INTRODUCTION
The award of the 1987 Nobel Prize in chemistry to Charles Pedersen, Donald Cram and Jean-Marie Lehn marks an important turning point in the history of organic chemistry. For most of the 150 years between Wohler’s synthesis of urea and the present time, the focus of organic chemists has been on molecules containing only covalently linked atoms. This Nobel Prize delineates that time in history when the focus changed from covalent to non-covalent interactions.

Macrocyclic compounds are novel cyclic lipophilic organic molecules that contain heteroatoms like O, N, S and P capable of forming electron rich interior cavities and possess the ability to complex ions or molecules via ion-dipole or dipole-dipole interactions. Initially they were well defined, as they possess at least three heteroatoms as a part of the ring. Nowadays it has been broadened to the lateral meaning which indicates a cyclic compound having high molecular masses. That is how calixarenes, resorcinarenes, catenanes, rotaxanes and cyclodextrines are also included to the list of crown ethers and cryptands.

The host-guest chemistry has opened a new era in the field of research from the day of discovery of certain macrocyclic entities viz. crown-ethers, cyclodextrin and calixarenes. Molecular recognition is taking place due to fixed diameter or depth of reagent, which are much more specific and selective, which can be further modified by functionalization.

Crown ethers are very interesting molecules as they can be designed according to the need, by modifying cavity size or jumbling hetero atoms. All oxygen crowns strongly complex alkali and alkaline earths and those of all nitrogen cyclams, strongly complex heavy-metal cations. The mixed complexation properties make aza-crowns much more interesting to researchers as they have enhanced complexing ability for transition metal ions and ammonium ions too.
Crown compounds can be designed by the following methods, to get the desired applicability of the macrocycles which make them more specific.

- The ‘n’ crown ‘m’ ether can be regarded as a base, which can be designed separately by introducing different heteroatoms as well as various moieties with hydroxyl group.
- The cavity size for the interaction of metal ion can be modified by changing the number of ‘n’ and ‘m’.
- The crown compounds are generally rigid and so more specific for a particular metal ion. The flexibility can be introduced by synthesizing open crown known as ‘podant’.
- The modification can be done either by using specific moiety as a raw material to form crown or by attaching the specific group (chromophoric or fluorophoric) to crown by various means.
- Any macrocycle can be made more selective by functionalizing it with crowns.

The macrocyclic compounds like crown ether are more selective for the metal ions due to the presence of fixed size cavity. The selectivity of the binding is controlled by changing the size of the crown ether cavity and introducing the various combinations of the O, N, S heteroatoms in the crown ether cycle. Such molecule finds application in the field of metal extraction, ion selective electrode, phase transfer catalysis, ion transportation and in chromatographic separation.

Attachment of various functional groups to crown ethers often results in some unique complexing properties of the macrocyclic ligands. The molecule can be made more specific for the use in the metal complexation by the introduction of proton-ionizable chromophoric
groups. The introduction of photo and electro active \(-N=N-\) or \(-N(0)=N-\) residues into crown ethers can result in highly selective chemical sensors. Ditopic ligands containing macrocyclic unit attached to another metal-ion binding site have been used to prepare luminescent or electrochemical sensors. Photo-responsive supramolecular systems are of great significance particularly for their potential application to nanoscale devices for cation sensor and switches. The design and synthesis of photosensitive complexing molecules are actively pursued for the development of supramolecular photoactive devices. The application of selective molecular recognitions for the development of functional chemical switching or information converting devices, based on interactions with electrons, ions or photons, has been strongly stimulated by the progress achieved by the chemical modifications of crown and azacrown ethers.

The modifications by functionalisation of crown ethers have been exhaustively covered in the recent reviews, as in the last two decades field of macrocyclic compounds has been the most exploited fields by the analytical chemists.

