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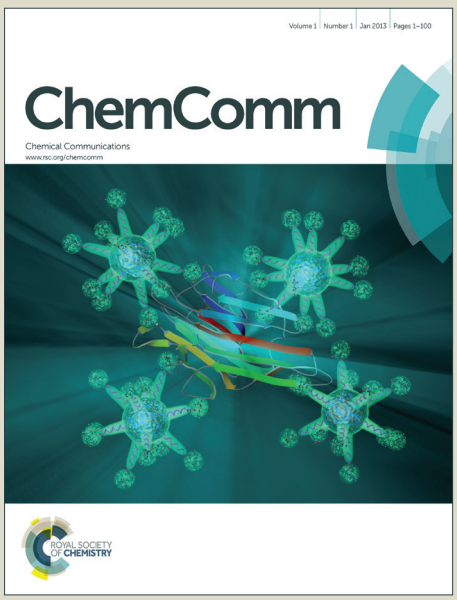

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ARTICLE TYPE

Recent developments in anion induced capsular self-assemblies

Ranjan Dutta[a] and Pradyut Ghosh*[a]

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This feature article covers recent developments in anion induced capsular self-assemblies, with particular focus on important reports from 2011-2013. Contemporary studies on the capsular binding of environmentally and biologically relevant anions in aqueous medium are described. Emerging reports of such systems reveal their potential utility towards various functional aspects like anion separation, CO_2 fixation, hydrated halide recognition and anion transportation. This article also highlights potential applications of anion induced molecular capsules.

1. Introduction

Non-covalent synthesis of supramolecular structures with an internal cavity to accommodate guest molecules has attracted much attention in recent times. This is because, these aggregates are important in molecular recognition, selective guest-inclusion and in the catalysis of specific reactions.[1-10] In particular, anions have shown to be very versatile templates for the synthesis of a wide range of supramolecular assemblies over the last ten years.[11-19] This article aims to present a comprehensive update on the most important reports on capsular recognition of anions published in the last few years. As a proceeding of our previous article,[20] more importance will be given to studies in aqueous solvents and potential application towards environmental and industrial issues.

In recent times, new platforms are introduced to design synthetic receptors for capsular recognition of anions which will be a part of our discussion. Nature's sulfate binding protein binds SO_4^{2-} in its synthetic pocket *via* neutral functionalities[21] which indeed inspires researchers to design synthetic neutral receptors for capsular recognition of anions in highly competitive aqueous medium. Thus, special attentions are also directed towards recognition of anions in aqueous medium by capsular assemblies which may resemble to the natural-world. However, there are other systems for anion recognition studies in aqueous medium which are not included in this article.[22]

One of the major reasons for global warming is due to the increase of CO_2 concentration in the atmosphere.[23] Metal-organic frameworks (MOFs), organic cages, zeolites, amines etc. are widely explored for the removal and storage of CO_2.[24-26] One of the possible remedies to control aerial CO_2 concentration is its chemical conversion to other species. Synthetic anion receptors are emerging to accomplish this purpose *via* CO_3^{2-} encapsulation from aerial CO_2.[27-30] On the other hand, anions present in groundwater, specifically, few inorganic oxyanions can be toxic to the human health even at submicromolar concentration.[31-34] Removal of SO_4^{2-} from radioactive nuclear waste is essential for improved vitrification of the waste and excess SO_4^{2-} is also responsible for permanent hardness of water.[35] Competitive crystallization technique or liquid-liquid anion exchange technology provides suitable strategy for SO_4^{2-} removal using synthesized anion receptors.[35,36] Importance will be given to studies which have potential applications towards the above mentioned environmental and industrial issues. In that direction, interesting properties of capsular assemblies such as capsular binding of CO_3^{2-} *via* sequestration of aerial CO_2 and separation of SO_4^{2-} from water will be discussed in separate sections (Chart 1). Anion binding within covalent capsules and metal-coordinated capsules will not be the part of our discussion.

Chart 1 Schematic presentation of various features of anion induced molecular capsules.

2. Anion induced dimeric capsular assembly

In this section, recent development of anion receptors on different platforms namely (i) tris(2-aminoethyl)amine (tren), (ii) rigid platforms like benzene, cyanuric acid, triazine and iii) macrocyclic backbone which are relevant in capsular assembly will be discussed.

