

**Electronic Supporting Information**

**Unusual Red-Orange Emission from Rhodamine Derived  
Polynorbornene while Selectively Binding to Fe<sup>3+</sup> ions in the Aqueous  
Environment**

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## Experimental section

### Materials:

Rhodamine B, ethylenediamine and Cis-5-Norbornene-exo-2,3-dicarboxylic anhydride, toluene, dichloromethane (DCM), CD<sub>3</sub>CN were purchased from Aldrich, Acros, Merck and used as received. DCM was distilled over calcium hydride and used for reactions. The stock solutions of metal salts used were CdCl<sub>2</sub>, HgCl<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, FeCl<sub>2</sub>·4H<sub>2</sub>O, CuSO<sub>4</sub>·5H<sub>2</sub>O, NaCl, KCl, MgCl<sub>2</sub>, NiCl<sub>2</sub>·6H<sub>2</sub>O, CoCl<sub>2</sub>, ZnCl<sub>2</sub>, SnCl<sub>2</sub>·2H<sub>2</sub>O, FeCl<sub>3</sub>. Deionised water was used to make the metal salt solutions.

### Methods:

#### NMR Characterization:

NMR spectroscopy was carried out on a Bruker 500 MHz spectrometer using CDCl<sub>3</sub>, CD<sub>3</sub>CN as a solvent. NMR spectra of solutions in CDCl<sub>3</sub>, CD<sub>3</sub>CN were calibrated to trimethylsilane as internal standard ( $\delta$ H 0.00).

#### Fluorescence Measurements:

Fluorescence emission spectra were recorded on a Fluorescence spectrometer (Horiba Jobin Yvon, Fluoromax-4, 250-900 nm). Emission spectra for all solutions were measured with an excitation wavelength of 520 nm. Typically the slit widths were 2 nm and the scan rate was 400 nm/min. Slit widths and scan rates were adjusted to allow adequate intensity, if needed.

#### UV-Vis experiments:

UV-visible absorption measurements were carried out on Perkin-Elmer Lambda35 UV-Vis spectrometer, with a scan rate of 480 nm/min. The absorption spectra for all solutions were measured in a quartz cell of 1 cm.

#### ESI-MS Analysis:

HRMS analyses were performed with Q-TOF YA263 high resolution (Waters Corporation) instruments by (+)ve mode electrospray ionization.

#### Advanced Polymer Chromatography (APC)

Molecular weights and molecular weight distributions [dispersity ( $\bar{M}_w/\bar{M}_n$ )] of polymers were determined by Waters ACQUITY APC. The instrument contains a 1500 series HPLC pump, an ACQUITY refractive index detector, and one ACQUITY APC XT 2002 5  $\mu$ m (4.6  $\times$  7.5 mm) column in THF at 45 °C at 0.25 mL/min flow rate. Poly (methyl methacrylate) standards were used to calibrate the instrument.

#### Sample preparation for UV-Vis and fluorescence studies:

The stock solutions of **NR** and **PNR** were initially prepared in CH<sub>3</sub>CN medium and further dilution was made accordingly for different experiments. For UV-Vis and fluorescence titration studies, solutions of fixed concentration of **NR** and **PNR** were prepared in different vials and treated with increasing concentration of Fe<sup>3+</sup> ion. In case of **NR** all the sets were incubated for 30 minutes and for **PNR** the incubation time was 3 minutes. Further, the UV-Vis and fluorescence spectral measurements were performed. For the selectivity experiments fixed concentration of NR (20  $\mu$ M) was treated with different metal ions of 50  $\mu$ M concentration and the corresponding UV-Vis and fluorescence spectra were measured.

## Synthesis and characterization

### Synthesis of Compound 1:

In a 250 round bottom flask Rhodamine B (1 g, 2 mmol) was added and dissolved in 30 mL of EtOH. After stirring for 10 minutes, the mixture was charged with 1.3 mL of ethylenediamine and the mixture was stirred in refluxing condition for overnight. After completion of the reaction, solvent was evaporated and the residue was dissolved in DCM. Organic layer was washed with water followed by brine solution for several times. Organic layers were collected and dried over anhydrous sodium sulphate and evaporated in reduced pressure. Crude product was purified using column chromatography. Obtained product was dried well in vacuum to get **Compound 1**. **Yield:** 0.9 g (89%).

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz), δ (ppm):** 1.13(t, 12H), 2.18(s, 2H), 2.44(t, 2H), 3.19(t, 2H), 3.32(q, 8H), 6.24-6.26(dd, 2H), 6.36(d, 2H), 6.40(s, 1H), 6.41(s, 1H), 7.05-7.06(m, 1H), 7.40-7.41(m, 2H), 7.86-7.87(m, 1H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz), δ (ppm):** 12.47, 40.63, 43.3, 44.2, 64.97, 97.66, 105.41, 108.1, 122.65, 123.71, 127.94, 128.51, 130.99, 132.33, 148.74, 153.17, 153.38, 168.65.

### Synthesis of NR:

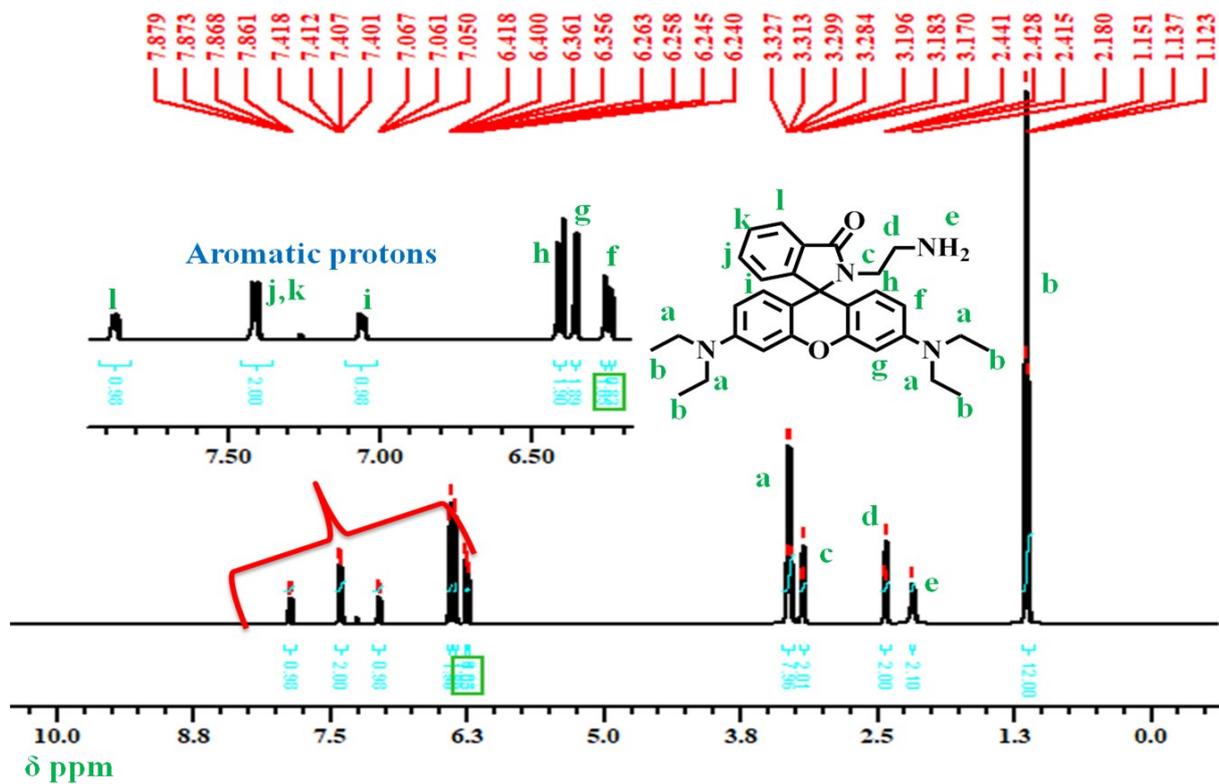
0.8 g (1.6 mmol) of compound 1 was dissolved in 30 mL of toluene and stirred for 30 minutes. Cis-5-Norbornene-exo-2,3-dicarboxylic anhydride (0.27 g, 1.6 mmol) was added to the stirring mixture and kept in refluxing condition for 12 hours. Completion of the reaction was monitored using TLC. After completion of the reaction, excess solvent was removed using reduced pressure. The solid was dissolved in DCM and washed with water for several times followed by brine wash. Organic layers were collected and dried over anhydrous sodium sulphate and the crude was purified by column chromatography using hexane/ethyl acetate as eluent to obtain NR as faint pink crystalline solid. **Yield:** 0.8 g (77%).

