

**Chemical Research Society of India
Sixth National Symposium
Indian Institute of Technology, Kanpur**

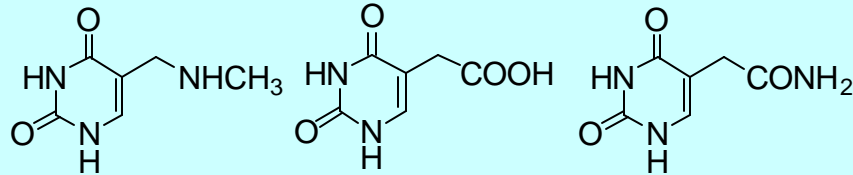
Photoactive Receptors for Metal ion Recognition

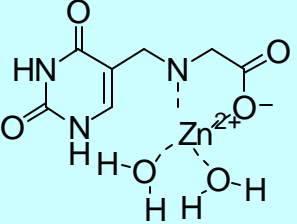
Subodh Kumar

Department of Chemistry, Guru Nanak Dev University,
Amritsar – 143 005.

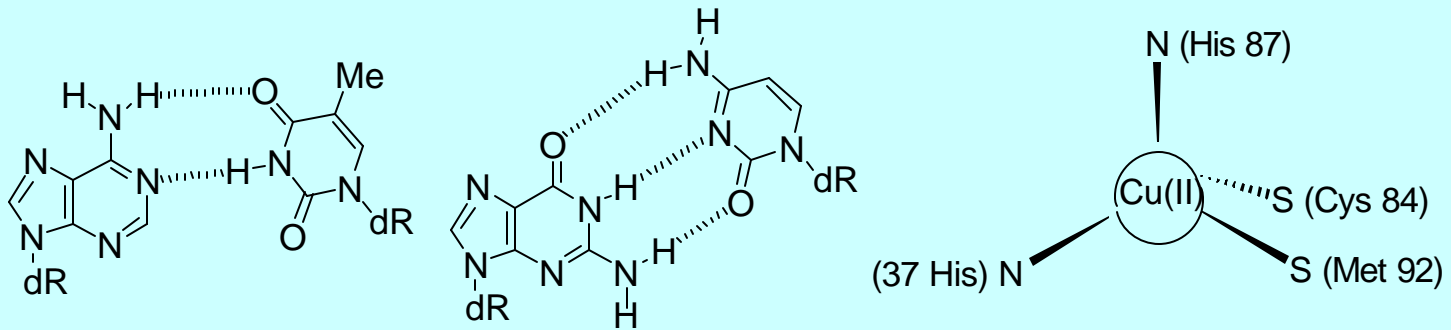
MOLECULAR RECOGNITION IS BASIS OF LIFE

- RNA WORLD - PREBIOTIC PERIOD
- NUCLEIC ACID WORLD



-  Bridge between RNA world & present state
- The side chains of amino acids attached at C-5 of uracil.
- **Limited metal ion selective pockets, poor recognition.**

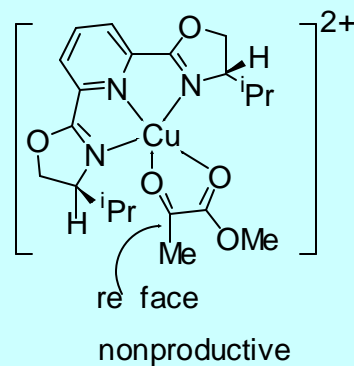
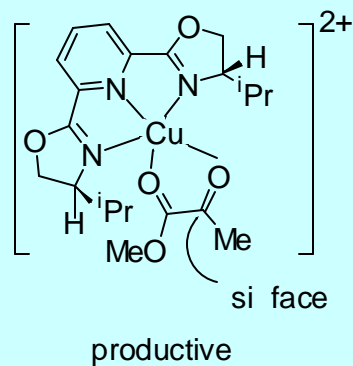
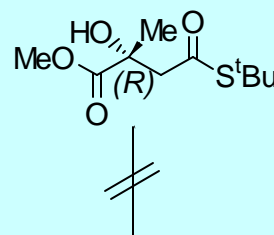
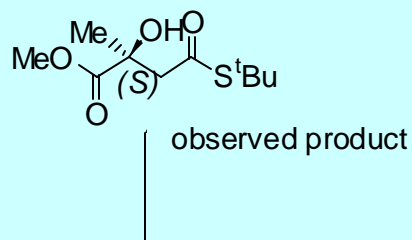
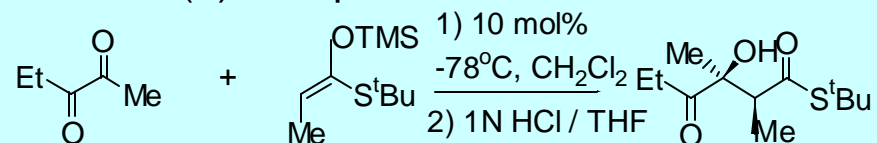
DNA - PROTEIN WORLD



- Adenine - Thymine Guanine - cytosine Cu(II) selective binding in protein
- Watson - Crick Model (1953) Plastocyanin

Molecular Recognition & Asymmetric Synthesis

- Evans' Bisoxazoline - Cu(II) Complexes

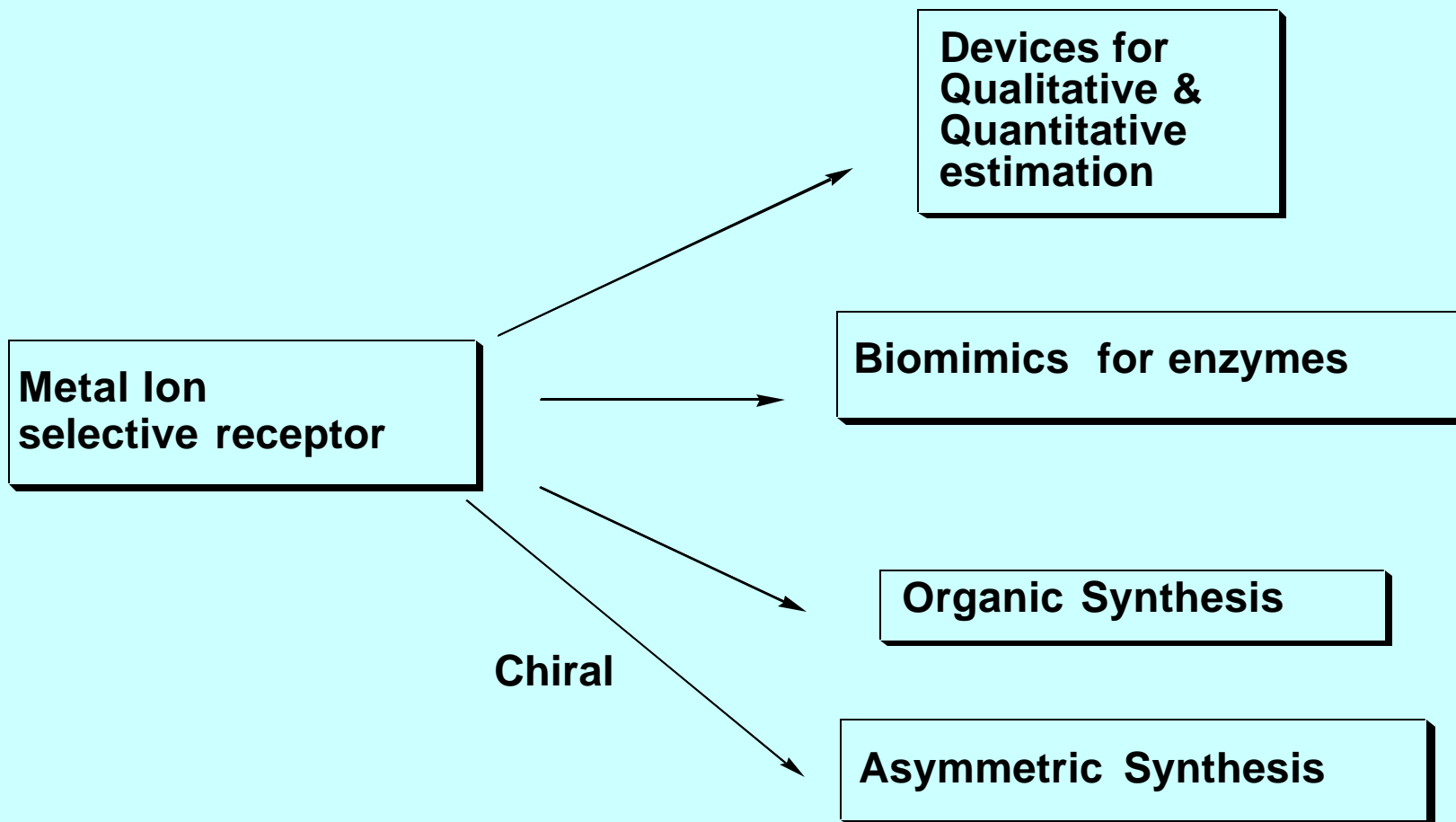


- D.A. Evans et. al. J. Am. Chem. Soc. **1999**, 121, 686-699.

Metal ions play the crucial role in organization of various moieties in Enzymatic and other catalytic reactions

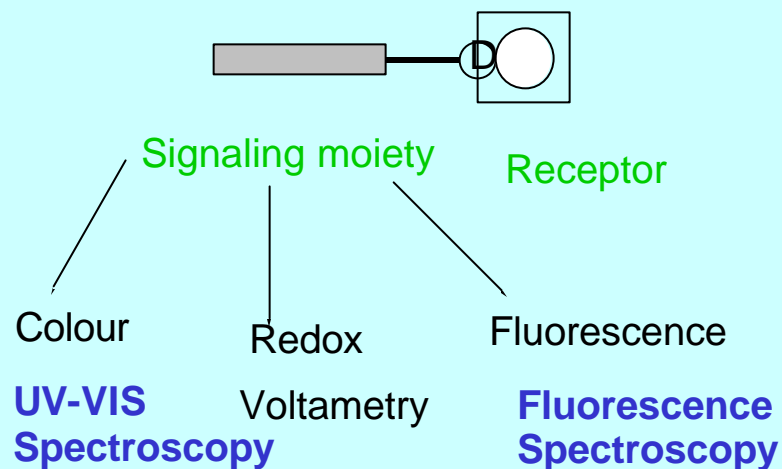
Development of receptors with selective metal ion binding features is necessitated for their estimations and other features

Possible applications



Objectives

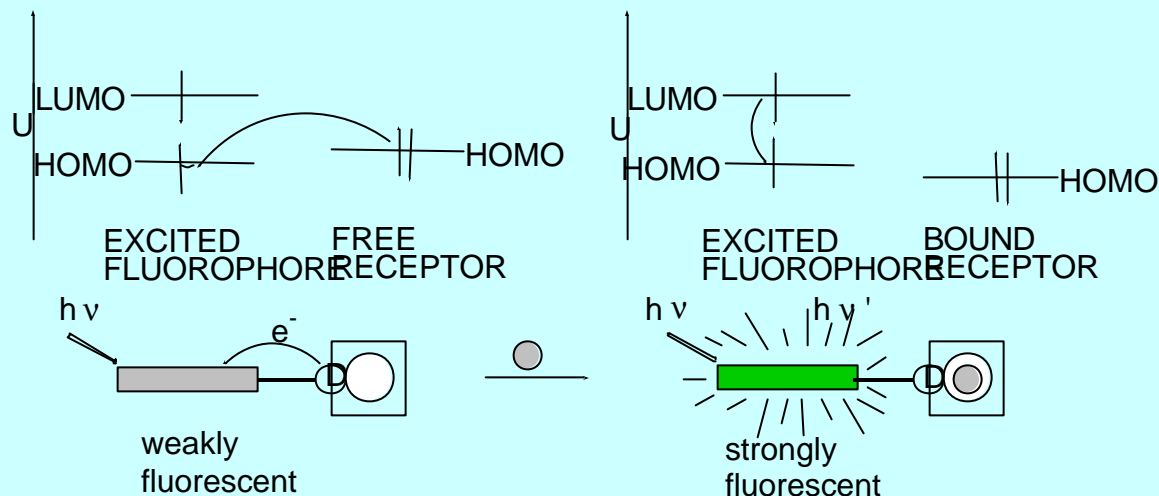
- ***Photoactive Receptors for Cu(II) and Ag(I)***
- *Conventional Techniques: Atomic absorption spectroscopy, ion selective electrodes, Flame photometry etc.
- More recent Techniques: Chemosensors and their based ion-selective electrodes



- **more sensitive and accurate**

Fluorescent Receptors

- Fluorescence Efficiency Before and after complexation (PET)

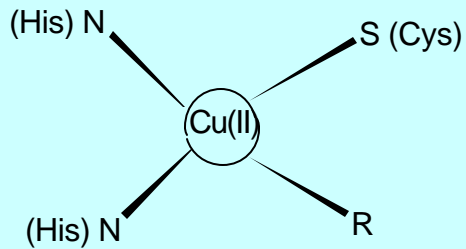


- -- nature of Fluorescent moiety (absorption and fluorescence wavelength and efficiency)
- -- interactions of ligating sites (N, S, O) of receptor with the guest species (**enhanc.**)
- -- interactions of fluorophore moiety with the guest species (**quenching**)
- -- paramagnetic effect in case of some metal ions (**quenching**)
- -- placement of fluorescent moiety in the receptor (**efficiency of above phenomena**)
- (distance of ligating sites from fluorescent moiety)

