

## CHAPTER IV

### CONCLUSION

#### 4.1 Anions and amino acid sensors

We have synthesized novel colorimetric anion sensors  $L^1H$ ,  $L^2H$  and  $L^3H$ . Interestingly,  $L^1H$  in the presence of  $F^-$ ,  $AcO^-$ ,  $BzO^-$  and  $H_2PO_4^-$  underwent the cleavage and deprotonation process on  $-NH_{car}CH_2N_{imi}^-$  and  $NH_{ant}$ , respectively. From the cleavage process,  $L^1H$  was changed to be  $L^3H$ . This result was confirmed using  $^1H$ -NMR and Mass spectroscopy. In the case of Trp into  $L^1H$ , it was found that the cleavage process was accounted but the deprotonation process would not occur. It indicated that  $-NH_{car}CH_2N_{imi}^-$  held with a weak bond and was easy to be cleaved in the presence of base ( $F^-$ ,  $AcO^-$ ,  $BzO^-$  and  $H_2PO_4^-$ ). All ligands have the deprotonation process at  $NH_{ant}$  resulting in the colour change and red shift of the maximum absorption band for  $F^-$  and  $AcO^-$ . From complexation study,  $L^2H$  prefer Y-shape anions over spherical anions. Moreover,  $L^2H$  like to bind benzoate due to  $\pi$ - $\pi$  stacking interactions. Unfortunately,  $L^3H$  could not calculate the association constant because  $L^3H$  contained only one NH amide which was enable to bind guests with a very weak interaction. In the electrochemical studies,  $L^1H$  was not evaluated because of deprotonation and cleavage by bases. In presence of  $F^-$  in  $L^2H$ , the cyclic voltammogram was shifted to more the negative potential because of the enhancement of negative charge in the system so it is difficult to reduce the anthraquinone. The CVs of  $L^2H$  with spherical anion showed a slightly shift of potential reduction because of less base than  $F^-$ . In the case of  $AcO^-$ ,  $BzO^-$  and  $H_2PO_4^-$ , the feature peaks were analogous because these are Y-shape anions and basicity are not different. In the case of amino acids, Phe was dramatically changed over Trp and Ala. The complexation between  $L^3H$  with guests could not be measured by  $^1H$ -NMR technique and UV-vis spectroscopy. However, the electrochemical studies of  $L^3H$  gave a selectivity with  $H_2PO_4^-$  according to the significant change of CV response which showed three reduction peaks. In the case of amino acid, D- and L-Trp, the CV response performed the similar peaks, but for D- and L-Phe, CV response exhibited the different peaks. Therefore,  $L^3H$  can differentiate enantioselectivity of Phe. Therefore,  $L^2H$  would respond to be electrochemical sensors for  $F^-$  and Phe. In the case of  $L^3H$  were electrochemical sensors for  $H_2PO_4^-$ , Trp and Phe.

## 4.2 Luminescent molecular logic gates

### 4.2.1 Self-assembled molecular logic gates in micelles

We have developed molecular logic gates in micelle using the self-assembled system created by hydrophobic receptors and fluorophores within the micelle. Moreover, the results show 'plug and play' behaviour since we can select a given combination of one or more receptors, fluorophore and micelle as the system for a particular use. PASS 0 logic was obtained when the fluorescence signal was maintained at the 'off' level at various pH. The case of PASS 1, which was inverse the PASS 0, as the fluorescence output remained in the 'on' state as the pH is changed. For the creation of proton-driven YES gates, it was found that the anions of 4-*tert*-butylphenol **27** and 4-octylphenol **28** were the best receptors. The best conditions also required the use of **27** as the fluorophore and Triton X-100 as the micelle. These systems showed strong fluorescence enhancements when protons are added to the system. A  $\text{Ca}^{2+}$ -driven YES gate was also demonstrated, by employing **10b** as the receptor at neutral pH, along with **23** as the fluorophore and Triton X-100 as the micelle. A  $\text{K}^{+}$ -driven YES gate was also demonstrated, though of lower efficiency, by employing **8b** as the receptor at neutral pH, along with hydrophobic tris(bipyridine)Ru(II) (number instead of shortened name) as the fluorophore and Triton X-100 as the micelle. A  $\text{Na}^{+}$ -driven YES gate was also examined using *tert*-butylbenzo-15-crown-5 ether **8b**, 9-cyanoanthracene **26** as the fluorophore and Triton X-100 as the micelle. The reduced efficiency in this case stemmed from the short fluorescence lifetime of the latter fluorophore.

