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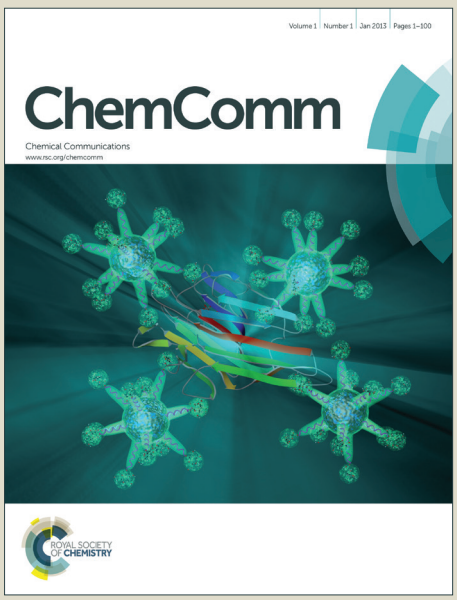

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ARTICLE TYPE

Artificial receptors for nitrate: A comprehensive overview

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This review article highlights recent developments in the field of synthetic receptors designed to recognize nitrate with a particular emphasis on: i) synthetic receptors for nitrate in competitive media, ii) assembly processes driven by nitrate recognition and iii) synthetic transporters and extractants for nitrate.

1. Introduction

Nitrate (NO_3^-) a trigonal planar anion consists of three equivalent N-O bonds. NO_3^- is the conjugate base of a strong acid and thus a weakly basic anion. The major outer source of NO_3^- in human body is vegetables, whereas endogenous NO_3^- source is the L-arginine–NO pathway. In plants, NO_3^- assimilation occurs via its active transportation across the cell by NO_3^- transporter protein followed by its reduction to NO_2^- by nitrate reductase.[1] NO_3^- binding in protein scaffold by structural characterization to 1.5 Å resolution is described for a nitrate specific receptor NrtA from Synechocystis.[2] The NO_3^- is bound in the cleft both by hydrogen bonding and electrostatic interactions (Fig. 1). One oxygen atom O1 is closer to positive charges of Lys269 and His196 and is hydrogen bonded to Gln155. Whereas, O2 is surrounded by hydrophobic side chains of Pro222 and Val239 and bonded to Gly240. Finally, O3 is close to the positive charge of His196 and hydrogen bonded to Trp102. Generally, natural nitrate sources cannot be controlled due to natural fixation of nitrogen. Thus, groundwater pollution due to elevated nitrate concentration always remains a serious threat.[3] According to World Health Organization guidelines, maximum contaminant level of NO_3^- in drinking water is established as 45 mg/L.[4] Emission of sulfur oxide and different nitrogen oxides released from different power plants and cars produce sulfuric acid and nitric acid, which are main component of acid rain.[5] Thus, nitrate is one of the major components of acid rain which make deep impact on aquatic systems, forests and architectures. Anthropogenic activities such as excessive use of fertilizers, on-site sanitation etc. cause eutrophication leading to the disruption in aquatic systems.[6] This higher nitrate levels associated with methemoglobinemia which causes the "blue baby" syndrome in infants.[7] Another health risk associated with excess nitrate is the potential formation of carcinogenic nitrosamine.[3] Thus, development of synthetic receptors for nitrate is demanding. Same time, it is very challenging to develop synthetic receptors that are selective towards nitrate because of its low basicity as well as high hydration energy (ΔG_h = -314 kJmol^{-1}). Position of NO_3^- in the Hofmeister series depicts the soft nature of this anion.[8] Over the years, chemists have designed strategies to overcome such problems and other selectivity issues to compete with anions of similar shape for recognition of NO_3^- by different charged and neutral hosts. Theoretical calculations by Hay *et al.* reveal that an ideal NO_3^- receptor should have six hydrogen bond donor site (D-H), where two protons share one oxygen atom of NO_3^-.[9]

Since the discovery of chloride encapsulation by macrobicyclic polyammonium cage by Park and Simmons in 1968, coordination chemistry of anions has attracted the attention of scientific community.[10] Fourteen years later first nitrate receptor is described by Lehn *et al.* in 1982, where the cavity binding mode of NO_3^- is shown inside a polyammonium cage.[11] Slow progress of the development of nitrate receptors is evident from the reports by Bowman-James[12] and Anslyn[13] *et al*. polyammonium and polyamide based macrobicycle respectively fifteen years later. Davis *et al*. have published one relevant review on different artificial and biological receptors for nitrate in 2008.[14] However, in the last six years the issue of selective binding of nitrate is particularly studied by different synthetic receptors. With the evolution of anion coordination chemistry different kinds of receptors having amide functionality, electron deficient core, metal coordinating site are also employed for NO_3^- binding. In some cases, selectivity for NO_3^- is demonstrated along with the structural evidences. Beside the simple recognition studies, NO_3^- triggered self-assembly process such as capsular aggregation, interlocked molecule formation etc. are recently documented. However, recognition of NO_3^- is comparatively less explored than the other anionic species such as tetrahedral oxyanions and halides. Reports for fluoride (Rissanen *et al.*),[15] sulfate (Ghosh *et al.*)[16] and phosphate (Anslyn *et al.*)[17] recognition studies have already been summarized in recent times. Herein we report a wide and up to date panorama on different classes of synthetic receptors employed for nitrate recognition, with more emphasis given to the work published in last six years. Development of receptors with various dimensions starting from acyclic, tripodal, metal-organic framework, macrocyclic, macrobicyclic and interlocked systems for selective binding, extraction and transportation of nitrate anion through recognition event will be discussed.

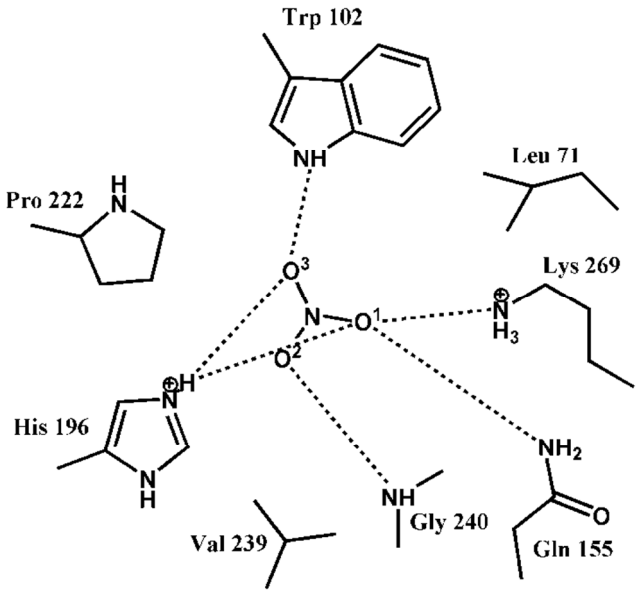

Fig. 1 Presentation of hydrogen bonding interactions between NrtA and NO_3^-.

2. Highlights on nitrate receptors prior to 2008

Since Davis *et al*. have already reviewed artificial and biological receptors for nitrate in 2008;[14] here we only highlight selective important nitrate receptors which have been published before 2008. All those receptors containing ammonium, amide, guanidium, pyrrolic etc. recognition elements (Fig. 2) bind nitrate exclusively via hydrogen bonding interactions.

Protonated amine receptors are most widely used for binding of anions.[18] Lehn *et al.* have first reported NO_3^- binding by a bis-tren cryptand **1** (Fig. 2) by potentiometric titration study and predicted binding modes of NO_3^- by the cryptand.[11] Binding constant (log K) of NO_3^- is measured as 0.50, 1.15, 1.52, 2.30, and 2.93 with the bis, tris, tetra, penta and hexaprotonated form of **1** using $NaClO_4$ as supporting electrolyte. This result suggests that the protonation of at least two secondary amine groups is required for NO_3^- and the hexaprotonated form of **1** has the highest affinity for NO_3^-. Thus, several N-H···O hydrogen bonding interactions are proposed for NO_3^- binding in the cavity of **1**.

Later on, Bowman-James *et al.* have shown one elegant example of two NO_3^- anions encapsulation in the cavity of a hexaprotonated octaazacryptand **2** (Fig. 2).[12] Protonation of **2** with HCl followed by anion exchange with $AgNO_3$ results the crystals of NO_3^- complex, where encapsulation of two NO_3^- is observed by N-H···O interactions with the protonated secondary amines. Each oxygen atom of the encapsulated NO_3^- acts as a bifurcated hydrogen bond acceptor and thus resulting six hydrogen bonds for each NO_3^- (Fig. 3). The C_3-symmetric geometry of the bicyclic cage provides ideal geometry of trigonal planar NO_3^-. Binding of two NO_3^- anions in the solid state is further supported by potentiometric titration data, where binding constant for first and second NO_3^- anion is estimated as 3.02 and 2.38 respectively.