**<sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz), δ (ppm):** 1.11(t, 2H), 1.23-1.39(m, 2H), 2.38(s, 2H), 3.01(d, 2H), 3.14-3.16(t, 2H), 3.31-3.39(m, 10H), 6.21(s, 2H), 6.33-6.38(m, 6H), 6.94-6.96(m, 1H), 7.47-7.49(m, 2H), 7.79(d, 1H).

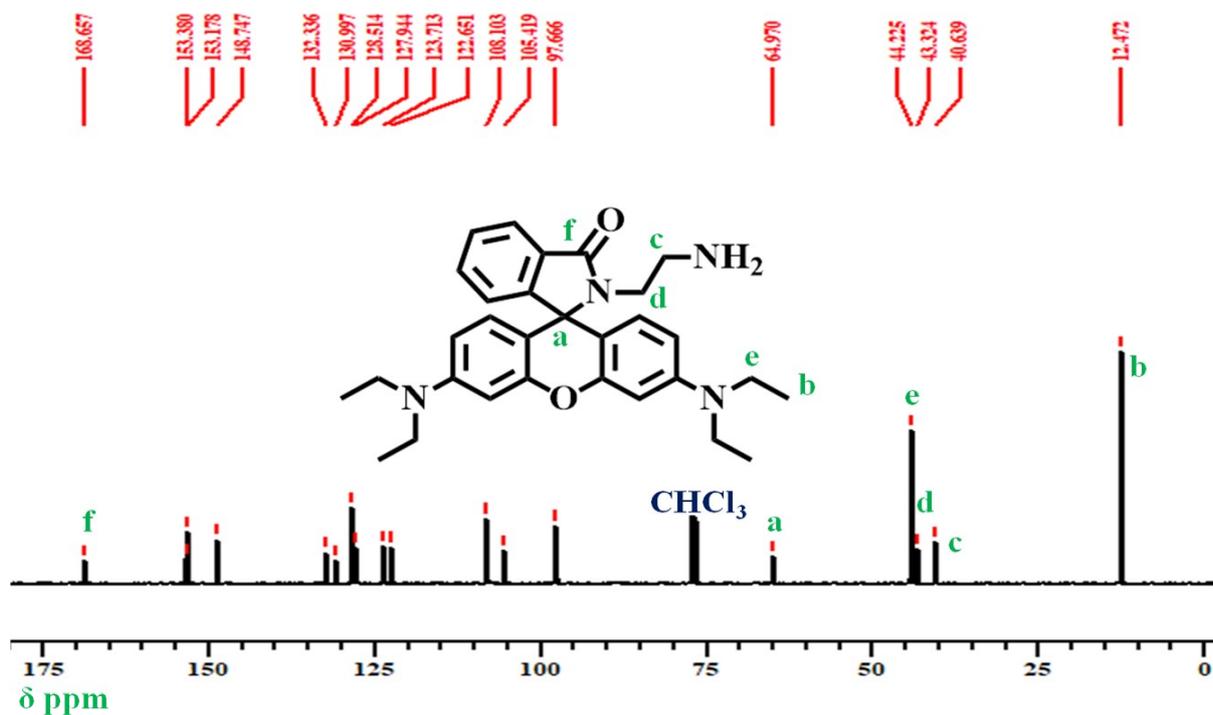
**<sup>13</sup>C NMR (CD<sub>3</sub>CN, 500 MHz), δ (ppm):** 12.89, 37.73, 38.79, 43.52, 44.95, 45.86, 48.70, 65.81, 98.41, 106.3, 109.3, 123.3, 124.5, 129.2, 129.6, 131.8, 133.6, 138.6, 149.9, 154.3, 154.9, 169.2, 178.6. ESI-MS calculated for C<sub>39</sub>H<sub>42</sub>N<sub>4</sub>O<sub>4</sub> [M+H]<sup>+</sup> 631.78 found 631.85.

### Synthesis of PNR:

100 mg of NR was taken in a 15 mL oven dried vial followed by the addition of 1 mL of dry DCM, under inert condition. After that 2 mg of Grubbs' 2<sup>nd</sup> generation catalyst (G2) was taken separately in a vial under N<sub>2</sub> atmosphere and dissolved in 0.5 ml of dry DCM. The catalyst solution was added to the reaction mixture and kept in stirring condition for 12 hours. The polymerization was quenched using ethyl-vinyl ether and polymer (PNR) was precipitated out in diethyl ether. Vanishing of 6.21 ppm peak in <sup>1</sup>H NMR spectroscopy, confirmed the polymer formation. APC traces also confirmed the homopolymer (PNR) formation with M<sub>n</sub>=35341, PDI=1.01.



