A Nanoparticle based chromogenic chemosensor for the simultaneous detection of multiple analytes.

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1. Experimental: Synthesis of 1 and 2.

Materials and Reagents.

Chemicals were purchased from Aldrich Co. and used as received without further purification. Green emitting CdSe-ZnS QD's were purchased from Evident Technologies, New York (product No ED-C10-TOL-0545). Receptor **1**[1] and its disulfde **3**[2] were prepared following literature procedures. Their ^{1}H nmr spectra are provided in Figures S11 and S12 respectively.

*Synthesis of QD-Receptor conjugate (**2**).*

The QD-Receptor conjugate was prepared with the ligand exchange reaction developed by Tomasulo et al.[3] A solution of CdSe/ZnS core based QDs (0.5 mL, 27 nmol) was added to receptor **1** (2.3 g, 0.01 mol) in dry chloroform. The reaction was allowed to reflux for 24 h. Upon completion of reaction, the solvent was removed under reduced pressure. The crude mass was suspended in acetonitrile (5 ml) and centrifuged at 12,500 rpm for 5 min. The supernatant solution was decanted off and the solid was again suspended in fresh acetonitrile. This step was repeated twice and the product was vacuum dried to obtain pure **2** as an orange coloured powder (0.02 g). The QD and QD conjugate concentration was determined by a literature method.[4]

Cation recognition studies.

The cation binding ability of **2** was determined by preparing solutions containing 4.0 X 10^{-8} M of QD-receptor conjugate and 50 μM of a particular metal salt in THF:H_2O (8:2, v/v) HEPES buffered solution (pH = 7.0 ± 0.1). The absorption spectrum of each solution was recorded. The cation recognition behavior of QD-receptor conjugate for the binding of a particular cation was evaluated from the changes in absorption spectrum of receptor upon addition of that metal salt.

QD-receptor conjugate vs. Metal ion titration

Volumetric flasks were taken each containing 4.0 X 10^{-8} M of **2** along with varied amounts of a particular metal salt in THF : H_2O (8:2, v/v) HEPES buffered solution (pH = 7.0 ± 0.1). The solutions were shaken thoroughly and their absorption spectra were recorded.

pH titration

The solutions were prepared under similar conditions as were used for QD-receptor conjugate vs. metal ion titration experiment, except that the solutions were not buffered at a fixed pH value.

2. Experimental: Equipment and Parameters

UV-Vis measurements were recorded on an Agilent UV-Vis Spectrometer using 10 mm quartz cuvettes. NMR spectra were recorded on a Bruker Ultrasheild 400 MHz. ^{1}H NMR samples were prepared by dissolving 5 mg of sample in 1.0 mL of $CDCl_3$.. Chemical shifts are reported in parts per million (δ) downfield of TMS. Particle size distributions were recorded on a Malvern NanoZS instrument at 25^{o}C in a 10 mm cuvette using a He-Ne laser of 633 nm. The average size is the average of 20 independent experiments and the standard deviation is taken as the error. Transmission Electron Micrographs were recorded with a JEOL-JEM 2011 electron microscope operating at 200 kV

Figure S1: Absorption spectra of **1** in the presence of various metal ions. [**1**] = 1 x 10^{-6} M; [ion] = 50 μM; in a 80% THF / 20% 0.01 M HEPES buffer solution at pH = 7.0.

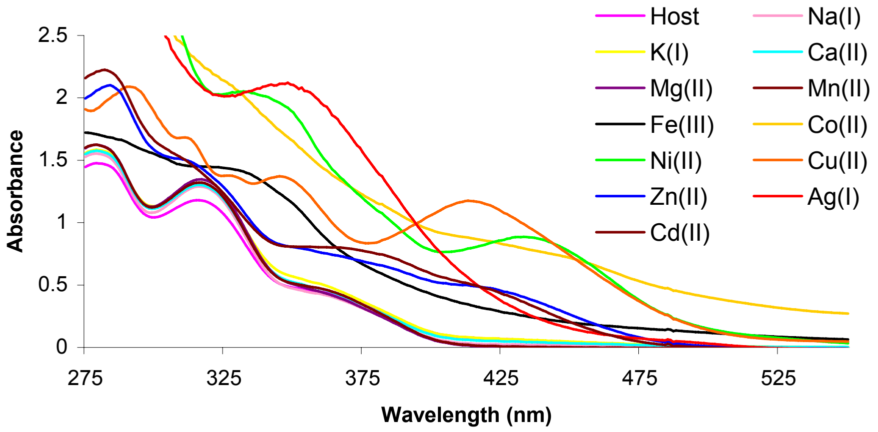


Figure S2: Absorption spectra of **3** in the presence of various metal ions. [**3**] = 1 x 10^{-6} M; [ion] = 50 μM; in a 80% THF / 20% 0.01 M HEPES buffer solution at pH = 7.0.