2.1 TREN based tripodal anion receptors

Literature survey reveals tren scaffold based tripodal receptors are widely used in the formation of anion induced capsular assemblies. Straightforward synthesis of tren based receptors and their complementarity with certain class of anions make them

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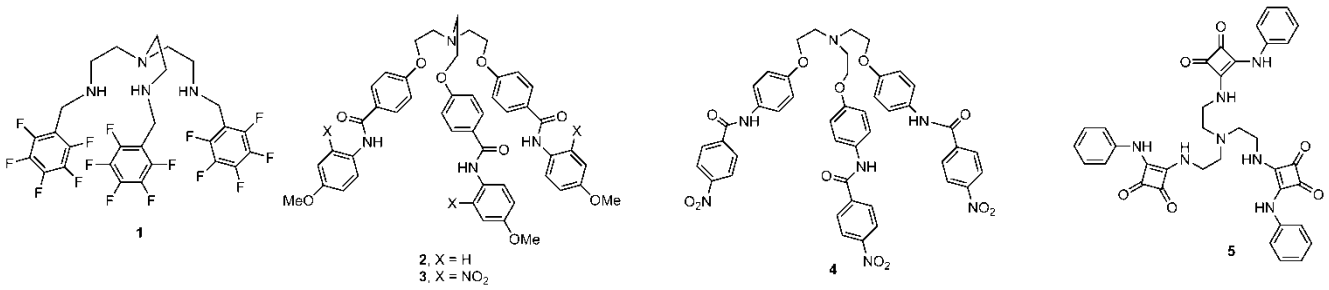

Chart 2

attractive scaffolds in anion coordination chemistry. A recent review has elaborated the development of self-assembled capsules of tren based urea/thiourea receptors towards tetrahedral oxyanion recognition and their separation.[37]

Generally, tripodal ammonium and amide receptors on tren scaffold do not have the tendency to form capsular assembly upon anion binding.[38-40] We have extended our investigation on the solid and solution states binding properties of triprotonated tripodal amine **1** (Chart 2) with wide varieties of anions. Tripodal amine **1** has previously shown monotopic recognition of Cl^- and Br^- in its triprotonated state.[41] Recently, it has been found that $[H_3\mathbf{1}]^{3+}$ also shows monotopic F^- encapsulation *via* C_{3v}-symmetric cleft formation as usual for spherical anion (Fig. 1a).[42] Interestingly, octahedral SiF_6^{2-} dianion induces dimeric capsular assembly of $[H_3\mathbf{1}]^{3+}$ *via* multiple N-H···F and C-H···F interactions (Fig. 1b). Monotopic F^- encapsulation *vs.* SiF_6^{2-} induced capsular assembly by $[H_3\mathbf{1}]^{3+}$ could be due to the difference in charge and shape of the encapsulated guest. However, potentiometric titration of $[H_3\mathbf{1}]^{3+}$ in MeOH/H_2O solvent shows high affinity towards more basic F^- and AcO^- over other anions.

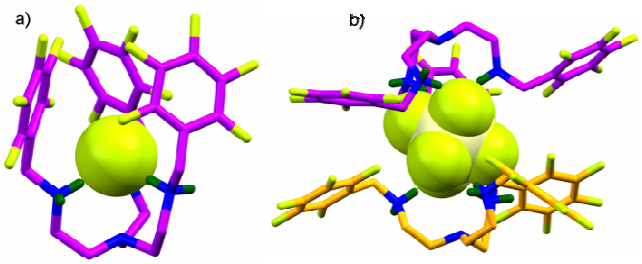

Fig. 1 Single crystal X-ray structures of anion complexes of $[H_3\mathbf{1}]^{3+}$ showing a) monotopic F^- encapsulation by $[H_3\mathbf{1}]^{3+}$ and b) encapsulation of SiF_6^{2-} in the dimeric capsular assembly of $[H_3\mathbf{1}]^{3+}$. Non-bonding hydrogens and lattice anions are omitted for clarity.

Sun and Singh have employed tren based extended tripodal amide receptor **2** (Chart 2) towards solvent dependent reversible nitrate binding and dimeric capsule formation.[43] Reaction of methanolic solution of **2** with aqueous HNO_3 yields **2·HNO$_3$**, which is structurally characterised as a NO_3^- encapsulated complex of $[H\mathbf{2}]^+$. Tris-amide **2** forms a mixture of NO_3^- complex of **2** and **3** upon treatment with HNO_3 in methanol/chloroform binary solvent. On the contrary, when HNO_3 is added to acetonitrile solution of **2**, formation of **3·HNO$_3$** is observed as evident from NMR and ESI-MS studies. Titration of **3·HNO$_3$** in DMSO-d_6 with less polar $CDCl_3$ results the formation of homodimeric capsular assembly of **3** with release of NO_3^- as evident from ^{1}H-NMR, ESI-MS studies (Chart 3). Upon lowering the solvent polarity, intramolecular H-bonding interactions between amide –NH and O atom of *ortho*-nitro group predominate over the interactions between amide and NO_3^-, thus, facilitate the formation of a homodimer $\mathbf{3_2}$ with the release of NO_3^-. Evaporation of $CDCl_3$ regenerates the NO_3^- encapsulated product **3·HNO$_3$**, which suggests the reversibility of the process. Interestingly, upon standing of DMSO/$CHCl_3$ solution of **3·HNO$_3$**, formation of NO_3^- trapped self-assembled capsule, $[\mathbf{NO_3^-}\cdot H\mathbf{3_2}]^+$ is observed, which is described as a thermodynamically stable product.