Itsikson and coworkers\(^5\) have reviewed synthesis, modification and properties of macrocycles, such as crown ethers, their open-chain analogs, i.e. pendants, calixarenes and resorcinarenes, having azaheterocyclic fragment. A recent review about ring closing reactions in the synthesis of natural compounds using macrocyclic compounds as a catalyst by Ivin\(^6\) demonstrate new route of synthesis. Gelmboldt\(^7\) and his coworkers have reviewed the synthesis, structure, and the properties of the host-guest compounds of boron, silicon, and germanium fluoro complexes and crown ethers or their aza analogs. Whereas Parker\(^8,9\) reported the syntheses of thia, oxa-thia and aza-thia crowns. Campbell\(^10\) and coworkers have reviewed synthesis of mono- and dibenzocrown ethers with fluorinated or chromogenic
Tsivadze\textsuperscript{11} and his coworkers have covered the main classes of crown compounds, e.g., crown ethers, aza- and thiacrown ethers, cryptands, catenands, spherands, hemispherands, cyclodextrins, catenands, calixarenes, podands, and lariats in their review. They have also discussed the physicochemical characteristics, structural features, selectivity, and complex formation properties of the synthesised molecules. The uses in the fields of separation, concentration, and determination of metals, isotope separation, and other areas are discussed in the same.

Tikhonova and coworkers\textsuperscript{12} have reviewed catalytic and complexing properties of two perfluorinated polymercuramacrocycles, where both the macrocycles can efficiently bind various anions to form unique complexes, in which the anionic species is simultaneously coordinated to all Lewis acidic atoms of the ring. The formation of unusual complexes of these compounds with various neutral Lewis bases, such as nitriles, carbonyl compounds, aromatic hydrocarbons, etc., were also described.

Kirkovits\textsuperscript{13} has reviewed uses of macrocycles in the field of ion-pair recognition, in which a host simultaneously binds both cationic and anionic guests. Details of these receptors, which combine crown ethers and calixarenes for cation complexation, with Lewis acid centers, pyrroles, amides or urea groups for anion recognition, was discussed in the same. Reetz\textsuperscript{14} reported the review on receptors that bind cations and anions simultaneously.

Clearfield\textsuperscript{15} in his review along with his coworkers has discussed three classes of metal phosphonates, which show promise for use in separation science and catalysis and for design of a wide variety of structures with built-in physical properties.

Simonov\textsuperscript{16} along with his coworkers reviewed inclusion compounds formed by the
interaction of silicon, germanium and boron fluorides with crown ethers. The crystallographic structures and interaction with ions were also discussed.

Kilburn\textsuperscript{17} and coworkers have reported cleft receptors and molecular bowls, self-assembling receptors, cyclophanes and calixarenes, and crown ethers and aza-analogs, cryptands, podands, and spherands.

Shinkai\textsuperscript{18} and coworkers have reviewed the basic concepts for molecular design toward such man-made molecular machines useful for artificial chemosensors. The discussions are emphasized on chromogenic crown ethers, photoresponsive crown actuators in action for ion and molecular recognition, cyclodextrins modified as mol. sensors, calixarenes modified as ion and molecular sensors and a new artificial sugar sensing systems in which the boronic acid-diol interaction combined with photoinduced electron transfer.

Li, De-jiang\textsuperscript{19} and coworkers reviewed the chemistry of various types of chromogenic crown ethers. The synthesis and applications of some species are discussed in detail.

**Chromogenic and fluorophoric functionalised crown ethers**

Most of the research work reported recently is based on functionalization with proton-ionizable chromogenic or fluorogenic ionophores. Substituents are also incorporated as part of the macrocyclic framework.

Huszthy\textsuperscript{20} and his coworkers have synthesized seven new proton-ionizable chromogenic and fluorogenic ionophores containing NO\textsubscript{2} group(s) and/or Br or Cl atom(s) in the aromatic rings, starting from acridono-18-crown-6 ligand by electrophilic substitution. These compounds found binding ability with water molecule and DMF in their cavities by multipodal hydrogen bonding.

Luboch\textsuperscript{21} and coworkers have synthesised new derivatives of azobenzene crown ethers. Which include compounds with alkyl, alkoxy, hydroxy or dimethylamino group in
aromatic residue(s) as side substituents. Their chromoionophoric properties and properties in ion-selective membrane electrodes have been studied.