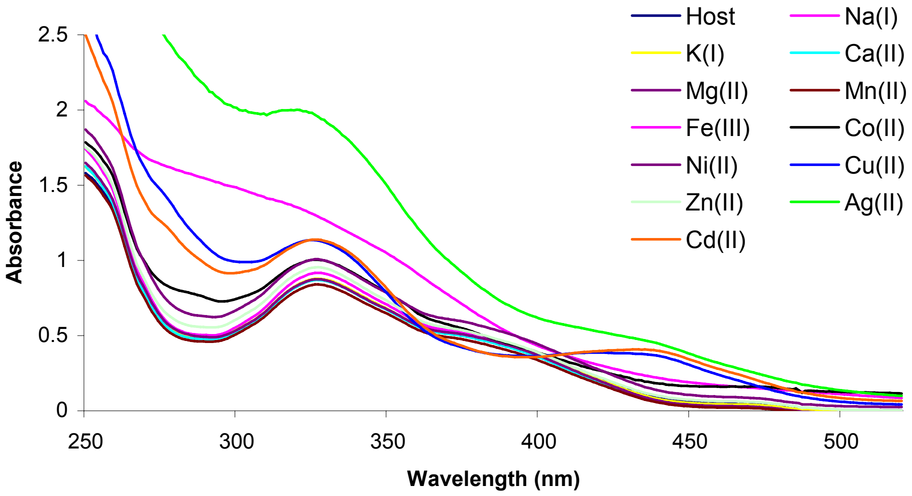


Figure S3: Expansion of the aromatic region for Receptor **1** (A) and QD-receptor conjugate **2** (B).

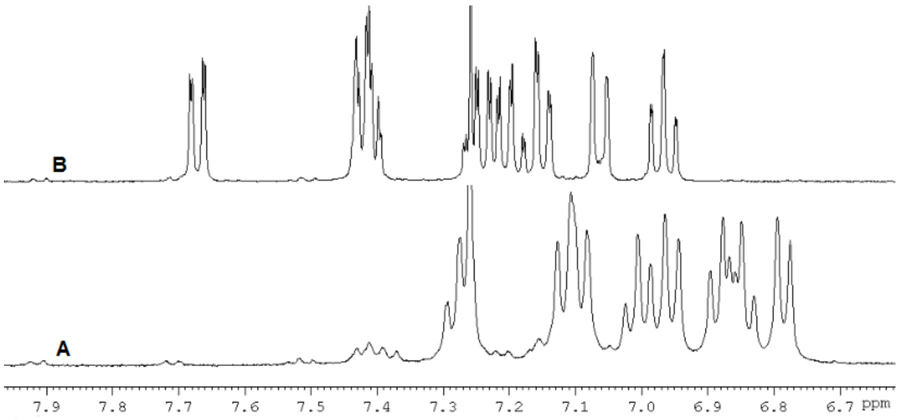


Figure S4: Absorption spectrum of **2** recorded in THF showing the visible region. The first exciton peak is the broad absorption centered at 510 nm. [**2**] = 2.0 x 10^{-6}. M.

