60 mL) and water (20 mL) were mixed in a 250 mL flask. The mixture was stirred at 40°C for 1 h. Then, it was poured into 200 mL of water and extracted three times with ethyl acetate . The combined organic phase was dried over anhydrous $MgSO_4$. After reaction, the solvent was removed by rotary evaporation. Remaining pyrrole impurities were removed by extracting the crude mixture in a mixture of ether (30 mL), THF (30 mL), and 20% $NaOH_{(aq)}$. The upper layer of the mixture was collected and concentrated. After evaporation, pure compound **3** was observed.

Yield= 77%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.2 (s, 3H, N$\underline{H}$), 6.7 (s, 3H, ArH), 6.12–6.16 (t, 3H, ArH), 6.07 (s, 3H, ArH), 3.58 (s, 6H, $NC\underline{H_2}$).
Molecular formula: $C_{15}H_{18}N_4$ (254 g/mol).

Synthesis of Tris(5-formylpyrrol-2-ylmethyl)amine (H_3tpa^{CO}) (4)

The intermediate **4** was acquired from the Vilsmeier−Haack formylation of **3**. The intermediate **3** (2 g) was dissolved in dimethylformamide (40 mL) and cooled to -10°C. $POCl_3$ (4.4 mL) was added dropwise over 10 minutes with vigorous stirring, and the solution became dark red. The mixture was removed from the ice bath and heated to 60°C for 2 h. An aqueous NaOH solution (6.00 g) were prepared and poured into the mixture. Then, the mixture was heated to 80°C for 1 h. After the reaction, it was cooled to room temperature and extracted with DCM:chloroform (1:1). The solvent was removed by rotary evaporator, yielding an oily crude product. This oily crude product was stirred with a large excess of acetonitrile for 16 h to precipitate the product **4**. The precipitate was filtered, washed with acetonitrile and dried. Product **4** was obtained as pale brown solid [15].

Yield= 73%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 11.19 (s, 3H, C<u>H</u>O), 9.39 (s, 3H, N<u>H</u>), 6.91–6.92 (d, 3H, ArH), 6.17–6.18 (d, 3H, ArH), 3.69 (s, 6H, NC<u>H$_2$</u>).
FTIR (KBr, ν_{max}/cm^{-1}): 3457 (NH), 2766 (CHO), 1612 (CO).
Molecular formula: $C_{18}H_{18}N_4O_3$ (338.36 g/mol).

Synthesis of Pyrryl-Rhodamine Chemosensor (PR)

A solution of ethylenediaminyl Rhodamine B (1.18 g, 0.74 mmol) in anhydrous ethanol (50 mL) was added to the intermediate **4** (0.25 g, 2.44 mmol) and stirred for 2 days at 80°C. After completion of the reaction, the solvent was removed by rotary evaporation. The crude product was further purified and isolated by column chromatography (silica gel, 100–200 mesh) using methanol in DCM (10% v/v) as eluent.
Yield= 70%. ^{1}H-NMR (400 MHz, DMSO) δ: 10.98–11.95 (s, 3H, N<u>H</u>), 7.72–7.90 (s, 3H, C<u>H</u>N), 7.41–7.71 (m, 9H, ArH), 6.99–7.10 (d, 3H, ArH), 6.24–6.39 (m, 21H, ArH), 5.92–5.97 (d, 3H, ArH), 3.12–3.50 (m, 42H, NC<u>H$_2$</u>), 1.01–1.10 (t, 36H, CH_2C<u>H$_3$</u>). ^{13}C-NMR (400 MHz, $CDCl_3$) δ: 168 (<u>C</u>O), 154 (<u>C</u>HN), 149 (Ar), 134 (ArH), 132 (Ar), 129 (ArH), 128 (ArH), 127 (ArH), 124 (ArH), 122 (ArH), 118 (ArH), 118 (ArH), 116 (Ar), 98 (ArH), 78 (Ar), 77 (Ar), 65 (N<u>C</u>-Ar), 50 (N<u>C</u>H$_2$), 44 (N<u>C</u>H$_2$CH$_3$), 42 (CHN-<u>C</u>H$_2$), 41 (N<u>C</u>H$_2$), 17 (CH_2<u>C</u>H$_3$).
Mass spectrum (FAB, m/z): 1739 (M), Molecular formula: $C_{108}H_{120}N_{16}O_6$ (1738 g/mol).