A good quality proton-driven NOT gate was obtained using 4,4'-bipyridine **31** as the receptor, **23** as the fluorophore and SLS as the micelle. A similarly good proton-driven NOT gate was obtained by changing the receptor to 4-octylpyridine **30** and the fluorophore to pyrene **25** while maintaining Triton X-100 as the micelle. The NOT gate gave a high fluorescence signal in alkaline solution because the pyridine receptor is not a suitable electron acceptor.

OR and AND gates were two-input logic gates that were demonstrated in this work. Protons and calcium served as two inputs. The OR gate was assembled using **23** as the fluorophore and Triton X-100 as the micelle, along with **10b** to serve as a receptor for  $\text{Ca}^{2+}$  and also as a receptor for high concentrations of  $\text{H}^{+}$ . In other words a non-selectivity

condition was chosen and maintained for **10b**. It was found that the fluorescence was enhanced with high levels of either protons or calcium.

The AND gate was assembled by using **23** as the fluorophore and Triton X-100 as the micelle, along with the anion of 4-*tert*-butylphenol **27** as the proton receptor and **10b** as the  $\text{Ca}^{2+}$  receptor. The operating conditions had to be chosen rather carefully so as to maintain the necessary selectivity of the two receptors for their respective guests. For instance, the fluorescent 'on' state was attained at pH 8 and 0.2 M  $\text{Ca}^{2+}$ .

Overall, the 'plug and play' approach to the creation of molecular logic gates is found to be quite successful. Its flexibility is a positive feature compared to the covalently bound systems employed previously. However, the smaller fluorescence enhancement factors found (as compared with those for covalently bound systems) represent a negative feature.

#### 4.2.2 Molecular logic gates on beads

We have synthesized several new pyrazolines for use as fluorescent sensors and switches responding to protons for eventual use on bead surfaces. Some of these pyrazolines behave in homogeneous solution as reconfigurable molecular logic gates. This happens because one pyrazoline can act as two types of logic gates by monitoring their fluorescence at different wavelengths. For instance, compound **12b** showed YES gate behaviour at 469 nm and PASS 0 at 650 nm. The internal charge transfer (ICT) nature of pyrazoline excited states was confirmed by the red shift of the emission band as the polarity of the solvent is increased.

Compound **18b** was designed to respond to temperature via a photofission process. Preliminary studies in toluene showed weaker fluorescence intensity at lower temperatures as expected.

While still in its preliminary stages, the connection of molecular logic gates to beads has shown several good results. YES logic behaviour can be transported from solution phase to the wet solid phase of the beads. As a bonus, some of the precursor compounds show interesting aspects of reconfigurable logic.

### 4.3 Suggestion for future works

#### 4.3.1 Anion and amino acid sensors

1. X-ray crystal structures of  $L^1H$ ,  $L^2H$  and  $L^3H$  and their complexes with various anions and amino acids are to understand the structure of their coordination chemistry in DMSO.
2. The possibility of using compound as a molecular device should be explored using many techniques such as carbon pasted electrode.

#### 4.3.2 Luminescent molecular logic gates

1. The development of self-assembled molecular logic gate systems in micelles can be used to create more types of logic gates such as XOR, NOR etc.
2. The possibility of using molecular logic gates as practical molecular devices should be explored using them as tags for solid-phase beads.