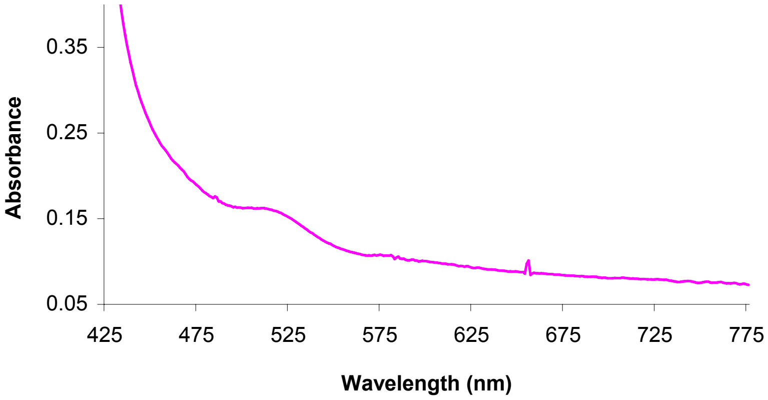
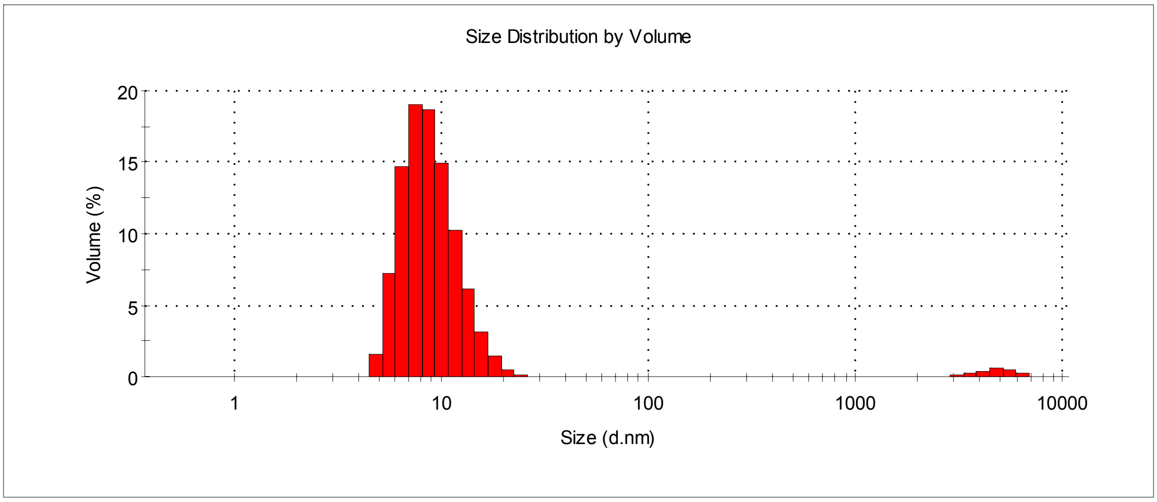


Figure S5: Dynamic Light Scattering measurements of CdSe/ZnS QD's (top) and **2** (bottom). Solvent = THF, [CdSe/ZnS QD's] = 1.0 x 10^{-6} M, [**2**] = 1.0 x 10^{-6} M.



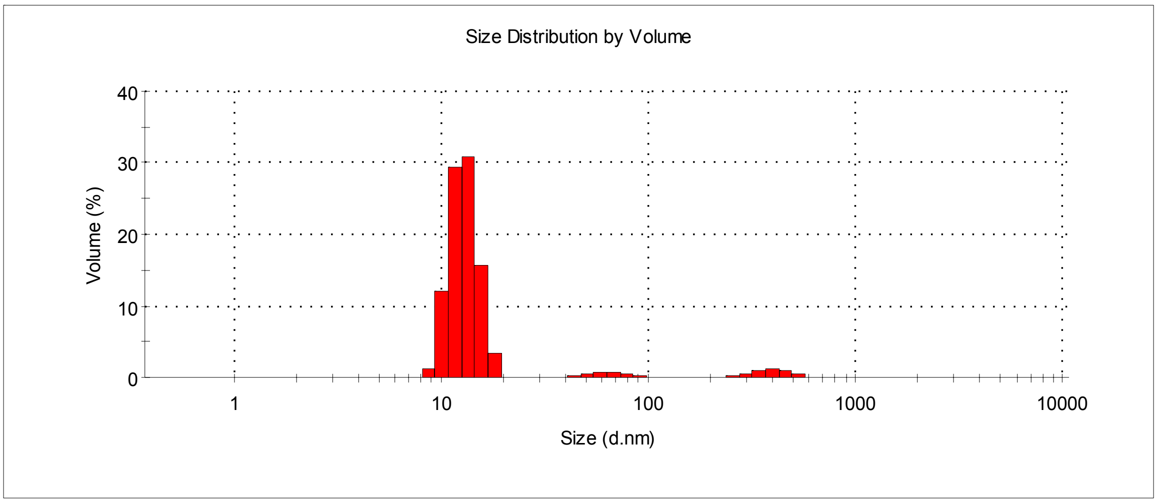


Figure S6: TEM image of **2**.