Cu(II) Binding sites in enzymes

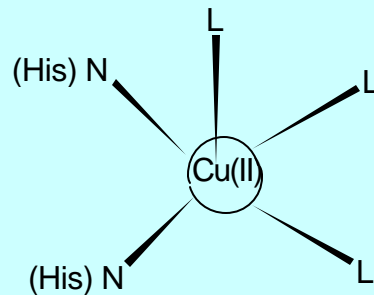
Tetragonal , Jahn-Teller effect

Type I



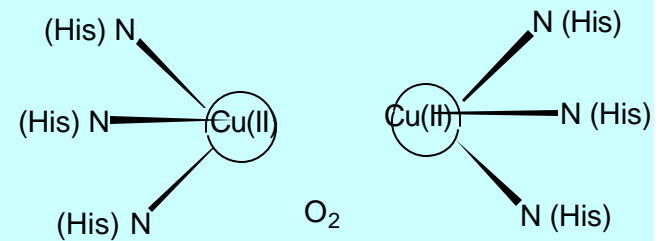
R = Met (azurin, Plastocyanin)
R = N / O donor (stellocyanin)

Type II



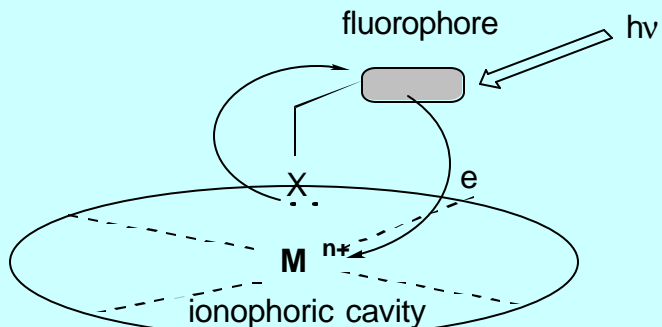
lacasse

Type III

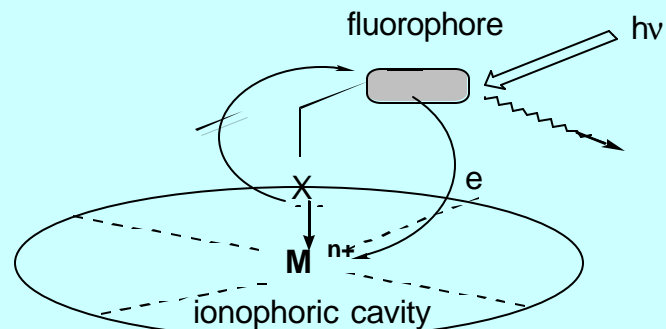


Tyrosinase,
Hemocyanin

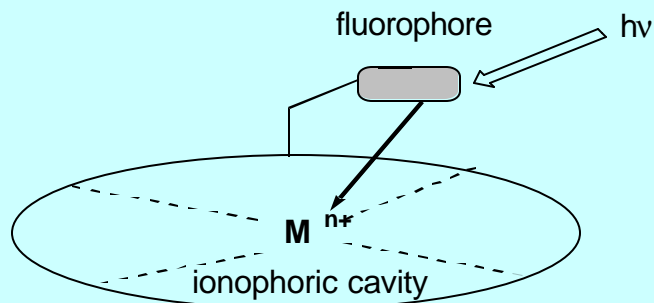
Various phenomena for the metal induced fluorescence enhancement / quenching (PET)



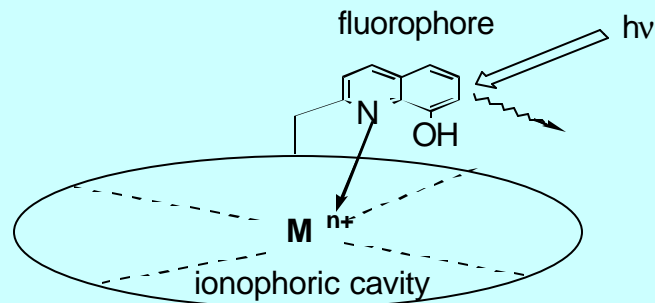
fluorescence quenching



fluorescence enhancement



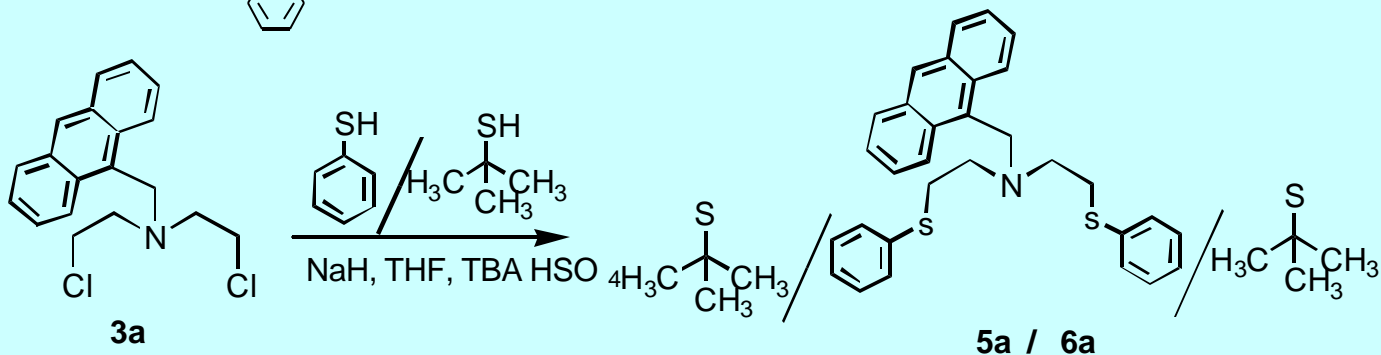
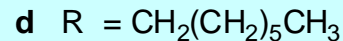
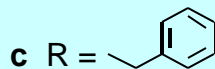
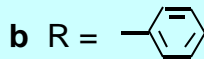
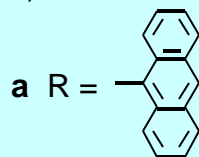
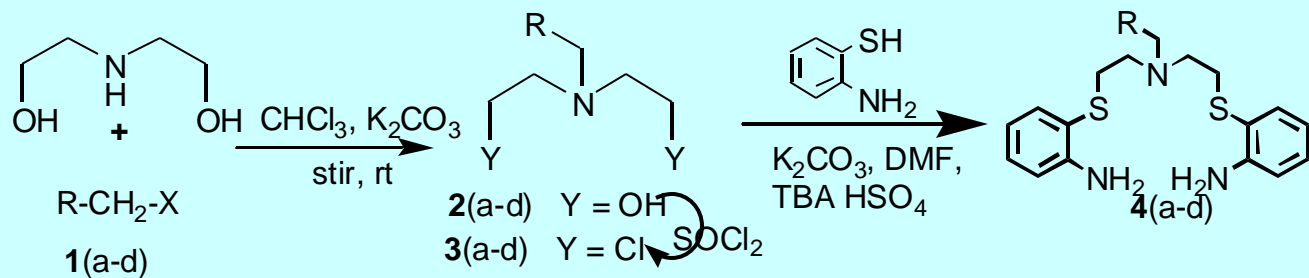
fluorescence quenching



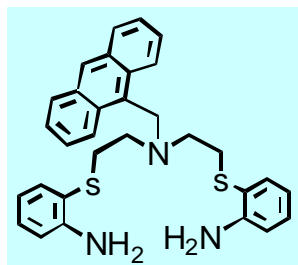
fluorescence enhancement

Anthracene based ionophores

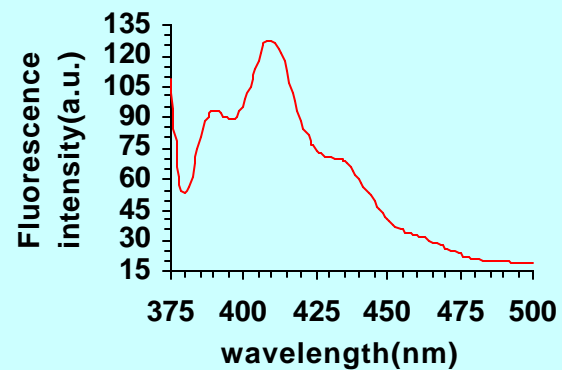
- Synthesis



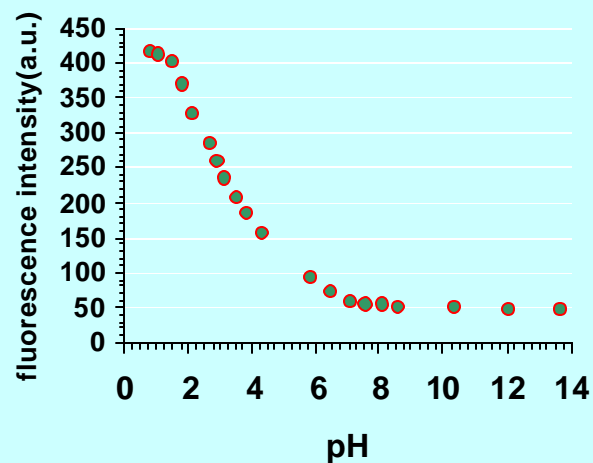
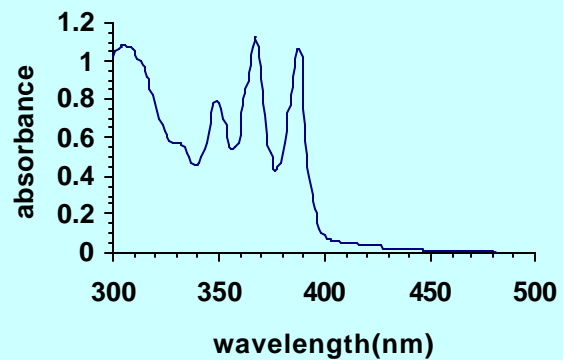
Anthracene based ionophores



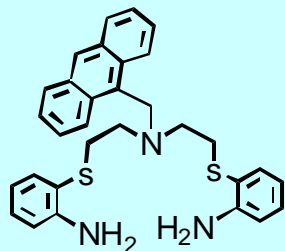
Fluorescence spectrum



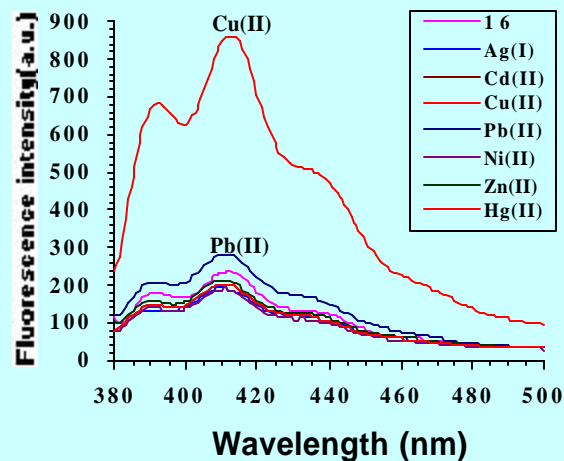
UV-visible spectrum



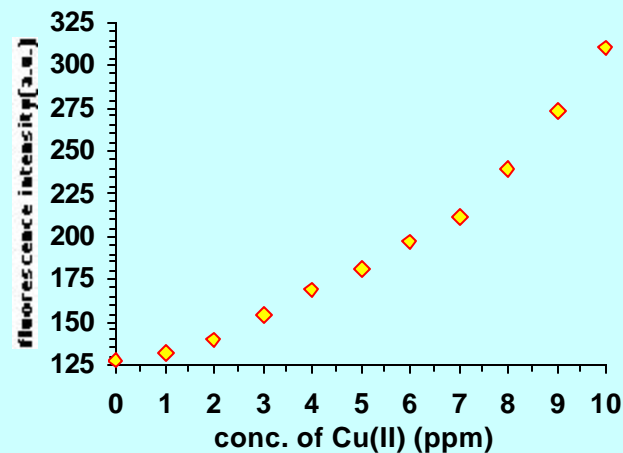
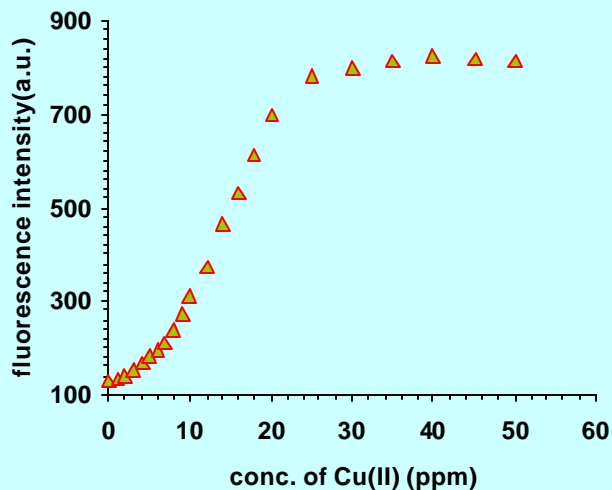
Anthracene based ionophores



[4a] = 10^{-5} , $\lambda_{\text{ex}} = 365 \text{ nm}$, $\lambda_{\text{em}} = 410 \text{ nm}$
in $\text{CH}_3\text{CN} : \text{H}_2\text{O} 4:1$ at pH 7 (HEPES 10 mM)



