

## CHAPTER IV

### CONCLUSION

The compounds, 25,27-*N,N'*-di-((2-ethoxy)benzyl)ethylenediamine-*p-tert*-butylcalix[4]arene-dihydrochloride (4a), 25,27-*N,N'*-di-((2-ethoxy)benzyl)ethylenediamine-*p-tert*-butylcalix[4]arene (5a) and 25,27-di-(4-pyridylmethoxy)-*p-tert*-butylcalix[4]arene (6) has been synthesized. Ligand (5a) was achieved *via* the reduction of its Schiff's base (3a) with NaBH<sub>4</sub> and then protonation with HCl/CH<sub>3</sub>OH to afford the ammonium derivative in 83%. The ligand (4a) was then neutralized with NaOH/CH<sub>3</sub>OH to obtain the neutral form (5a) in 66%. Ligand (6) was prepared through the alkylation of hydroxy group on *p-tert*-butylcalix[4]arene by 4-(chloromethyl)pyridine hydrochloride to give the required product in 44%.

Diaza benzo crown *p-tert*-butylcalix[4]arene containing 2,3 and 4 carbons as linkage (ligands (5a)-(5c)) are used to investigate the hydrogen bond interaction through various basic anions such as chloride, bromide, iodide, nitrate, carbonate, sulfate and phosphate using <sup>1</sup>H-NMR titration in chloroform-*d* or a mixed solvent (methanol-*d*<sub>4</sub> and chloroform-*d*) depending on the solubility of anions. Plots between CIS and equivalents of anions revealed that ligands (5a)-(5c) could not form complexes with the previously mentioned anions. The repulsion of negative charge of anions by the ligands as well as the cavity size of the ligands are accounted for the failure.

The ligand (6) containing hydrogen bond acceptors was investigated its interactions towards hydrogen bond donors such as 1,3-dialdehyde crown *p-tert*-butylcalix[4]arene (ligands (2-1) and (2-2)), acetylacetone, 1,2-diaminoethane, 2,6-diaminopyridine, catechol, resorcinol, hydroquinone, phthalic acid, isophthalic acid

and terephthalic acid. Only catechol, resorcinol and phthalic acid was found to form complexes with ligand (6). Ligand (6) selectively bound resorcinol in a 1:1 stoichiometry with very high stability constant ( $\log K > 20.8$ ). The structure of 6-resorcinol disclosed by NOESY experiments showed the polymeric nature of the complex. The resorcinol molecule interacted with N-pyridyl moieties of ligand (6) *via* its O-H while the aromatic part was included into an upper rim cavity of another calix[4]arene unit. Ligand (6) also forms a 1:1 complex with phthalic acid with a stability constant ( $\log K$ ) of 5.41. NOESY and ROESY experiments revealed that phthalic acid was included into the lower rim cavity of ligand (6). Catechol was also found to form a weak complex with ligand (6). The 6-catechol complex was suggested by NMR experiments to be a 1:4 complex linked each other *via* hydrogen bonding into a polymeric manner. The recognition of ligand (6) towards dialcohols and diacids are as follows: resorcinol  $\gg$  phthalic acid  $>$  catechol. Besides hydrogen bonding, hydrophobic interaction and the matching between size and shape of hosts and guests play an important role in strengthening the stability of the complexes.

#### **The suggestion for future works:**

Future works should be focused on:

1. The anion receptors should be attached the electron withdrawing group (eg. carbonyl or sulfonyl) or lewis acid center (eg.  $\text{Ni}^{2+}$ ) in order to increase the ability of anion inclusion.
2. The structures of neutral complexes should be supported with other methods such as ESI-MS, VPO measurement<sup>50</sup>, GPC and single crystal X-ray crystallography<sup>51-52</sup>.
3. Ligand (6) shows a high recognition towards certain dialcoholic molecules. It should be modified to be a sensor for these neutral molecules by attaching a sensory unit to the upper or lower rim of calix[4]arene.