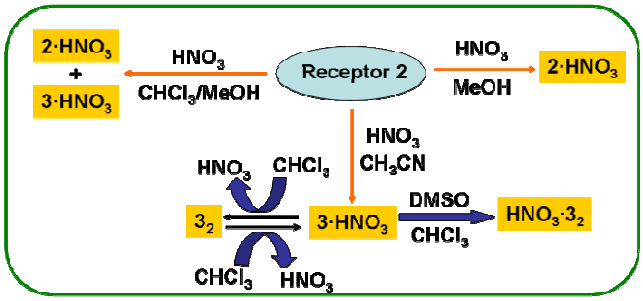

Chart 3 Solvent dependent formation of different NO_3^- complexes of **2**, **3** and dimeric capsules of **3**.

Apart from the works by Sun and co-workers, Das *et al.* have reported halide induced dimeric capsular assembly of a tren based extended amide receptor **4** (Chart 2).[44] They have designed tren scaffold based highly organized amide receptor **4** where the amide groups are placed far away from the bridgehead nitrogen. Upon protonation of the bridgehead nitrogen with HCl/HBr, dimeric capsular assembly of $[H\mathbf{4}]^+$ is observed. Dimeric assemblies are found to encapsulate a halide-water cluster with the composition $[X_2(H_2O)_2]^{2-}$ (X= Cl^-, Br^-) (Fig. 2a,b). Widely spaced amide groups in **4** are forced to bind planar parallelogram shaped $[X_2(H_2O)_2]^{2-}$ cluster rather than a single halide anion. Dimension of the capsular assemblies vary from 20.62 Å to 20.75 Å moving from smaller Cl^- to Br^- anion. Authors have claimed

solution state existence of $[X_2(H_2O)_2]^{2-}$ clusters by 2D-NOESY NMR, where strong NOE coupling between the amide NH and the encapsulated water is observed. However, I^- induces polymeric assembly of $[\mathbf{H4}]^+$ with the rearrangement of C_{3v} to C_{2v} conformation of the receptor. Squaramide functionalization on tren scaffold also results suitable receptors for different oxyanions in solution. Squaramide-based tripodal receptor **5** (Chart 2) forms the dimeric pseudo-capsular assembly with SO_4^{2-} (Fig. 3), where the SO_4^{2-} binding occurs in the cleft of **5** in 2:2 (host/guest) stoichiometry. Solution state selective binding of SO_4^{2-} is observed *via* 1:1 (host/guest) stoichiometry.[45]

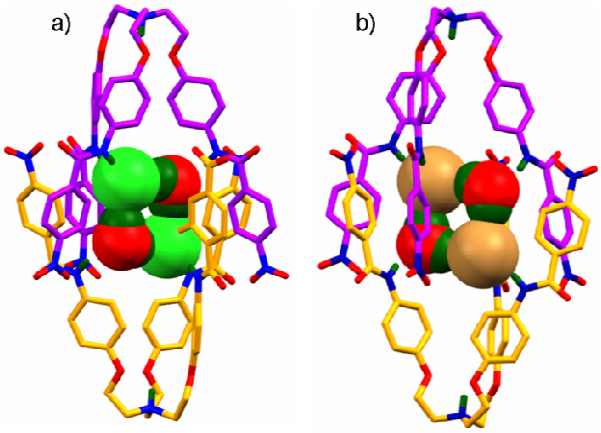

Fig. 2 X-ray crystal structures of dimeric capsular assemblies of $[\mathbf{H4}]^+$ showing encapsulation of a) $[Cl_2(H_2O)_2]^{2-}$ and b) $[Br_2(H_2O)_2]^{2-}$ cluster. Non-bonding hydrogens are omitted for clarity.

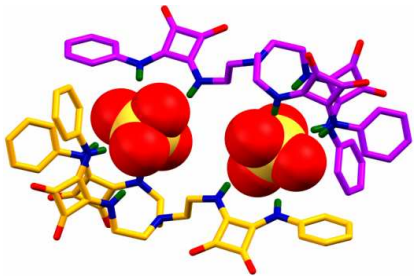

Fig. 3 View of binding of two SO_4^{2-} in the dimeric assembly of **5**. Non-bonding hydrogens and countercations are omitted for clarity.