Effect of metal ions

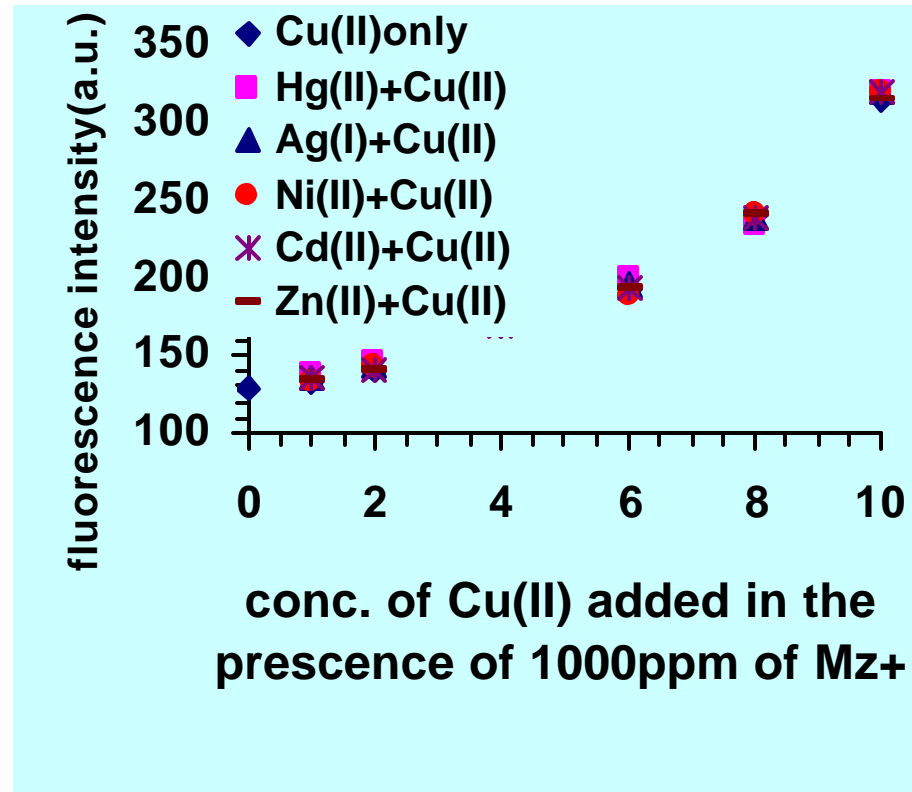


Titration with Cu(II)

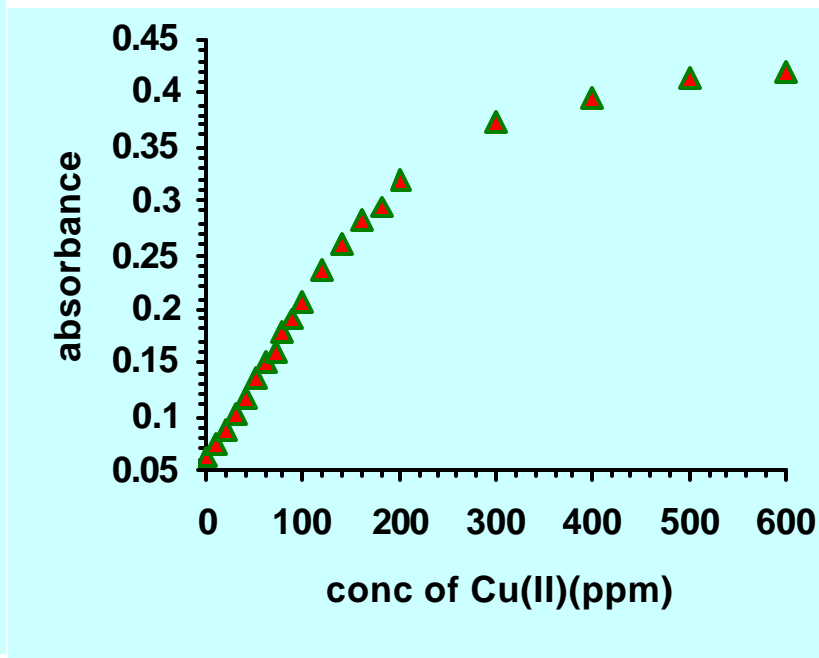
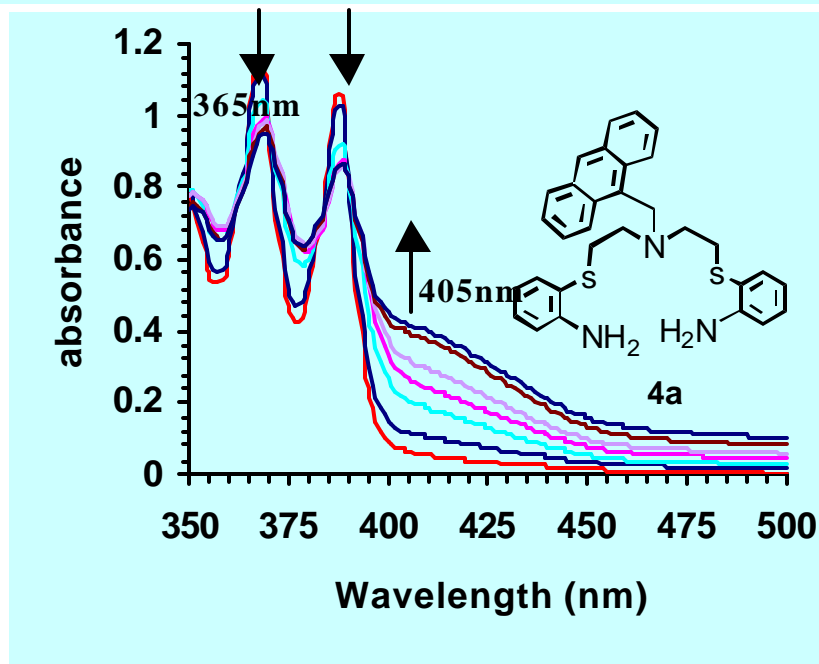
S. Kaur and S. Kumar, J. Chem. Soc. Chem. Commun. 2002, 2840.

Anthracene based ionophores

Interference of other metal ions



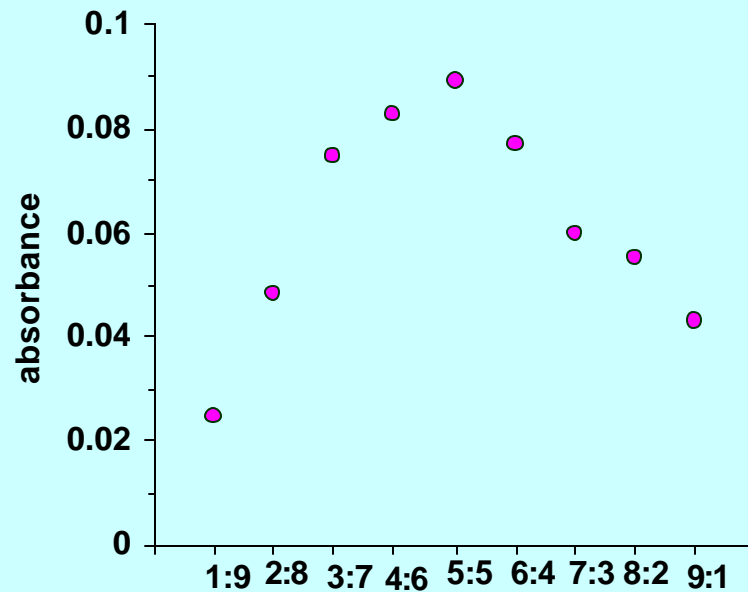
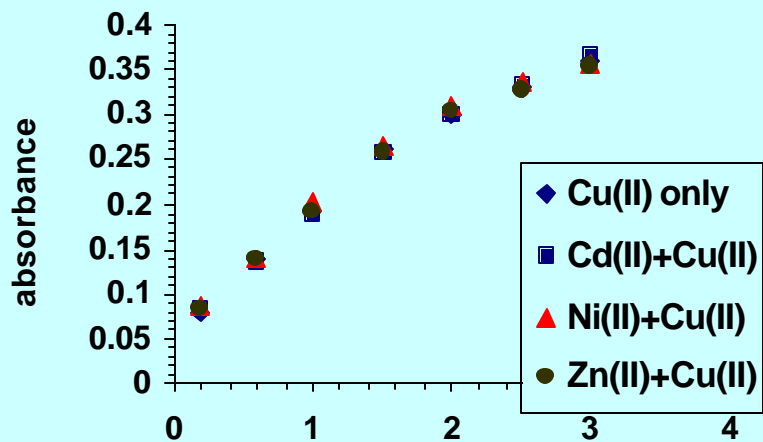
Anthracene based ionophores



- Effect of Cu(II) on UV-Vis spectrum
-

$[4a] = 10^{-4}M$, $[Cu(II)] = 10^{-5}M$
 $-10^{-6}M$ titration with Cu(II)

Anthracene based ionophores

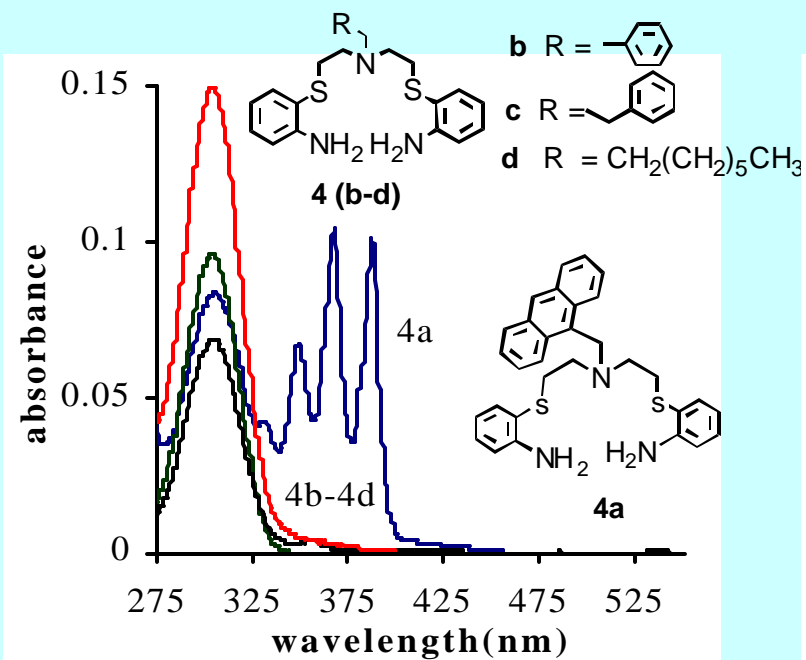


- Interference of other metal ions

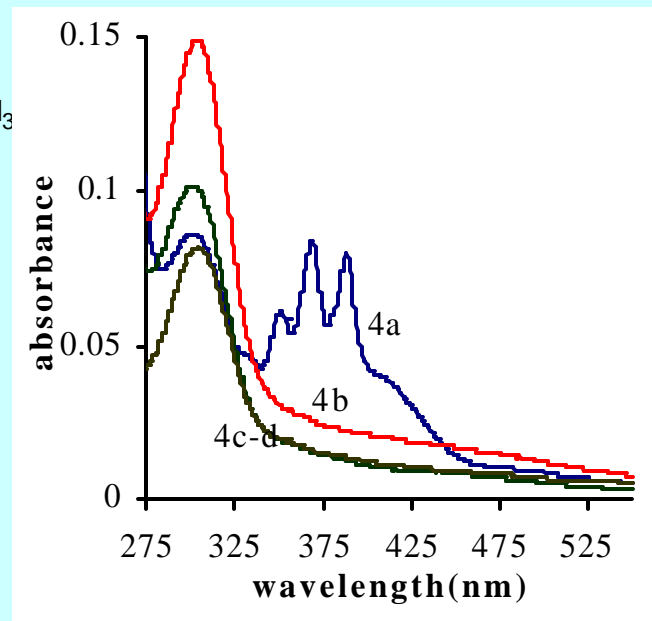
- Job plot

Anthracene based ionophores

Effect of appendage on UV-Vis spectrum

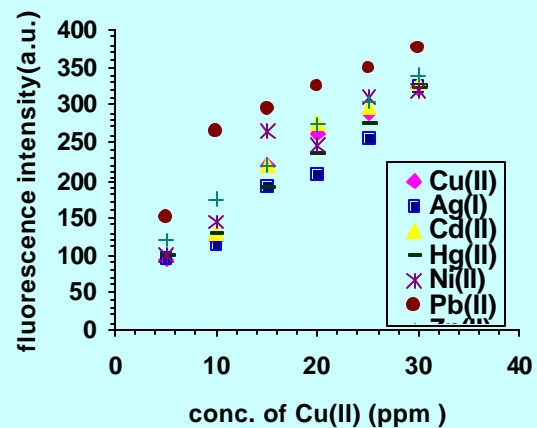
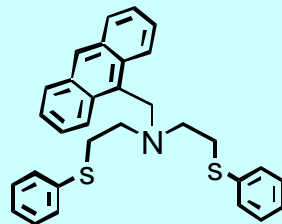
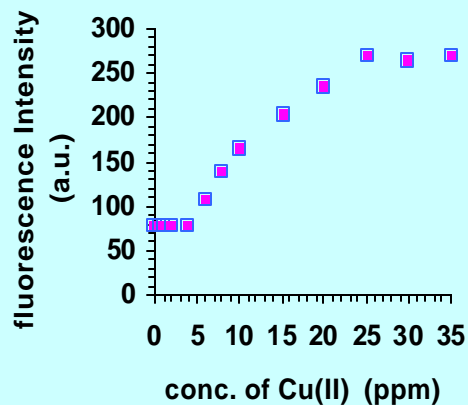