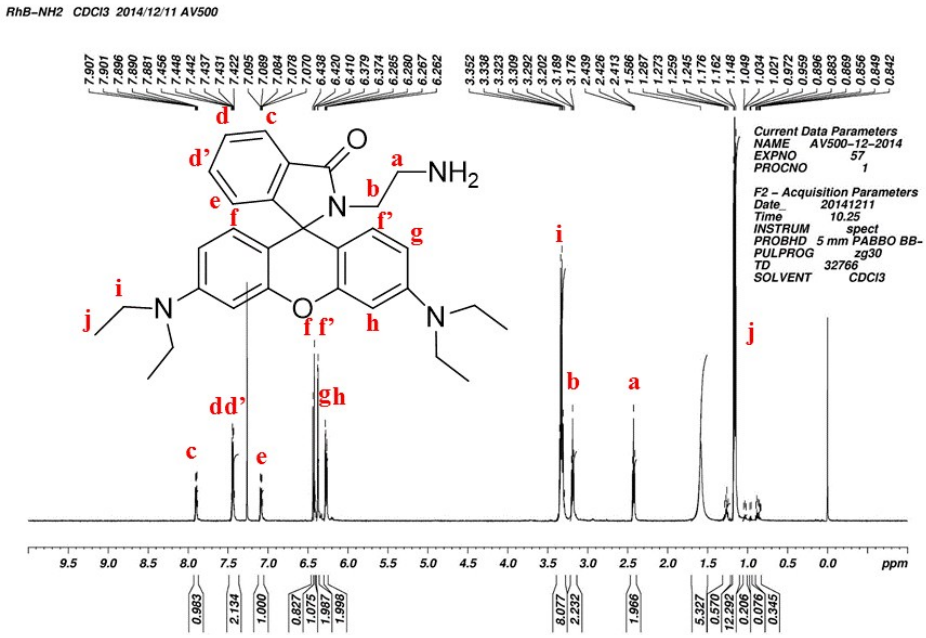

Fig. S1 ^{1}H-NMR spectrum of compound RhB1 in $CDCl_3$

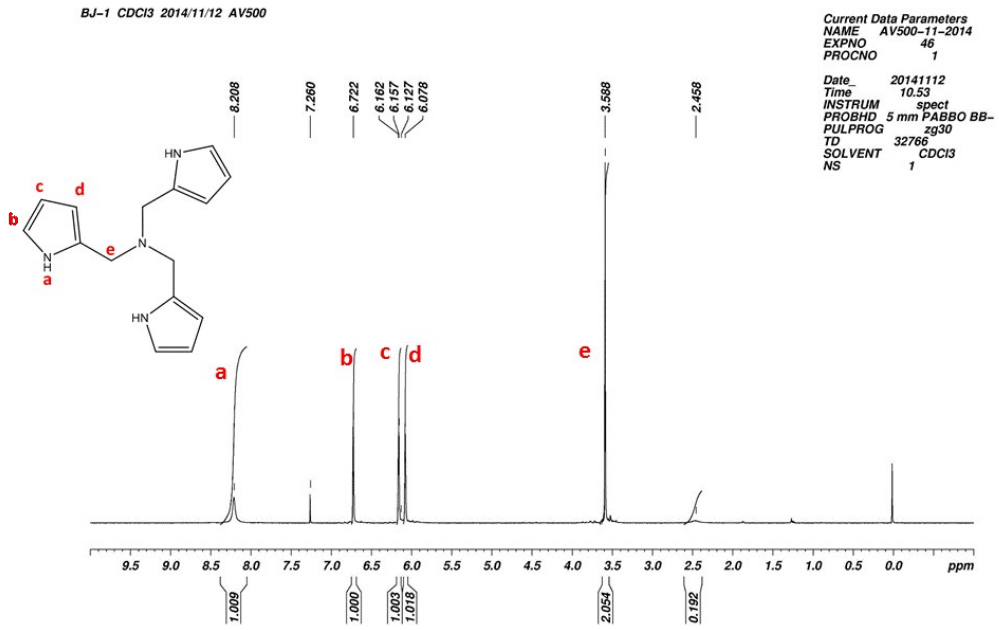

Fig. S2. ^{1}H-NMR spectrum of compound H_3tpa in $CDCl_3$.

