Supporting Information

A highly selective and sensitive probe for colorimetric and fluorogenic detection of Cd^{2+} in aqueous media

Shyamaprosad Goswami,[*a] Krishnendu Aich[a], Sangita Das[a], Avijit Kumar Das[a], Abhishek Manna[a] and Sandipan Halder[b]

[a]*Department of Chemistry, Bengal Engineering and Science University, Shibpur, Howrah, INDIA, 711 103, Tel. +91-33-2668 4561-3 ext. 498; Fax. +91-33-2668 2916.*

e-mail spgoswamical@yahoo.com

[b]*Department of Chemistry, Indian Institute of Technology, Kanpur, India*

CONTENTS

General method of UV-vis and fluorescence titration:

By UV-vis method

UV-vis spectra were recorded on a JASCO V-530 spectrophotometer using a dissolution cell of 10 mm path and the fluorescence spectra were recorded on a PTI spectrophotometer using a fluorescence cell (10 mm). For UV-vis titrations, stock solution of receptor was prepared (c = 6 x 10^{-6} ML^{-1}) in CH_3OH-H_2O (1:4 *v/v*) in the presence of HEPES buffer solution (pH 7.1). For fluorescence titrations, stock solution of receptor was prepared (c = 3 x 10^{-6} ML^{-1}) in CH_3OH-H_2O (1:4 *v/v*) in the presence of HEPES buffer solution (pH 7.1). The solution of the guest cations using their perchlorate salts in the order of 2 x 10^{-5} M were prepared in deionised water. Solutions of various concentrations containing host 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.

$$1/(A\text{-}Ao) = 1/\{K(A_{max}–Ao)\,[M^{x+}]^n\} + 1/[A_{max}\text{-}A_o]$$

Here Ao is the absorbance of receptor in the absence of guest, A is the absorbance recorded in the presence of added guest, A_{max} is absorbance in presence of added $[M^{n+}]_{max}$ and K is the association constant. The association constant (K) could be determined from the slope of the straight line of the plot of $1/(A\text{-}Ao)$ against $1/[M^{x+}]$ and is found to be 1.656 x 10^{-5} M.

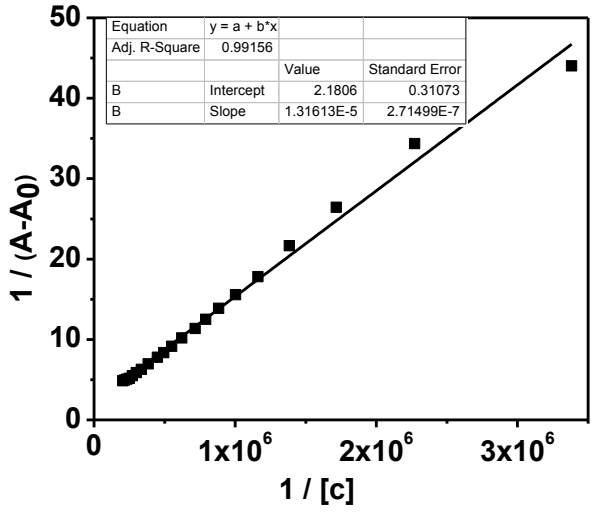


Figure S1: Benesi-Hildebrand plot from absorption titration data of receptor (6 µM) with Cd^{2+}.

General procedure for drawing Job plot by UV–vis method

Stock solution of same concentration of the receptors and the guest were prepared in the order of ca. 1.0 x 10^{-5} ML^{-1} CH_3OH-H_2O (1:4, *v/v*). 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 Cd^{2+} with receptor has been determined from the emission intensity data following the modified Benesi–Hildebrand equation,[2] $1//\Delta I = 1//\Delta I$ 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 receptor considered in the absence of Cd^{2+}, at an intermediate Cd^{2+} concentration, and at a concentration of complete saturation where K is the binding constant and [C] is the Cd^{2+}concentration respectively. From the plot of [1 / (I_{min} –I)] against $[C]^{-1}$ for receptor, the value of K has been determined from the slope. The association constant (K_a) as determined by fluorescence titration method for the receptor with Cd^{2+} is found to be 6.808 x 10^5 M^{-1} (error < 10%).

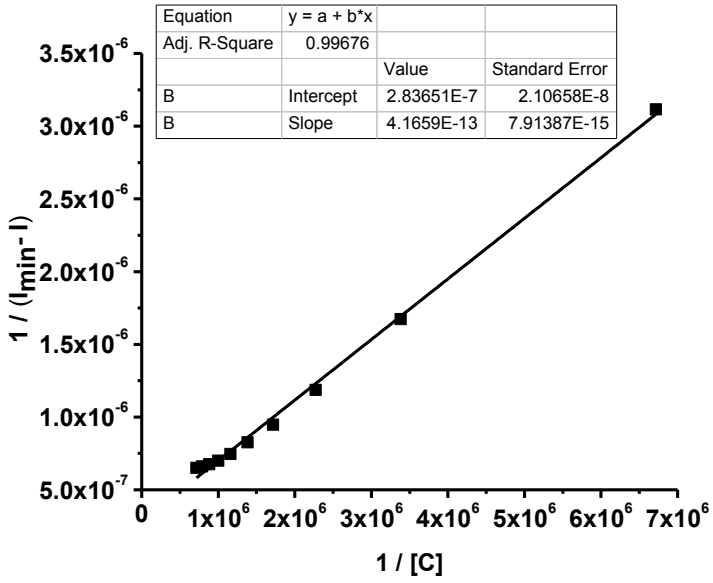


Figure S2: Benesi–Hildebrand plot from fluorescence titration data of receptor (3 μM) with Cd^{2+}.