According to Harris and his coworkers, there exists an increasing need for creative ligand designs capable of performing fundamental mechanical motions at the molecular level. To this end they synthesized a series of oligobipyridines linked by flexible pseudo-crown-ethers, which function as mechanical switches through the encapsulation of small alkali ions. These switches visibly display ion guest encapsulation through the reversible interaction of two facially attracted d8 square planar transition metals. The host cavity produced by these flexible oligomers is not selective based on ion size, but rather will encapsulate many different guest ions producing a different photo-response for each. The display of different colors is based upon the molecular orientation of the switch and the relative distance between transition metal centers. Few chromogenic crown-ether sensors are known and most display is selectivity based on ion size, inhibiting multiple ion sensitivity. These flexible architectures form the basis for controlled mechanical switches that are useful for ion sensing applications.

Kim and his coworkers have reported the synthesis of dinitro derivative of calix[4]arene-crown ethers and their ionophoric properties toward representative alkali and alkaline earth metal ions. The research work was reported as part of the development of efficient and selective chromogenic sensing materials for barium ions. Wagner-Wysiecka and coworkers also have synthesised chromogenic azocrown ethers possessing a phenol moiety. A template effect on the macrocyclization step has been observed by them. Color reactions of the crown ethers with alkali metal cations are described. Stability constants of lithium, sodium and potassium complexes were determined along with X-ray structures.
Other proton ionizable moieties are reported by Talanova\textsuperscript{25} and his coworkers. They have claimed twelve new proton-ionizable, picrylamino-type chromogenic lariat ethers derived from dibenzo-14-crown-4, dibenzo-16-crown-5 and dibenzo-19-crown-6 and all of them demonstrate good selectivity and remarkable color response upon extraction of alkali metal cations from basic aqueous solutions into CHCl\textsubscript{3}.

Skwierawska\textsuperscript{26} and coworkers have synthesized proton-dissociable chromogenic azocrown ethers (1; \( R = \text{Me, CMe}_3, n = 1; \ R = \text{Me, n} = 2 \)) the group being the part of the macrocyclic system. Color reactions of 1 with metal cations were described. A high selectivity for lithium complex formation was found by spectrophotometry.

![Azocrown ether with alkyl substitution](image)

Inerowicz\textsuperscript{27} and coworkers have synthesised chromogenic crown ethers having an intraannular aza and phenolic hydroxy subunits which have been used as complexing reagents for alkali metal cations in aqueous dioxane. The most pronounced spectral changes were observed for lithium ion.

Wagner-Wysiecka\textsuperscript{28} and coworkers have synthesised macrocyclic chromogenic derivatives of pyrrole and imidazole. The complexing properties of these compounds with metal cations were investigated spectrophotometrically in acetonitrile. The synthesized
Crown ethers were also tested as ion carriers in ion-selective membrane electrodes. The X-ray structure of one isomer of 18-membered pyrrole crown ether is also reported.

Tsubaki et al. have reported two binaphthyl crown receptors containing phenylboric acid and 2,4-dinitrophenylurea as lariat parts, 2a and 2b, which are prepared from the optically active binaphthyl crown alcohol 2c in two and four steps, respectively. Host 2a showed 30% extraction efficiency for GABA by a solid-liquid extraction method in DMSO. Chromogenic host 2b discriminated guest linear amino acids by molecular length, and the information was revealed through color changes. The structures of the compounds are as follows.

Binaphthyl crown receptors containing phenylboric acid and 2,4-dinitrophenylurea
A ferrocene-based ditopic receptor containing a urea and a benzocrown ether unit\textsuperscript{30}, e.g., 3, shows a remarkable color switching (ON-and-OFF) function induced by anion and cation recognition.

![Ferrocene-based ditopic receptor](image)

Structurally variable compounds and fibrous organic compound bound to capture structure for capturing target molecules and use in detection application are claimed by Kinoshita\textsuperscript{31} and his coworkers. α-Helical proteins, DNA, or amylose, in particular, having amphipathic characters, are used as fibrous organic compounds. The capture structures are inclusion compounds and have cavities of tube, layer (stratified), or basket shape, and rely on physical or chemical adsorption for capture. Compounds undergoing light-induced, heat-induced, or electronic field-induced structural change, or geometrical isomers, liquid crystal molecules, may be used. Azobenzene compounds are preferred.

New chromogenic azo-crown ethers possessing sulfur atoms and two azo groups in the macrocycle are described by Szczygelska-Tao\textsuperscript{32} and coworkers. These synthesized macrocycles have been applied as ion carriers in ion-selective membrane electrodes. Their selectivity and sensitivity were studied towards alkali and transition metal cations.