**Figure S1:**  $^1\text{H}$ NMR spectrum of Compound 1 in  $\text{CDCl}_3$ .



**Figure S2:**  $^{13}\text{C}$ NMR spectrum of Compound 1 in  $\text{CDCl}_3$ .

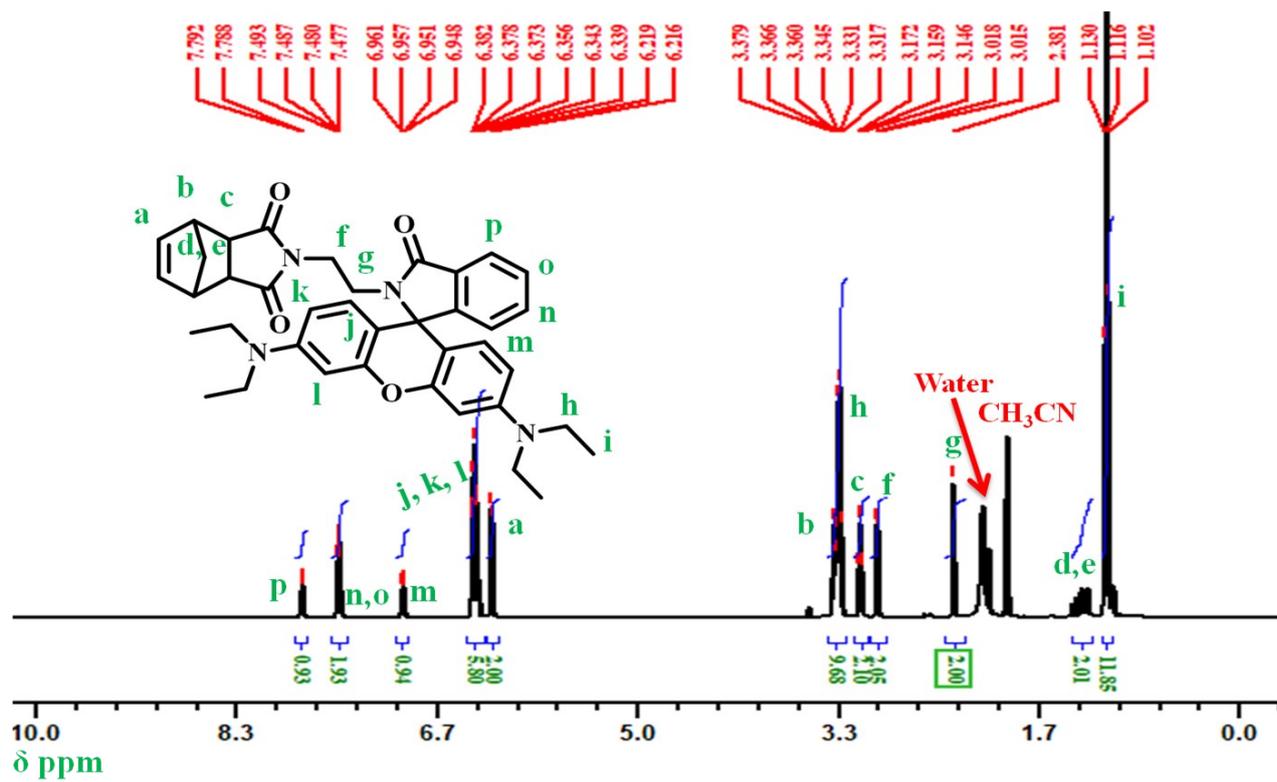


Figure S3: <sup>1</sup>H NMR spectrum of NR in CD<sub>3</sub>CN.

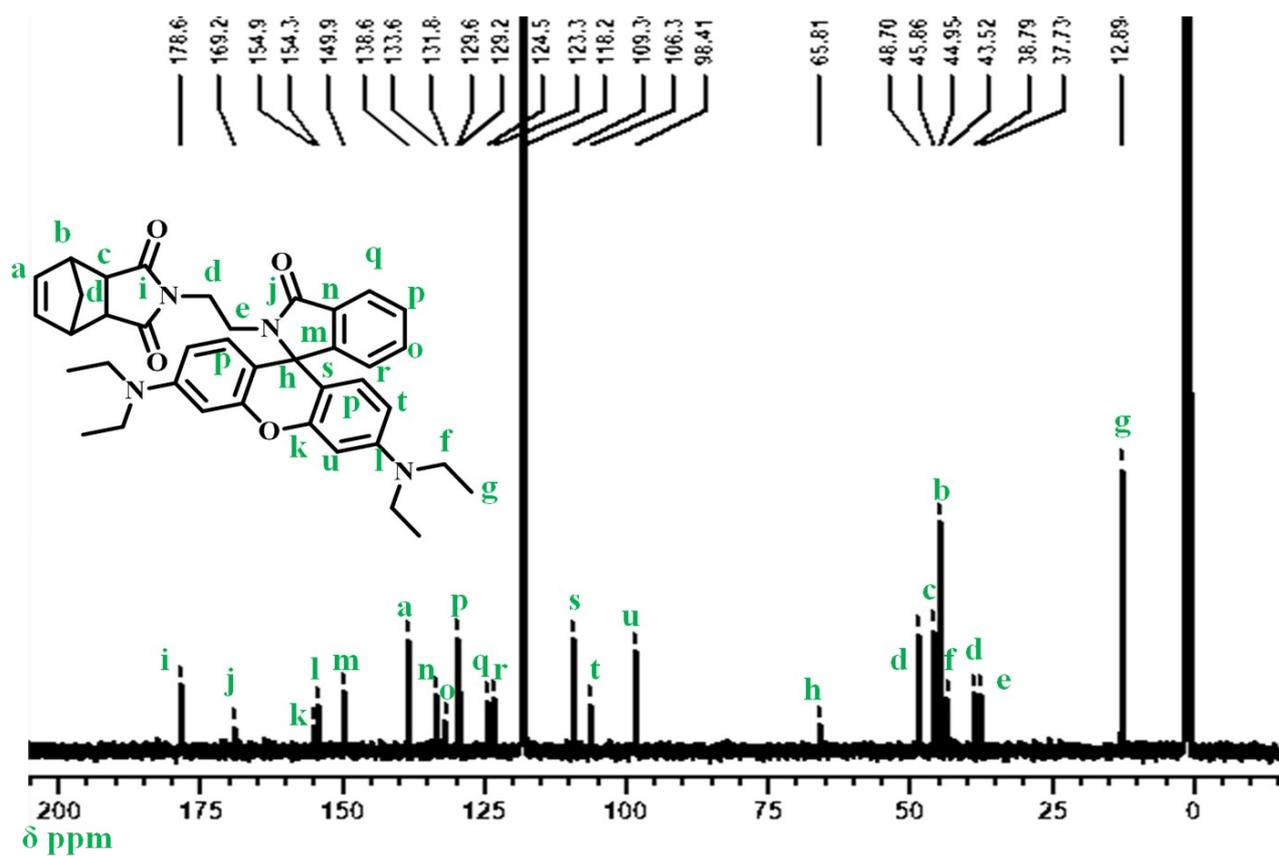


Figure S4:  $^{13}\text{C}$ NMR spectrum of NR in  $\text{CD}_3\text{CN}$ .