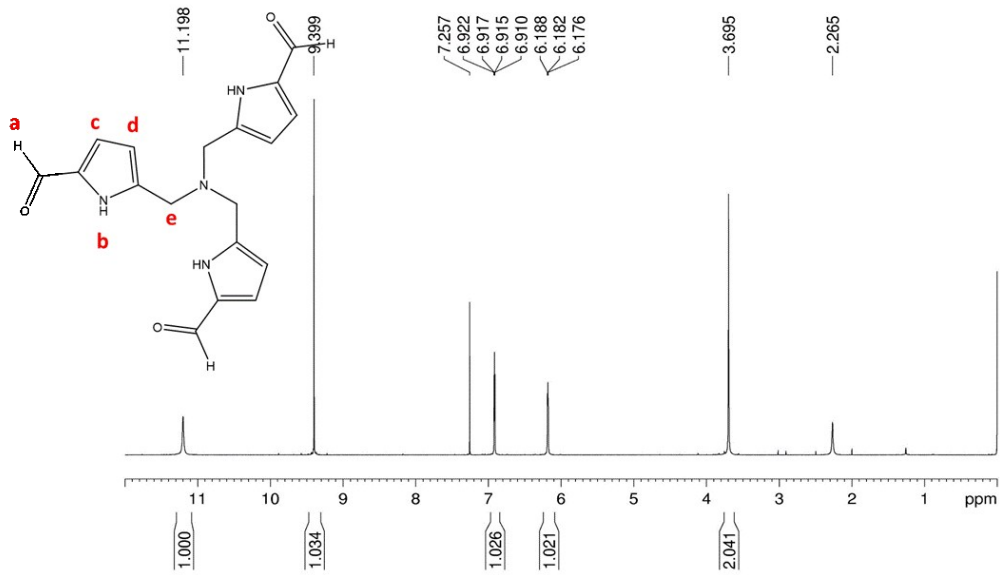

Fig. S3. ^{1}H-NMR spectrum of compound H_3tpa^{CO} in $CDCl_3$.

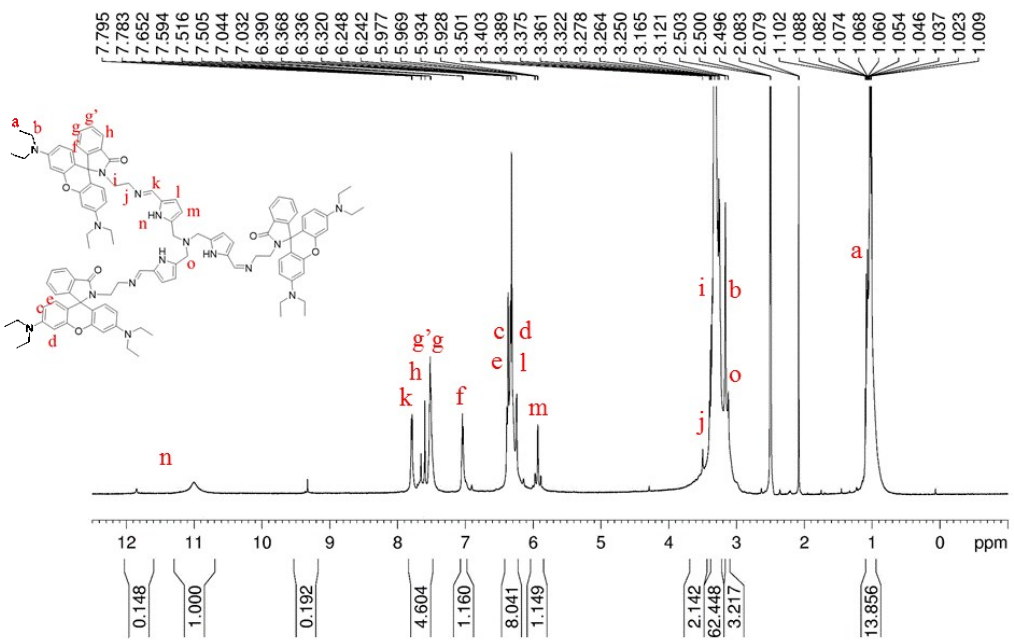

Fig. S4. ^{1}H-NMR spectrum of probe the **PR** in DMSO-d_6.

