Supplementary Material (ESI) for New Journal of Chemistry

Electronic Supplementary Information

for

Reversible colorimetric switching of thiophene hydrazone based on complementary IMP/INH logic functions

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Experimental

General remarks

The IR Spectrum for the receptor 1 was recorded on JASCO-FTIR Spectrophotometer while ^{1}H NMR spectra were recorded on a Bruker-400 Avance NMR Spectrometer and JEOL AL 300 FT NMR Spectrometer. Electronic spectra were recorded at room temperature (298 K) on a UV-1700 pharmaspec spectrophotometer with qurtz cuvette (path length=1 cm).

Materials:

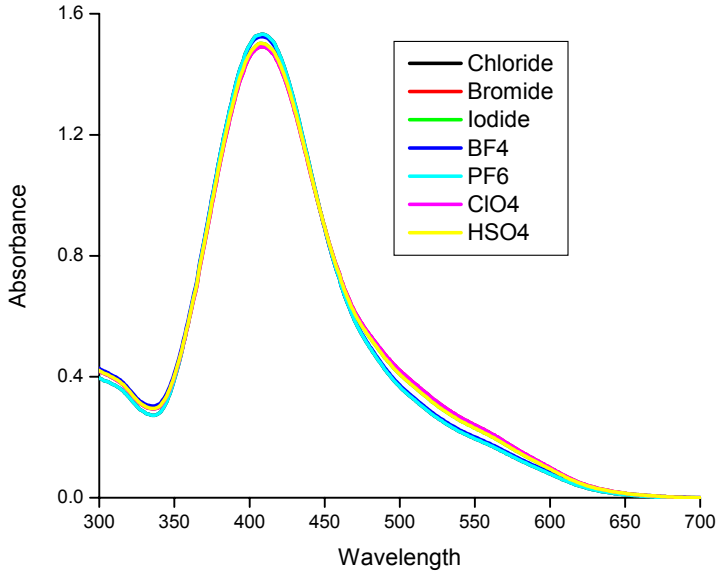
All reagents for synthesis were purchased from Sigma-Aldrich and were used without further purification. For UV-visible experiments the DMSO of HPLC grade was purchased from Spectrochem pvt. Ltd. Mumbai, India. The tetrabutylammonium salt of anions used for titration experiments were purchased from Sigma-Aldrich.

General Method:

All titration experiments were carried at room temperature. For UV-visible titrations a $5x10^{-5}$ M solution of receptor and solutions of tetrabutylammonium salts of the respective anions and chloride salt of metal ions were prepared in DMSO. The ^{1}H NMR titrations were carried out in DMSO-d_6 using TMS as internal reference standard. The $5x10^{-3}$ M solution of the receptor was prepared in DMSO-d_6 and the varying equivalents of CH_3COO^- were added as its tetrabutylammonium salt solution in DMSO-d_6. The M^{II} as its chloride salt was prepapred in DMSO-d_6. The titration data were exported to Excel, decimated to give absorbance in 10 nm increments, and the processed using Hyperquad. All systems except the fluoride system gave acceptable fits (Chi-squared < 12.5 indicating a 95% confidence level). The reported constants are uncertain by ±0.2 in logβ and ±2000 in ε.

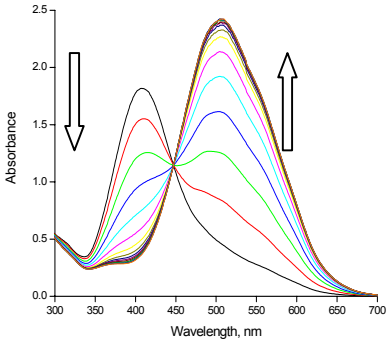
Figures and Captions

Figure 1:

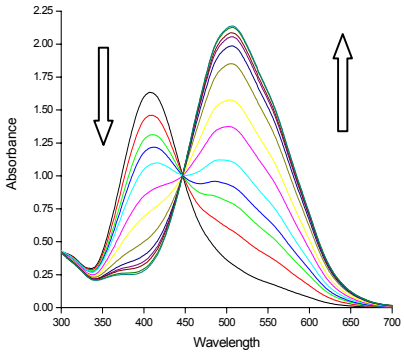


Effect of non-coordinating anions such as Cl^-, Br^-, I^-, BF_4^-, HSO_4^-, ClO_4^- and PF_6^- on the UV-visible spectral pattern of Receptor 1