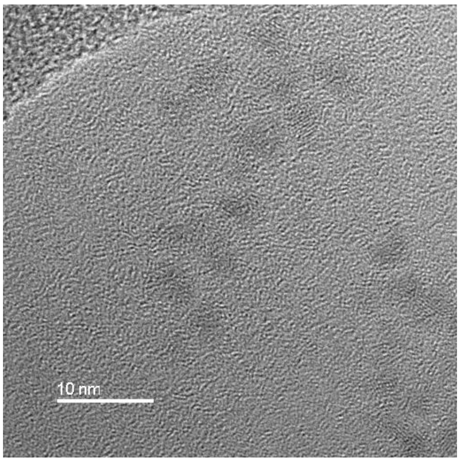


Figure S7: UV/Vis - pH titration of **2**. [**2**] = 4 x 10^{-8} M in a 80% THF / 20% H_2O solution. Inset lists the pH values tested.

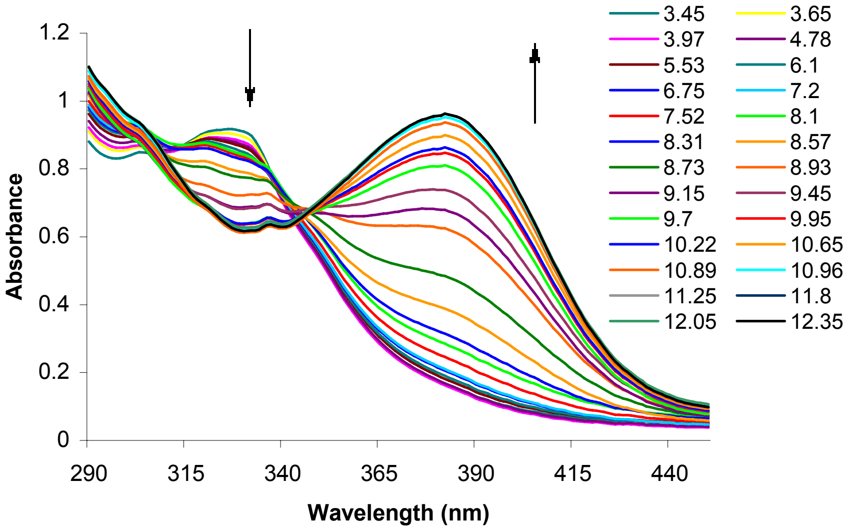


Figure S8: Plot of absorbance intensity against pH for **2**. [**2**] = 4.0 x 10^{-8} M in a 80% THF / 20% H_2O solution.

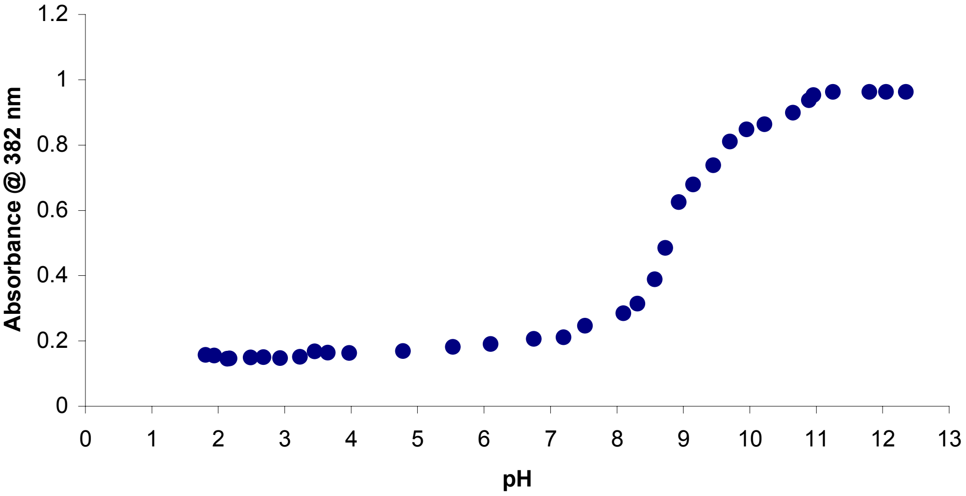


Figure S9: Competition study of **2** for Cu(II) in the presence of Fe(II). The values shown in the inset are the μM concentrations of Cu(II) with Fe(II) being present at 25% of this concentration. Solutions prepared in a 80% THF / 20% 0.01 M HEPES buffer solution at pH = 7.0. [**2**] =4.0 x 10^{-8} M.