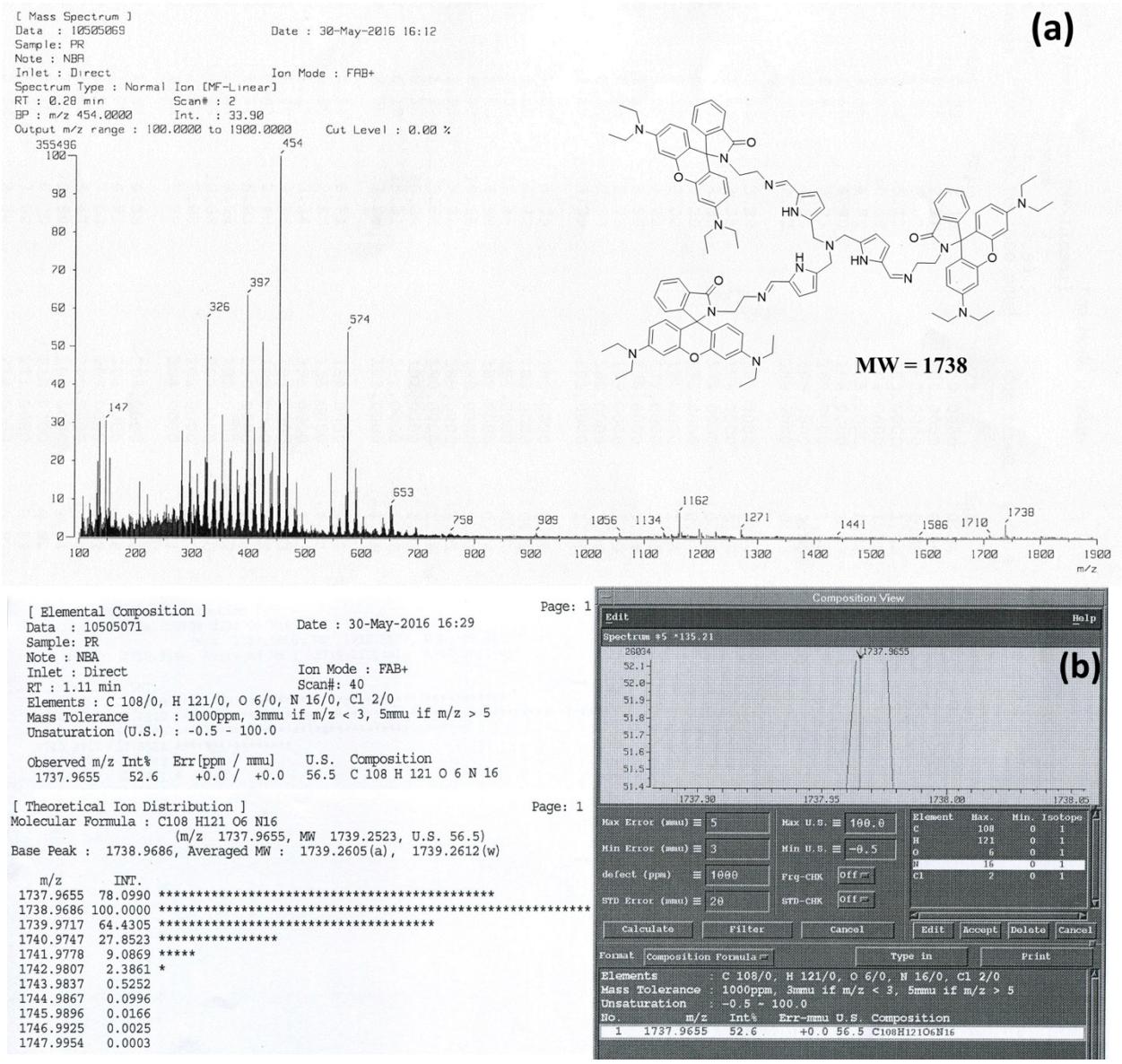

Fig. S5. Mass spectrum of the probe **PR** (a) low resolution (b) high resolution mass spectral data with spectrum