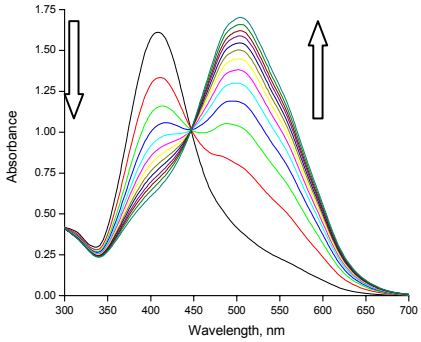
Figure 2:



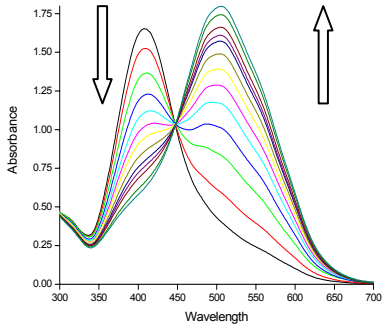
(a) CH_3COO^-



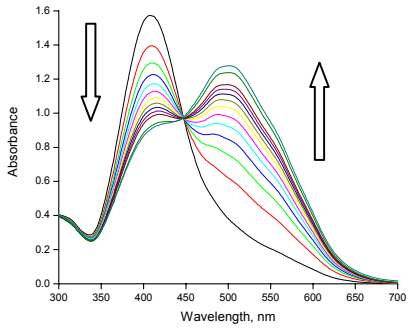
(b) F^-



(c) $C_6H_5COO^-$



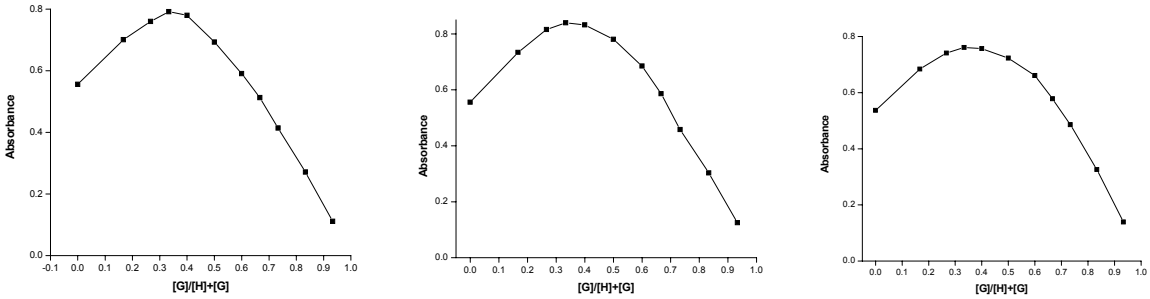
(d) $H_2PO_4^-$



(e) $HCOO^-$

UV-visible titration spectra of the Receptor 1 upon concomitant addition of anions (a) CH_3COO^- (b) F^- (c) $C_6H_5COO^-$ (d) H_2PO_4- and (e) $HCOO^-$

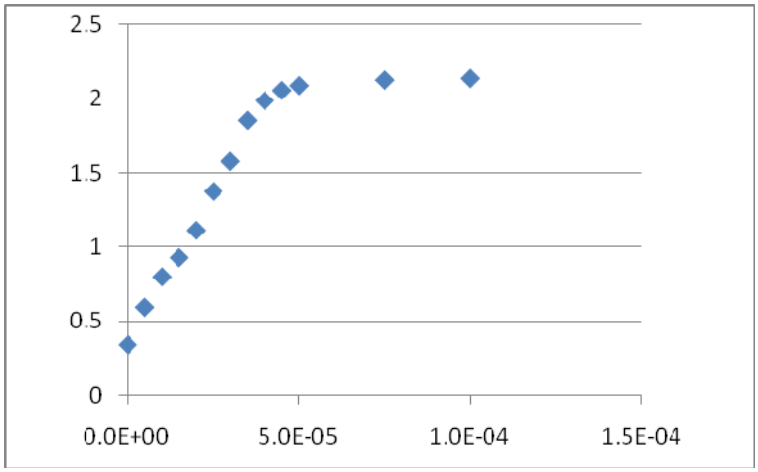
Figure 3:



(a) **(b)** **(c)**

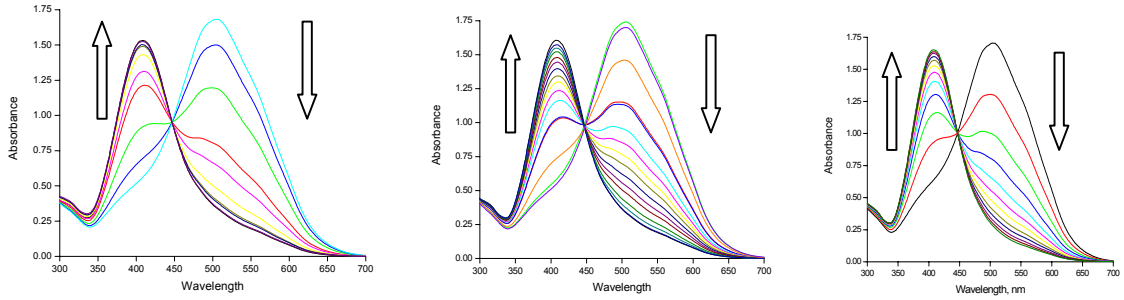
The stoichiometry analysis of complex between receptor 1and anions by Job's plot (a) CH_3COO^- (b) $C_6H_5COO^-$ and (c) F^-

Figure 4:



Sample titration data for fluoride and receptor 1 at 505 nm. Note the slight inflection about 2.5E-05 M indicating a possible 1:1 complex in addition to the 2:1 complex indicated by the Job plot.

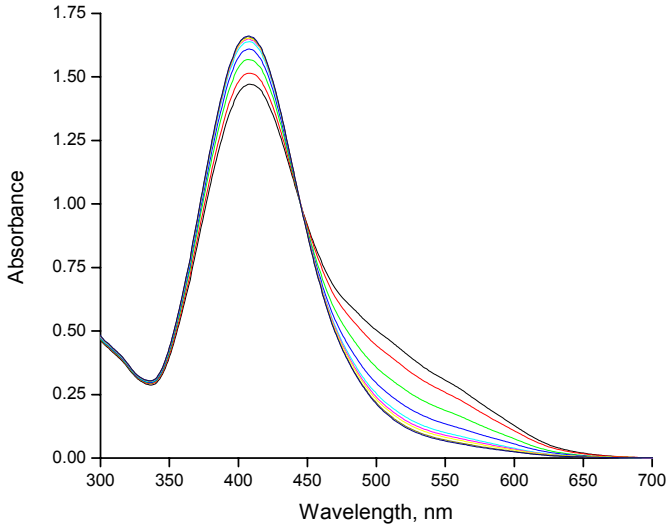
Figure 5:



(a) Zn^{II} **(b) Cd^{II}** **(c) Hg^{II}**

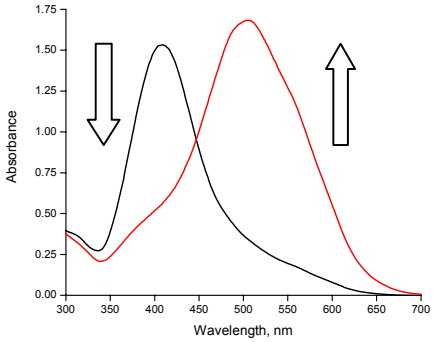
Reversal of UV-visible spectral pattern of Receptor 1 with 0.5 Equiv. of CH_3COO^- upon concomitant additions of (a) Zn^{II} (b) Cd^{II} and (c) Hg^{II}

Figure 6:

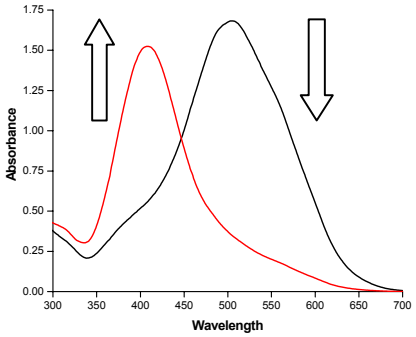


Changes in UV-visible spectral pattern of Receptor 1 upon concomitant addition of Zn^{II}

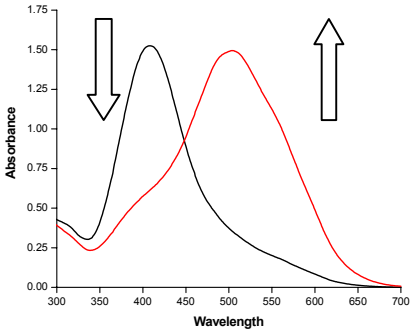
FIGURE 7: Three Cycle reversibility of receptor 1 upon addition of acetate and Zn^{II} ion respectively;