Determination of detection limit:

The detection limit (DL) of **RQ** for Cd^{2+} was determined from the following equation:

DL = K* Sb1/S

Where K = 2 or 3 (we take 3 in this case); Sb1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

For UV-vis:

From the graph, we get slope = 43180.32, and Sb_1 value is 0.010213

Thus using the formula we get the Detection Limit = 7.09×10^{-7} M i.e. RQ can detect Cd^{2+} in this minimum concentration through UV-vis method.

For Fluorescence:

From the graph we get slope = 1.44×10^{12}, and Sb_1 value is 94366.66

Thus using the formula we get the Detection Limit = 1.97×10^{-7} M i.e. RQ can detect Cd^{2+} in this minimum concentration through fluorescence method.

ESI MS spectra of compound B:

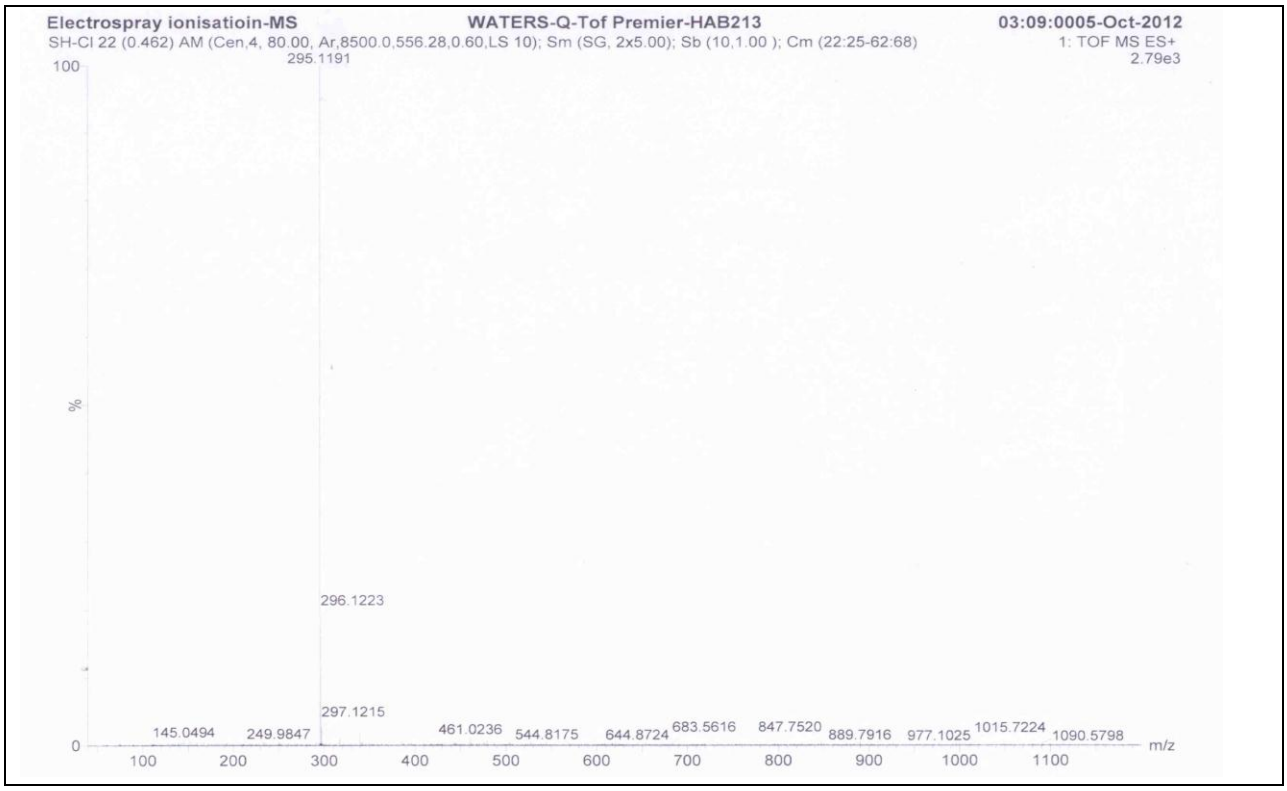


Figure S3: ESI TOF mass spectra of the compound B.

^{1} H NMR spectra of the compound B:

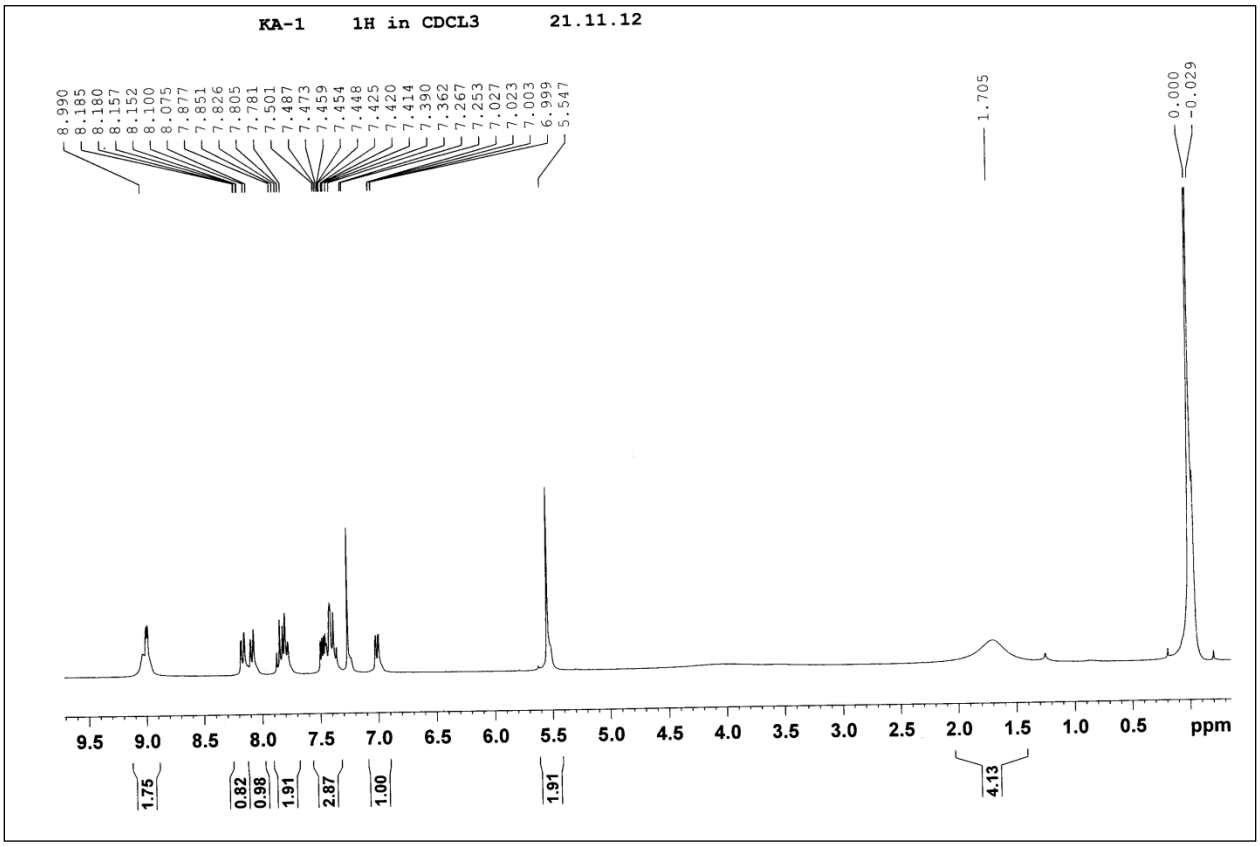


Figure S4: 1H NMR (300 MHz) spectra of compound B in $CDCl_3$.

^{1} H NMR spectra of the receptor:

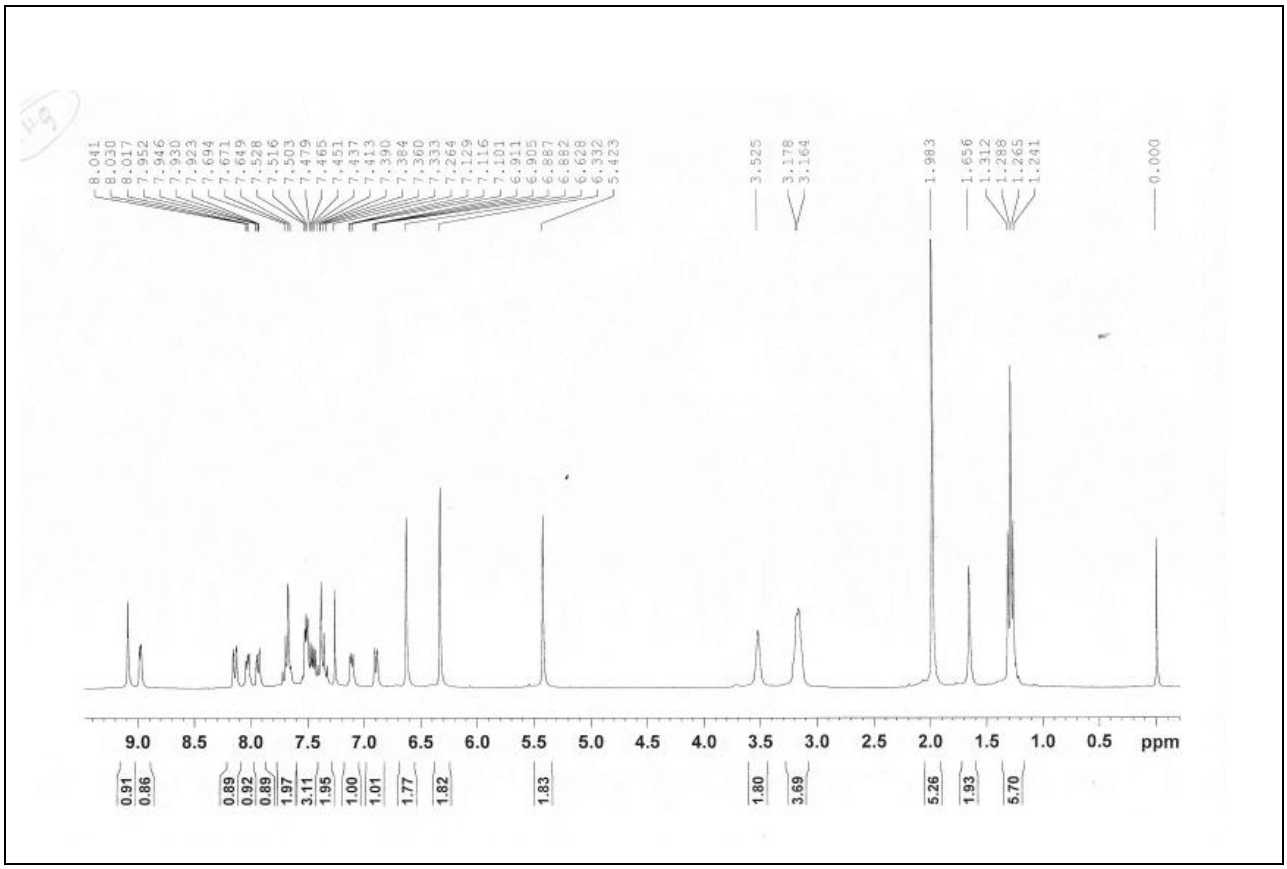


Figure S5: 1H NMR (300 MHz) spectra of the receptor in $CDCl_3$.

ESI MS spectra of the receptor:

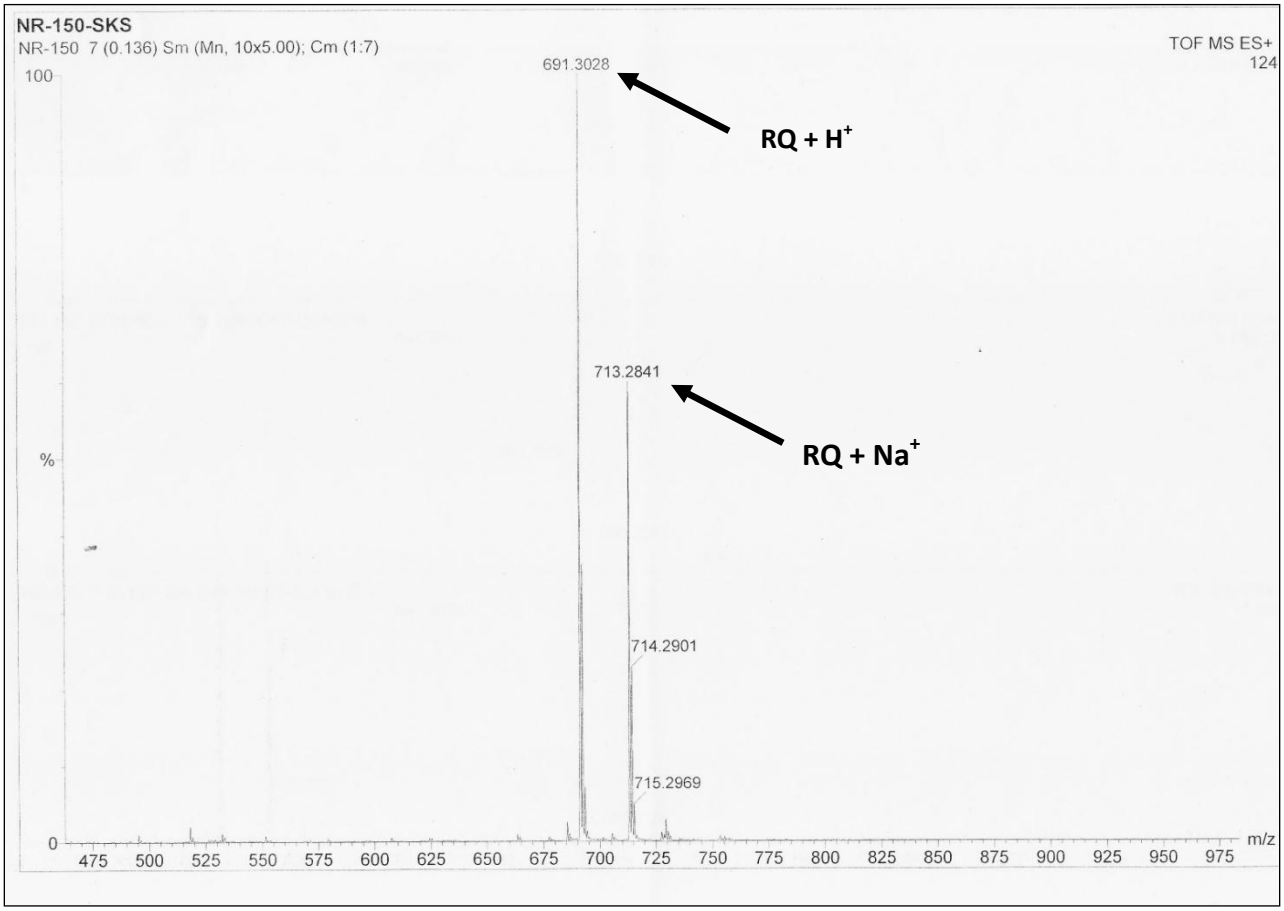


Figure S6: ESI TOF mass spectra of the receptor.