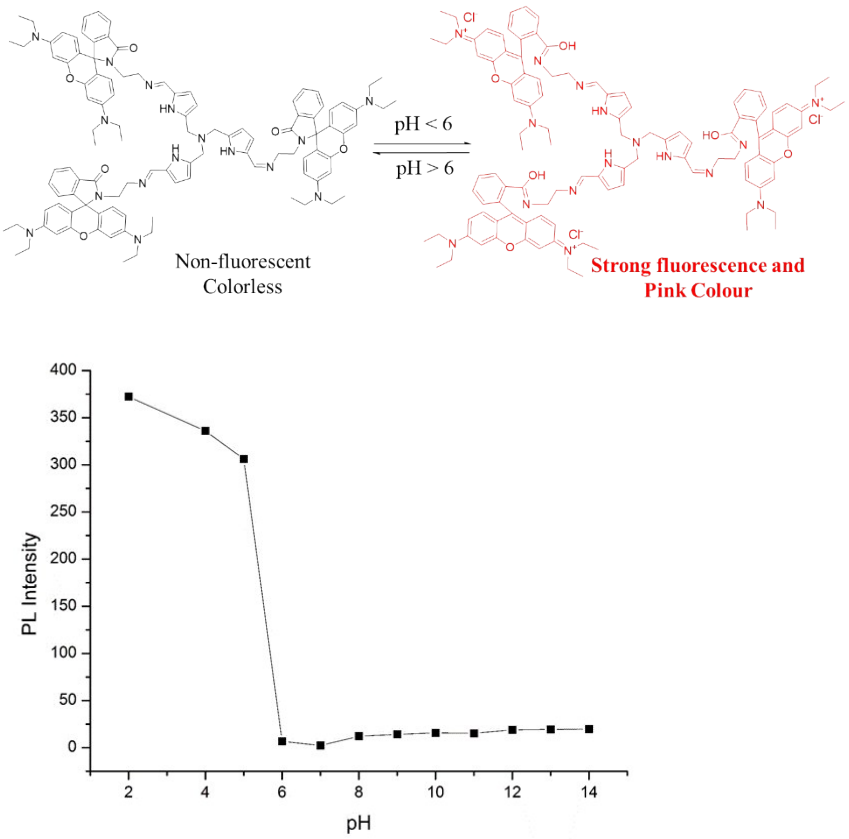

Fig. S6. Effect of pH on fluorescence intensity of **PR** in CH_3CN:H_2O (1:1 v/v) at 577 nm. The pH of the solutions was adjusted by HCl (1 M) and NaOH (1 M), λ_{ex} = 520 nm