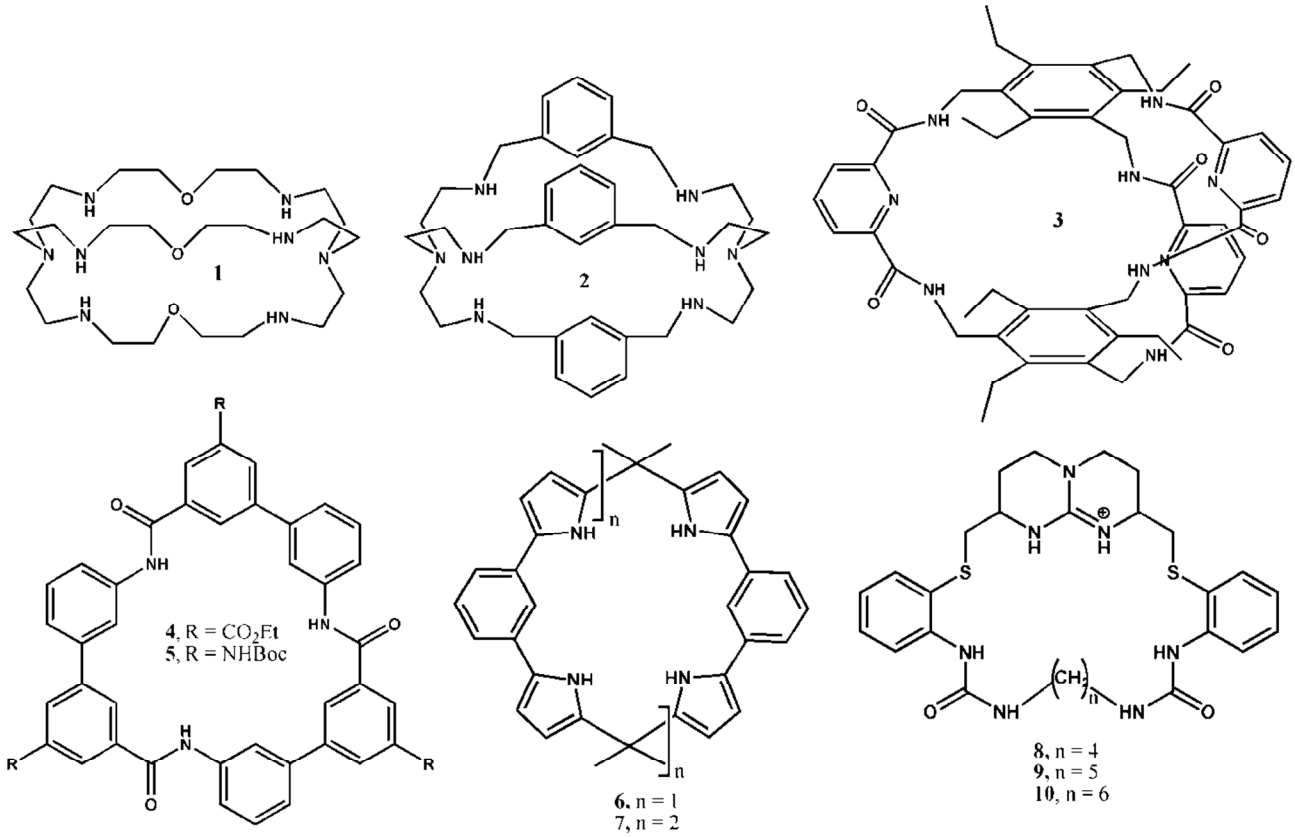

Fig. 2 Chemical structures of bicyclic azacryptand **1**-**2**, amide cryptand **3**, amide macrocycles **4**-**5**, calix[4]pyrroles **6**-**7** and guanidium based macrocycles **8**-**10**.

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Almost same time, Anslyn *et al.* have reported one of the earliest synthetic receptor, an amide functionalized C_{3v}-symmetric cyclophane **3** (Fig. 2) for the recognition of NO_3^-.[13] Crystal structure analysis of acetate complex of **3** reveals encapsulation of AcO^- in the bicyclic cavity by six hydrogen bonding interactions. ^{1}H-NMR titration study with different anions shows high affinity for AcO^- (770 M^{-1}) and NO_3^- (300 M^{-1}) over other anions. This remarkable observation leads to the conclusion that although NO_3^- is 106 times less basic than AcO^-, an efficient binding of NO_3^- is found due to shape complementarity with the host.

In 2003, Hamilton *et al.* have designed elegant macrocyclic receptors **4-5** (Fig. 2) for moderate NO_3^- binding in polar solvent.[19] Apart from ammonium and amide based receptors, few other synthetic receptors for NO_3^- binding are also documented where structural characterization of NO_3^- complex provides useful information of NO_3^- recognition although most of the receptors do not have NO_3^- selectivity. Suitably modified calix[4]pyrrole receptors, **6-7** (Fig. 2) are explored by Sessler *et al.* to evaluate anion binding affinity by ^{1}H-NMR titration.[20] Receptors **6** and **7** show moderate binding affinity towards NO_3^- in CD_2Cl_2, although none of them are selective towards NO_3^-. Crystal structure analysis reveals binding of two oxygen atoms by the pyrrolic –NH group in **6** (Fig. 4a), whereas each of three oxygen atoms are hydrogen bonded to pyrrolic –NH of **7** (Fig. 4b). Another crystal structure of the NO_3^- complex of cyclic guanidium receptors **8-10** (Fig. 2)[21] are reported by Mendoza *et al.* Crystal structure analysis reveals in all cases NO_3^- fits well into the macrocyclic cavity (Fig. 5) and each oxygen atom is hydrogen bonded to two –NH groups each thus showing an ideal geometry for NO_3^-. In addition few other neutral and charged receptors are also reported for NO_3^- binding in early 2000s.[22-25]

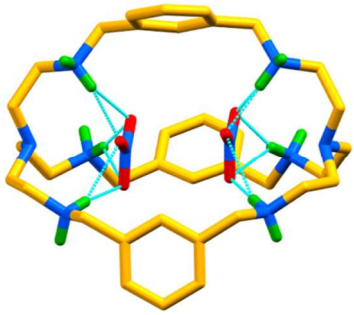

Fig. 3 X-ray structure of two NO_3^- encapsulation in the cavity of $[H_6\mathbf{2}]^{6+}$. Lattice nitrates and non-bonding hydrogens are removed for clarity.

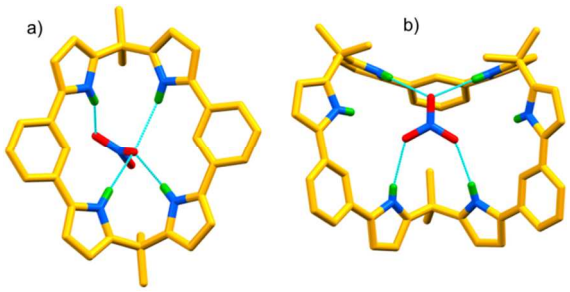

Fig. 4 View of NO_3^- binding in the cleft of calix[4]pyrrole a) **6** and b) **7**.

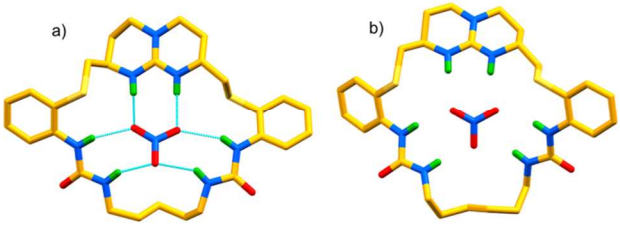

Fig. 5 View of complimentary binding of NO_3^- in a) **9** and b) **10**.

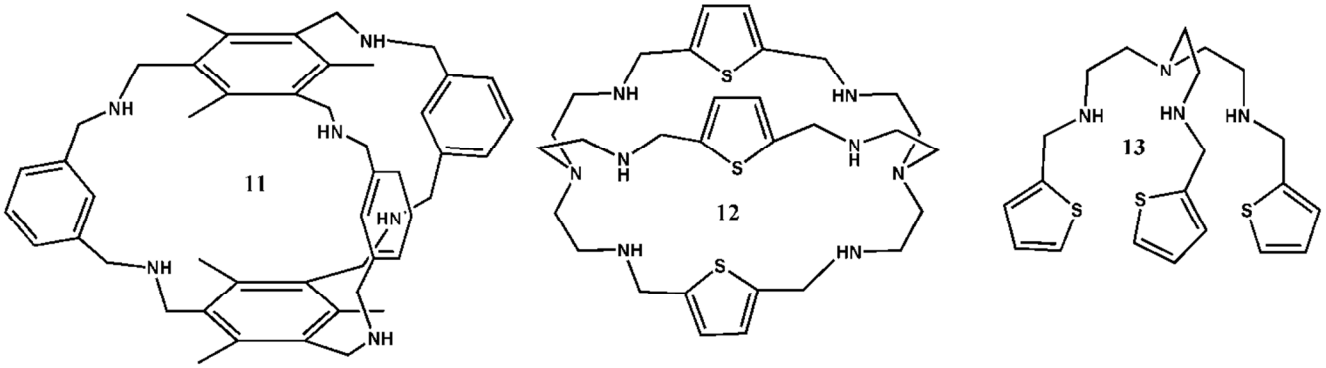

Fig. 6 Chemical structures of azacryptands **11** and **12** and tripodal amine **13**.

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In recent years, scientists have adopted new strategies to address the selectivity issue of nitrate binding along with the conventional hydrogen bonding interactions. Furthermore, nitrate directed self-assembly processes and synthetic nitrate transporters and extractants are recently reported in the literature which are discussed in the following sections.

3. Hydrogen bonding based receptors

Cryptand molecules with six secondary amine groups are found to be suitable host for NO_3^-. In this context, structural investigation of guest complexation study of the bicyclic cyclophane **11** (Fig. 6)[26] by our group have revealed inclusion of π-rich solvents such as DMF, DMSO, MeCN, Me_2CO inside the cyclophane cavity. Protonation of the cyclophane **11** with HNO_3 and $HClO_4$ results hexaprotonation of **11** with recognition of NO_3^- and ClO_4^- in the cleft and cavity respectively (Fig. 7a). Isothermal Titration Calorimetric (ITC) measurements of **11** with different anions at pH = 2 in MeOH/H_2O (1:1) binary solvent reveal moderate selectivity towards NO_3^- (3.14) over ClO_4^- (2.25).

Hossain *et al.* have reported an unusual NO_3^- binding mode of an octaprotonated azacryptand **12** (Fig. 6).[27] Structural analysis of NO_3^- complex of **12** reveals protonation of six secondary amines and two bridgehead tertiary amines by HNO_3. Now binding of three NO_3^- anions is observed in the cleft of **12** in between the bridgehead -NH groups (Fig. 7b). Each -NH group is in trifurcated hydrogen bonding interaction with one oxygen atom of NO_3^-, forming a trigonal bipyramidal geometry of the three oxygen atoms sitting inside the cavity. This triply bridged anions, $[NH(NO_3)_3HN]^+$ resembles anion bridged Werner type transition metal coordination complex. However, the protonated secondary amine groups (NH_2^+) are not hydrogen bonded to NO_3^-. ^{1}H-NMR titration in D_2O shows a 1:1 stoichiometry with a binding constant value 4.30 (log K) in D_2O, although, DFT calculation supports both 1:1 and 1:3 complexes.

A tripodal amine receptor **13** (Fig. 6)[28] is established for efficient NO_3^- binding via encapsulation in the C_{3v}-symmetric cleft. Protonation of **13** with HNO_3 yields crystals of nitrate complex, where encapsulation of a single NO_3^- is observed *via* six N-H···O interactions with the protonated secondary amine groups of **13** (Fig. 7c). Each oxygen atom of NO_3^- is hydrogen bonded to amine groups which is also established as a preferred binding mode for NO_3^- *via* DFT calculation study. In contrast, no such C_{3v}-symmetric cleft formation is observed for I^- complex of **13**, which suggest complementarity between C_{3v}-symmetric host and trigonal planar NO_3^-. Moreover, moderate solution state selectivity of **13** towards NO_3^- (315 M^{-1}) is established by ^{1}H-NMR titration in $CDCl_3$, where a 1:1 binding mode is observed with the binding order: $NO_3^- > Br^- > Cl^- > F^- > ClO_4^- > I^-$.