Absorption spectra of **4a-d** (10^{-5} M)

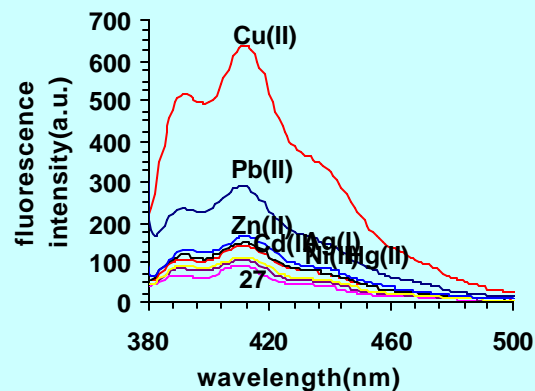


Absorption spectra of **4a-d** (10^{-5} M)
on addition of Cu(II) (5×10^{-5})

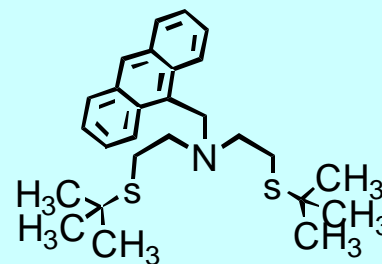
Anthracene based ionophores



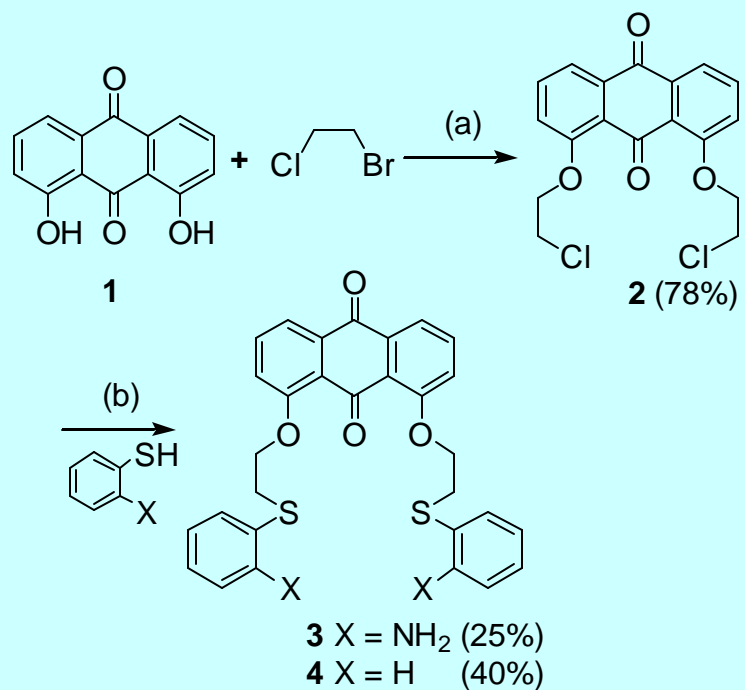
Titration with Cu(II)



Interference of other metal ions

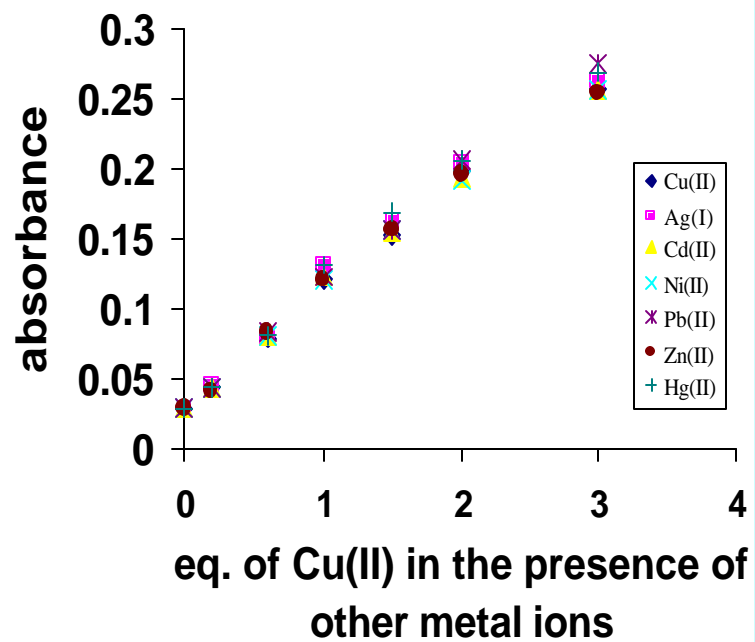
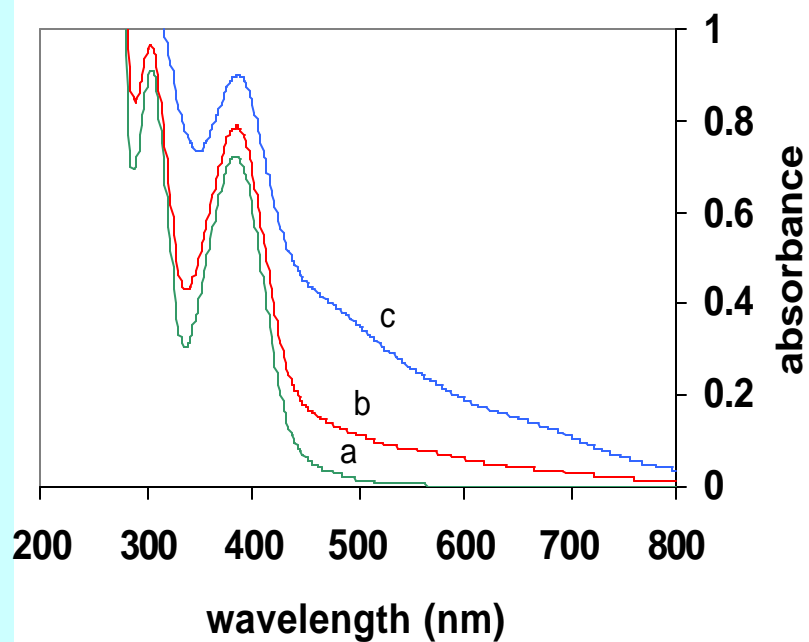
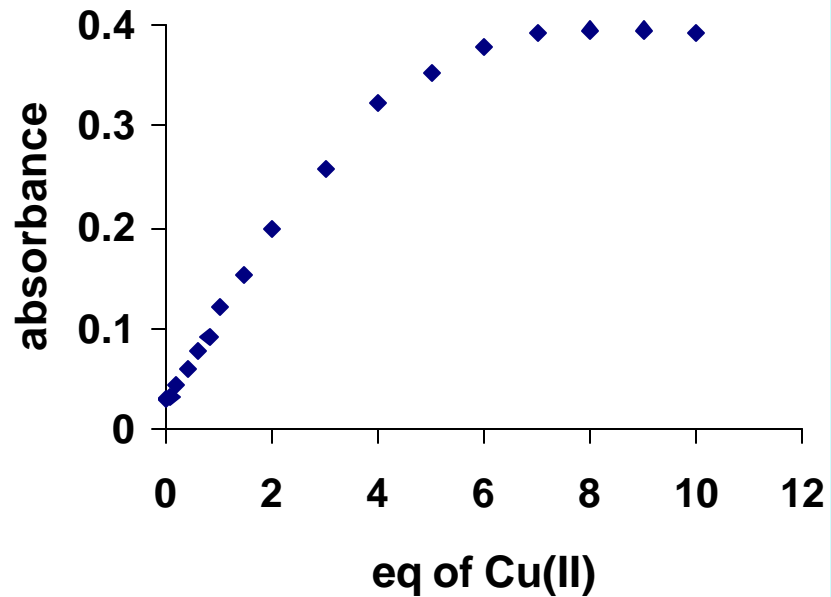
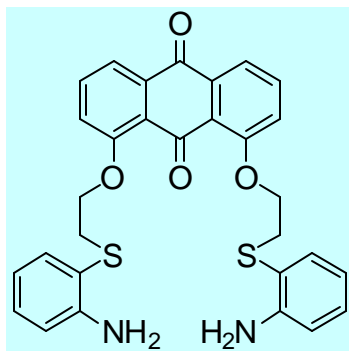


Synthesis of anthraquinone based Receptor



(a) K₂CO₃, DMF, tetrabutylammonium HSO₄, 18-Crown-6, 80°C, 48h

(b) K₂CO₃, DMF, TBA-HSO₄, 12h

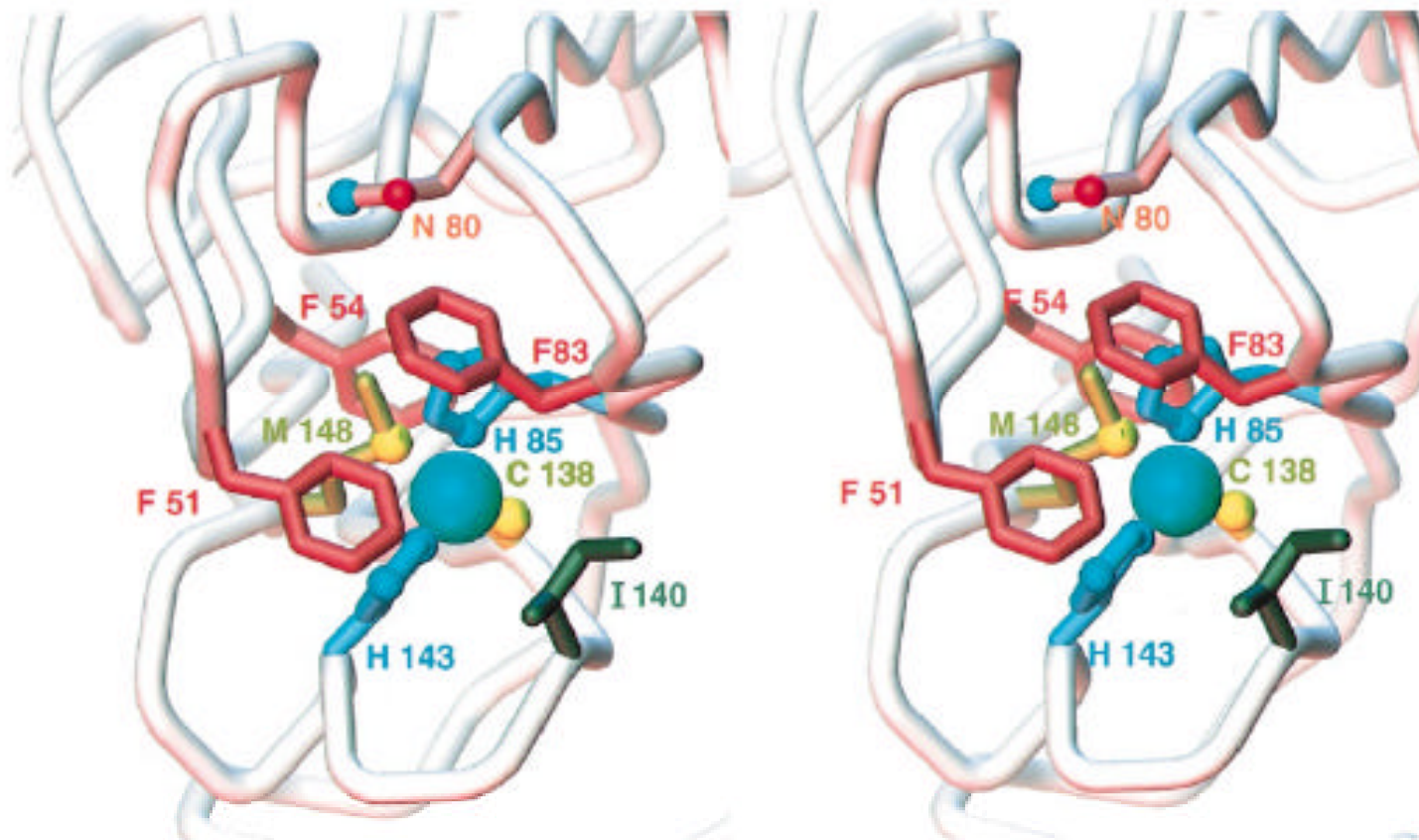


Cu(I) Rusticyanin from Thiobacillus Ferrooxidans

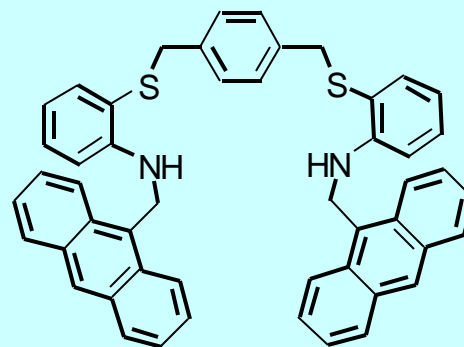
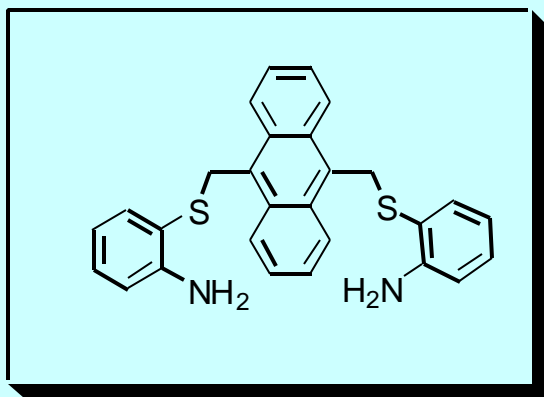
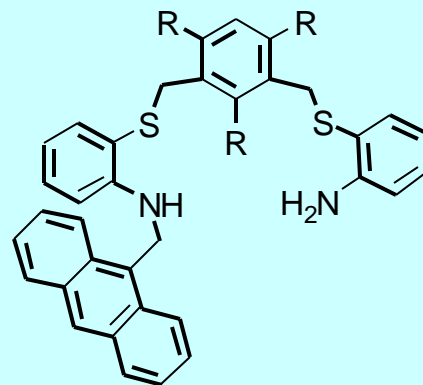
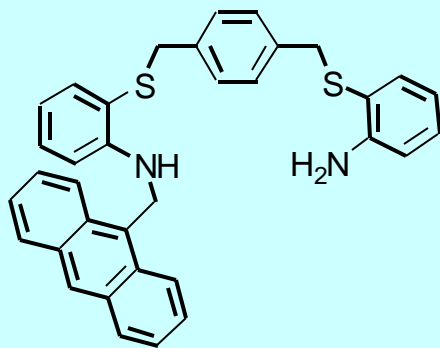
Structural basis for extreme stability