A method for the preconcentration and trace determination of Th with crown hydroxamic acid is reported\textsuperscript{33} from our laboratory. The extraction of Th from the monazite
sand and from sea water was studied. Similar extraction procedures were developed for U(VI) and La(III).58

Goodman34 and coworkers have described about a chromogenic receptor comprising a self-assembled chromogenic compound having at least one intrinsic binding site in their framework. The chromogenic compound is characterized by the property of producing a reversible color change responsive to binding a target substrate to the receptor. The ligand is selected from the group consisting of substituted phenanthroline, substituted 2,2'-bipyridine and substituted 2,2':6',2''-terpyridine. The transition metal is selected from the group consisting of Cu(I), Cu(II), Ag(I), Ni(II), Fe(II), Fe(III), Ru(II), Co(III), and Os(II). Self-assembly can be effected in the presence of Cu(I) to form receptors for dicarboxylic acids, carbohydrate, amino acids, steroids and pyrophosphates. The receptors are characterized by the formation of a 2:1 complex of the target substrate with the receptor producing a visible color change from orange to red and a measurable change in its luminescence. Methods of using these receptors are also disclosed.

Chromogenic and fluorophoric functionalised azacrown ethers

McSkimming35 and coworkers have synthesised and characterized aza-crown ethers 4 and 5 with anthracene-containing pendant. Both compounds bind Group 1 metal cations in solution, forming complexes of 1:1 stoichiometry. The properties of compound 5 and its complexes have been studied by a range of techniques, including NMR, UV and fluorescence spectroscopy and X-ray crystallography. The pendant arms can adopt either a cis or a trans geometry, the cis geometry favored with larger cations. The geometry of the complex affects the fluorescence properties of the system, with larger cations giving higher excimer/monomer ratios. Upon irradiation at 9 $\geq$ 300 nm, coronand 4 forms the cryptand 6 through a reversible intramolecular [4π+4π] cycloaddition reaction. The rates of the forward and reverse
reactions of this photochromic process are cation dependent; in particular the rate of the thermal reverse reaction is decreased by smaller cations and increased by larger cations, especially with Rb⁺. The metal binding constants in methanol for 4 and 5 have been determined, revealing that the cryptand 5 binds Na⁺ and Rb⁺ more weakly than crown ether 4 by over two orders of magnitude.

Sibert and coworkers have reported a molecule having hybrid, macrocyclic structure based on o-phenylenediamine and azacrown ether 7 which promotes an intimate mutual interaction with a bound potassium ion as chelation by the redox-active moiety. A general synthetic method and properties are described for the first member of a new class of redox-active, lariat-type macrocycles 7 called the o-Wurster's crowns. The electrochem. properties of the pendant arm azacrown ether and of its alkali metal complexes are discussed. The
crystal structure of the potassium complex, KL(PF6) (L = I), was also determined.

Wilhelm et al. carried out reaction between lipoyl imidazolide and aza-15-crown-5 (1,4,7,10-tetraoxa-13-azacyclopentadecane) or aza-18-crown-6 (1,4,7,10,13-pentaoxa-16-azacyclooctadecane) to afford new N-lipoylated azacrown compounds in good yields. These compounds transformed into 1,3-dithiols and amines by reduction with complex hydrides of the disulfide and/or amide group of the lipoyl chain. The new pendant-arm macrocycles react as heteroditopic ligands by forming dithiolate and disulfide complexes with the soft metal ions Ni\(^{2+}\) and Pd\(^{2+}\), respectively, and an amine complex with the hard Li\(^{+}\) ion.

Ishifune along with his coworkers reported the electro reduction of Me decanoate (1) by using alkali metal ion-free Bu\(_4\)NCIO\(_4\) as a supporting electrolyte and platinum as anode and cathode in the presence of alkali metal ions. The use of Bu\(_4\)NCIO\(_4\) as a supporting electrolyte without alkali metal ions gave only a trace amount of the reduced product. It is plausible that alkali metal (0) species are electrogenerated from alkali metal ions and react as active reductants to reduce the aliphatic esters and the mediatory system is established in this electrolysis system.