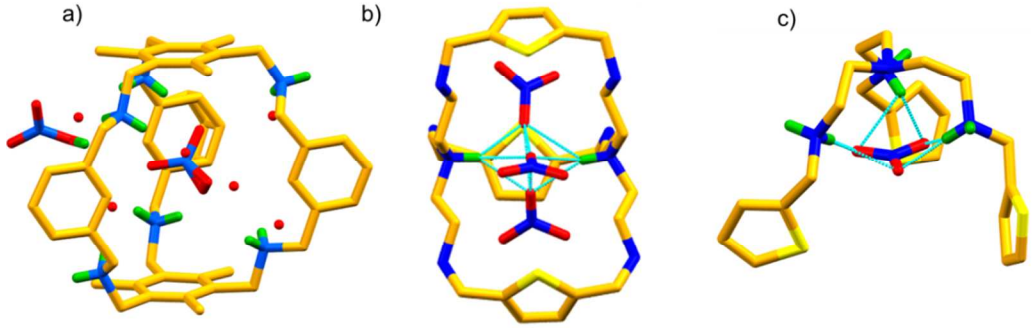

Fig. 7 Structural representation of a) hydrated NO_3^- binding in the protonated cleft of $[H_6\mathbf{11}]^{6+}$, b) triply bridged anion $[NH(NO_3)_3HN]^+$ in $[H_8\mathbf{12}]^{8+}$ and c) NO_3^- encapsulation in the C_{3v}-symmetric cleft of $[H_3\mathbf{13}]^{3+}$. Lattice nitrates and non-bonding hydrogens are removed for clarity.

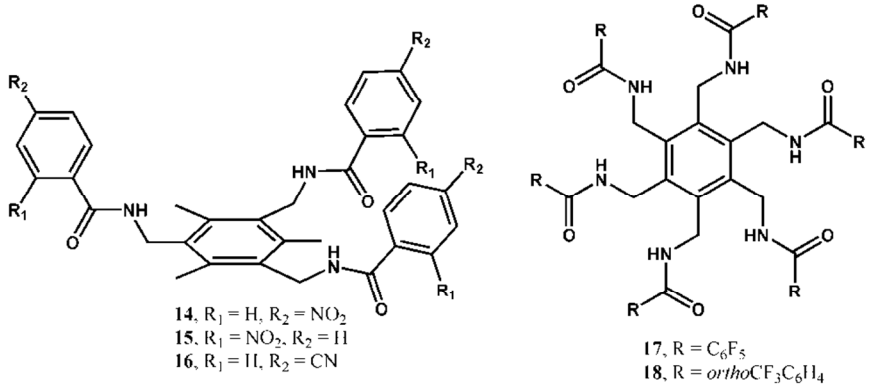

Fig. 8 Chemical structures of benzene platform based tris-amides **14-16** and hexa-amides **17-18**.

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Receptors having amide functionality are also employed for NO_3^- recognition using hydrogen bonding interactions. We have structurally demonstrated NO_3^- binding property of benzene platform based *para* and *ortho* nitrophenyl terminated tripodal amide receptors **14** and **15** respectively (Fig. 8).[29,30] Interestingly, encapsulation of two NO_3^- is observed in the dimeric capsular assembly of **14** (Fig. 9a). Similar dimeric capsular assembly of **14** with hydrated forms of AcO^-, F^- and Cl^- are also observed, whereas **15** shows distorted capsular-type monotopic encapsulation of NO_3^- (Fig. 9b). However, selective formation of $[F_2(H_2O)_4]^{2-}$ templated dimeric capsular assembly formation is demonstrated for **15**.[30] Similar evidence of two NO_3^- encapsulation in the dimeric capsular assembly is also reported in case of *para* cyanophenyl terminated tripodal amide receptor **16** (Fig. 9c).[31] In fact, a general trend of planar anion, such as AcO^-, NO_3^- encapsulation is observed for benzene based tripodal amide receptors.

Our exploration of new generation benzene based hexapodal receptors results compartmental recognition of four NO_3^- in the tripodal amide cleft of hexa-amide **17** (Fig. 8).[32] The solid state structure of NO_3^- complex of **17** reveals the unusual encapsulation of four NO_3^- anions and two water molecules in a single receptor unit, indicating 1:4 binding of **17** to NO_3^- (Fig. 10a). This compartmental recognition of NO_3^- allows trapping of one of the hexapodal conformers with alternating arms are pointed up and down. ^{1}H-NMR titration study with NO_3^- in acetone-d_6 shows 1:2 (host/guest) stoichiometry with log K1 and log K2 values 2.83 and 4.91 respectively. In contrast, *ortho* -CF_3 functionalised hexa-amide receptor **18** (Fig. 8)[33] shows encapsulation of NO_3^- by an unusual hexapodal conformer with four arms pointing one side and other two arms in opposite side (Fig. 10b). However, solution state ^{1}H-NMR and ITC measurement do not show any appreciable binding with NO_3^- in DMSO.

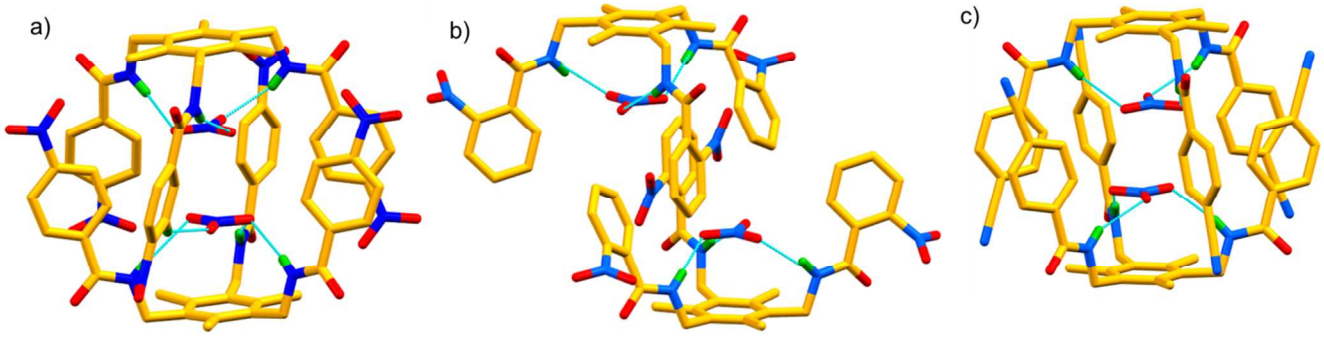

Fig. 9 X-ray crystal structures of a) two NO_3^- encapsulation in the dimeric capsular assembly of **14**; b) NO_3^- assisted non-capsular assembly of **15** and c) two NO_3^- encapsulation in the dimeric capsular assembly of **16**. Countercations, non-acidic hydrogens and lattice solvents are omitted for clarity.

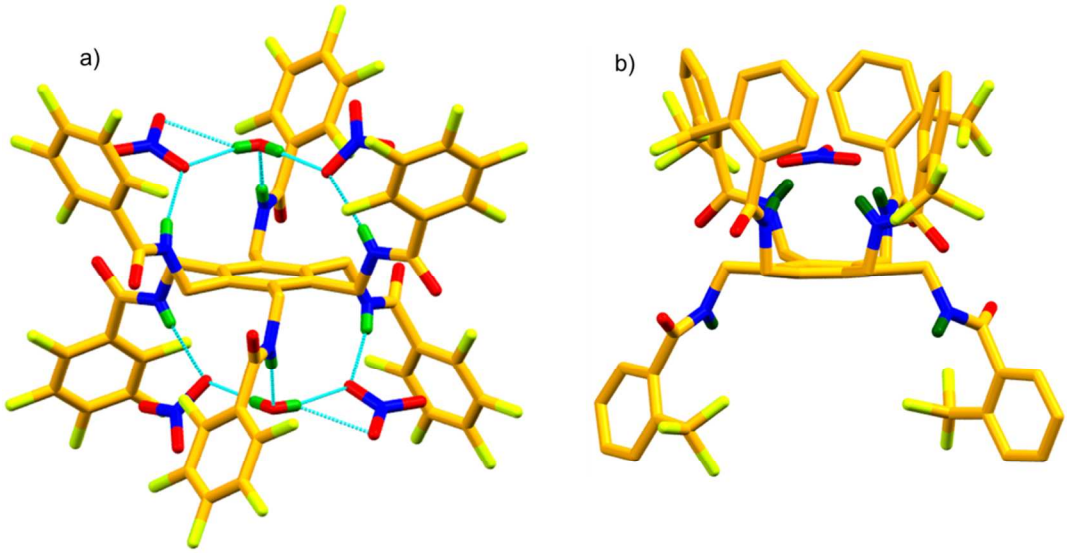

Fig. 10 View of a) nitrate-water recognition in the compartmental cleft of **17**, b) monotopic NO_3^- binding in the cleft of **18**. Non-acidic hydrogens and countercations are omitted for clarity.

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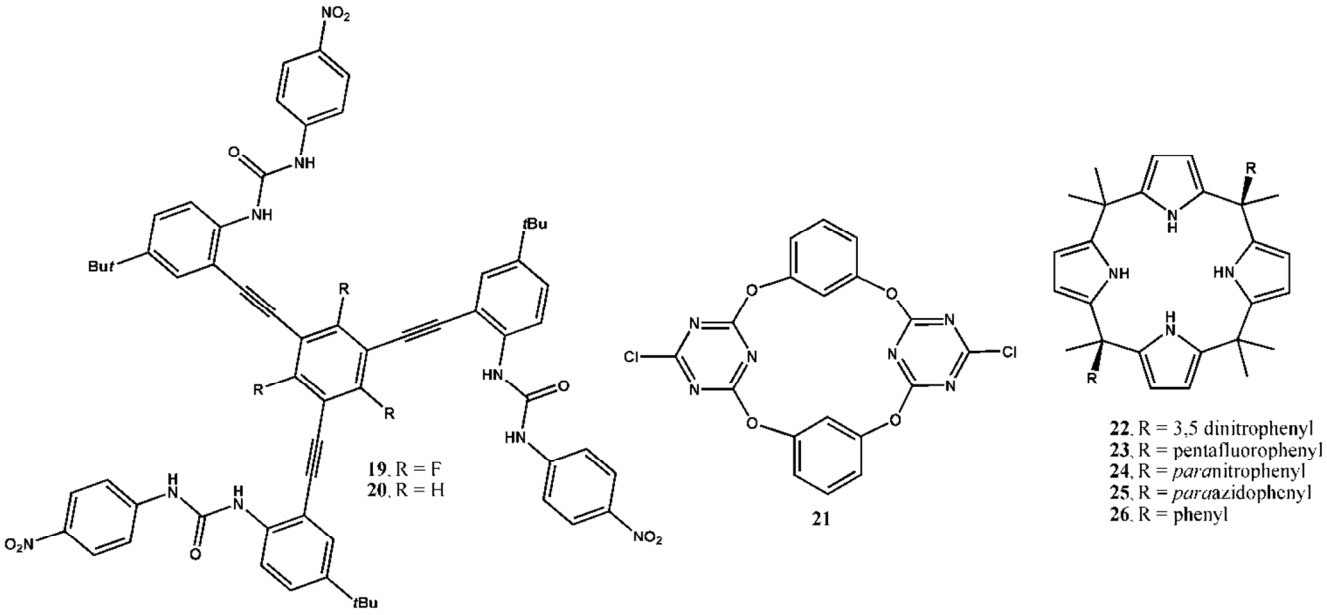

Fig. 11 Chemical structures of benzene platform based urea receptors **19** and **20**, triazine based receptor **21** and calix[4]pyrroles **22-26**.