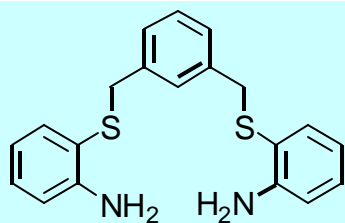
Disposition of ligands and spatially close side chains in the copper site

High density of aromatic rings immediately surrounding the Cu(II) site

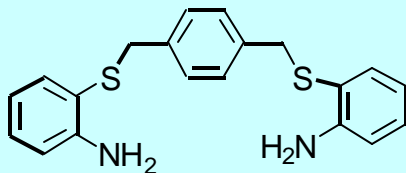


Possible Models for Cu(II) Cavity

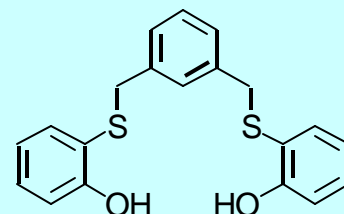




% ext. Ag⁺ = 97.6
Ag⁺ / Pb²⁺ sel. = 1085

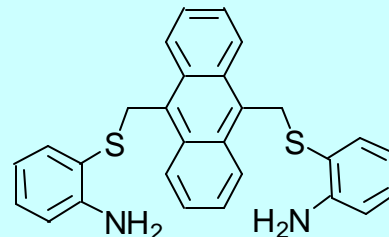
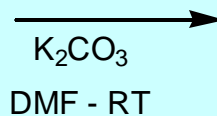
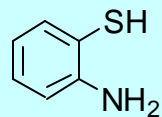
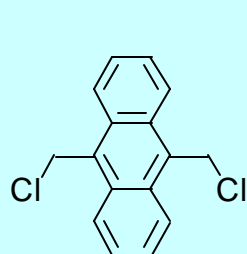


% ext. Ag⁺ = 59
Ag⁺ / Pb²⁺ sel. = 212



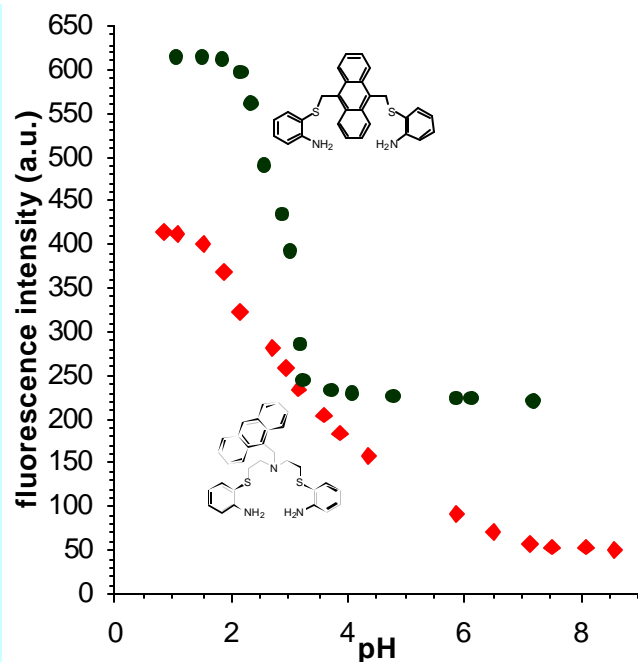
% ext. Ag⁺ = 60
Ag⁺ / Pb²⁺ sel. = >2000

(0.01 M L, 0.01M metal picrate)

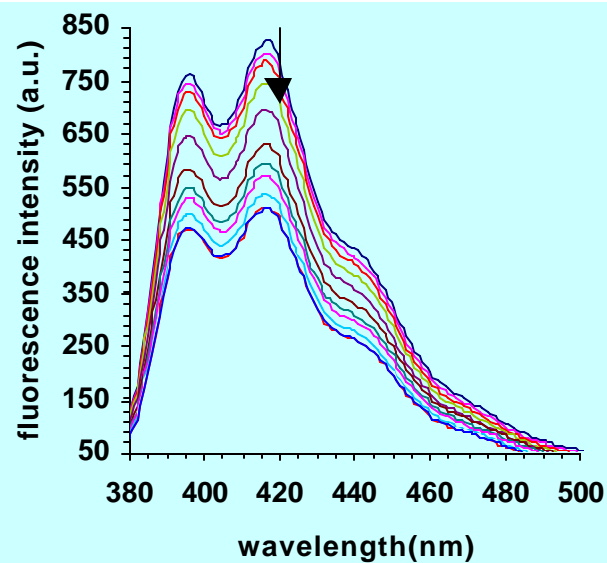


% Ext. Ag⁺ = 7.48, Pb²⁺ 0.2
Ag⁺ / Pb²⁺ sel. 374
(0.001 M L; 0.001 M metal picrate)

9,10-anthracene based fluorescent Cu(II) sensor

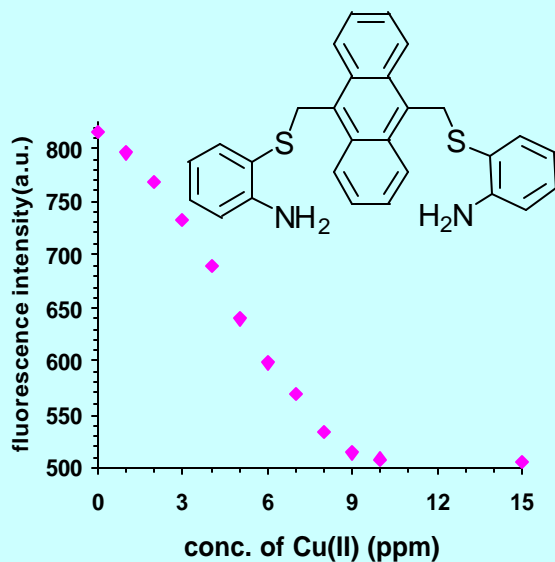


Effect of pH on the fluorescence intensity of fluoroionophores

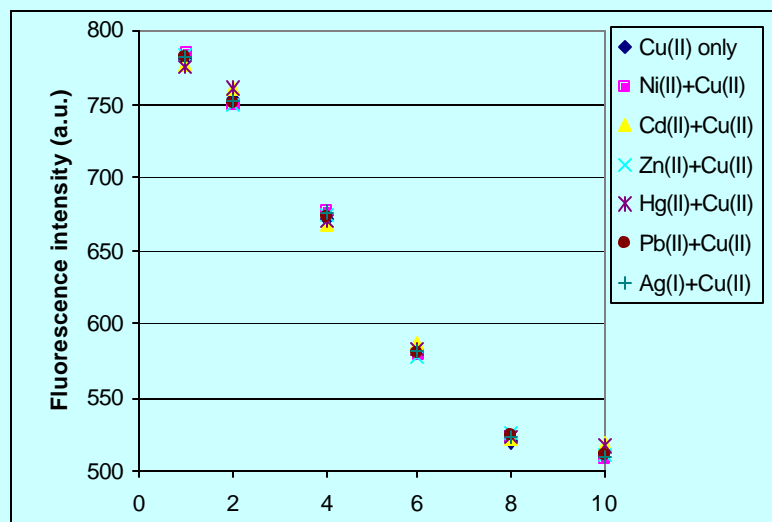


The effect of Cu²⁺ on the Fluorescence of Fluoroionophore (5 mM)

9,10-anthracene based fluorescent Cu(II) sensor

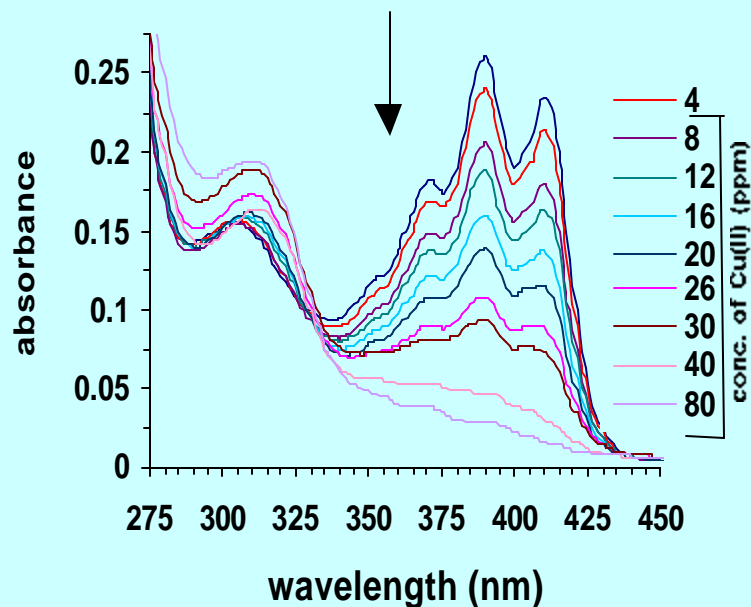


Plot of conc. of Cu²⁺ vs fluorescence of fluoroionophore

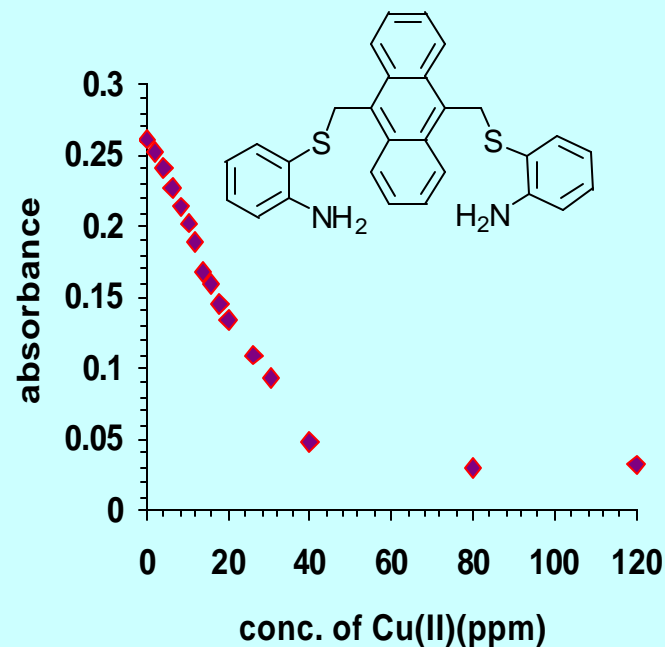


The estimation of Cu²⁺ in the presence of Ni²⁺, Cd²⁺, Zn²⁺, Hg²⁺, Ag⁺ and Pb²⁺ (5000mM)