Kele and coworkers have synthesised two novel fluorescent chemosensors in which an aza-crown is linked to 4-coumaryl fluorophores by a methylene spacer for sensing saxitoxin. Fluorescence enhancement was observed upon binding of the dicationic toxin molecule, whereas several metal ions produced no effect. Another ionophore is reported by
Brunet and coworkers by attachment of coumarins to azacrown ethers. The alkaline-earth complexes of these new ligands were studied from their UV-visible, NMR, and fluorescence data. Some systems displayed bathochromic shifts and fluorescence decreases upon complexation with Ca$^{2+}$ that may make them useful signaling devices of this metal.

The emission behavior of the 4,4'-bis(dimethylamino)biphenyl subunit covalently attached to aza-crown ethers is studied by Costero and his coworkers. Some new ligands were synthesized by them to test the properties of this new fluorophore. The fluorescence of these new ligands and some other compounds previously described was studied in acetonitrile in the presence of Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, Cd$^{2+}$ and also in the presence of some alkali and alkaline-earth cations.

Arya and coworkers made structural studies on a range of Ag$^+$ and Pb$^{2+}$ complexes of N-allyl and N-butenyl lariat ethers. In the case of smaller ligands with allyl side arms ($L = \text{N-allylaza-15-crown-5 and N-azaallyl-18-crown-6}$), coordination polymers $[\text{Ag}(L)]^+\infty$ exhibiting Ag$^+-\pi$ interactions are observed. Increasing the length of the side arm to N-butenylaza-18-crown-6 gives a monomeric 'scorpionate' species in which the Ag$^+$ ion is simultaneously bound to the macrocyclic portion and side arm of a single ligand. NMR titration results indicate that the Ag$^+-\pi$ interactions persist in solution. In the case of Pb$^{2+}$ complexes no side arm involvement is observed in any case. The novel protonated complex ($\text{H}_3\text{O})(\text{N-allylaza-18-crown-6})[\text{Cu}_2\text{I}_3]$ is also reported.

Li-Qian and coworkers have synthesized a novel crown ether, 2,3-naphtho-10-aza-15-crown-5 (NAC), which does not show strong fluorescence and phosphorescence due to photoinduced intramolecular electron transfer from the N lone pair of electrons to the singlet excited state of the naphthalene chromophore. Complexation with heavy-metal ions results
in the quenching of the fluorescence and enhancement of the phosphorescence significantly. These observations were interpreted in terms of the binding interactions, between the N lone pair electrons and the metal cation, which prevent photoinduced intramolecular electron transfer, and the heavy-atom effects which induce quenching of the fluorescence and enhancement of the phosphorescence. These aza crown and heavy-metal-based systems could be useful as potential chemical sensors and molecular photonic devices.

The interaction of Na$^+$ and K$^+$ ions with the N3 site of the DNA base adenine azacrown in a model system was studied by Gibson$^{44}$ and coworkers. The N9-(2-chloroethyl)adenine was condensed with 1-aza-18-crown-6 to give a crown ether linked adenine ligand (L). Reaction of L with NaBPh$_4$ gives the 7-coordinate sodium complex, [NaL(H$_2$O)](BPh$_4$) (1), in which the sodium ion is bonded to the 6 N and O atoms of the azacrown ether moiety and a water molecule and has no direct interaction with the adenine. Reaction of L with KPF$_6$ results in the potassium complex [KL] in which the N3 of adenine bonds to the potassium in addition to the 6 N and O atoms of the azacrown ether. Crystal structures of both complexes were obtained. Calculations were performed on 1 and 2, as well as on 9-methyladenine and N3-protonated 9-methyladenine to determine the changes in electron distribution upon complexation.

Chen, Jau-An$^{45}$ and coworkers have reported ureyleno crown ethers 8 (I, R = H, 2, R = pyrenylmethyl 3, CH$_2$), which bind with 2 equivalent of Li$^+$ cooperatively and selectively over other alkali metal ions such as Na$^+$, K$^+$, and Cs$^+$. The binding constant for 2-Li$_2^{2+}$ is 3.0 \times 10^7 (L/mol)$^2$ and its crystal structure determined. The fluorescence of 3 and its 1:2 lithium complex is also reported.
Inerowicz\textsuperscript{46} and coworkers have synthesised novel chromogenic 21-membered crown ether having an intraannular aza and hydroxy subunits and used as a complexing reagent for alkali metal cations. The complex formation was detected by visible spectroscopy and formation constants were calculated. The most pronounced spectral changes were observed for lithium ion.