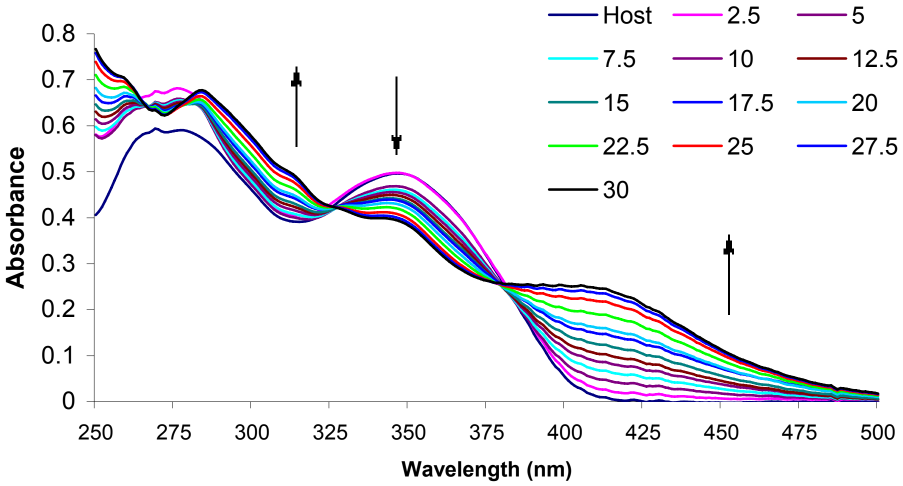


Figure S10:Competition study of **2** for Fe(III) in the presence of Cu(II). The values shown in the inset are the μM concentrations of Fe(III) with equimolar concentration of Cu(II). Solutions prepared in a 80% THF / 20% 0.01 M HEPES buffer solution at pH = 7.0. [**2**] =4.0 x 10^{-8} M.

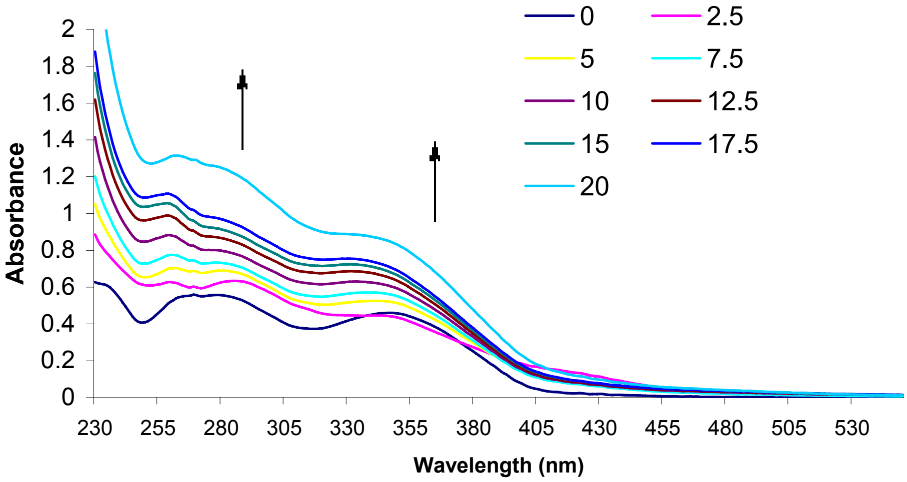


Figure S11: ^{1}H NMR spectra of **1** in $CDCl_3$.