4. Anion-pi based receptors

Interactions between anionic species and electron deficient rings namely anion-pi interaction has recently been explored by theoretical and experimental studies.[34,35] Johnson *et al.* have recently reported the synthesis of a benzene scaffold based electron deficient tripodal urea **19** (Fig. 11)[36] and have shown the preferential binding towards anion in competitive hydrogen bonding solvents such as acetone-d_6 and 10% DMSO-d_6/$CDCl_3$. A strong binding of anions is observed in 10% DMSO-d_6/$CDCl_3$ solvent and the association affinity of **19** trends: NO_3^-> Cl^-> Br^-> I^-, with a moderate selectivity towards NO_3^- (24100 M^{-1}). This type of NO_3^- selectivity in competitive solvent is rare in literature with synthetic receptors. Although, the urea protons mainly act as hydrogen bond donors, the electron deficient core also facilitates NO_3^- binding by favourable anion-pi interaction. Crystal structure of NO_3^- complex shows proximity of NO_3^- and electro deficient alkynyl core, suggesting possible mode of anion-pi interaction with NO_3^- (Fig. 12). The NO_3^- anion aligns close to the π-system of **19** at a distance less than 3.7 Å (Fig. 12). This mechanism of NO_3^- selectivity over Cl^- is verified binding properties of a control receptor **20** (Fig. 11) which lacks electron deficient core. In contrast, receptor **20** shows selectivity towards Cl^- over NO_3^- with reduced association constant for NO_3^- (11800 M^{-1}). Binding studies of **20** support the existence of a favorable anion–pi interaction by reporting a loss of NO_3^- selectivity and Cl^- selectivity by additional hydrogen bond donor in **20**.

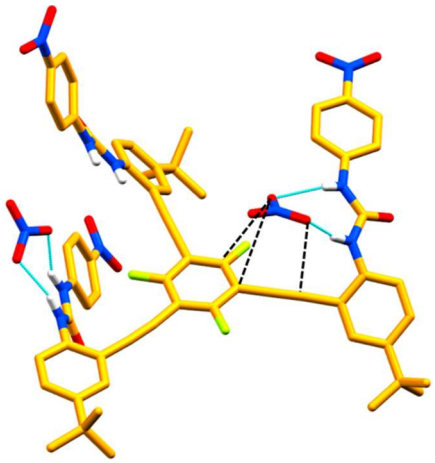

Fig. 12 Structural view of NO_3^- binding to urea –NH group of **19** and close proximity of NO_3^- to electron deficient alkynyl core. Black dotted lines present anion-pi interactions. Countercations are omitted for clarity.

Wang *et al.* explored tetraoxacalix[2]arene[2]triazine, **21** (Fig. 11)[37] having electron deficient triazine core towards anion recognition with anion-pi interaction as an exclusive tool. Fluorescence titration of **21** in acetonitrile reveals appearance of new emission band at 450 nm with NO_3^-, SCN^-, BF_4^- and PF_6^-. Job's plot analysis reveals 1:1 binding stoichiometry with all these anions and binding constant follow the order: NO_3^-> BF_4^- >

PF_6^- > SCN^-. Thus, NO_3^- selectivity with high binding affinity (16950 M^{-1}) is estimated for **21**. Interestingly, ^{1}H-NMR titration of **21** in CD_3CN with anions does not affect the ^{1}H-NMR spectra of host. This observation rules out possibility of noncovalent arene C-H···anion interactions and supports anion-pi interaction in solution. ESI-MS study of a mixture of **21** and different anions show peaks corresponding to the **21**·anion complexes which suggest formation of anion-pi complex in gas phase. Finally, anion-pi interactions of **21** with anions are unambiguously established by structural isolation of the anion complexes. Structural analysis reveals that the macrocyclic host **21** accommodates one anion in π-electron deficient core, which is composed of two triazine ring. In case of NO_3^- complex, close proximity of nitrate and triazine is observed, with a distance 2.953 Å (oxygen to triazine plane) and 3.084 Å (oxygen to triazine centroid) (Fig. 13). Besides anion-pi interaction weak σ-interaction is found between the oxygen atoms of NO_3^- and one triazine ring. Similar structural observation is also described for BF_4^-, SCN^- and PF_6^- anions.

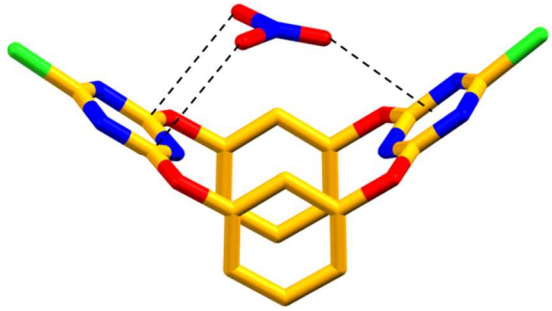

Fig. 13 Structural presentation of anion-pi interactions between NO_3^- and triazine in **21**. Countercations are omitted for clarity.

Ballester *et al.* have recently employed a series of calix[4]pyrrole receptors **22-26** (Fig. 11)[38] with suitable aromatic substitutions at two walls to evaluate their NO_3^- binding affinity. ^{1}H-NMR titration study with $TBANO_3$ in CD_3CN shows significant downfield shift of pyrrolic –NH protons whereas no such shift are observed for the aryl C-H protons of the side walls. This chemical shift pattern suggest binding of NO_3^- deep into the aromatic cleft and aromatic systems do not interact with NO_3^- via C-H···O interactions. However, anion-pi interaction between NO_3^- and axially oriented aromatic rings is predicted to be operational. 3,5 dinitrophenyl substituted receptor, **22** shows highest affinity towards NO_3^- (1550 M^{-1}) in CD_3CN. Now a control calix[4]pyrrole system, **26** is selected to quantify the value of possible anion–pi interactions *via* the difference in free energy of binding. In all calix[4]pyrrole receptors with various substitution, similar change in pyrrolic –NH signal is found which suggest difference in binding affinity is governed by anion-pi interaction. Thus, by subtracting binding free energy changes of the receptors with the control receptor, provides the value of nitrate-pi interactions which is calculated as maximum (-0.9 $kcalmol^{-1}$ for each side wall) for **22**. Two set of NO_3^- bonded structure of **22** are isolated, where one of them corroborate solution state binding mode. The NO_3^- is located perpendicular above the plane of the electron deficient aromatic wall and involved in N-H···O interaction with pyrrolic –NH protons (Fig. 14). Further, one oxygen atom of NO_3^- is located above 3.0 Å over the carbon atom of the aromatic ring, suggests the presence of weak sigma interactions.

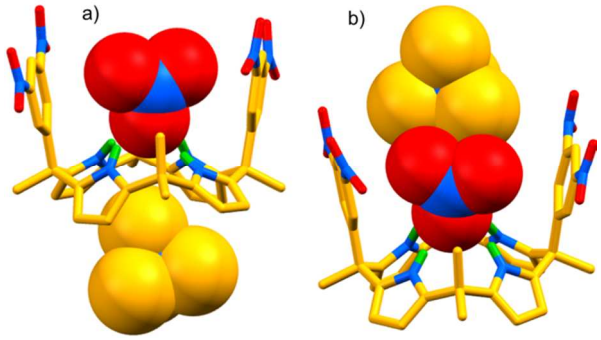

Fig. 14 View of two different NO_3^- binding geometry in $[Me_4N]^+[NO_3]^-$ ⊂**22**. Solvents and non-acidic hydrogens are removed for clarity.

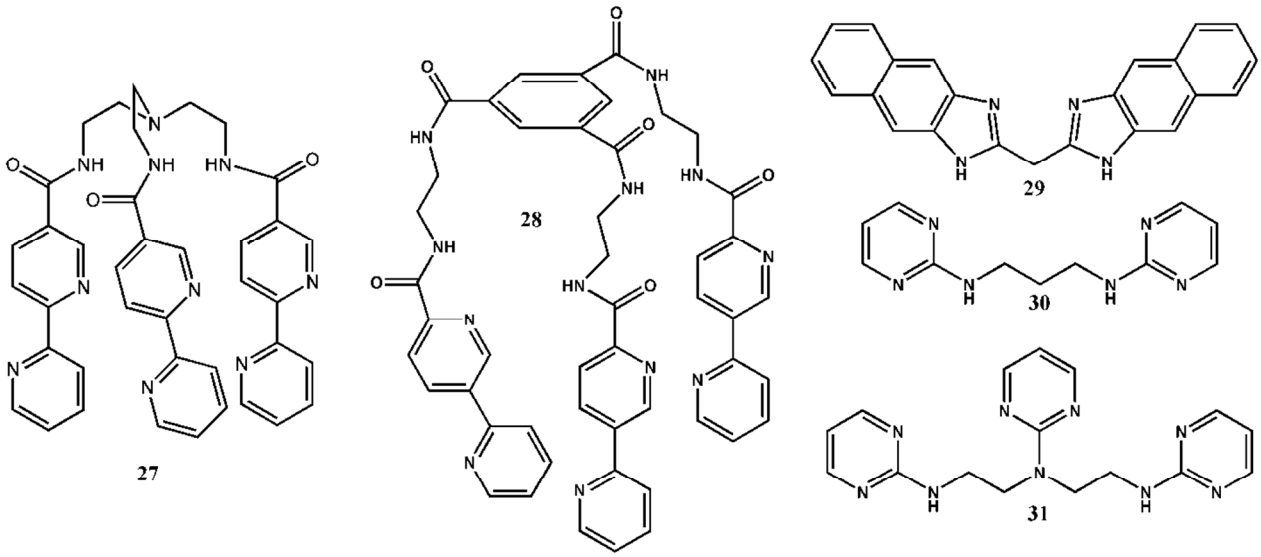

Fig. 15 Chemical structures of receptors, **27-31** employed for metal assisted NO_3^- binding.