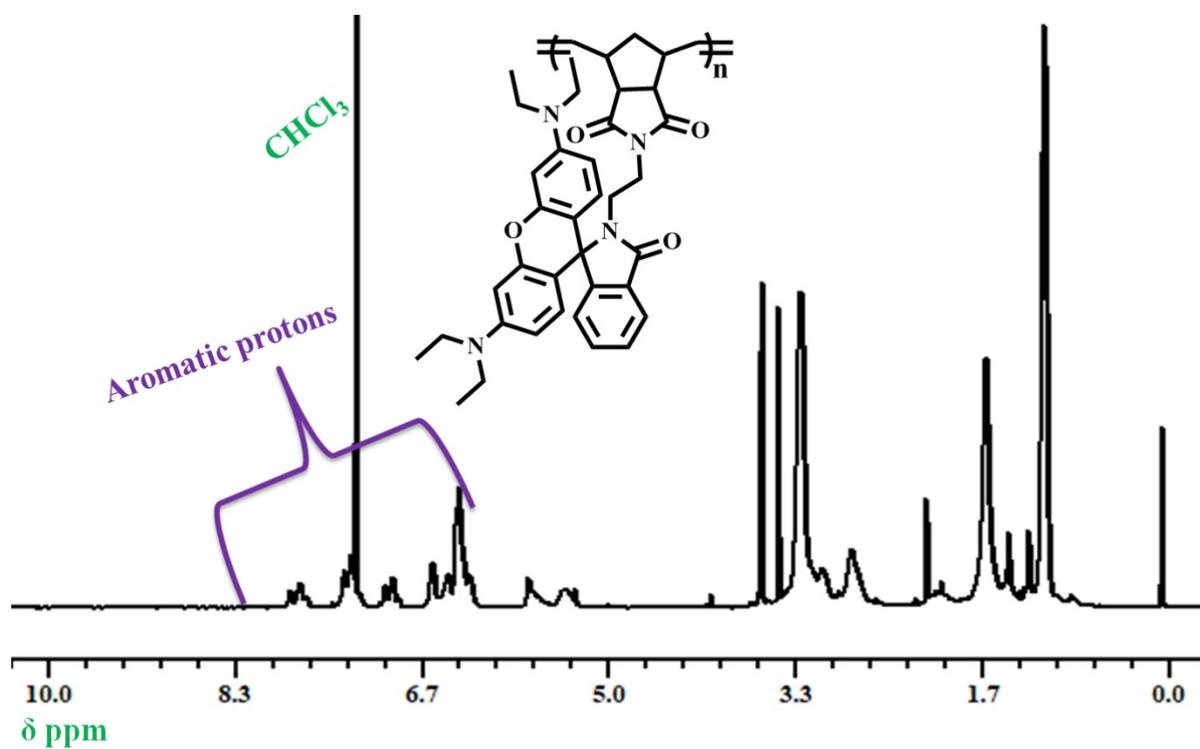
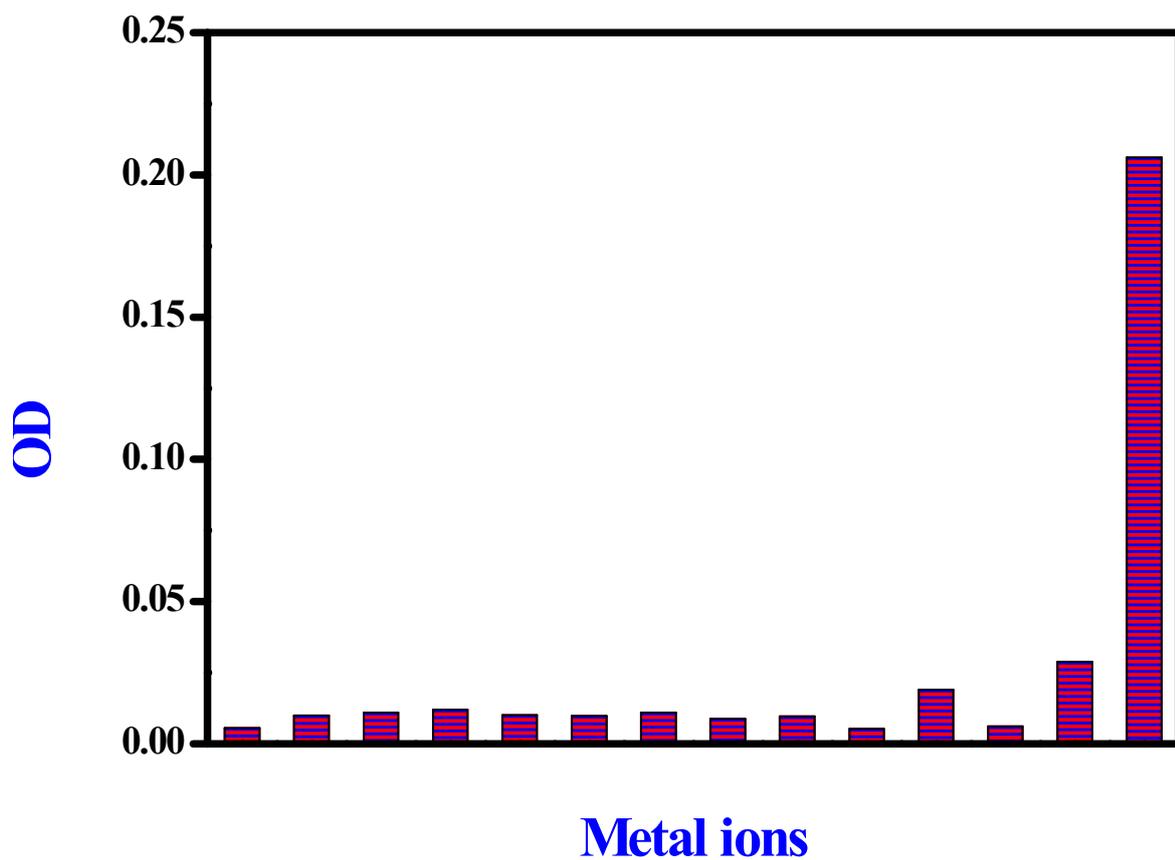
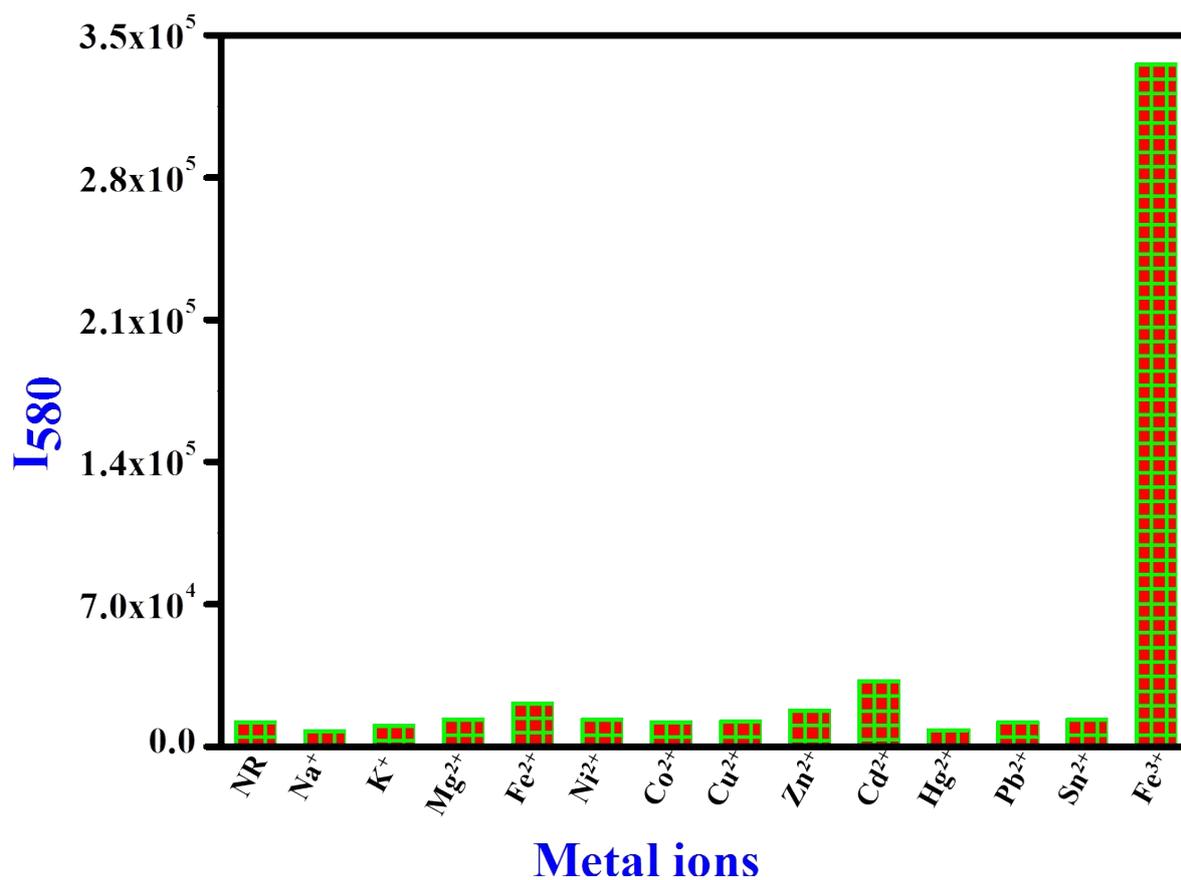