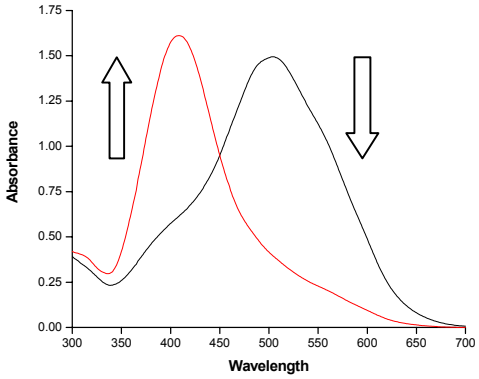
Receptor 1 +AcO^-



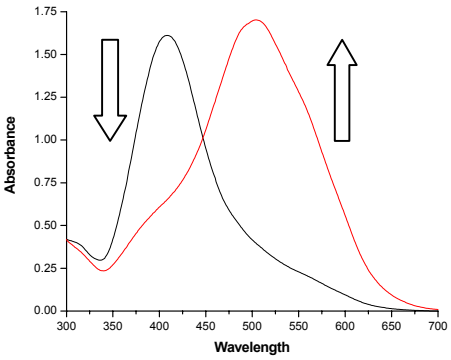
Receptor 1 +AcO^- + Zn^{II} ---------- Cycle 1