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5. Metal based receptors

Synthetic organic receptors functionalized with anion binding group are also reported which undergo assembly in presence of suitable metal and exhibit NO_3^- binding property. In some cases, metal-organic assemblies are triggered by NO_3^- anion. Few such examples of metal-based nitrate receptors are discussed. Unusual NO_3^- selectivity is demonstrated by an amide functionalized Ru(II) cryptate of **28** (Fig. 15).[39] The tripodal ligand consists of anion binding amide functionality and metal chelating bipyridyl groups and its Ru(II) complex is explored for anion binding studies. Structural analysis of the $[Ru\mathbf{28}]^{2+}$ shows presence of cavity in the amide cleft suitable for an anionic species. Fluorescence titration study of $[Ru(\mathbf{28})][PF_6]_2$ with NO_3^-, HSO_4^-, Cl^- and Br^- shows significant decrease in the luminescence, which suggest possible binding of these anion in the amide cleft. This data is corroborated by ^{1}H-NMR titration study of $[Ru(\mathbf{28})][PF_6]_2$ in CD_3CN, where significant downfield shift of amide NH group is observed with NO_3^-, Br^- and Cl^-. The complex illustrates a very high selectivity for NO_3^-, (log K_1 > 6) over Cl^- and Br^-. This remarkable NO_3- selectivity of $[Ru(\mathbf{28})][PF_6]_2$ is presumably due to the presence of complementary C_3-symmetric hydrogen bond donor having six –NH groups. On the other hand, $[Ru(\mathbf{27})][PF_6]_2$ (Fig. 15) having smaller cavity do not show any significant spectroscopic changes with nitrate and halides.

Anion switchable movement of a metal-organic framework derived from a flexible ligand **29** (Fig. 15)[40] and its anion binding property is investigated by Pan *et al.* Complexation of **29** with one equivalent of $[(tmen)Pd(NO_3)_2]$ (tmen = *N,N,N',N'*-tetramethylethylenediamine) in acetone/H_2O yields complex $[M_2\mathbf{29}_2\cdot(NO_3)_4]$ [M = $(tmen)Pd^{II}$] with bowl shaped conformation. Crystallographic analysis reveals formation of a bowl-shaped structure made up of two **29** units connected with Pd(II) atoms. Interestingly, one NO_3^- is recognized at the bottom of the bowl by C-H···O interactions with **29** (Fig. 16). ^{1}H-NMR and ESI-MS study of Pd(II) complex also imply presence of NO_3^- bound cone conformer in solution. In contrast, addition of sodium tetraphenylborate (BPh_4) to the nitrate complex in H_2O/MeCN results the switching of the bowl shaped conformer to chair shaped conformer. Formation of such chair conformer is characterized by X-ray crystallography, ^{1}H-NMR and ESI-MS study. The details of conformational transformation are also studied by ^{1}H-NMR titration experiment in solution. New set of signals are observed upon addition of NO_3^- to BPh_4 complex corresponding to the formation of bowl shaped conformer. Other anions like HSO_4^-, $H_2PO_4^-$ and carboxylates also switch the partial chair conformer to bowl shaped conformer. Anion binding affinity of BPh_4-complex with different anions are calculated from the degree of conformer conversion and chemical shift. The order of anion binding affinity of BPh_4-complex follows the order: NO_3^- (5800 M^{-1}) > HSO_4^-> terephthalate> $H_2PO_4^-$> $CF_3SO_3^-$ ~ ClO_4^-> PF_6^-.

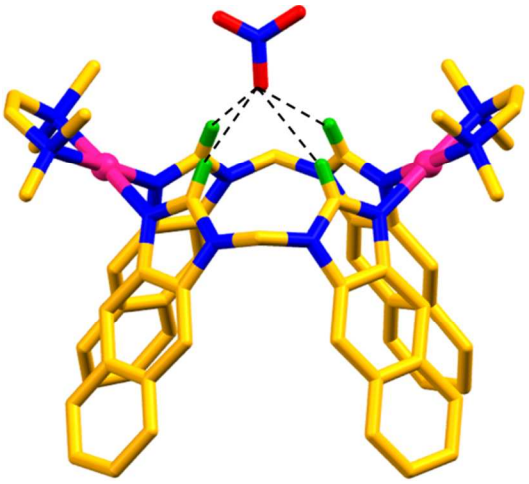

Fig. 16 Crystal structure of NO_3^- binding in $[(tmen)Pd^{II}\mathbf{29}_2\cdot(NO_3)_4]$. Lattice NO_3^-, solvents and non-acidic hydrogens are removed for clarity.

Frontera *et al.* have designed and structurally characterized self-assembled metallomacrocycle derived from **30** and **31** (Fig. 15) for anion binding by hydrogen bonding and electrostatic interactions.[41] Complexation of **30** with $AgNO_3$ leads to the formation of a self-assembled macrocycle having two incorporated NO_3^- (Fig. 17a) *via* the coordination of pyrimidyl nitrogen to Ag^+, where the NO_3^- binding is facilitated by hydrogen bonding interaction with –NH group and direct coordination to Ag^+. Similar structural arrangement is observed for OTs^- counteranion, where two anions sit outside the cavity. In contrast, an infinite chain of coordination polymer is formed in case of BF_4^- anion. In case of **31**, similar incorporation of two NO_3^- is observed in the self-assembled macrocyclic cavity with additional number of C-H···O interactions (Fig. 17b).

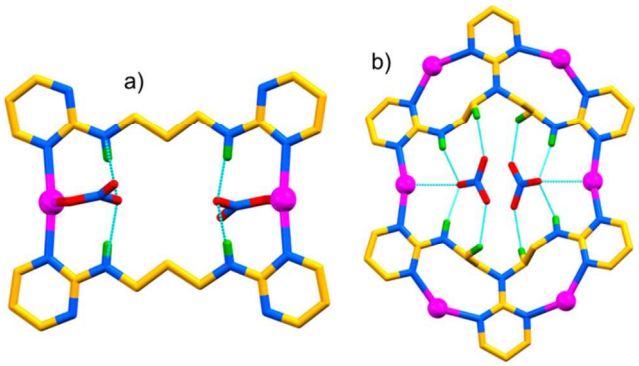

Fig. 17 Partial View of two NO_3^- binding in self-assembled metallo-macrocycles of a) **30** and b) **31**. Non-acidic hydrogens are removed for clarity.

6. Nitrate assisted assembly

Anions are widely used as template for the synthesis of self-assembled supramolecular architectures. Hydrogen bonding interactions are dominant force in case of organic supramolecular self-assembly. Trigonal planar NO_3^- anion has been explored for various self-assembly processes such as capsular/non-capsular assembly, interlocked molecules.

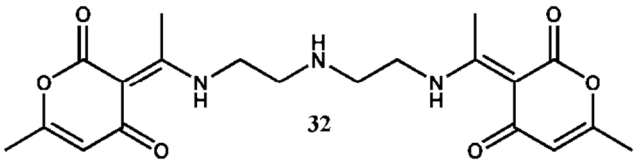

Fig. 18 Chemical structure of receptor **32**.

6.1. Capsular and non-capsular assembly

Cindrić *et al.* reported anion templated supramolecular assembly of a flexible ligand **32** (Fig. 18),[42] having anion binding ammonium group. Protonation of **32** with HNO_3/H_2SO_4 result the formation of pseudo-macrocyclic hosts assisted by NO_3^- (Fig. 19) and SO_4^{2-}. Anion templated assembly of three acyclic unit results the formation of a C_3-symmetric supramolecular complex with one incorporated NO_3^-. Crystallographic analysis shows that only the central amino group is protonated, whereas side amino group remains unprotonated but participate in resonance assisted hydrogen bonding interactions with the anions. Formation of such anion templated pseudo-macrocyclic host is established to be very specific only with NO_3^- and SO_4^{2-}. Each of the oxygen atom of NO_3^- acts as a tetrafurcated hydrogen bond acceptor thus results twelve coordination number of NO_3^- which is rare with synthetic receptors.

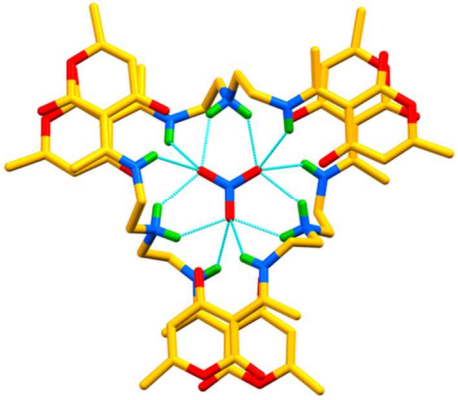

Fig. 19 Structural representation of NO_3^- assisted formation of C_3-symmetric supramolecular complex $[((H\mathbf{32})_3NO_3]^{2+}$. Non-acidic hydrogens are removed for clarity.

We have demonstrated nitrate triggered dimeric capsular assembly and chloride induced disassembly of a benzene capped tripodal receptor **33** (Fig. 20).[43] Tripodal receptor **33** having benzimidazole unit forms dimeric capsular assembly stitched by six NO_3^- and two water molecules upon protonation with HNO_3. The ligand undergoes conformational changes upon triprotonation and organizes in such a way that the $[H_3\mathbf{33}]^{3+}$ moiety forms a bowl shaped cleft. Now two such bowl shaped $[H_3\mathbf{33}]^{3+}$ shares six NO_3^- and two H_2O molecules to form discrete staggered capsule (Fig. 21). Interestingly, addition of Cl^- to the NO_3^- capsules disrupts the capsular assembly by expelling one NO_3^-. This selective NO_3^- assisted formation of capsular assembly is validated by protonating **33** with HCl, where similar non-capsular aggregates with infinite hydrogen bonded network of the receptor with Cl^- and H_2O is observed.

We have further extended our investigation on NO_3^- directed assembly with a series of tripodal and dipodal receptors **34-36** (Fig. 20).[44] Protonation of **34** having imidazole substitution with HNO_3 results the formation of a bowl shaped cavity with one encapsulated water and three hydrogen bonded NO_3^- at the cleft. Two units of such triprotonated **34** form infinite distorted capsular assembly (Fig. 22a) compared to the discrete staggered capsular assembly in case of **33**. On the other hand, protonation of **35** having dimethyl pyrazole substitution with HNO_3 results formation of a NO_3^- templated assembly of **35** to form a macrocyclic structure (Fig. 22b). Two pyrazolium rings of two different **35** units are connected by two bridging NO_3^- anions and a macrocyclic structure is formed by four such receptor units.

An interesting structural finding is observed during protonation of dipodal receptor **36** (Fig. 20) with HNO_3. Two diprotonated **36** units are bridged by one NO_3^- anion and form a polymeric zigzag chain (Fig. 22c). Remaining NO_3^- ion exist as an unusual proton bridged dinitrate species i.e $[NO_3\ldots H\ldots NO_3]^-$.