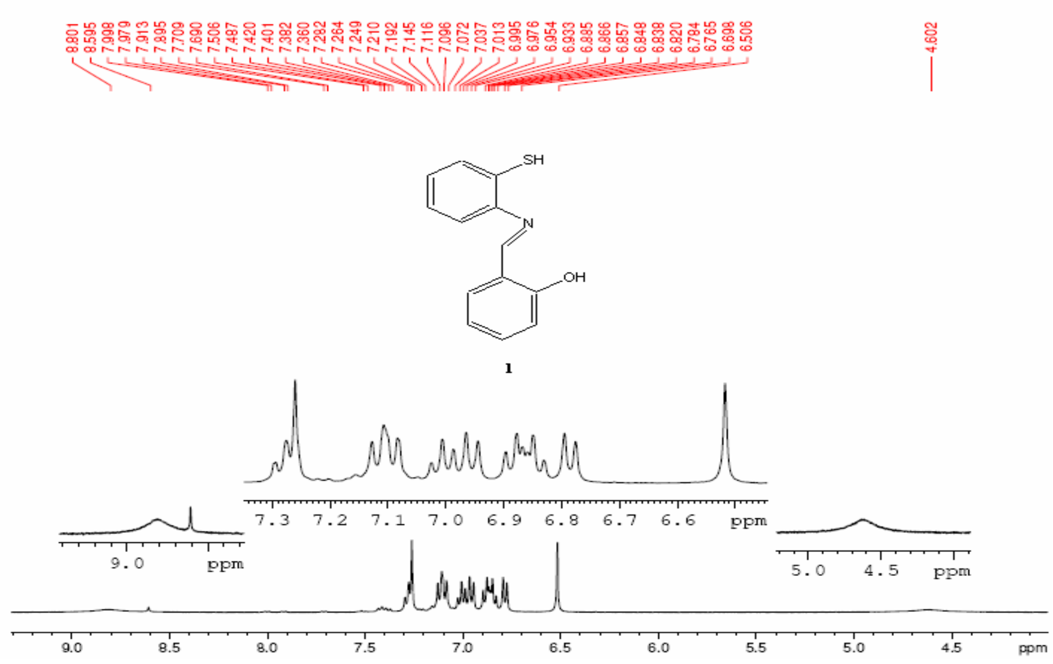


Figure S12: ^{1}H NMR spectra of **3** in d_6-DMSO

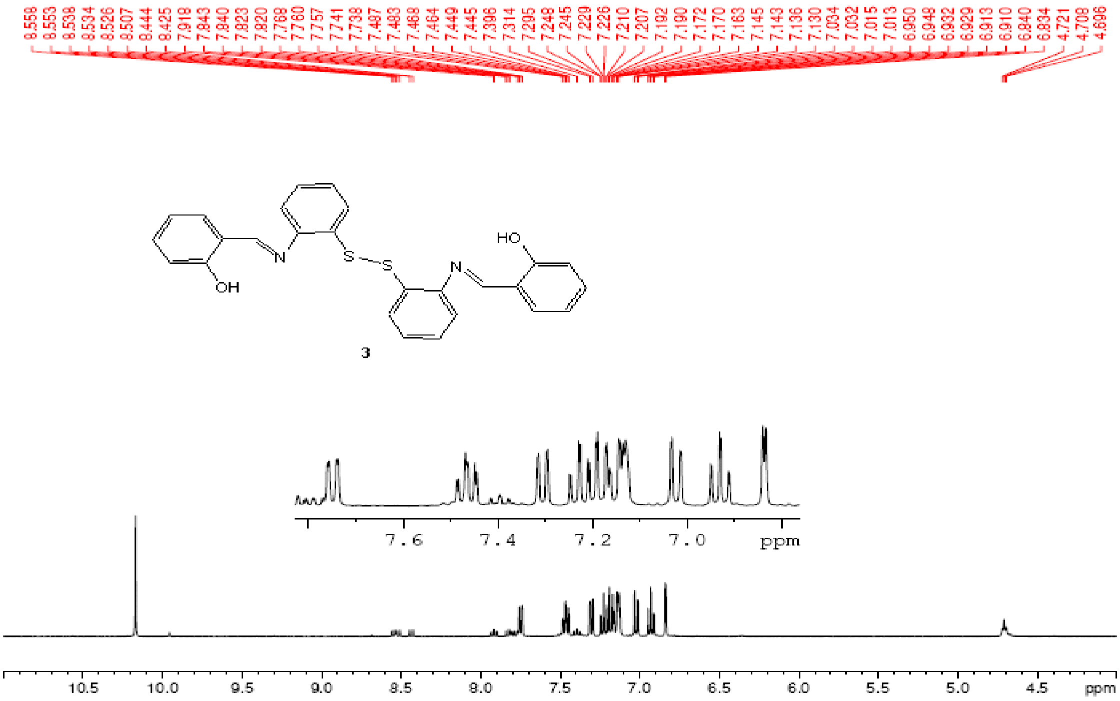


Table 1. Illustrating the dA/A$_o$ ratios for various metal ions at λ_{max} = 325 and 410 nm.

	dA/Ao 325	dA/Ao 410
Na(I)	0.164	1.025
K (I)	0.086	1.140
Mg(II)	0.029	1.099
Ca(II)	0.171	1.073
Mn(II)	0.509	1.092
Fe(III)	1.500	9.716
Co(II)	0.509	3.271
Ni(II)	0.159	2.748
Cu(II)	0.342	22.717
Zn(II)	0.259	2.977
Ag(I)	0.194	2.822
Cd(II)	0.261	2.410

The reported values are the average of independent determinations and are within error range of ± 5%.

References

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3 M. Tomasulo, I. Yildiz, S.L. Kaanumalle, and F.M. Raymo, *Langmuir*, 2006, **22**, 10284-10290.

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