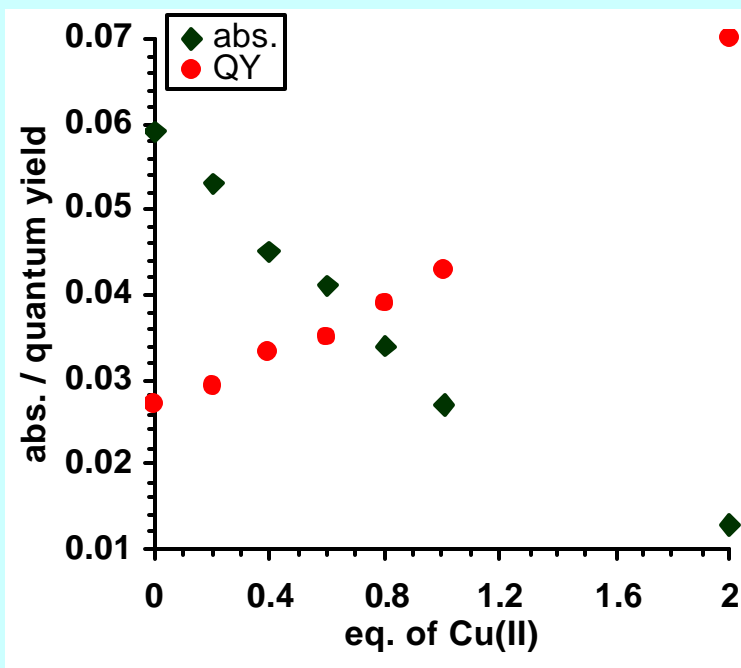
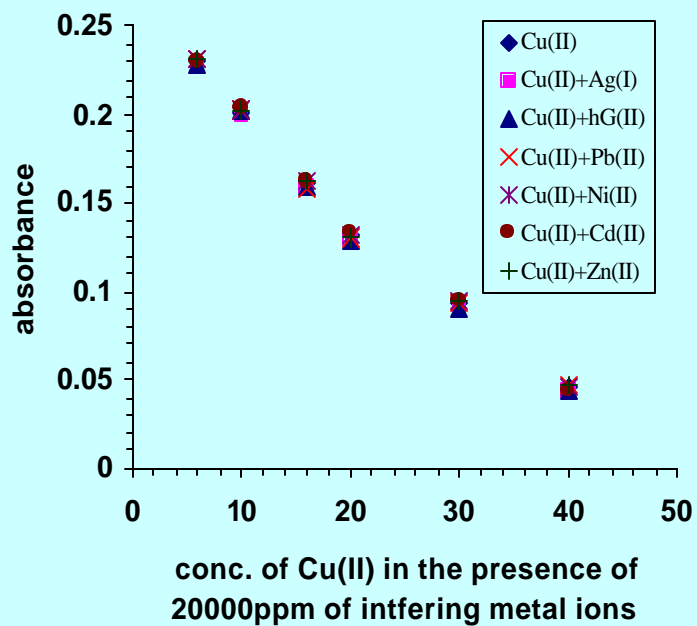
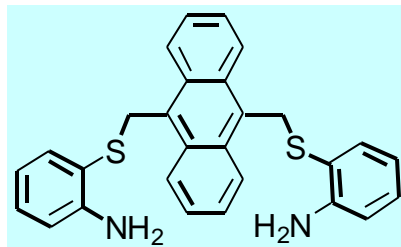
9,10-anthracene based fluorescent Cu(II) sensor



The effect of Cu^{2+} on the UV-vis spectrum of fluoroionophore



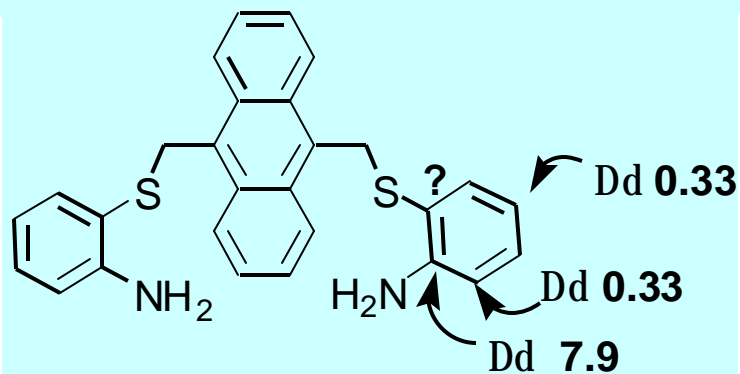
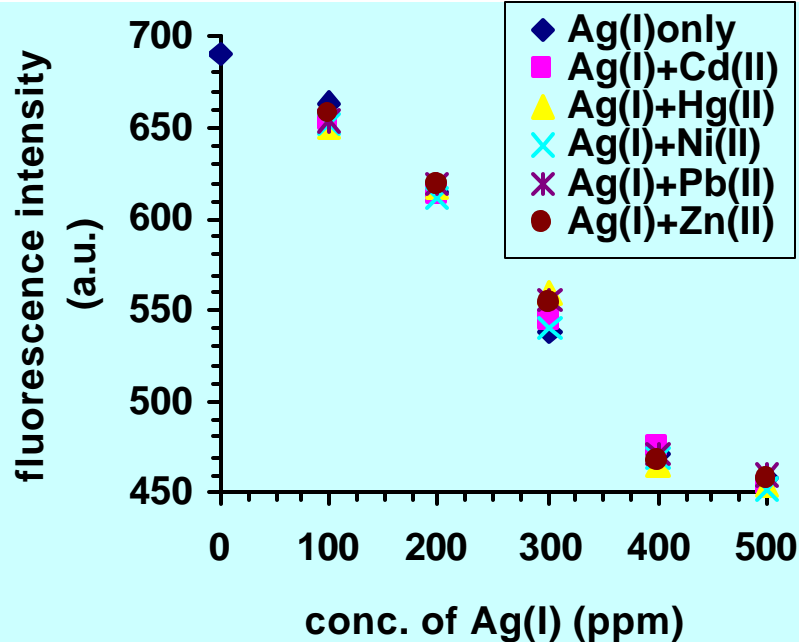
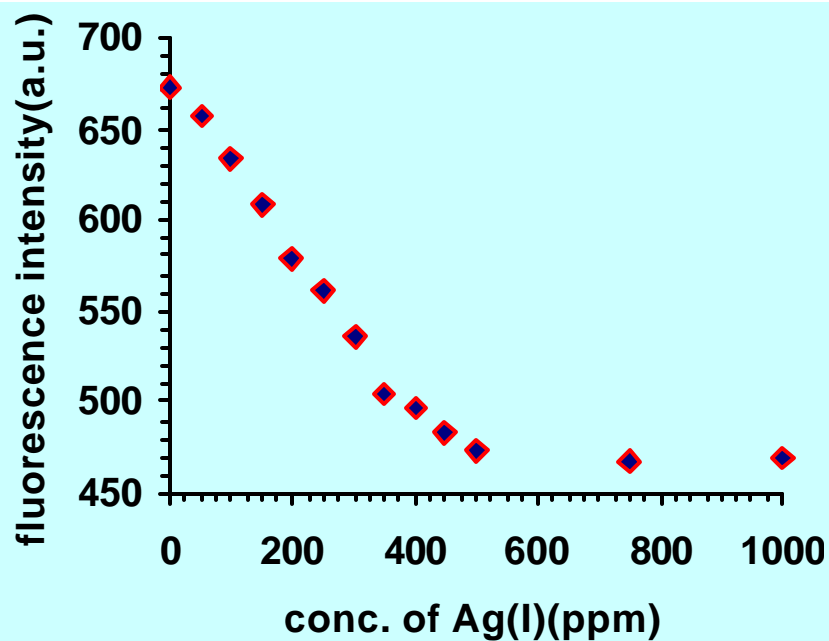
Plot of absorbance Vs concentration of Cu^{2+} at 415 nm



- Estimation of Cu (II) in the presence of other competing metal ions (20mM)

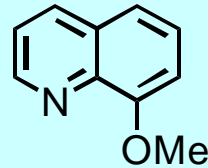
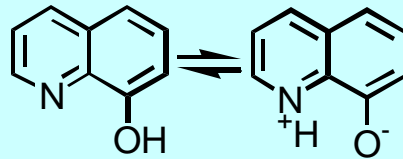
Plot of abs. / quantum yield Vs. Eq. of Cu(II)

Estimation of Ag(I)



Change in the chemical shifts of carbon signals on addition of AgNO_3 (1 equiv.) to a solution of fluorophore in $\text{CD}_3\text{CN}:\text{CDCl}_3$ 1:1

8-Hydroxyquinoline based ionophores



- **non-Fluorescent**

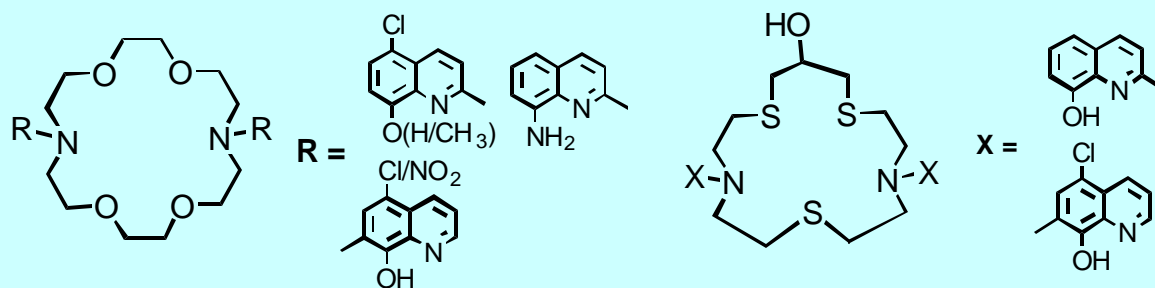
- **Fluorescent**

- The most frequently used complexing agent after EDTA
- The proton transfer from O to N during excitation turns it non-fluorescent moiety
- undergoes colour changes during complexation

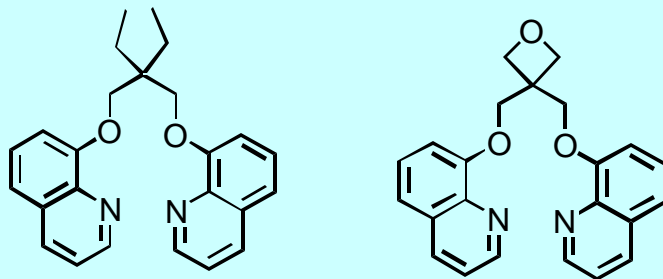
8-Hydroxyquinoline based ionophores

Literature reports

- Recognition is mainly dependent on ionophore core

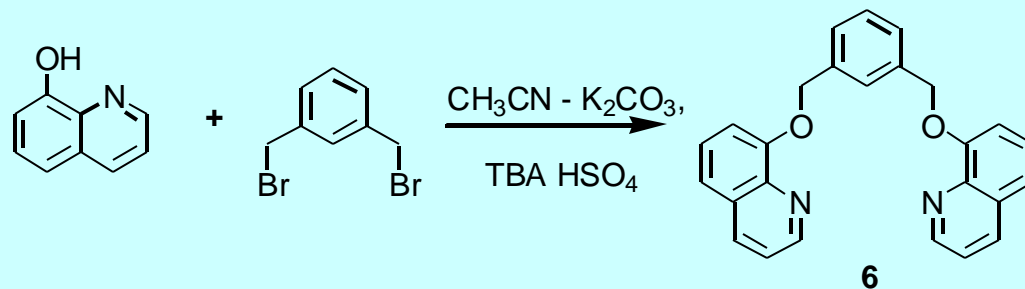
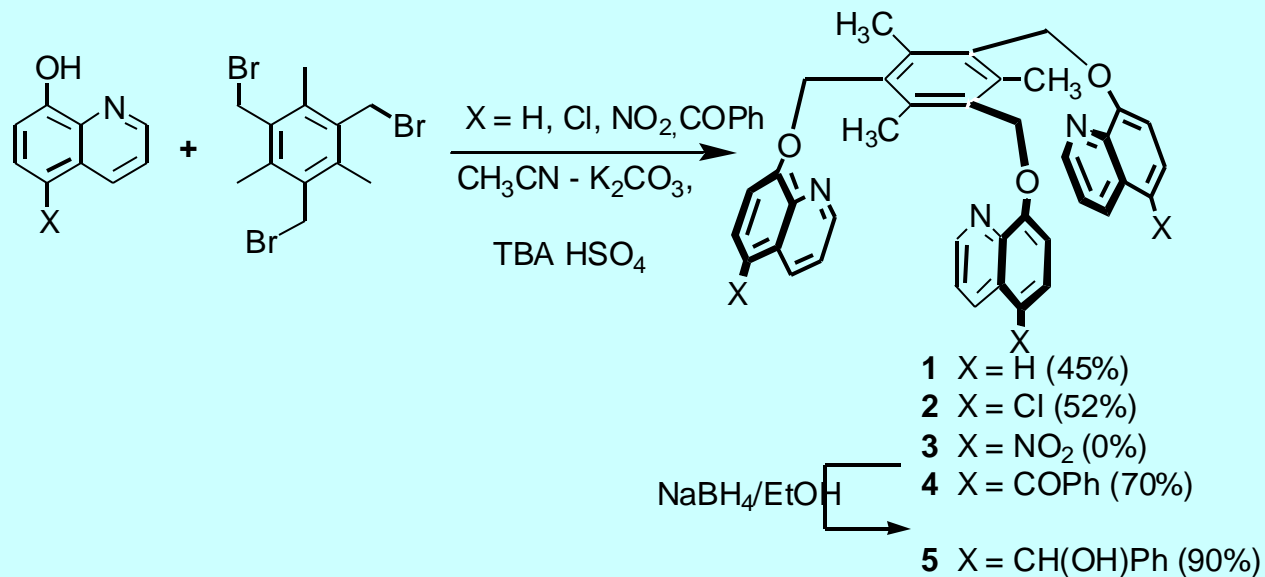