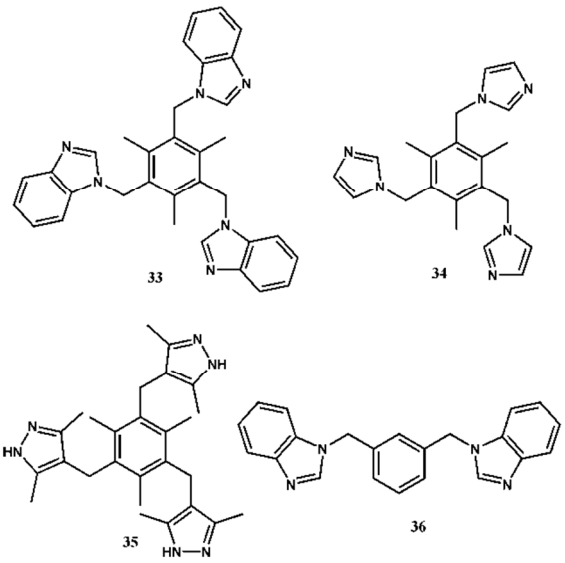

Fig. 20 Chemical structures of benzene platform based tripodal receptors **33-35** and dipodal receptor **36**.

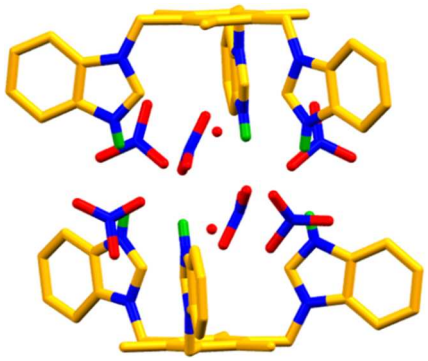

Fig. 21 View of NO_3^- stitched dimeric capsular aggregate of $[H_3\mathbf{33}]^{3+}$. Non-acidic hydrogens are omitted for clarity.

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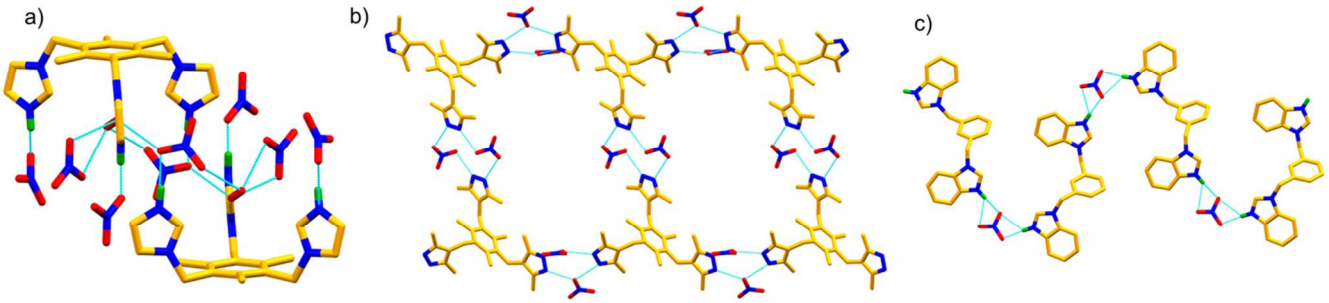

Fig. 22 View of a) NO_3^- assisted distorted capsular assembly of $[H_3\mathbf{34}]^{3+}$, b) NO_3^- assisted macrocyclic structure in the crystal packing of **35** and c) NO_3^- assisted polymeric chain of $[H_2\mathbf{36}]^{2+}$. Non-acidic hydrogens are removed for clarity.

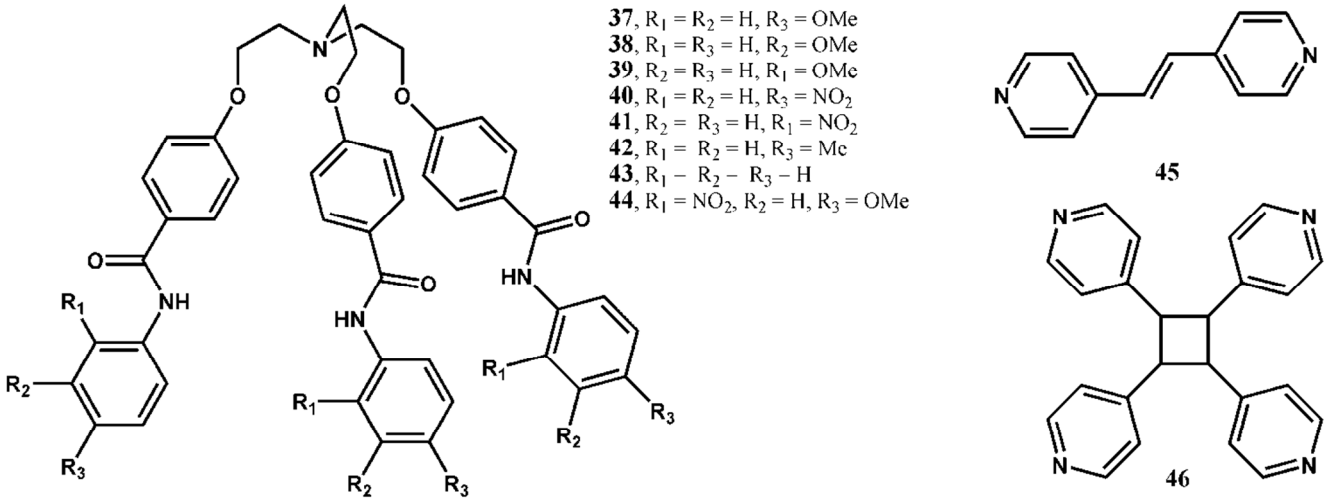

Fig. 23 Chemical structures of tripodal amide receptors **37**-**44** and trans isomer of **45** and its [2+2] photocyclized product **46**.

Sun *et al.* have demonstrated NO_3^- encapsulation by tripodal amide receptor and solvent driven dynamic self-assembly/disassembly *via* conversion between the nitrate complex and self-assembled dimer.[45] Reaction of **37** (Fig. 23) in $CHCl_3$ with aqueous methanolic HNO_3 yields the mixture of NO_3^- complex of **37** and **44**, where the bridgehead nitrogen is protonated. Formation of **44** from **37** is rationalized by the electrophilic nitration in *meta* position relative to methoxy group of **37** with HNO_3. Crystal structure analysis of NO_3^- complex of **37** shows encapsulation of one NO_3^- via the N-H···O interaction from the amide –NH groups (Fig. 24a). However, protonation of **37** with HNO_3 in CH_3CN results the formation of NO_3^- complex of **37** as a single product. When a DSMO-d_6 solution of NO_3^- complex of **44** is titrated with $CDCl_3$, a new species is formed as evident from ^{1}H-NMR spectra. At 1:1 (v/v) $CDCl_3$/DMSO-d_6 mixture, the self-assembled dimeric capsule of **44** is formed with the release of NO_3^-. Evaporation of $CDCl_3$, results the formation of NO_3^- complex of **44**. Thus, solvent polarity driven reversible conversion between NO_3^- encapsulated complex and self-assembled dimer of **44** is demonstrated.

Sun *et al.* have generalized the above findings with a series of tripodal amide receptors, **37**-**44** (Fig. 23) with both electron withdrawing/donating groups and studied their NO_3^- recognition affinity.[46] All the studied receptors except **42** forms NO_3^- encapsulated products upon treatment of HNO_3 with the receptors in $CHCl_3$/MeOH binary solvent. On the other hand, analytically pure NO_3^- complex of **42** is obtained by the reaction of **42** and HNO_3 in MeOH. Crystal structure analysis of the nitrate complex of **42** reveals encapsulation of a single NO_3^- in the tripodal cleft via N-H···O interactions with three amide –NH groups (Fig. 24b). The ^{1}H-NMR titration study of the ClO_4-complex of the receptors in acetone-d_6 results downfield shift of –NH signal with 1:1 binding stoichiometry. Among the studied receptors, **38** and **40** having *meta* -OMe (1550 M^{-1}) and *para* -NO_2 (1080 M^{-1}) group respectively show highest affinity towards NO_3^-. This enhanced NO_3^- affinity is explained by the polarization of amide –NH group by *meta* -OMe and *para* -NO_2 groups.

Role of nitrate template for stereoselective solid-state synthesis of photochemical [2+2] adduct by supramolecular encapsulation/release of anion template is nicely demonstrated by Sun *et al*.[47] Initially single crystals of NO_3^- complex of **44** is structurally characterized upon reaction of **44** and HNO_3 in aqueous methanol. [2+2] photo-adduct, **46**·2HNO_3 is obtained in quantitative yield by irradiation of **45**·2HNO_3 at 365 nm in solid state within 2.5-3h (Fig. 23). Previously, solvent polarity dependent NO_3^- encapsulation and release is demonstrated for tripodal amide receptor **44**. Reaction of **45** in presence of nitrate complex of **44** forms the nitrate adduct **45**·2HNO_3 in filtrate and self-assembled capsule of **44**·**44** in the precipitate as determined by ^{1}H-NMR study. Subsequent photo irradiation **45**·2HNO_3 yields the single isomer **46**·2HNO_3 with 100% yield. Now an aqueous ethanolic or methanolic solution of capsule **44**·**44** and **46**·2HNO_3 are reacted to regenerate the nitrate adduct of **44** as precipitate and nitrate free photocyclized product **46** in filtrate.

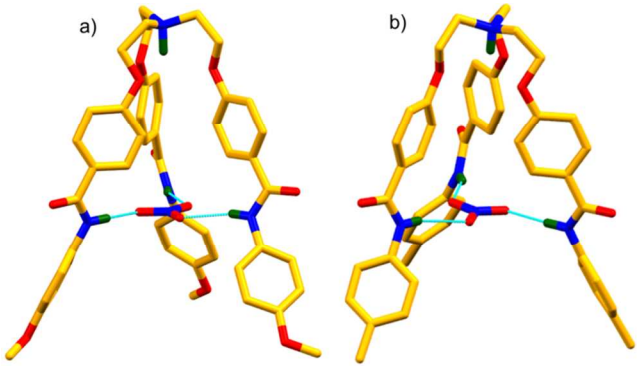

Fig. 24 View of NO_3^- encapsulation in the tripodal cleft of a) **39** and b) **42**. Non-acidic hydrogens are omitted for clarity.