Chromogenic crown ethers having an intraannular aza and phenolic hydroxy subunits have been used as complexing reagents for alkali metal cations in aqueous dioxane by Inerowicz\textsuperscript{47} and coworkers. The complex formation was studied by visible spectroscopy and formation constants were calculated. These value vary depending on addition of triethylamine or tetraethylammonium hydroxide in the reaction solution. The most pronounced spectral changes were observed for lithium ion.

Pearson\textsuperscript{48} and coworkers have synthesised two p-phenylenediamine derivatives, having aza-crown ether substituents, are described which show high selectivity for Mg\textsuperscript{2+} over Na\textsuperscript{+} in their fluorescence behavior.

Witulski\textsuperscript{49} et al have described a novel alkali cation selective probe, which exhibits unique ICT and binding properties, allowing the ratiometric titrations of sodium cations in the presence of other alkali metal ions.
The work published by Hojo and coworkers describes the complex formation constants between alkali metal ions and monoaza- or diazacrown ethers (L) in acetonitrile obtained by the analytical method of d.c. polarogram, in which a positive shift in E1/2 of the mercury-dissolution wave of L in the presence of a large excess of M⁺ is utilized. By the conventional method using a negative potential shift of the reduction of ML⁺ in the presence of a large excess of L, similar values of the complex formation constants were given for the 1:1 interaction (ML⁺ formation) between M⁺ and L. According to them the interaction between alkaline earth metal ions and L was too strong to obtain the formation constant.

Warmke and coworkers studied the influence of metal cations Li⁺, Na⁺, K⁺, Cs⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Pb²⁺ and Al³⁺ on the spectroscopic properties of the dansyl (1-dimethylaminonaphthalene-5-sulfonyl) group covalently linked to monoaza crown ethers 1-aza-15-crown-5 (1,4,7,10-tetraoxa-13-azacyclopentadecane) (A15C5) and 1-aza-crown-6 (1,4,7,10,13-pentaoxa-16-azacyclooctadecane) (A18C6) by means of absorption and emission spectrophotometry. They found interactions of the alkali metal ions with both fluoroionophores weak, while alkaline earth metal ions interact strongly causing 50 and 85 % quenching of dansyl fluorescence of N-(5-dimethylamine-1-naphthalenesulfonylo)-1,4,7,10-tetraoxa-13-azacyclopentadecane (A15C5-Dns) and N-(5-dimethylamine-1-naphthalenesulfonylo)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane (A18C6-Dns), respectively. The observation for Cu²⁺, Pb²⁺ and Al³⁺ cations, indicated strong interaction very strongly with dansyl chromophore, causes a major change in absorption spectrum of the chromophore and forms non-fluorescent complexes, whereas the Co²⁺, Ni²⁺, Zn²⁺, Mg²⁺ cations interact moderately with both fluoroionophores causing quenching of dansyl fluorescence by several percent only.
Rurack\textsuperscript{52} and coworkers studied the spectroscopic properties of 1-phenyl-3-benzothiazol-2-yl-5-(4-R-phenyl)-Δ2-pyrazolines which are strongly dependent on both the electronic nature of the substituent R and solvent polarity. As revealed by spectroscopic studies as a function of solvent polarity as well as temperature, for electron-rich amino donor substituents in polar solvents, deactivation of the strongly emissive charge transfer (CT) state of the basic 1-phenyl-3-benzothiazol-2-yl-Δ2-pyrazoline chromophore has to compete with a fast intramolecular electron transfer (ET) quenching reaction. In the case of the dimethylamino derivative (R = DMA), the rate constant of ET in acetonitrile was determined.

A series of novel N-chromogenic calix[4]arene azacrown ethers such as 9 were synthesized by Kim\textsuperscript{53} and coworkers as selective extractants of potassium ion. 9 was prepared reacting dipropyloxybis(chlorooxapentyl)calix[4]arenes with p-toluenesulfonamide in the presence of potassium carbonate; reductive removal of the tosyl group and alkylation of the amine with 2-hydroxy-5-nitrobenzyl bromide gave calix[4]arene azacrown ethers such as 9 in moderate yields.