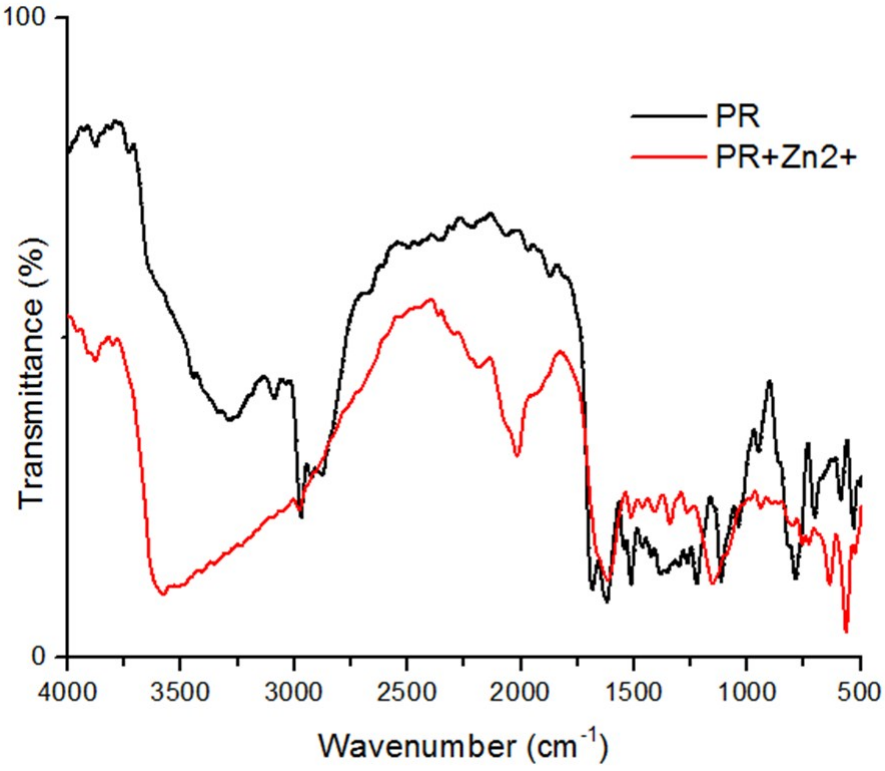

Fig. S7. FT-IR spectra of **PR** and PR-Zn^{2+} complex

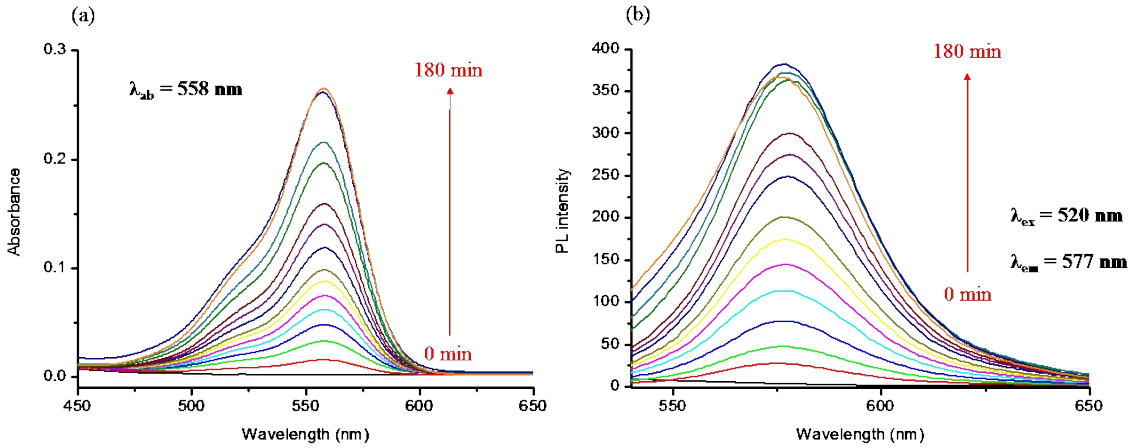

Fig. S8. Time dependent UV-vis spectra (a) and PL spectra (b) of **PR** with 100 equivalents of Zn^{2+} in CH_3CN/water (1:1 v/v).

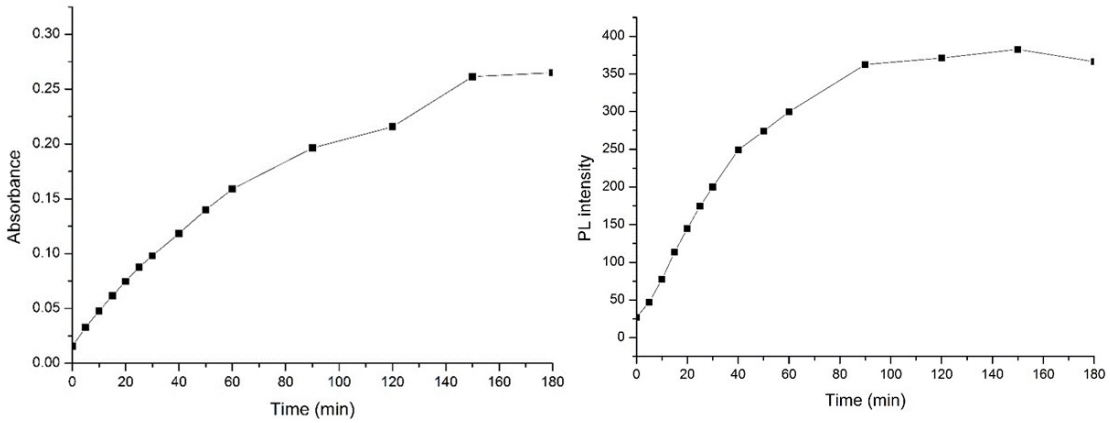

Fig. S9. Plots of absorbance (a) and fluorescence intensity (b) time dependence

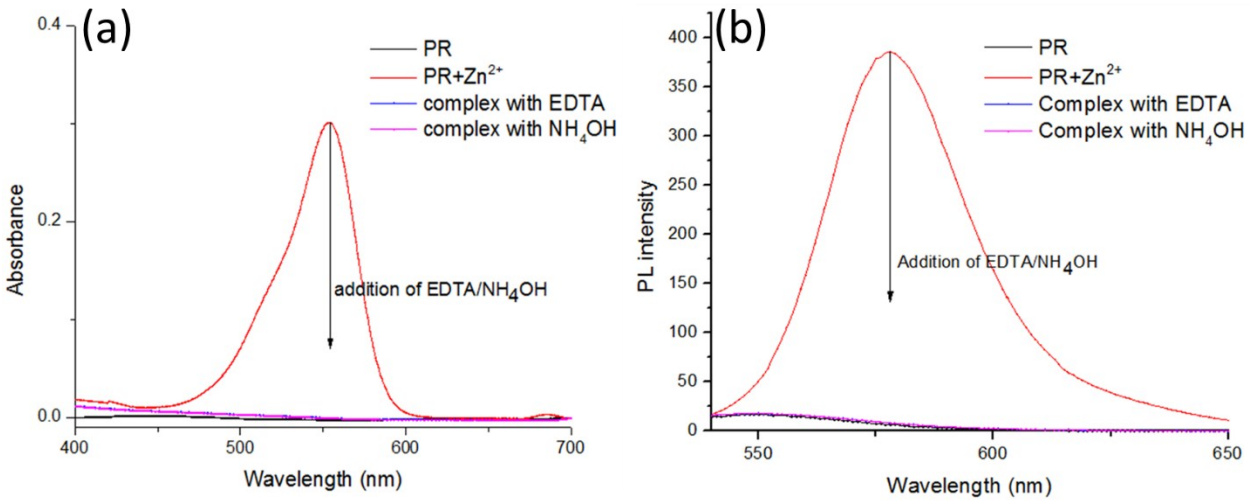

Fig. S10. Reversible process in UV-vis spectra (a) and PL spectra (b).