6.2. Nitrate templated interlocked molecules

Use of discrete anion template such as chloride, bromide, sulfate etc. for the formation of interlocked molecules has been well established by Beer *et al*.[48] Recently, they have demonstrated first NO_3^- templated assembly of interlocked molecules towards the formation of a [2]rotaxane **49** (Chart 1).[49] They have synthesized NO_3^- templated [2]pseudorotaxane where both the threading component **47** and macrocycle **48** consists of complimentary binding motifs (-NH) for NO_3^-. Upon successful formation of [2]pseudorotaxane, copper(I) catalysed stoppering strategy is employed for the synthesis of [2]rotaxane **49** by click chemistry between threading component with azide terminal and a bulky alkyne. Synthesis of [2]rotaxane **49** is failed in absence of NO_3^- which suggest the vital role of NO_3^- template. Furthermore, anion recognition property of PF_6^- salt of the [2]rotaxane is investigated by ^{1}H-NMR titration study in $CDCl_3/CD_3OD/D_2O$ (45 : 45 : 10) solvent mixture. 1:1 host/guest binding propensity of [2]rotaxane with NO_3^- (Ka = 430 M^{-1}) is observed with the selectivity over more basic anion HCO_3^- and $H_2PO_4^-$. This impressive NO_3^- selectivity is reasoned from the complementarity of NO_3^- with tridentate hydrogen bonding cavity of the [2]rotaxane **49**.

They have recently extended their NO_3^- templated strategy for the synthesis of more complex interlocked structure i.e [2]catenane **52** (Chart 2).[50] The initial macrocycle precursor **51** consists of two hydrogen bonding donor sites for two oxygen of NO_3^- and vinyl end functionality to facilitate ring closing metathesis (RCM) for catenane formation. In presence of $TBANO_3$ in dry CH_2Cl_2 an initial pseudorotaxane assembly is formed via the threading of **50** to macrocycle **51** that contains another set of hydrogen bond donor for NO_3^-. Finally, RCM reaction of this pseudorotaxane assembly using Grubbs second generation catalyst yields the final [2]catenane product **52**·NO_3. Crucial role of NO_3^- template is also verified by the use of other templating anions. Moreover, anion complexation property of **52**·PF_6 in $CDCl_3/CD_3OD/D_2O$ (45 : 45 : 10) reveals selectivity for NO_3^- (Ka = 250 M^{-1}) over HCO_3^-, $H_2PO_4^-$, AcO^- and Cl^-. Complementary binding sites of catenane **52** comprising of six –NH group renders selective NO_3^- recognition affinity of the catenane **52**.

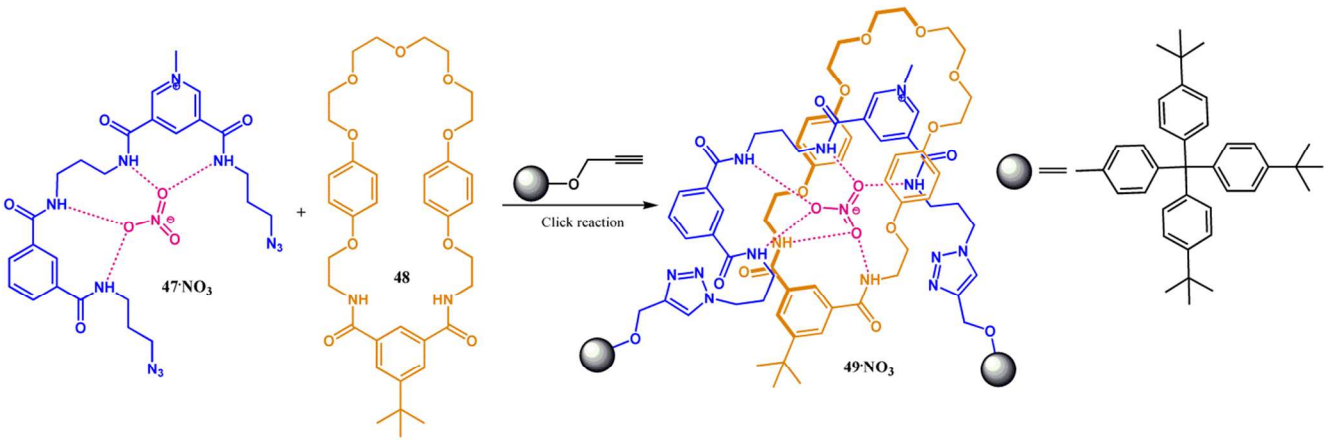

Chart 1 Synthesis of [2]rotaxane **49** via nitrate anion templation.

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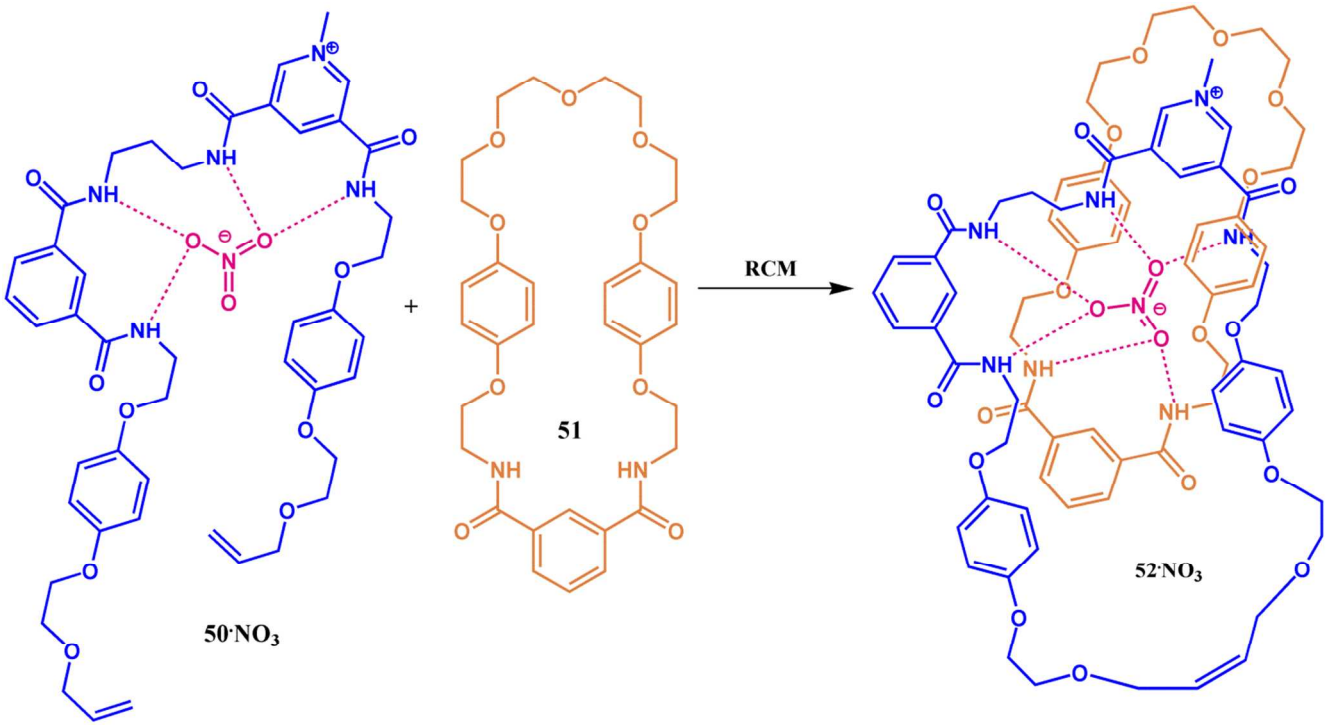

Chart 2 Synthesis of interlocked [2]catenane **52** via nitrate anion templation.

7. Binding constant of NO_3^- of selected anion receptors.

Due to the lower basicity of NO_3^-, most of the synthetic receptors show lower affinity towards NO_3^-. This observation is more prominent in polar solvent where competition from solvent further lowers the binding strength. We have summarized the binding constants for selected NO_3^- selective receptors as determined by different spectroscopic techniques such as ^{1}H-NMR, potentiometry, ITC, fluorescence, UV-Vis etc. (Table 1). Thus, most of the charged and neutral receptors show binding affinity for NO_3^- in the order of 10^2 to 10^3 M^{-1}. However, few of the recently developed anion receptor such as **19** and **21** show high affinity (10^4 M^{-1}) for NO_3^-.

Table 1. Binding constant of NO_3^- of selected anion receptors

Receptor	Solvent	log K
$[\mathbf{H_61}]^{6+}$	H_2O	2.93[a]
$[\mathbf{H_62}]^{6+}$	H_2O	3.02, 2.38[a]
3	CD_2Cl_2/CD_3CN (1:3)	2.48[c]
8	CH_3CN	0.86[b]
9	CH_3CN	1.18[b]
10	CH_3CN	1.87[b]
$[\mathbf{H_611}]^{6+}$	MeOH/H_2O (1:1)	3.14[b]
$[\mathbf{H_812}]^{8+}$	D_2O	4.30[c]
$[\mathbf{H_313}]^{3+}$	$CDCl_3$	2.50[c]
17	Acetone-d_6	2.83, 4.91[c]
19	$CDCl_3$/DMSO-d_6(9:1)	4.38[c]
21	CH_3CN	4.23[d]
22	CD_3CN	3.19[c]
[Ru(**28**)][PF_6]$_2$	CD_3CN	6.4, 9.2[c]
[Pd$_2$**29**$_2$][BPh_4]$_4$	CD_3CN	3.76[c]
H38·ClO_4	Acetone-d_6	3.19[c]
H40·ClO_4	Acetone-d_6	3.03[c]
49·PF_6	$CDCl_3/CD_3OD/D_2O$(45:45:10)	2.63[c]
52·PF_6	$CDCl_3/CD_3OD/D_2O$(45:45:10)	2.40[c]
53	DMSO-d_6	2.45[c]

a: potentiometry, *b*: Isothermal titration calorimetry, *c*: ^{1}H-NMR titration, *d*: fluorescence titration

8. Synthetic transporter and extractant for nitrate

8.1. Synthetic extractant for nitrate

A nice account on NO_3^- recognition as ion pair by a heteroditopic macrotricyclic host **53** (Fig. 25) is recently reported by Piątek *et al*.[51] The macrotricyclic host **53** consists of a tripodal anion binding domain and 4,10,16-triaza-18-crown-6 cation recognition unit. ^{1}H-NMR titration of **53** in presence of different anions shows selectivity towards NO_3^- (280 M^{-1}) and NO_2^- (290 M^{-1}) over other anions in DMSO-d_6. Interestingly, presence of NH_4^+ cation significantly increases the association constant of NO_3^- (1050 M^{-1}) with **53**. However, binding of Cl^- and Br^- are not enhanced in presence of co-bound NH_4^+ cation.