- ionophores with only 8-hydroxyquinoline as ligating sites



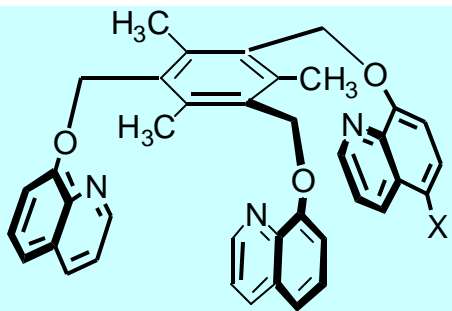
8-Hydroxyquinoline based ionophores

Synthesis of Tripod and Podand Ionophores

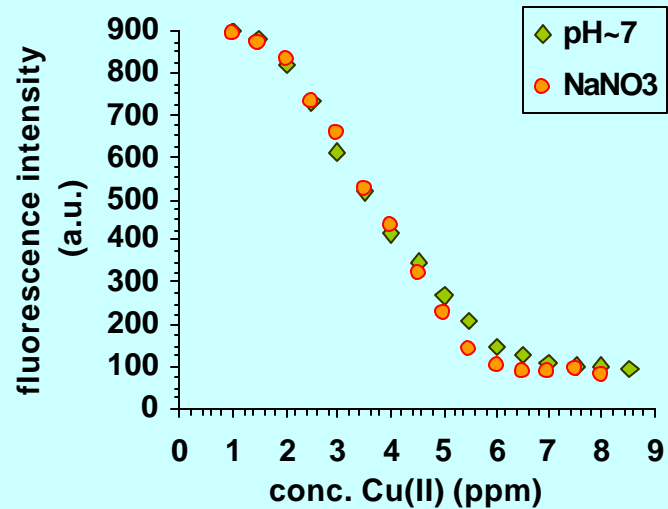
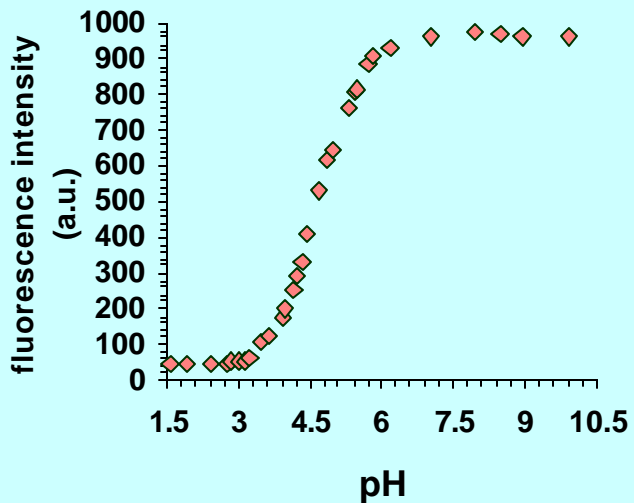
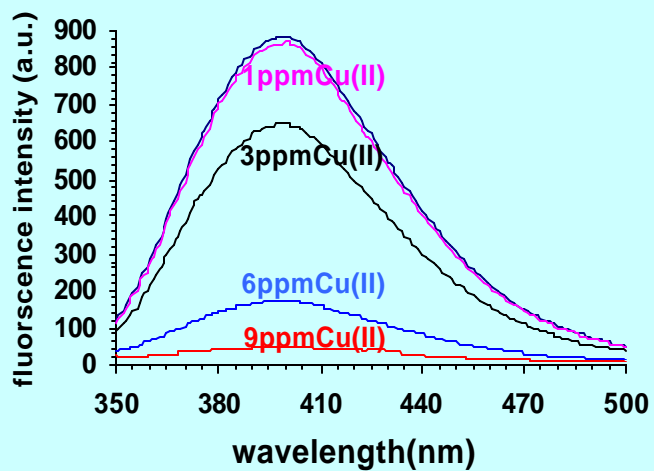


[1] = $1 \times 10^{-7} \text{M}$, $\lambda_{\text{ex}} = 305 \text{nm}$, $\lambda_{\text{em}} = 398 \text{nm}$

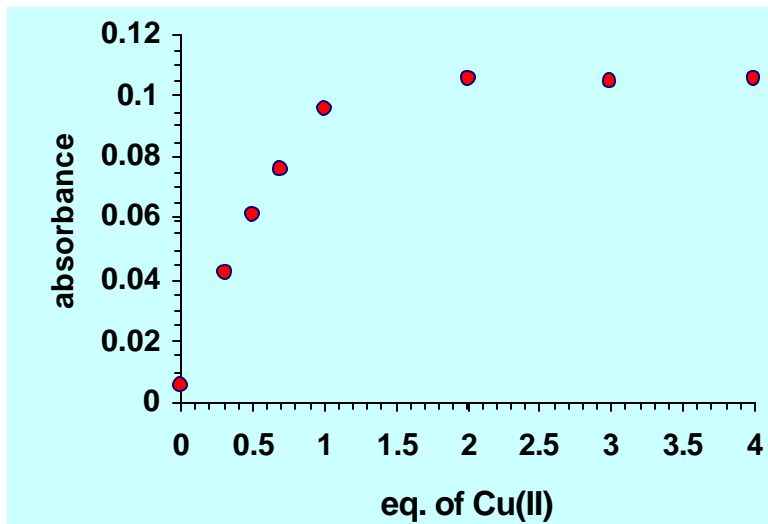
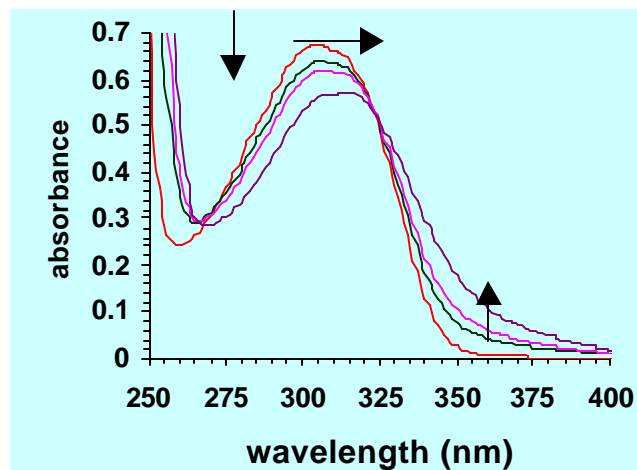
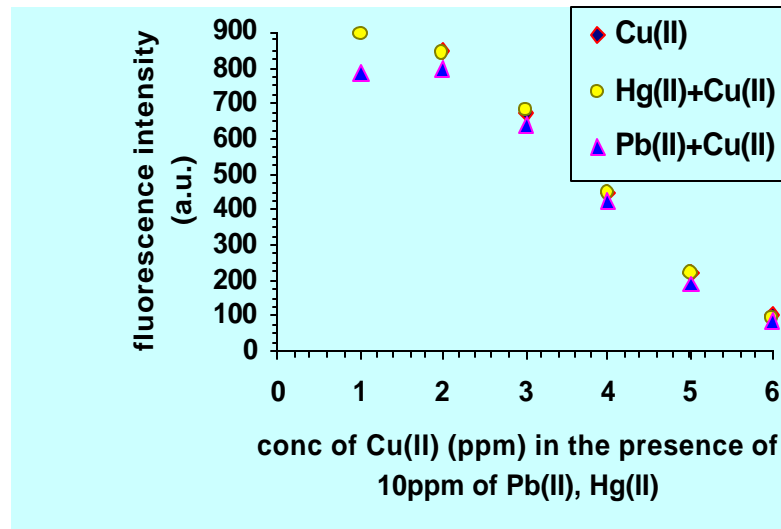
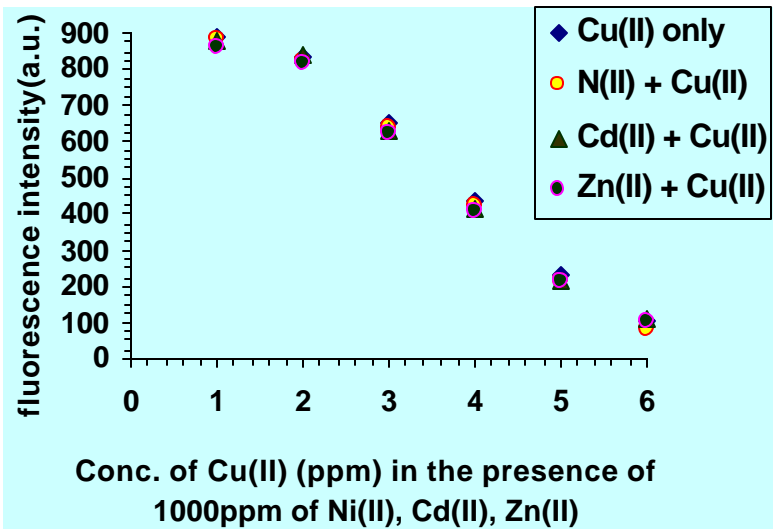
in $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ 4:1 (0.01M NaNO_3)

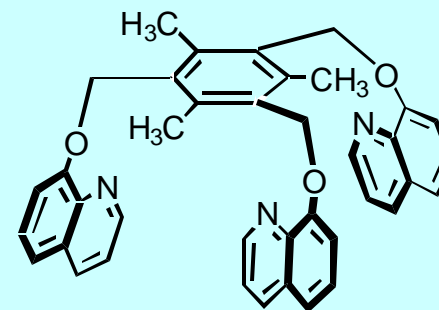
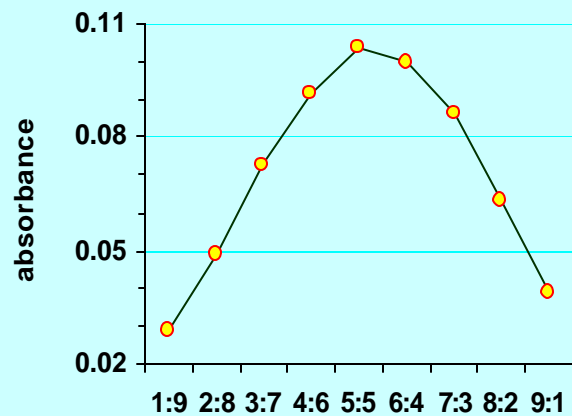