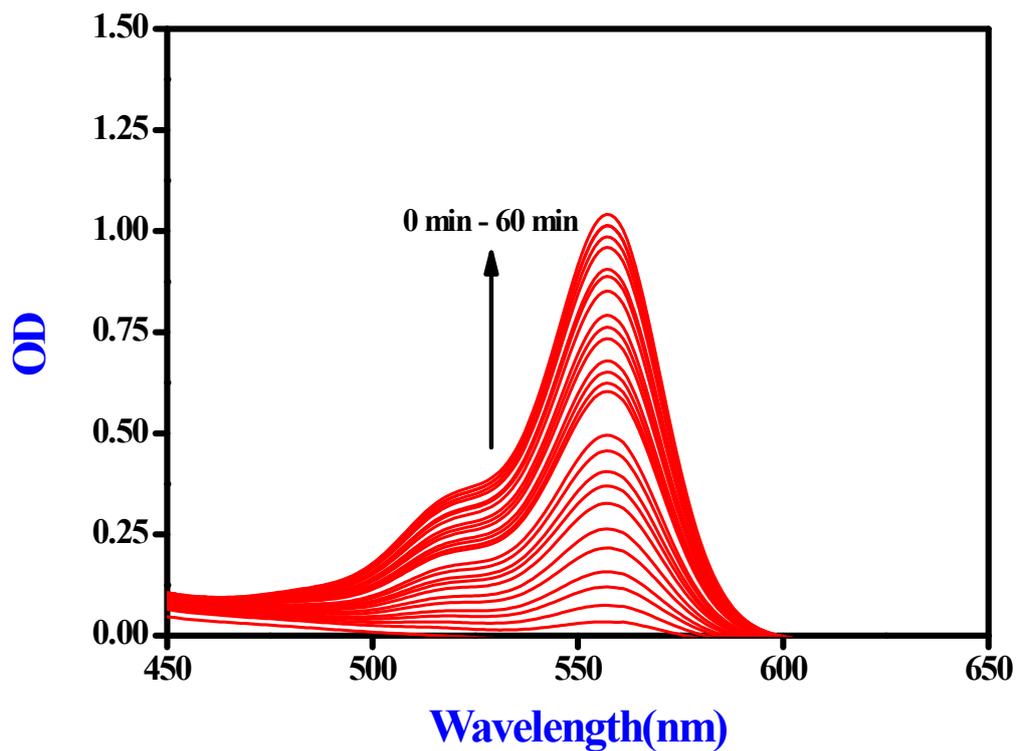
Figure S5:  $^1\text{H}$ NMR spectrum of PNR in  $\text{CDCl}_3$



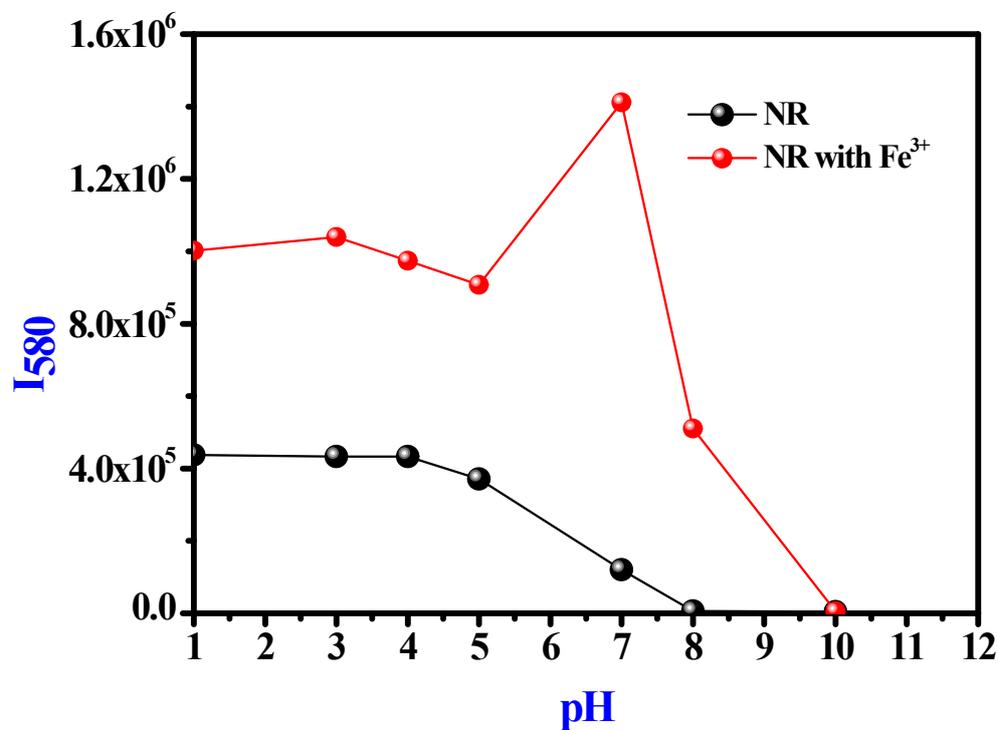
**Figure S6:** Bar plot of absorbance change of NR (20 μM) in presence of different metal ions like K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Sn<sup>2+</sup>, Fe<sup>3+</sup>.



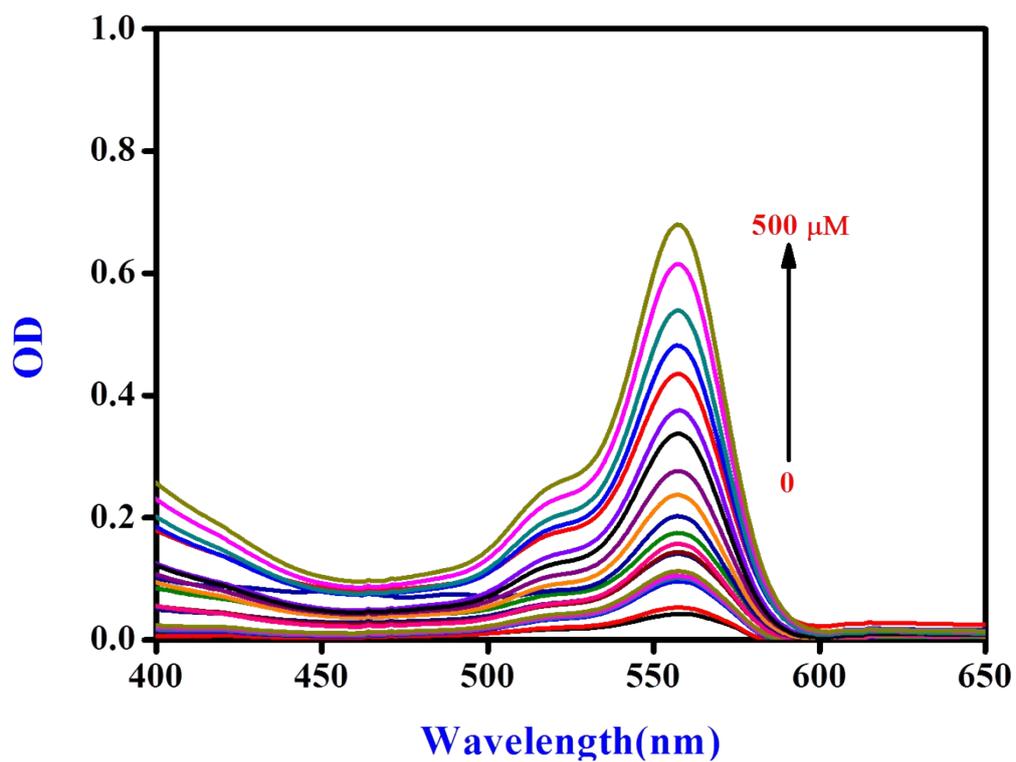
**Figure S7:** Bar plot for fluorescence intensity change of NR (20 μM) in presence of different metal ions like K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Sn<sup>2+</sup>, Fe<sup>3+</sup> in 1:1 CH<sub>3</sub>CN/H<sub>2</sub>O. ( $\lambda_{\text{ex}}$ =520 nm, Slit=2 nm).