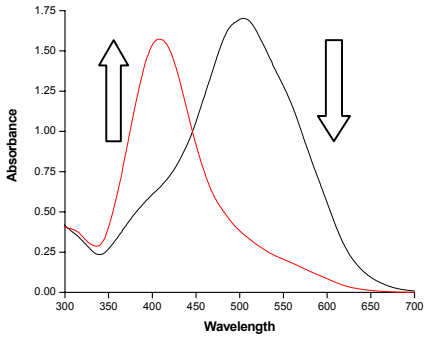
Cycle 1+ AcO^-



Cycle 1+ AcO^- +Zn^{II} ---------- Cycle 2

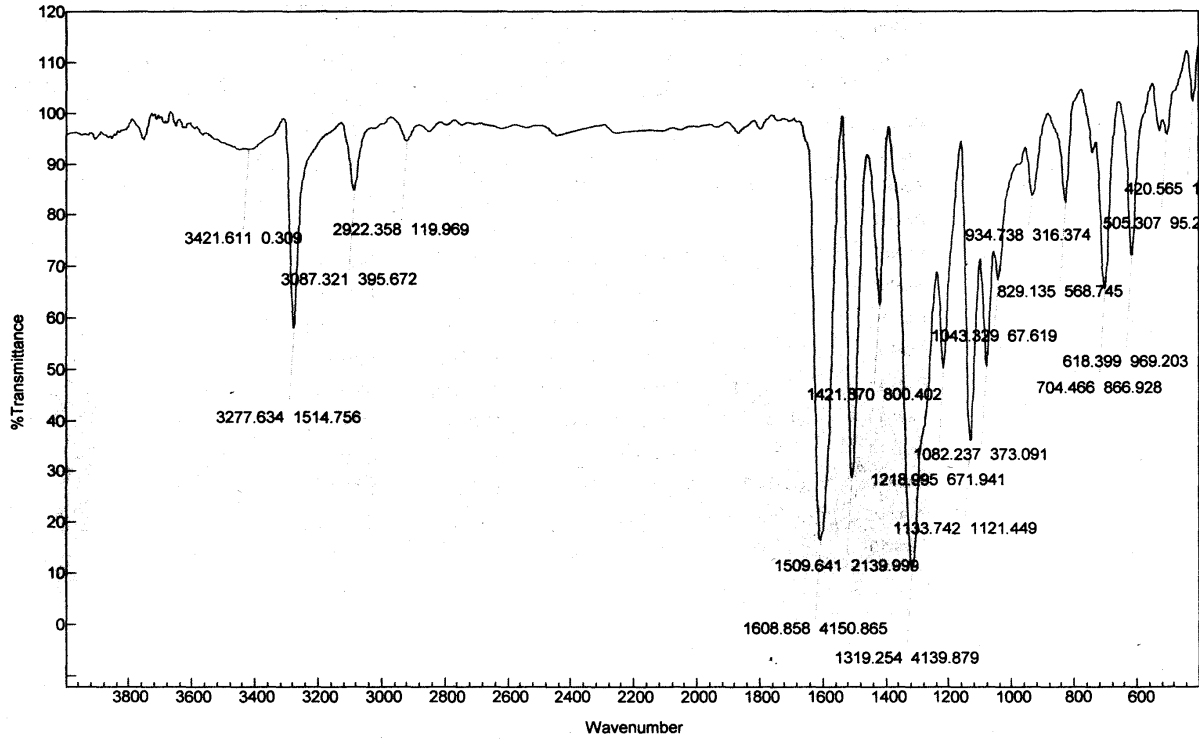


Cycle 2 + AcO^-

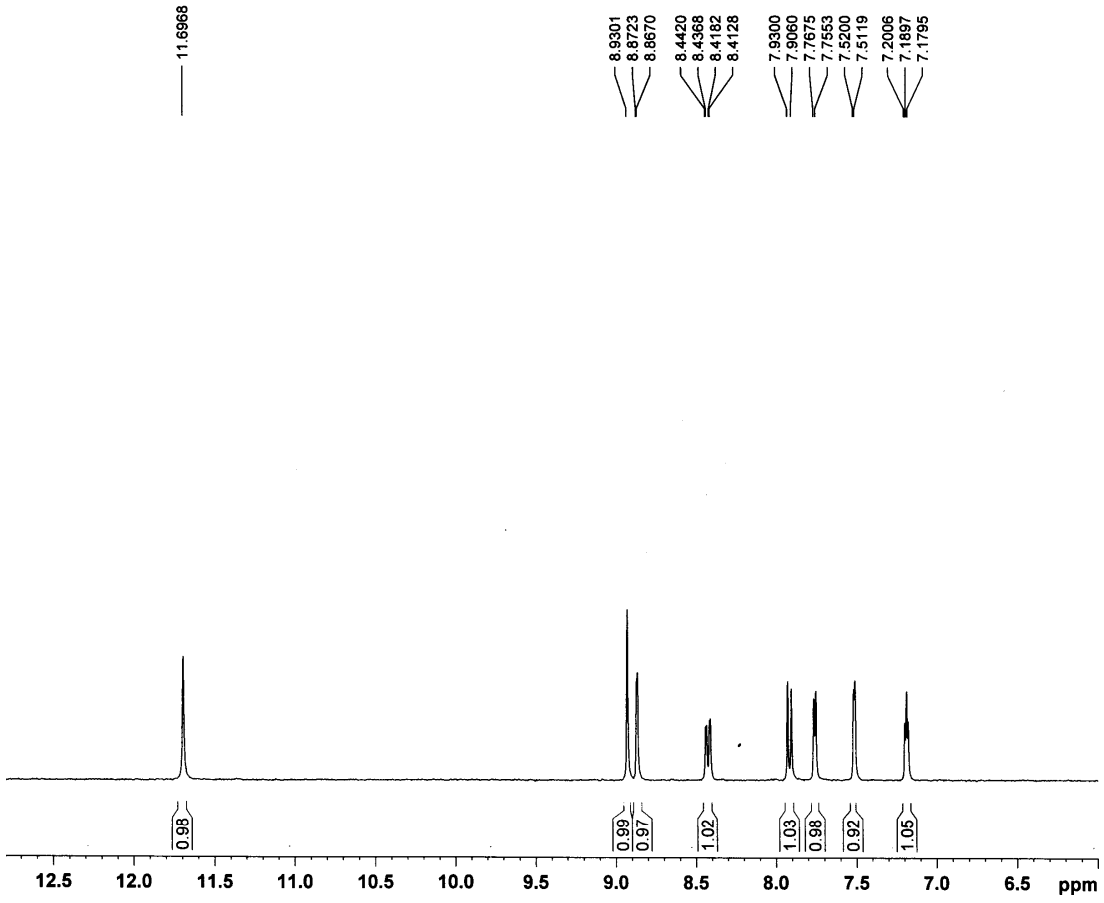


Cycle 1+ AcO^- + Zn^{II} ---------- Cycle 3

IR spectrum of Receptor 1:



^{1}H NMR Spectrum of Receptor 1:



Elemental analysis for Receptor 1:

Run Type Manual ID=TDN
Counter# 498 Run# 6 Wt= 1940. ug
PT=40 CT=10 FT= 53
BC=84 BH=170 BN=1646
KC=22.070 KH=70.700 KN=8.100
CR=20998 HR=5207 NR=6009
CZ=1745 HZ=1199 NZ=1458

R-Z=19253 R-Z=4008 R-Z=4551

RESULT= %C=44.771% %H=2.798 % %N=18.487% %R=33.944%

Analysis performed on Exeter Analytical Inc "Model CE-440 CHN Analyser" at Laboratory of Chemistry Department Faculty of Science BHU VARANASI-221005