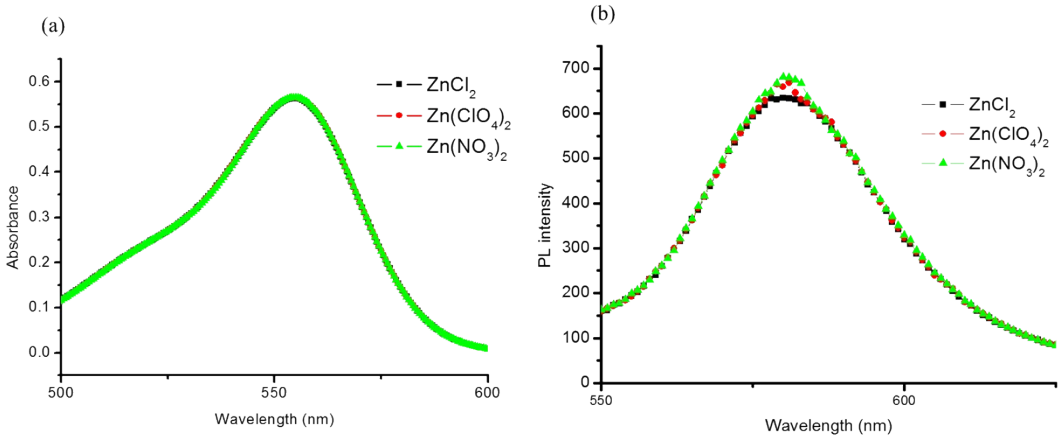

Fig. S11. (a) UV-vis spectra of **PR** in the presence of various zinc salts.

(b) PL spectra of **PR** in the presence of various zinc salts.

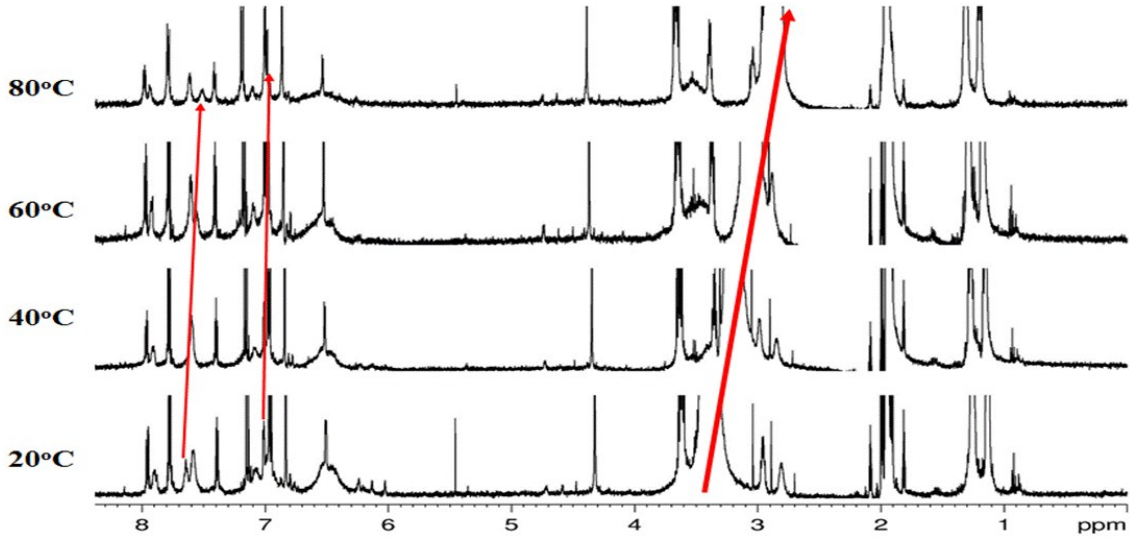

Fig. S12. Temperature dependent ^{1}H-NMR spectra of **PR** with Zn^{2+} over temperatures ranging from 20 to 80°C