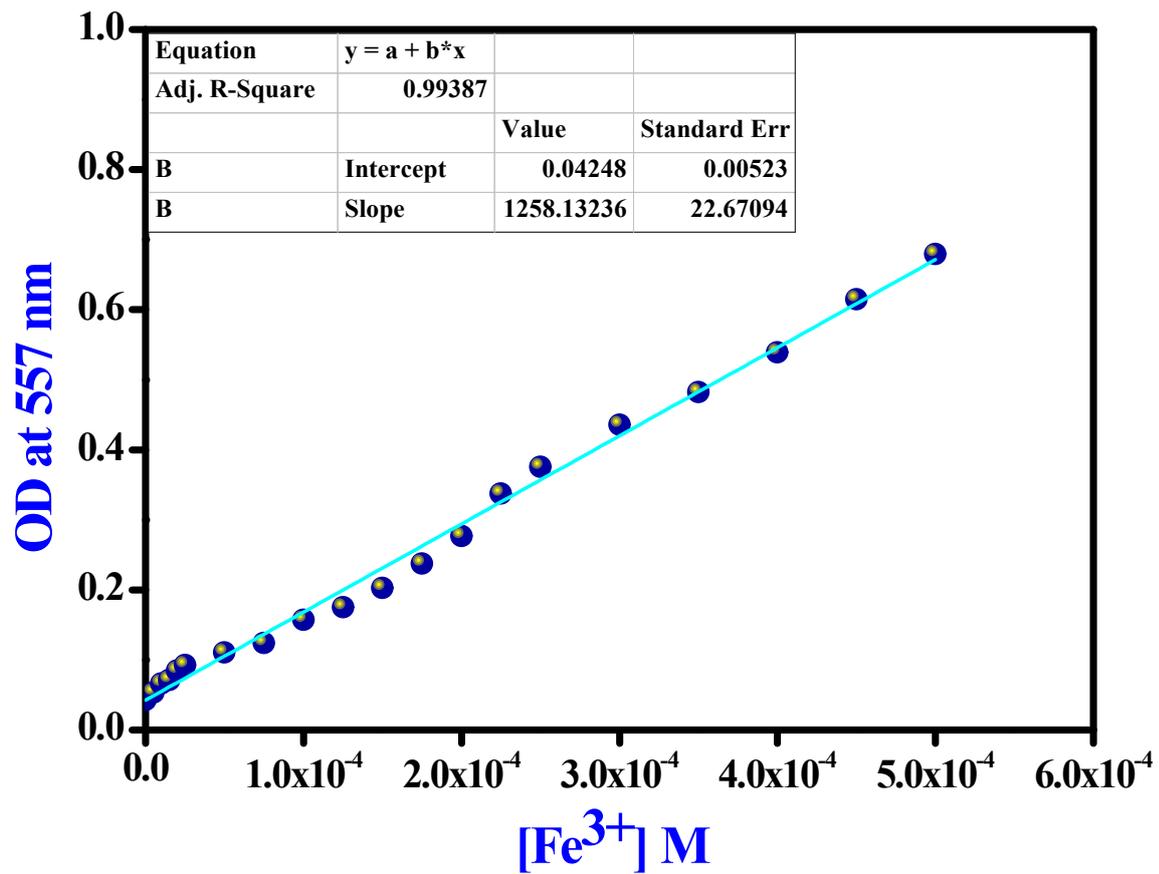
**Figure S8:** Change in absorbance of NR in presence of  $\text{Fe}^{3+}$  ion with time (minutes) in 1:1  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ .



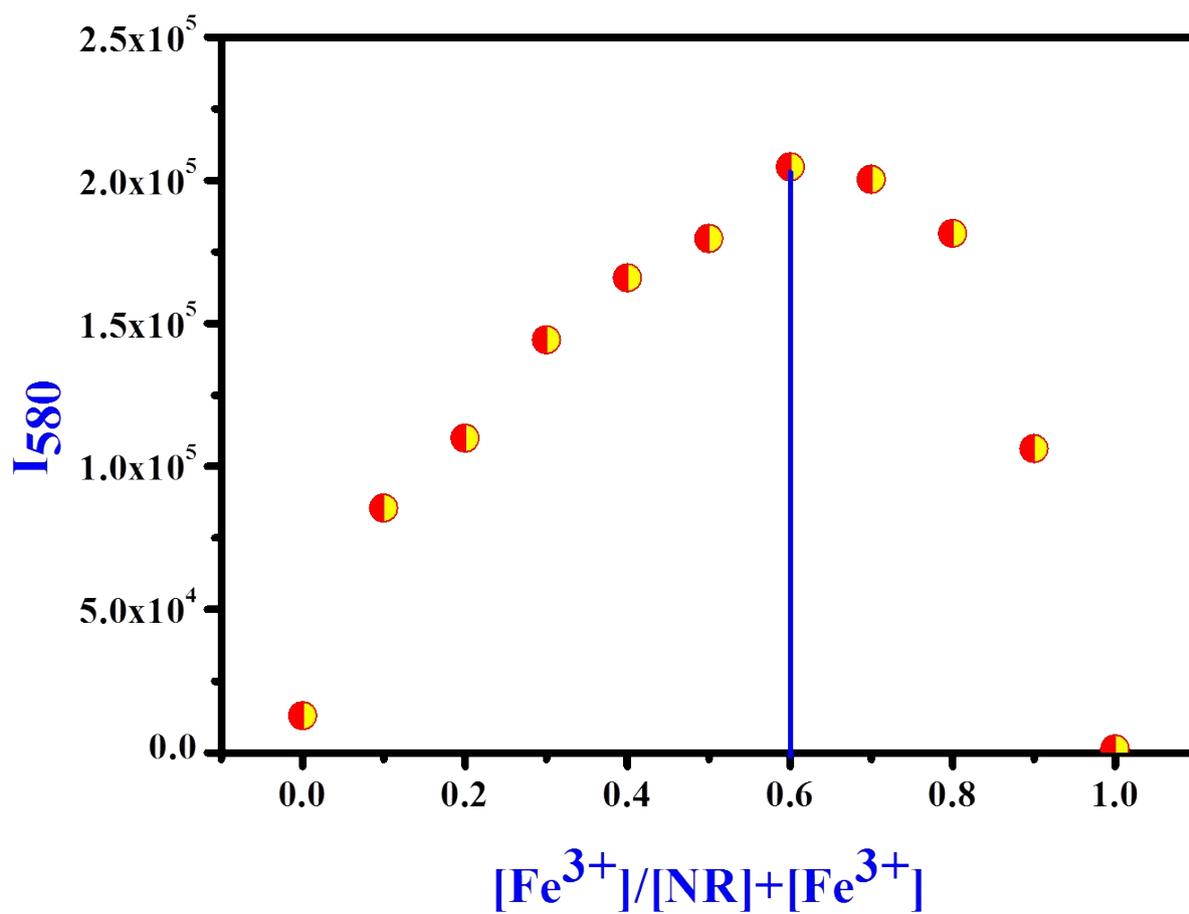
**Figure S9:** pH dependent study of NR in absence and presence of  $\text{Fe}^{3+}$  ion in 1:1  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ . ( $\lambda_{\text{ex}}=520$  nm, Slit=2 nm).