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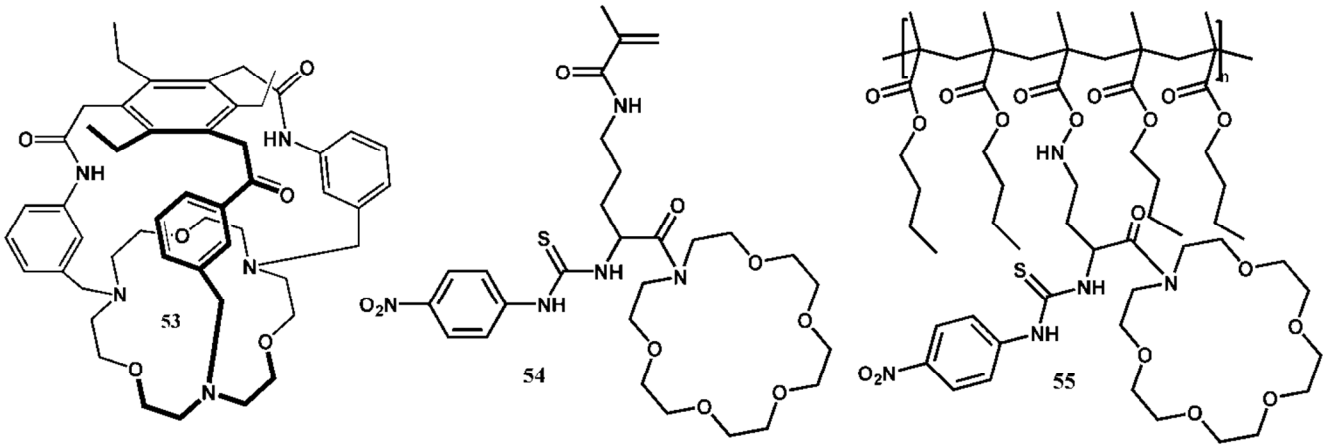

Fig. 25 Chemical structures of heteroditopic extractants **53** and **54** and polymer **55**.

Molecular modelling study supports formation of C_{3v}-symmetric host with encapsulated NH_4^+ cation and NO_3^- anion. The NO_3^- ion is located parallel to the plane of amide N-atoms and hydrogen bonded to three amide –NH groups. Whereas NH_4^+ cation resides near to the crown ether domain. Furthermore, efficient extraction of NH_4NO_3 from water is observed by **53** via liquid-liquid extraction study. An aqueous solution of NH_4NO_3 is mixed with $CDCl_3$ solution of **53** in a typical extraction experiment. ^{1}H-NMR analysis of the $CDCl_3$ layers reveals transfer of NH_4NO_3 from aqueous to organic layer with ~65% extraction efficiency. However, no extraction of $NaNO_3$ or NH_4Cl is observed in liquid-liquid extraction study, which further suggests cooperative effect for NH_4NO_3 binding. In this context, Smith *et al.* have previously reported such heteroditopic receptors for simultaneous complexation of alkali metal and nitrate anion.[52]

Piątek *et al*. have extended their work on NO_3^- extraction study to polymeric materials having NO_3^- recognition motif.[53] A heteroditopic receptor **54** (Fig. 25) with cation binding crown ether and anion binding thiourea units are explored for anion, cation and salt complexation study. ^{1}H-NMR titration studies with AcO^-, Cl^-, NO_3^- show very high binding affinity towards AcO^- and weak affinity for NO_3^-. Moreover, **54** shows selectivity for Na^+ over K^+ as determined by ^{1}H-NMR titration. Interestingly, AcO^- and Cl^- binding affinity is drastically reduced in presence of Na^+, whereas NO_3^- binding affinity increases by 2.5 fold. This observation is rationalized by positive cooperative effect in case of NO_3^-. However, **54** shows negligible liquid-liquid extraction property towards $NaNO_3$. Thus, the monomeric unit **54** is attached to the polymer **54** (Fig. 25) to tune the nitrate extraction property. An aqueous solution of $NaNO_3$ is extracted by a $CHCl_3$ solution of **55** and finally the organic layer is back titrated to distilled water to quantify the $NaNO_3$ extraction efficiency. The colorimetric nitrate-nitrite experiment of this aqueous solution reveals 32% extraction efficiency for nitrate.

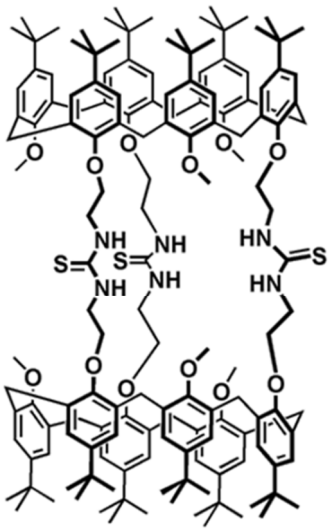

Fig. 26 Chemical structure of bis-calix[6]thiourea **56**.

Thiourea functionaised bis-calix[6]arene **56** (Fig. 26) having heteroditopic binding motif exhibits strong binding of SO_4^{2-} over other anions as a ion-pair triplet.[54] Interestingly, liquid-liquid extraction of NO_3^- is observed for **56** from water to chloroform solution as determined by ^{1}H-NMR study. Lower hydration energy of NO_3^- than SO_4^{2-} and binding complementarity inside **56** enable selective extraction of NO_3^-.

8.2. Synthetic transporter for nitrate

Davis *et al*. have first reported synthetic receptors which selectively transport NO_3^- over Cl^- across liposomal membranes.[55] First the tripod **57** (Fig. 27) having amide functionality is established as anion receptor by ^{1}H-NMR titration study. In CD_2Cl_2 solution **57** shows binding with Cl^- and NO_3^- via

the amide –NH protons. Moderate binding constant is evaluated for Cl^- (Ka = 816 M^{-1}) and NO_3^- (Ka = 326 M^{-1}) in CD_2Cl_2 solution. Nitrate transport across the phospholipid vesicle by **57** is monitored by UV-Vis spectroscopy where NO_3^- is reduced to NO_2^- by NADPH cofactor with concomitant oxidation to $NADP^+$ cofactor. The reduced NO_2^- is trapped to produce a Diazo dye. Thus, the whole process of NO_3^- transport by **57** is monitored by UV-Vis study. Although, higher Cl^- affinity is observed in solution, interestingly **57** shows transport selectivity for NO_3^- over Cl^- by antiport mechanism.

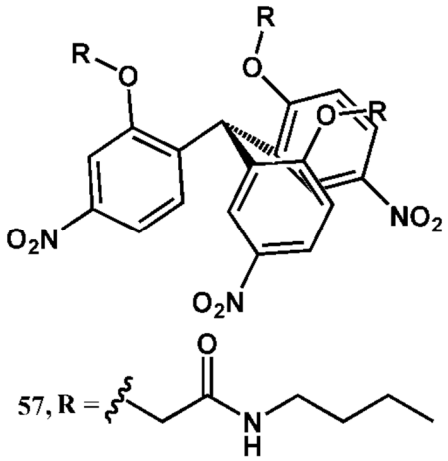

Fig. 27 Chemical structure of tripodal amide based nitrate transporter **57**.

Ballester *et al*. have studied the transport activity of the series of calix[4]pyrrole **22-26** (Fig. 11)[38] with different anion across a large unilamellar vesicle by EC50 value measurement. Among the investigated calix[4]pyrrole receptors **22** and **24** show highest anion transport activity. Although the receptor **22** shows higher binding affinity towards Cl^- and Br^- than NO_3^-, interestingly superior NO_3^- transport activity is observed for **22**.

9. Conclusion and outlook

In last five years, different new strategies have been introduced for selective binding of nitrate that includes nitrate-pi based receptors, metal coordination based assembly towards nitrate recognition and nitrate based assemblies. A wide variety of tris(2-aminoethyl)amine, arene-based receptors containing ammonium, amide, urea groups as anion recognition elements with increasing complexity from tripodal, macrobicycle, molecular capsule, hexapodal to interlocked systems have been evolved in recent times. Most importantly, particular attentions are given for quantitative evaluation of nitrate binding in solution by synthetic anion receptors. Furthermore, numerous structural evidences reveal new interaction modes and coordination geometries of nitrate. Hydrogen bond directionality and shape complementarity appears to be important criteria for designing nitrate selective receptors. Particularly, the necessity of shape complementarity is understood from the structural evidences of nitrate encapsulation by C_3-symmetric hosts. Some recent reports suggest anion-pi interactions could be a possible tool to design nitrate selective receptors even in competitive solvent media. However, nitrate templated syntheses of interlocked molecules employing the complimentary binding between nitrate and host molecules are only recently explored. Moreover, recent research on nitrate recognition has opened up opportunities to utilize such synthetic receptors for nitrate transporters and extractants. Thus, in future such potential nitrate receptors could be employed towards separation of nitrate from water as well as nitrate transportation in biology.

Pradyut Ghosh: Pradyut Ghosh is currently a Professor in the Department of Inorganic Chemistry, Indian Association for the Cultivation of Science (IACS), India. He received his PhD from the Indian Institute of Technology, Kanpur, under the direction of Parimal K. Bharadwaj in 1998. He spent two years as a postdoctoral fellow at Texas A&M University with Richard M. Crooks followed by an Alexander von Humboldt Fellowship at the University of Bonn, Germany, in Fritz Vögtle's group. Upon his return to India, he moved to IACS in 2007, after a brief stint at CSMCRI. His current research interests are recognition, separation and sensing of ions and interlocked molecules.

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Notes and references

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† Carbon: orange; oxygen: red; nitrogen: blue; hydrogen: green; fluoride: yellow green; sulphur: yellow.

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Graphical Abstract

Artificial receptors for nitrate: A comprehensive overview

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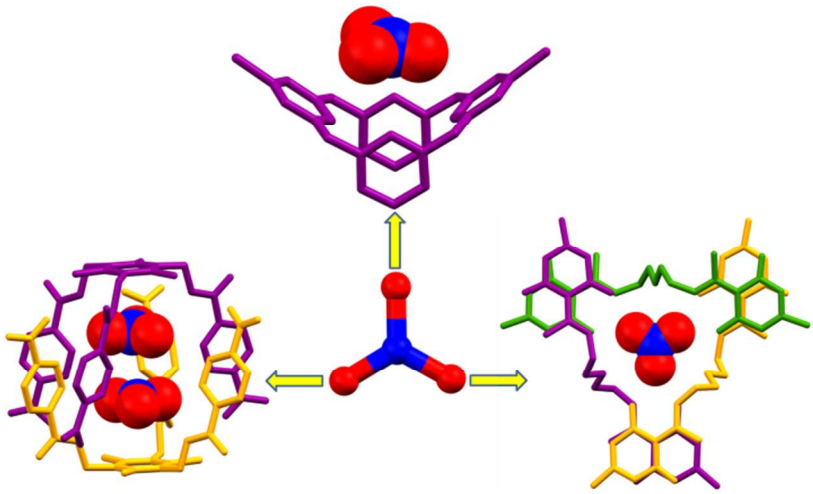

In this feature article, we describe current status and recent development of synthetic anion receptors for the recognition of nitrate.