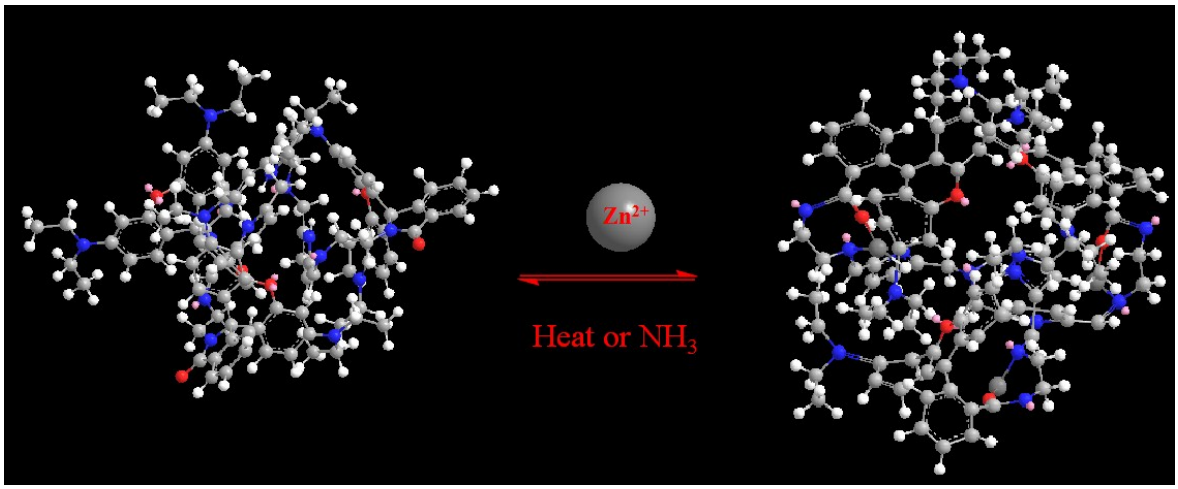

Fig. S13. Optimized structures of **PR** and **PR-Zn^{2+}**.

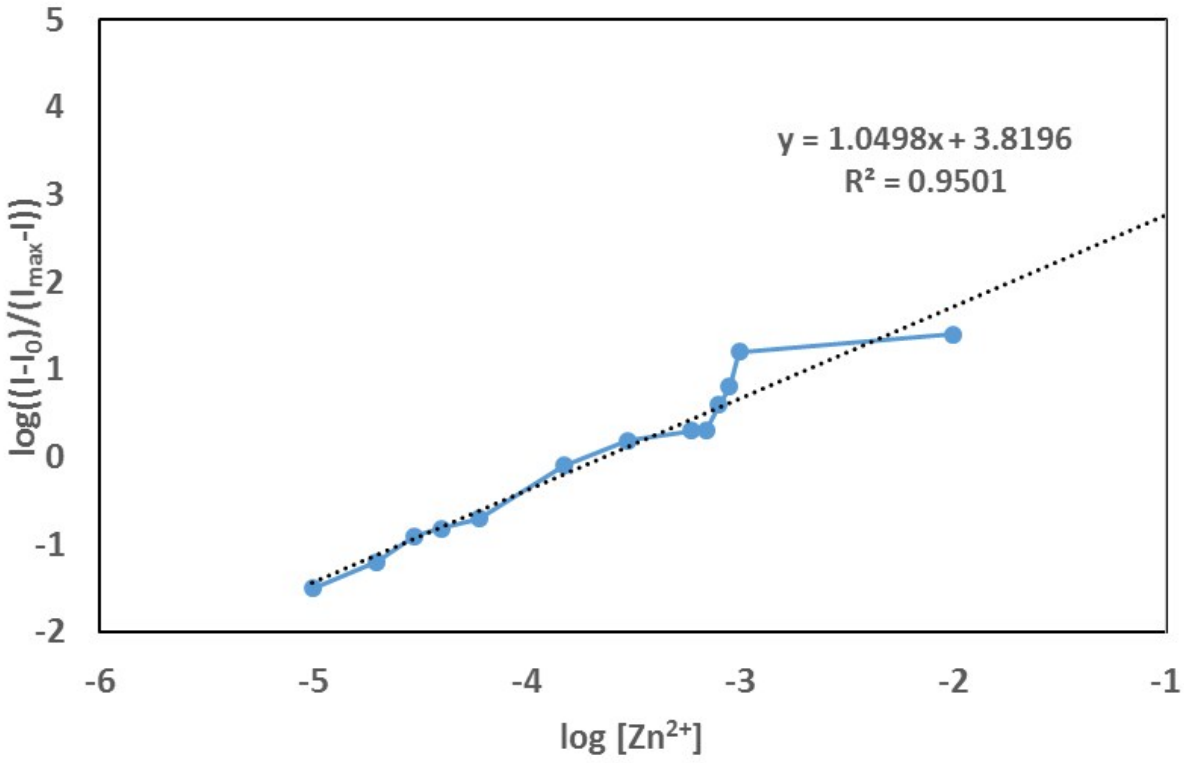

Fig. S14 Hill Plot of fluorescence probe PR with Zn^{2+}