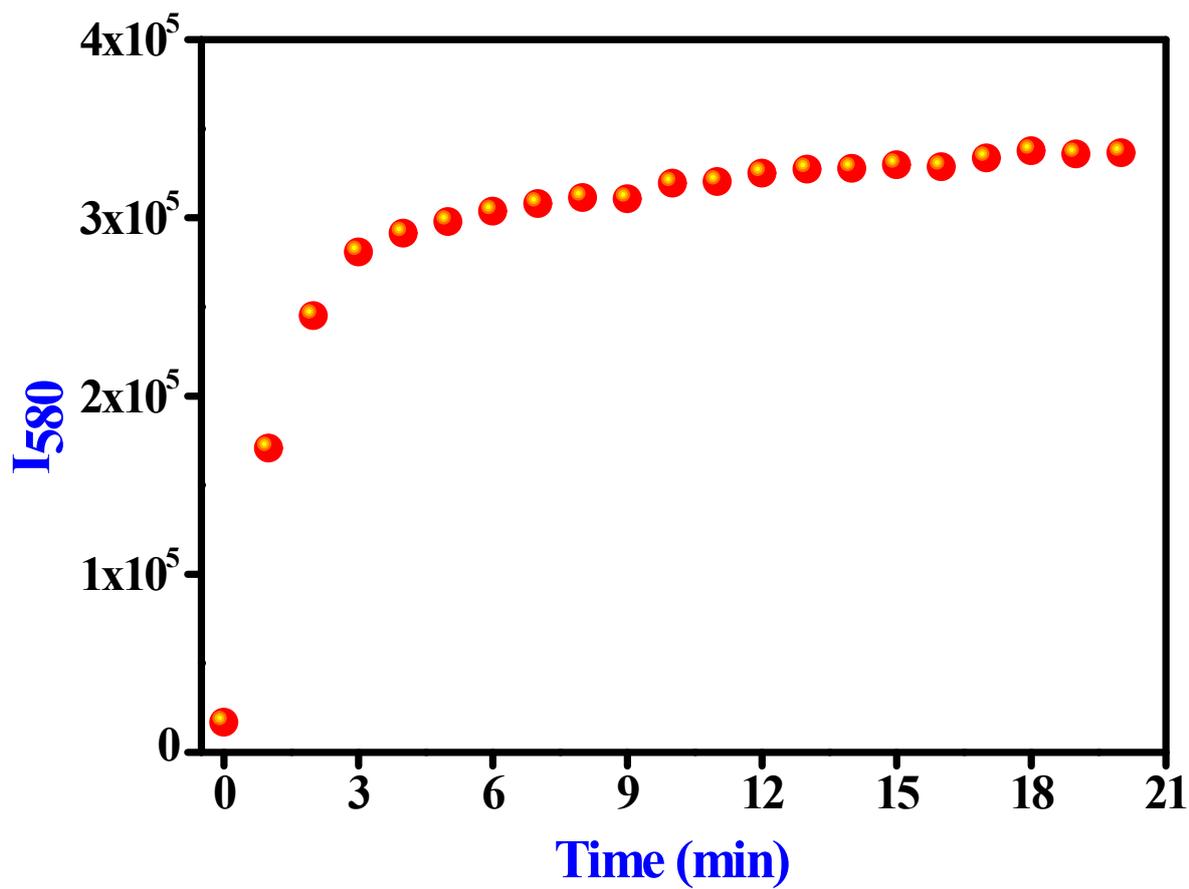
**Figure S10:** UV-Vis spectroscopy titration of NR (50 μM) in presence of Fe<sup>3+</sup> ion (0-500 μM) in 1:1 CH<sub>3</sub>CN/H<sub>2</sub>O.



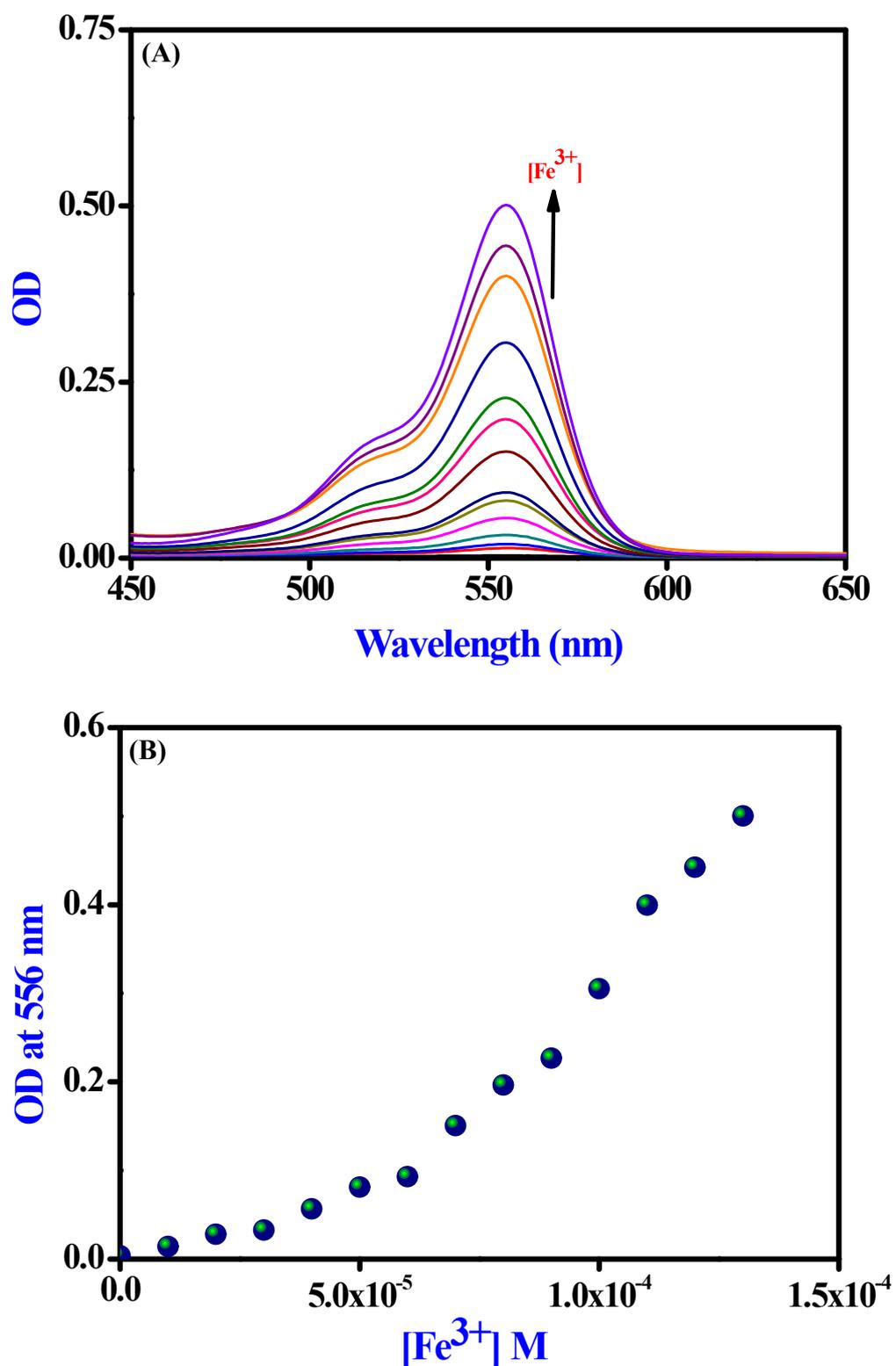
**Figure S11:** The plot of OD at 557 nm vs changing concentration of Fe<sup>3+</sup> (0-500 50 μM) ion for NR.



**Figure S12:** Job's plot using fluorescence spectroscopic technique to determine binding ratio between NR and  $Fe^{3+}$  ion.



**Figure S13:** Intensity (580 nm) vs. Time plot for **PNR** (0.05 mg/mL) in presence of  $\text{Fe}^{3+}$  (75  $\mu\text{M}$ ) ion. ( $\lambda_{\text{ex}}$ =520 nm, Slit=2 nm).



**Figure S14:** (A) UV-Vis study of PNR (0.1 mg/mL) with changing concentration of Fe<sup>3+</sup> ion (0-130 μM) (B) Corresponding OD<sub>556 nm</sub> vs. [Fe<sup>3+</sup>].