^{13}C NMR spectra of the receptor:

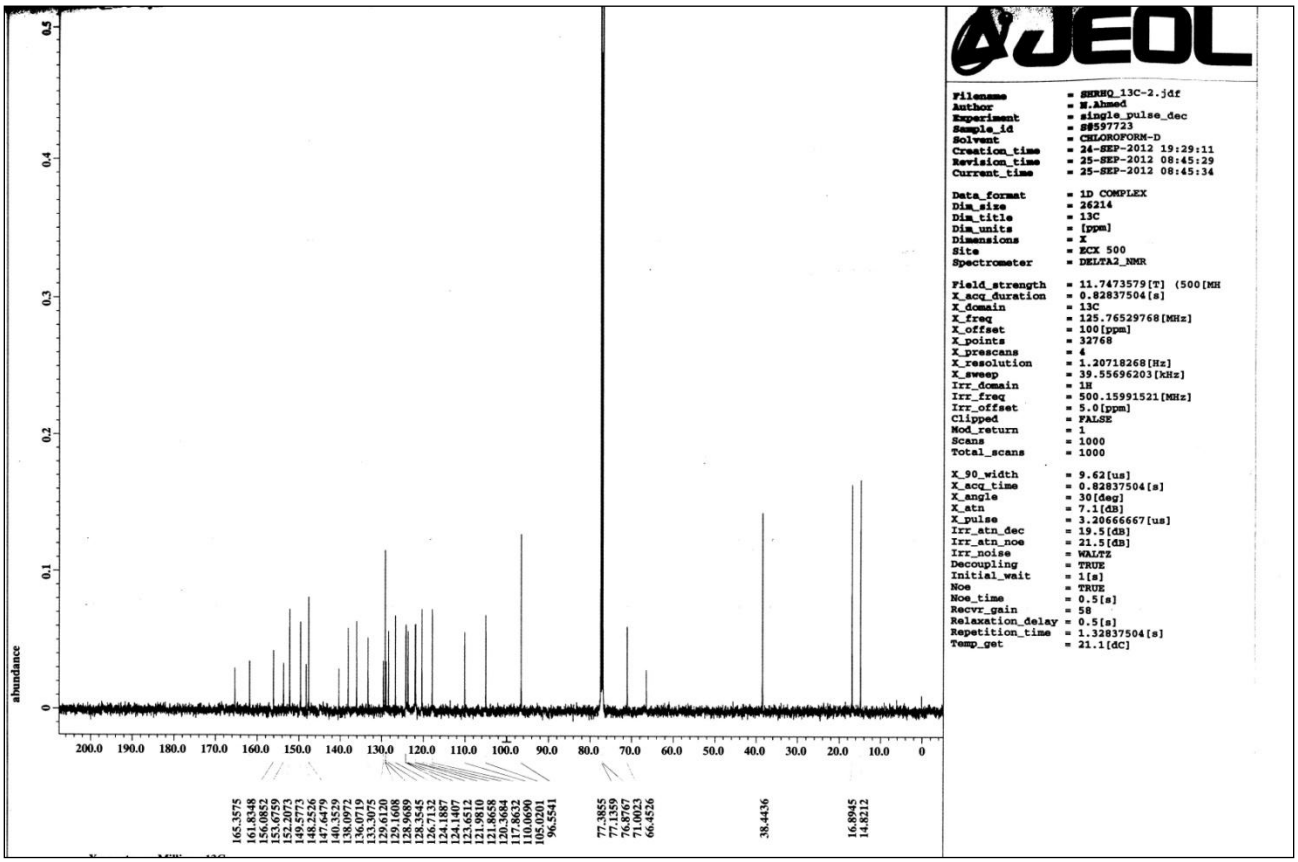


Figure S7: ^{13}C NMR (100 MHz) spectra of the receptor in $CDCl_3$.