1



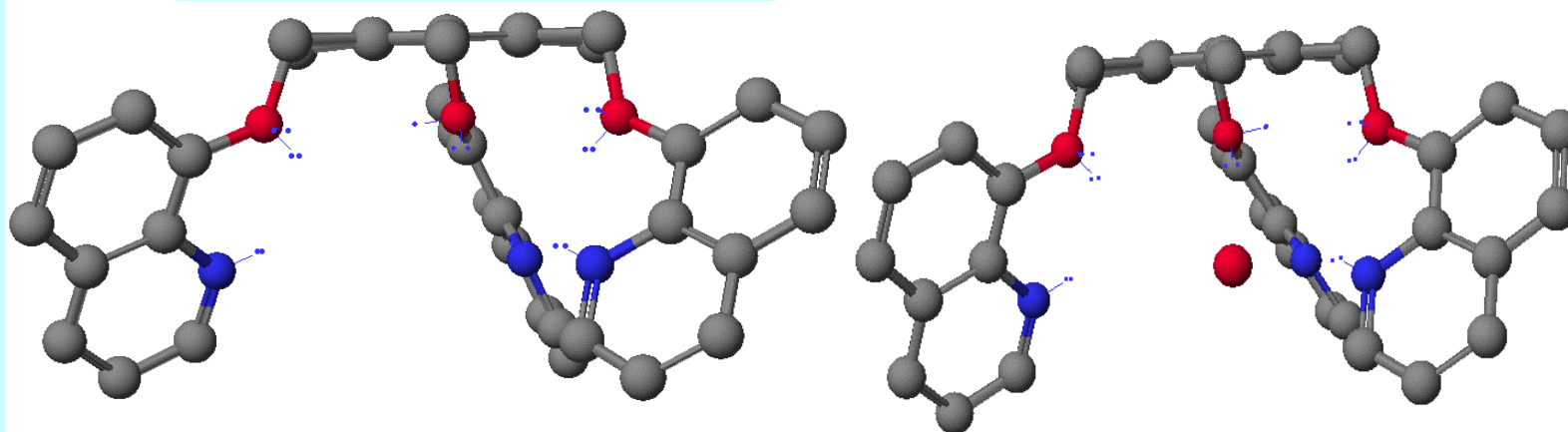
Interference of other metal ions



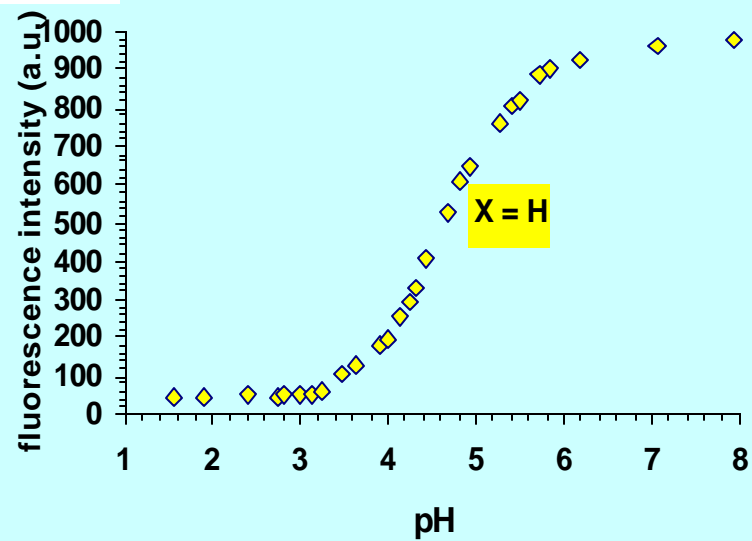
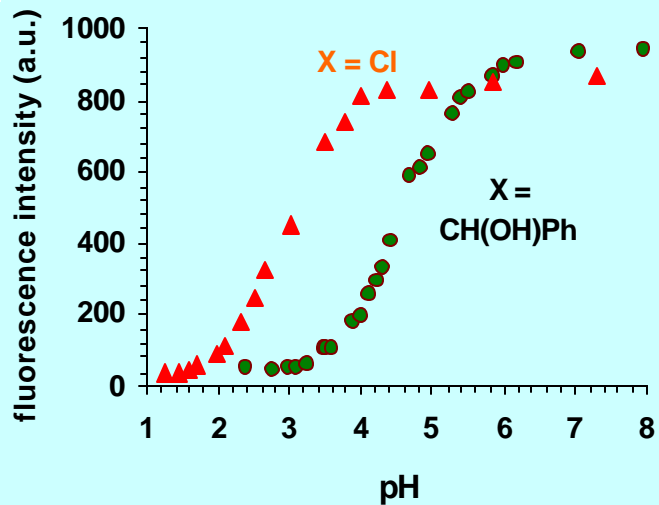
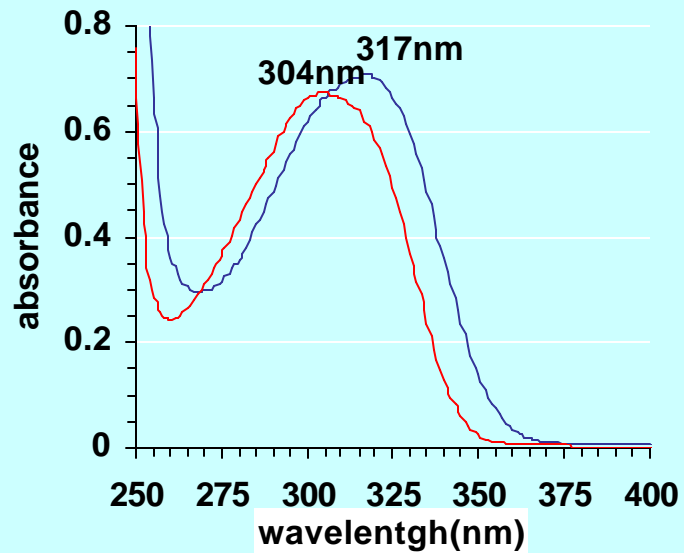
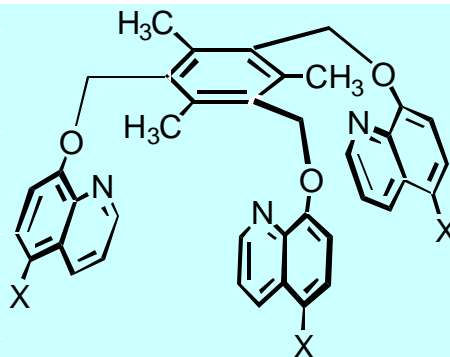
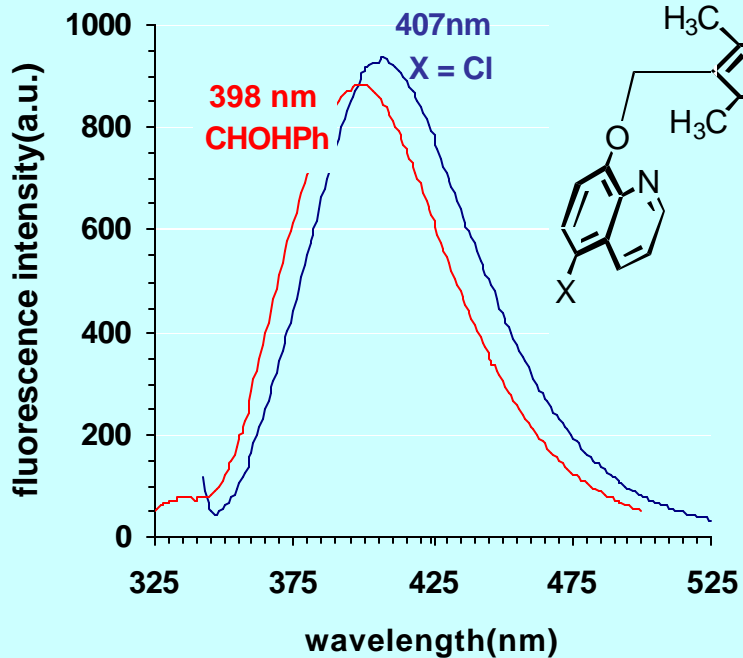


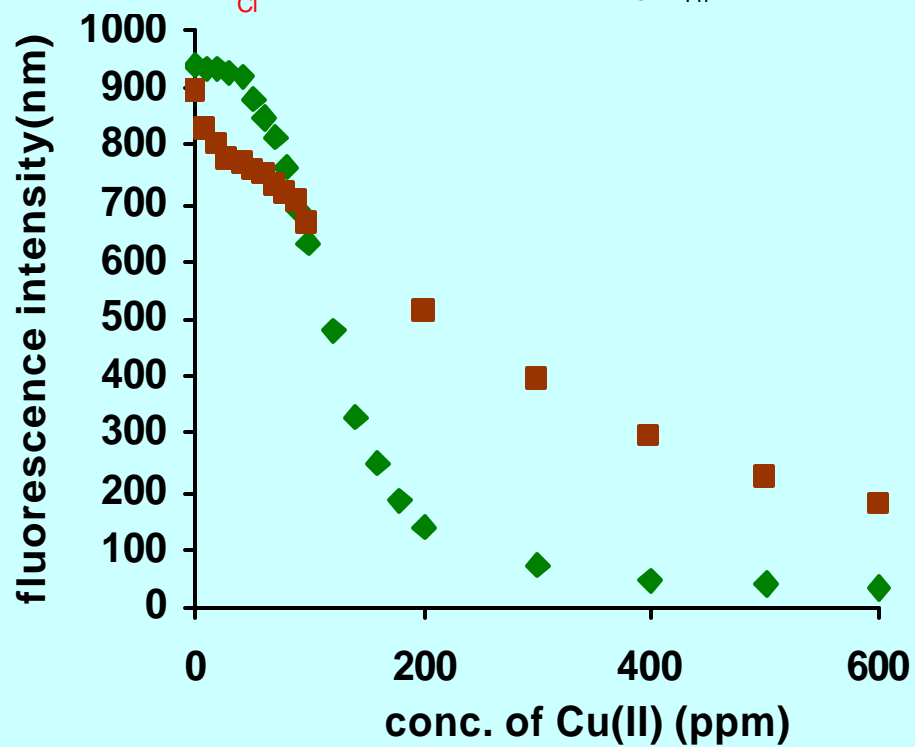
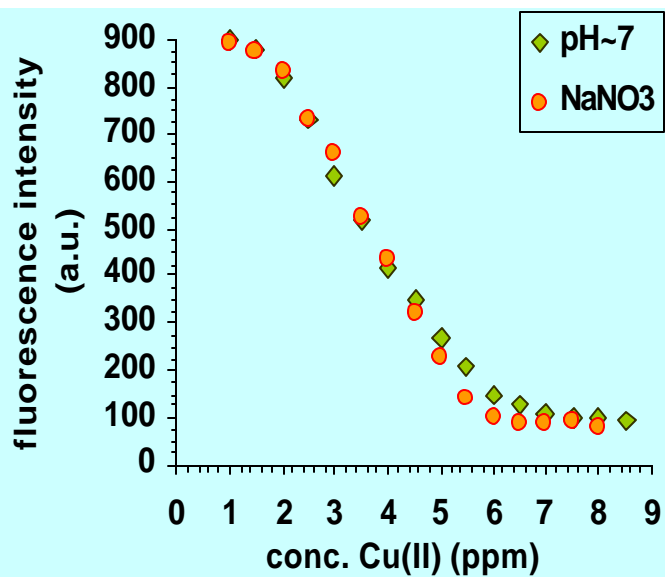
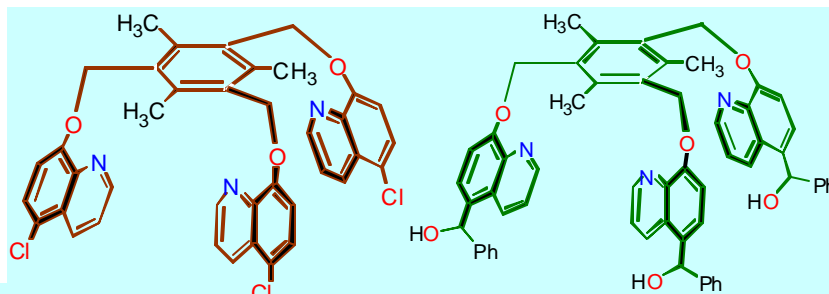
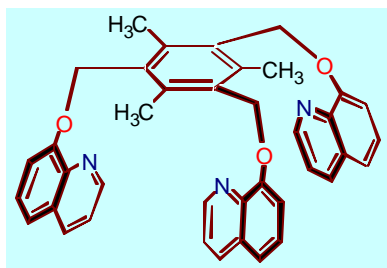
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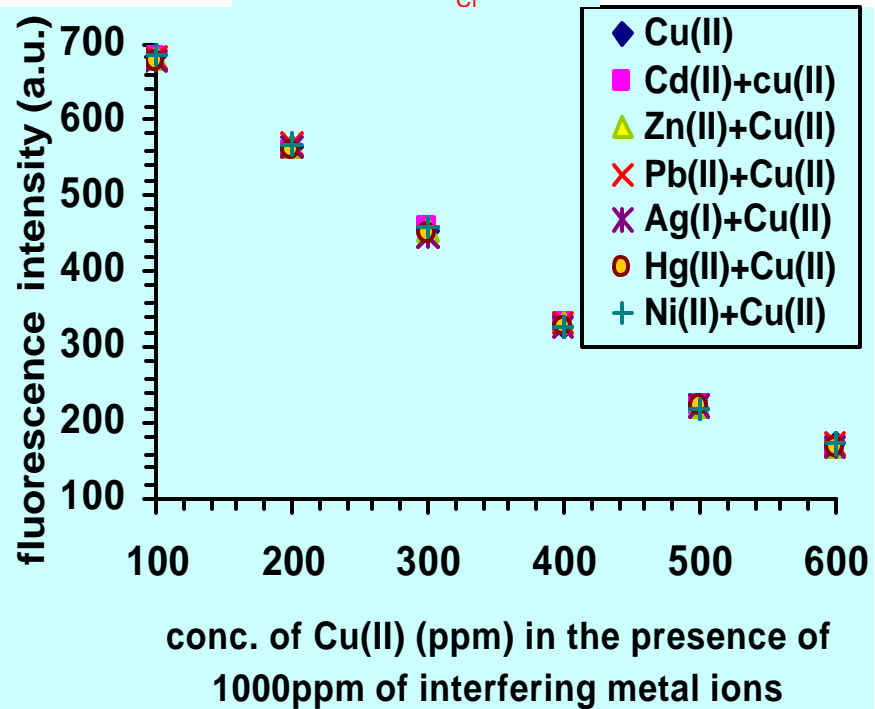
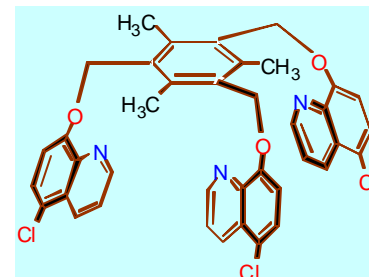
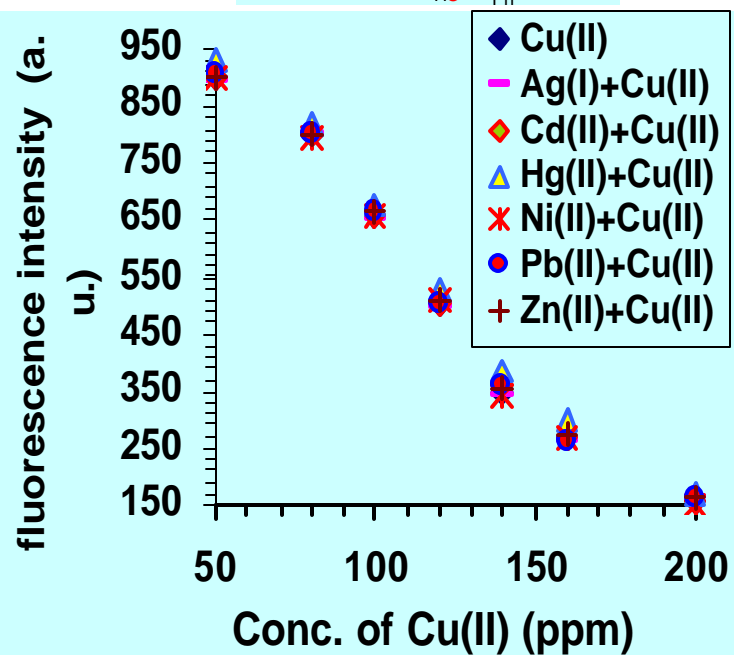
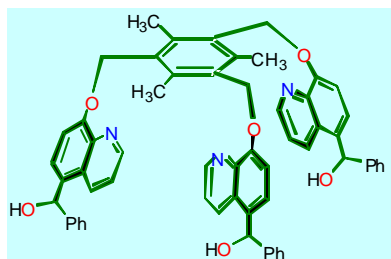
tripod 1 : Cu (II) ratio



- Energy minimized structures of tripod and its Cu(II) complex
- Planar Conformation = 66 Kcal / mol, tripodal conformation = 54 Kcal / mol, tripod : Cu(II) complex = 42 Kcal / mol







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Amritsar**