![Diagram of N-chromogenic calix[4]arene azacrown ethers](image-url)
9 shows high transport selectivity for potassium over other metal ions as shown by two-phase extraction, bulk liquid membrane, and $^1$H NMR studies on a ligand-metal complex. It is assumed that the -OH of the chromogenic group attached on nitrogen can assist the complexation by encapsulation of the metal.

Fluorescent PET (photoinduced electron transfer) sensors with monoaza-18-crown-6 or monoaza-15-crown-5 ether and boronic acid receptor units 10(10a, n=0; 10b, n=1) were synthesized by Cooper et al.

Costero et al have synthesised two new ligands ($X = NMe, Y = O; X = O, Y = NMe$), containing aza-crown ether moieties in their structures in addition to tetramethylbenzidine units 11. Their ability to complex transition metal cations has been studied by NMR and electrochemical techniques. Ligand 11 ($X = O, Y = NHMe$) gives rise to two diastereoisomeric complexes with Cd(NO$_3$)$_2$.
The same group\textsuperscript{56} have recently reported ligands derived from 4,4'-dinitrobiphenyl containing azacrown cavities in the 2,2' position and used in extraction and transport experiments. They studied controlled experiment with a system containing only one complexing cavity and demonstrated that the capability of forming a sandwich-type complex in the aforementioned ligand not only increases extraction but also the transport across a liquid membrane. Extraction studies by them have also shown that the complex present in the membrane has a 1:1 stoichiometry with regard to both ligands.

Ji, Hai-Feng\textsuperscript{57} and coworkers have synthesized four derivatives of alkylpyrene covalently bonded to aza-18-crown-6 at the nitrogen position, (12; n = 1-4), to study the effect of spacer length on the emission properties of pyrene fluorophore upon complexation of alkali metal ions by the crown moiety. They observed that in the absence of alkali metal ions, the parent molecule fluoresce weakly because its emission is partially quenched by photoinduced electron transfer (PET) from nitrogen lone pairs to the excited singlet state of pyrene, which increases greatly in the presence of alkali metals. They have examined the fluorescence behavior of these pyrene aza-crown ether derivatives in the presence of alkali metal ions to determine the magnitude of such an effect and its impact on the sensitivity of the fluorescent probe for detection purposes. Their results indicate that maximum efficiency for PET between the pyrene moiety and aza-crown ether is achieved when n ≤ 3.

Alkylpyrene supported azacrown
Aim and Scope

The literature on crown ethers reveals that a large number of chromogenic and fluorogenic crown derivatives have been synthesised to achieve highly selective ligands which may have great potential for the development of new sensors. The incorporation of a suitable ionophoric sensory group into the crown having a pre-organized binding site results in a chromogenic or fluorogenic receptor that exhibit pronounced molecular recognition. The functionalization also provides an ion-carrier molecule that is capable to form, with cations neutral ion-pairs which eventually are transferred into the organic phase. Most of the research work reported so far, are on crown ethers or aliphatic azacrowns. The mixed presence of both N and O donors makes the macrocycle more interesting to researchers in many areas. Only few substitutions have been reported on diaza-dibenzo-18-crown-6 whereas monoaza-dibenzo-18-crown-6 is the least studied system with only one report of alkyl substitution. Hence, in the present investigation monoaza-dibenzo-18-crown-6 has been synthesised and substituted with chromophoric and fluorophoric substituents. A fluorogenic azacrown has also been synthesized by using coumarin as a raw material to form the crown.

The functionalised azacrowns are synthesised by linking chromophores like 8-hydroxyquinolinine and alizarin as well as fluoroionophore like coumarin. This strategy combines the selectivity of the crown compounds and the sensitivity of the substituents. The molecules are designed for the extractive separation and transportation studies of toxic heavy metals viz. Cr(VI), Cr(III), Mo(VI), W(VI) and Zr(IV) and also for the trace determination of $F^-$ and amines. The fluorophore is designed for the trace level determination of Be(II) and
Al(III), which are least studied by the macrocyclic systems. The molecule will be applied for
the removal of toxic species like Cr(VI) and F$^-$ from the effluent samples and for the
separation of Zr(IV) from Hf(IV) by liquid membrane transportation.
References