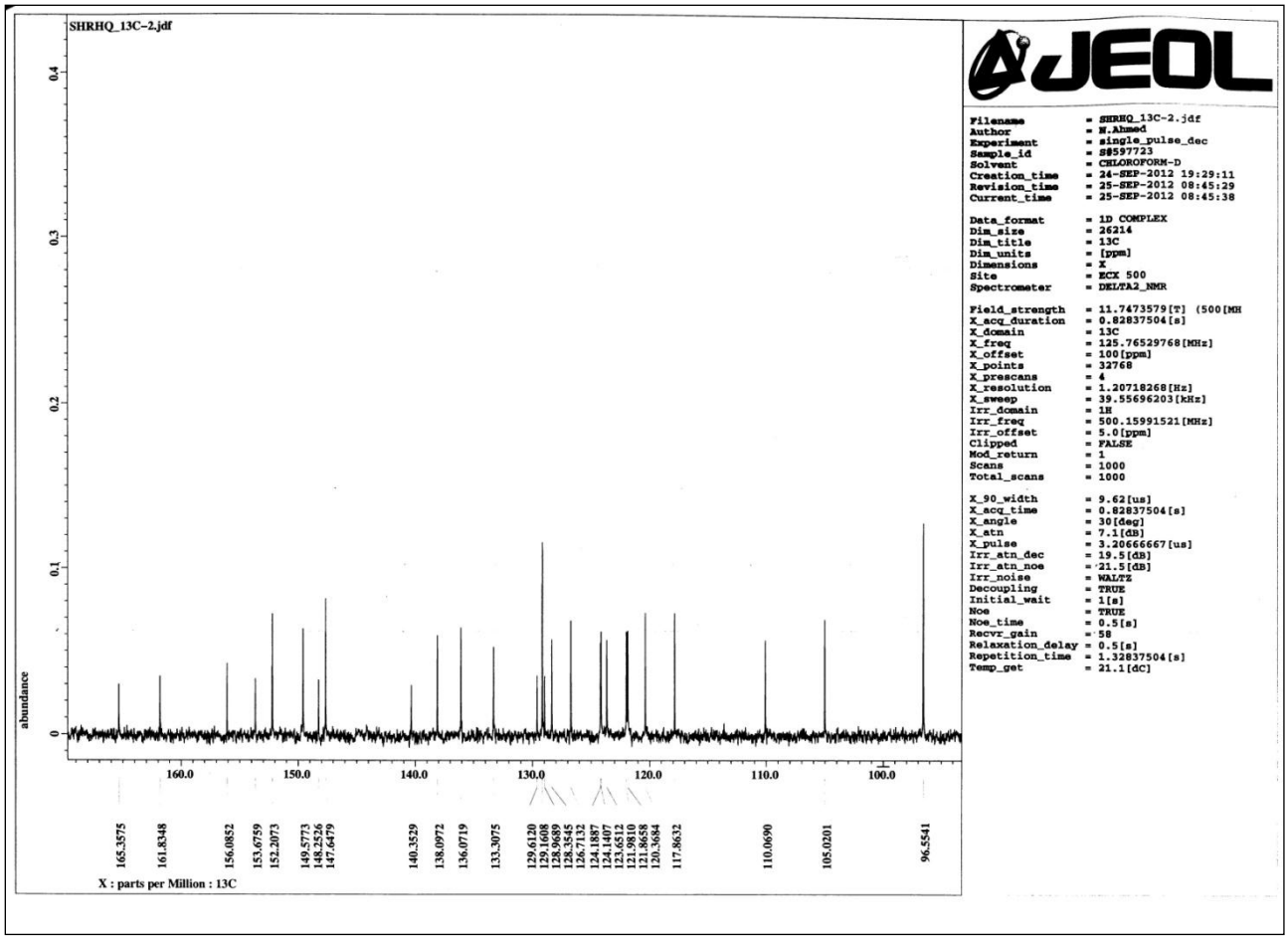


Figure S8: Expansion mode of the ^{13}C NMR spectra of the receptor in $CDCl_3$.

IR spectra of the receptor and its Cd^{2+} complex:

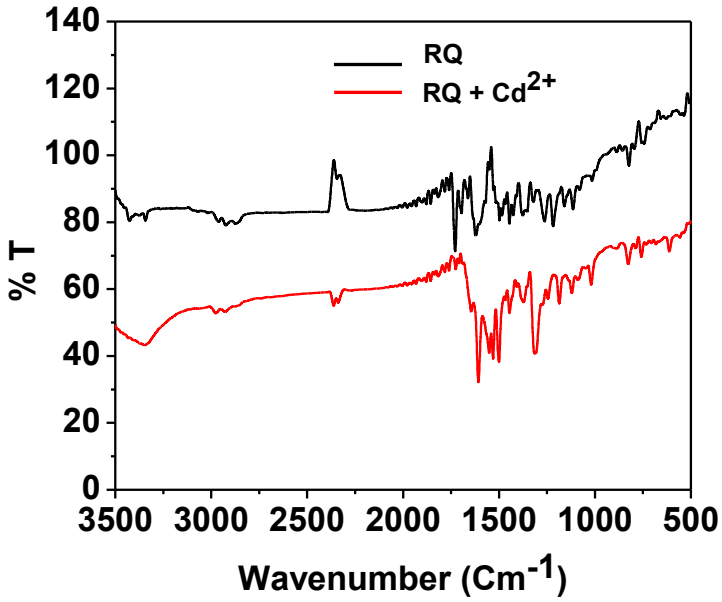


Figure S9: FT IR spectra of the receptor and its complex with Cd^{2+}.

ESI-MS of Cd^{2+} complex of the receptor:

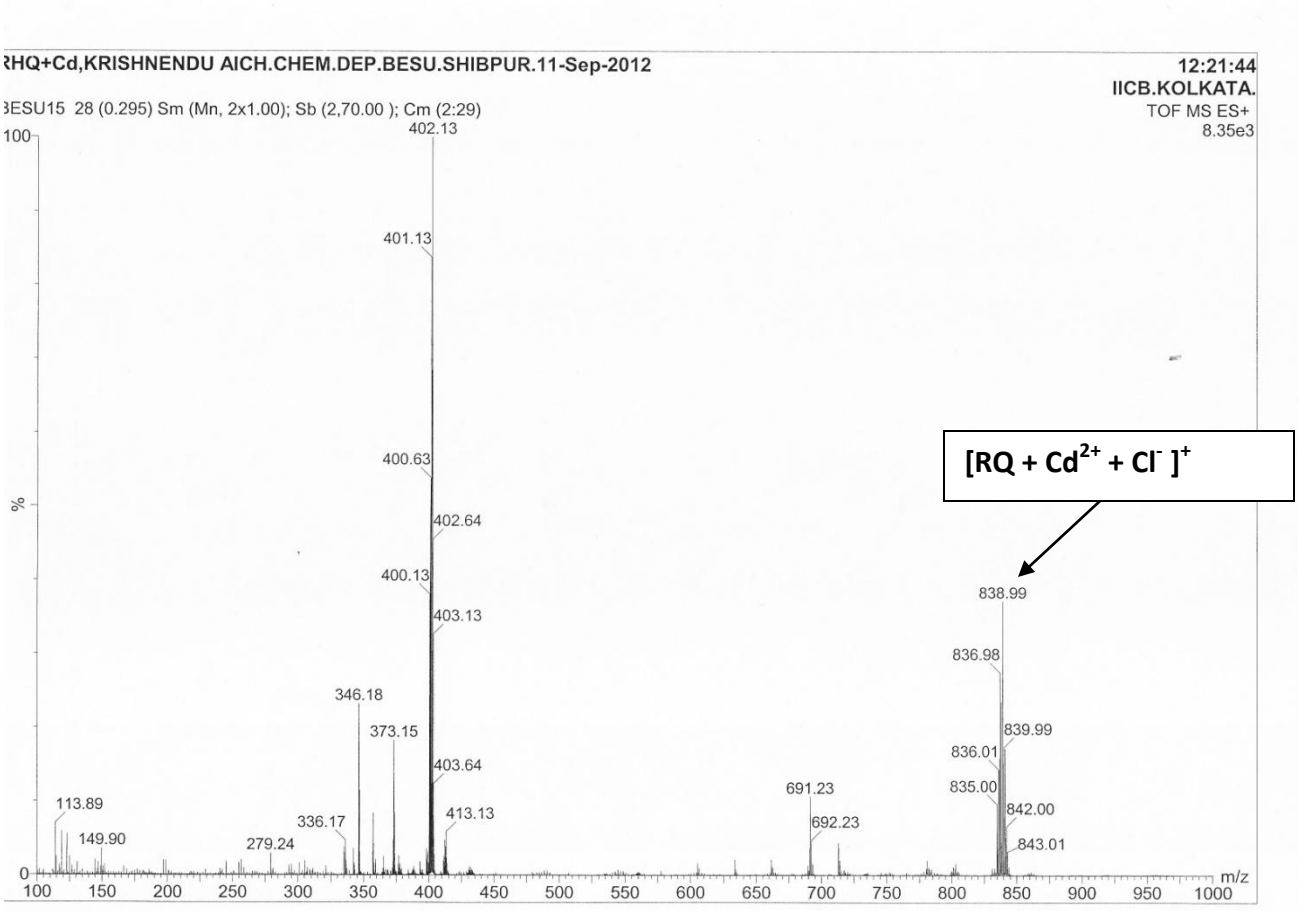
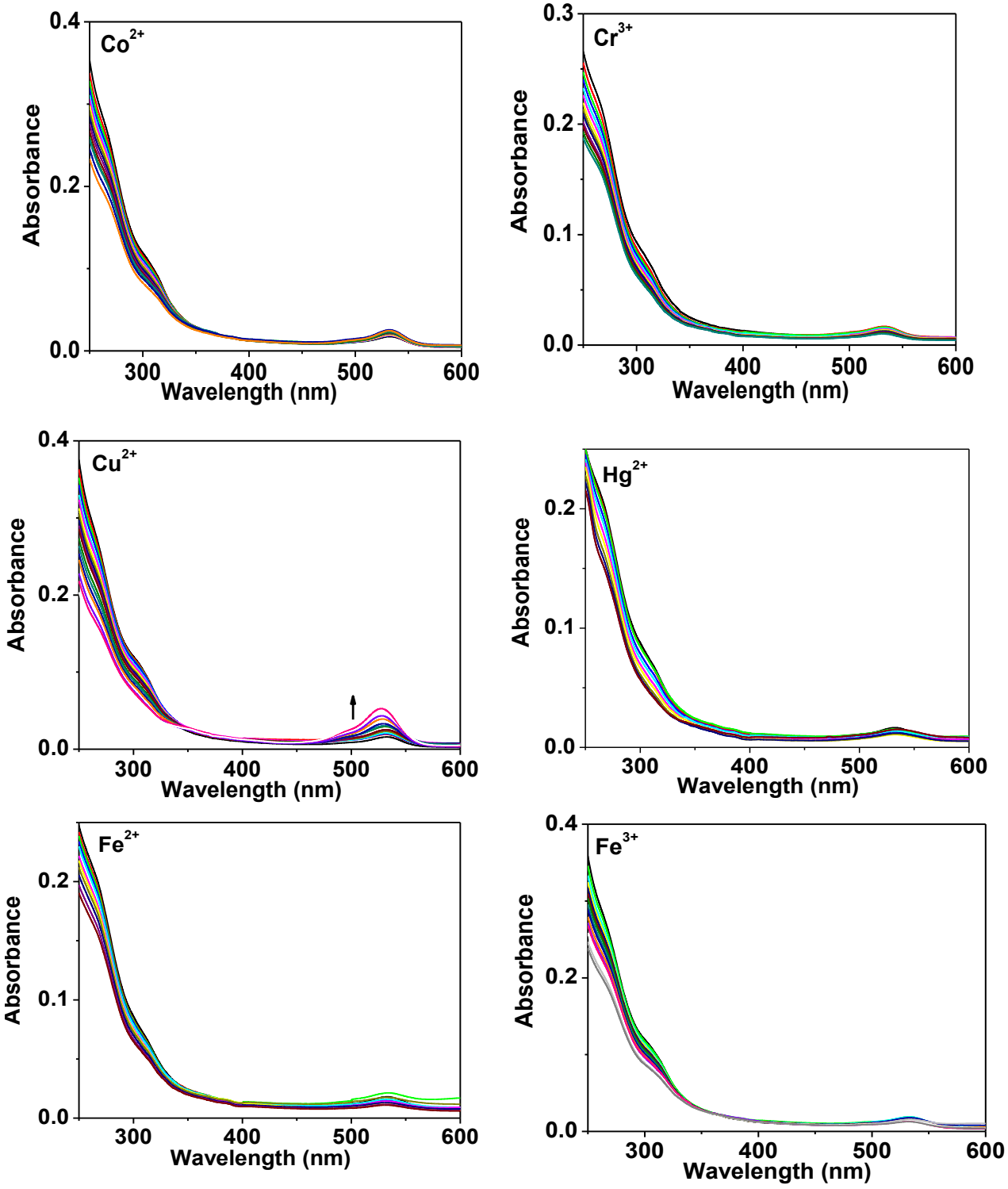
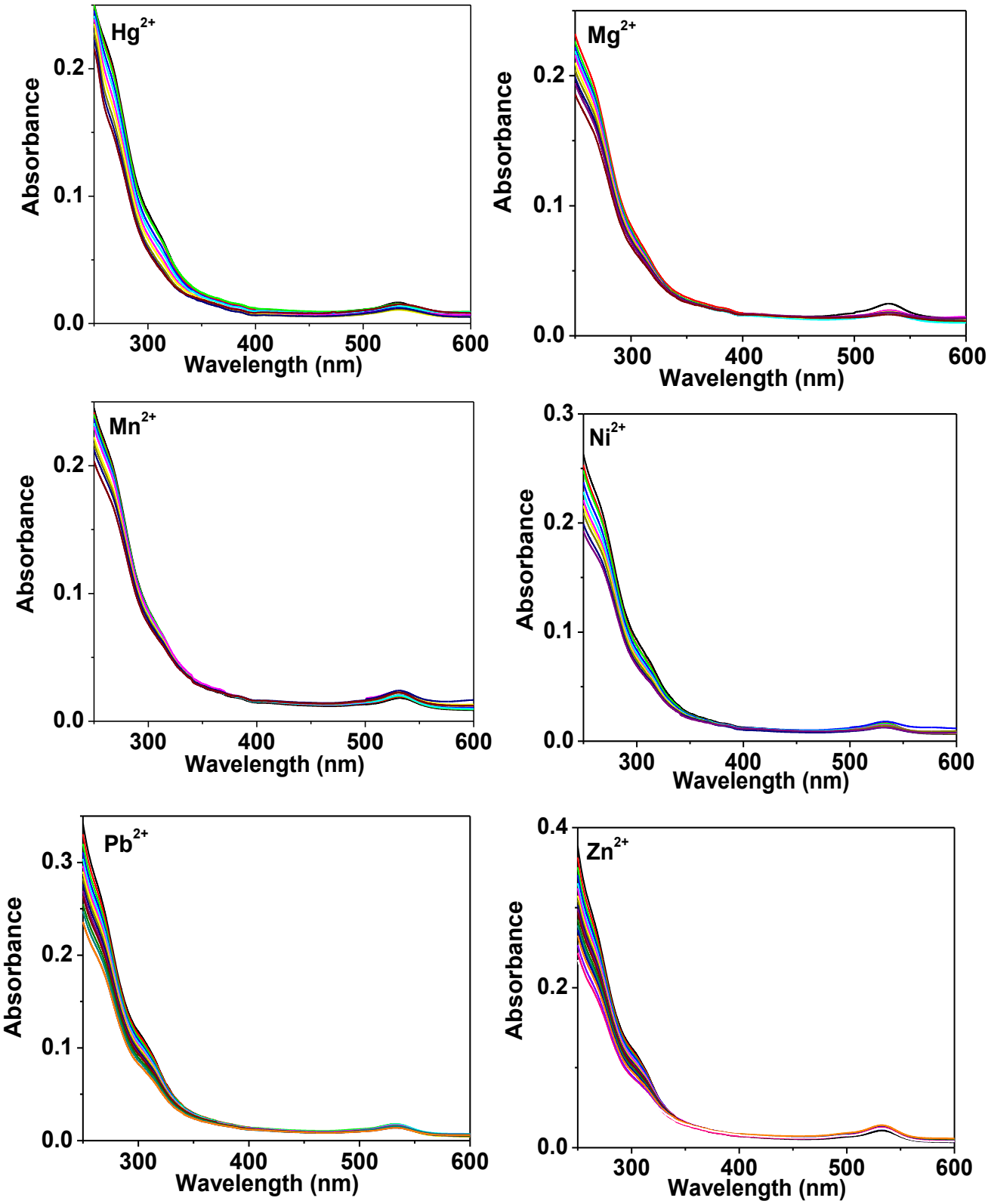


Figure S10: ESI TOF mass spectra of the Cd^{2+} complex of the receptor.

UV-vis titration spectra of the receptor with different guest cations in CH_3OH-HEPES buffer solution (1:4, *v/v*, pH= 7.1):





Fluorescence emission spectra of the receptor with different guest cations in CH_3OH-HEPES buffer solution (1:4, *v/v*, pH = 7.1):