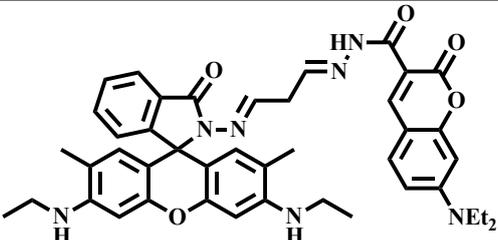
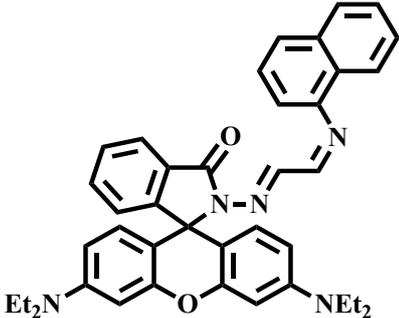
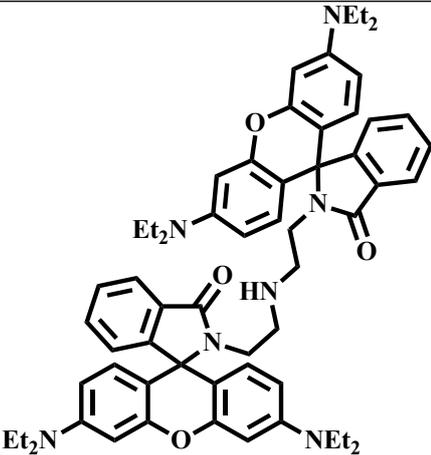
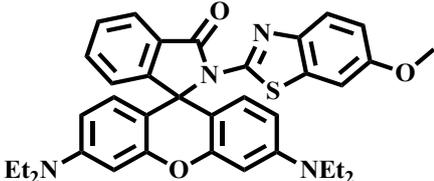
#### **Benesi-Hildebrand method**

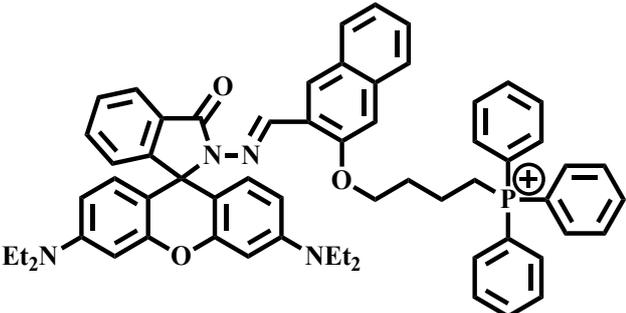
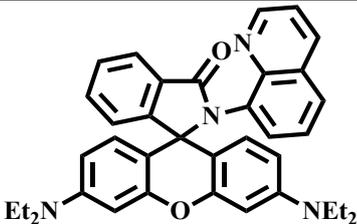
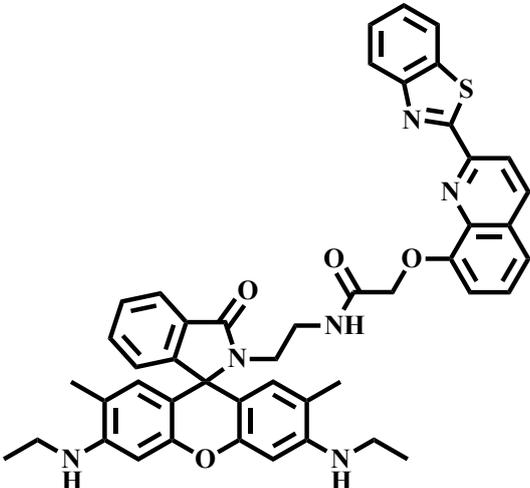
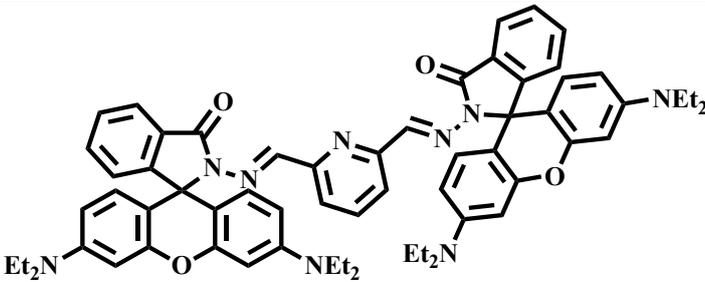
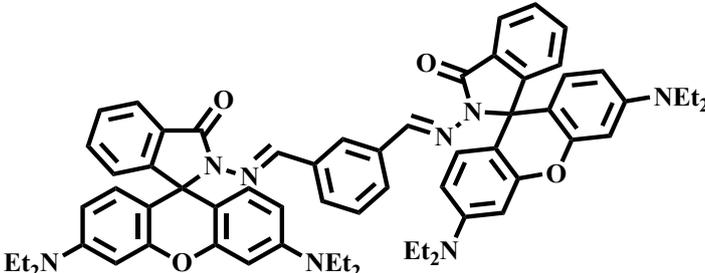
To elucidate the association constant for the interaction between NR and Fe<sup>3+</sup> we have utilized Benesi-Hildebrand equation (equation 1)

$$\frac{F_{\max} - F_0}{F - F_0} = \frac{1}{K_a [Fe^{3+}]^n} + 1 \quad \dots\dots\dots \text{equation 1}$$

Where  $F_0$  is the fluorescence of NR in the absence of  $Fe^{3+}$ ,  $F$  is the fluorescence recorded in the presence of  $Fe^{3+}$ ,  $F_{\max}$  is fluorescence in presence of  $[Fe^{3+}]_{\max}$ ,  $K_a$  is the association constant and  $n$  is the binding stoichiometry of metal. Here  $n=3/2$ .

**Table 1: Comparison of LOD and association/binding constant of Rhodamine based  $Fe^{3+}$  sensors**

Chemical structure	Association/ binding constant	LOD	References
	$5.2 \times 10^4$	$4.05 \times 10^{-6}$ M	1
	$0.25 \times 10^4$	$0.27 \times 10^{-6}$ M	2
	$10^4$	$10^{-5}$ M	3
	$4.52 \times 10^5$	$5 \times 10^{-6}$ M	4

	$(2.0 \pm 0.1) \times 10^4$	$6.93 \times 10^{-6}$ M	<b>5</b>
	NA	$3.2 \times 10^{-7}$ M	<b>6</b>
	$6.12 \times 10^5$	$5.39 \times 10^{-8}$ M	<b>7</b>
	$7.5 \times 10^3$	$50 \times 10^{-6}$ M	<b>8</b>
	$5.1 \times 10^3$	$70 \times 10^{-6}$ M	<b>8</b>

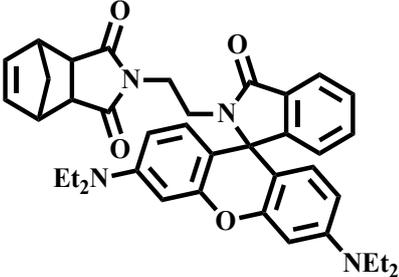
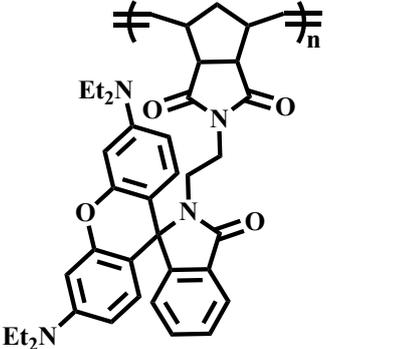
	6.25 x 10 <sup>6</sup>	49 x 10 <sup>-9</sup> M	This work
	NA	19 x 10 <sup>-9</sup> M	This work

Table 2: Calculation of recovered Fe<sup>3+</sup> concentration in tap water by fluorescence technique using NR and PNR.

Sample	Spiked(μM)	Obtained from tap water (μM)	% of recovery
1+NR	20	18.29	91.45
2+NR	40	37	92.50
3+NR	60	54.79	91.3
4+NR	80	72.95	91.2
5+NR	100	92.74	92.74
6+NR	120	112.7	93.9
7+NR	140	129.31	92.36
8+NR	160	148.09	92.5
9+NR	180	168.9	93.83
10+NR	200	185.87	92.9
1+PNR	20	19.5	97.6
2+PNR	40	37.76	94.4
3+PNR	60	57.2	95.3
4+PNR	80	76.8	96
5+PNR	100	92.7	92.7
6+PNR	120	115.3	96

<b>7+PNR</b>	<b>140</b>	<b>129</b>	<b>92</b>
<b>8+PNR</b>	<b>160</b>	<b>152.5</b>	<b>95.3</b>
<b>9+PNR</b>	<b>180</b>	<b>170.05</b>	<b>94.47</b>
<b>10+PNR</b>	<b>200</b>	<b>191.9</b>	<b>95.95</b>

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