Tren based urea/thiourea receptors are the intriguing class of anion receptors, particularly, towards the tetrahedral oxyanions.[37] Dimeric assembly of this class of receptors assisted by encapsulated tetrahedral anions is the most common feature observed in the reported anion complexes. From the first report of anion binding tren-based urea/thiourea receptors by Morán *et al.*[46] many groups have established 2:1 (host/guest) complexation with tetrahedral oxyanions. Recently, Gale *et al.* have reported the solid and solution states anion binding affinity of a series of fluorinated tren based urea/thiourea receptors **6-13** (Chart 4) and also studied their transmembrane transport activity.[47] Synthesis and anion binding studies of tris-urea **12** are well studied by our group previously.[30,48-50] Structural analysis reveals tendency of the thiourea receptors to form dimeric capsular assembly upon tetrahedral anion encapsulation. Both the sulfate and phosphate complexes of thiourea **7** show SO_4^{2-} and PO_4^{3-} templated dimeric assemblies of the receptor (Fig. 4a,b).

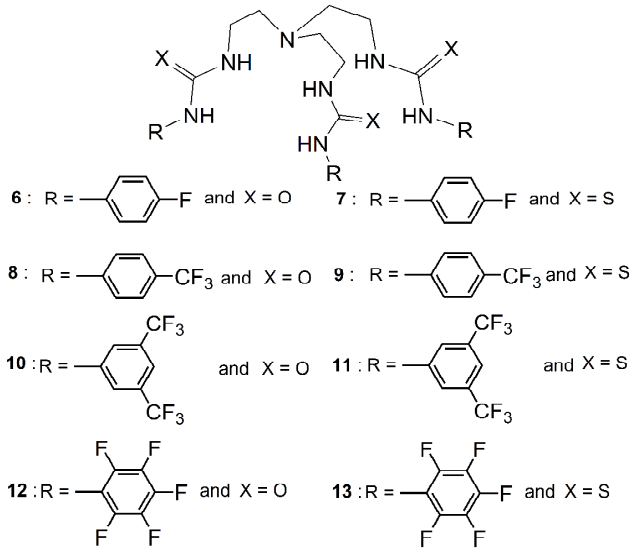

Chart 4

Dimension of the dimeric capsules are quite similar, 10.06 Å for SO_4^{2-} and 10.03 Å for PO_4^{3-}, as measured from the apical N···N distances. Tris-urea receptor **10** forms dimeric capsular assembly upon encapsulation of CO_3^{2-}, which is similar to our previously reported CO_3^{2-} complex of **12** (Fig. 4c).[30] Thiourea analogue of **10** i.e. **11** forms PO_4^{3-} templated dimeric capsular assembly of 10.13 Å (Fig. 4d). Single crystal X-ray structural analysis of phosphate complex of **13** shows encapsulation of two $H_2PO_4^-$ anions in the pseudo-capsular assembly of **13** (Fig. 5a) like $[(H_2PO_4)_2\mathbf{12_2}]^{2-}$ *via* multiple N-H···O and anion-π interactions.[48] Encapsulated $H_2PO_4^-$ anions are hydrogen bonded to each other as that observed in case of $[(H_2PO_4)_2\mathbf{12_2}]^{2-}$. On the other hand, SO_4^{2-} encapsulation by **13** is found to be assisted by two tetrabutylammonium countercations along with the urea –NH group of **13** (Fig. 5b). All the receptors show strong binding with SO_4^{2-} (log K $>10^4$) in DMSO-d_6/0.5%D_2O solvent with 1:1 host-guest stoichiometry as evident from ^{1}H-NMR titration study. Dihydrogenphosphate also shows moderate binding affinities even in highly competitive solvent medium. All the tris-urea receptors show higher binding affinity than the corresponding more acidic thiourea receptor. Furthermore, the binding affinities of the receptors decrease with the addition of increasingly electron-withdrawing groups. This reverse trend is rationalised by favourable interaction of the more electron-withdrawing groups with polar DMSO-d_6/D_2O solvent mixture.

Our continuous investigation of anion binding properties of tris-urea **12** have resulted many interesting properties like $H_2PO_4^-$,[48] SO_4^{2-} encapsulation,[49] CO_2 fixation[30] *etc*. Phosphate selectivity pattern of **12** is also established by ^{1}H-NMR titration study. Further we have demonstrated acid/base controllable capsular size modulation of phosphate capsules of **12**.[50] Crystallization of $H_2PO_4^-$ complex with TBAOH results the formation of HPO_4^{2-} encapsulated tight dimeric capsular assembly of **12** (Fig. 6b). HPO_4^{2-} encapsulation in **12** is observed *via* fifteen hydrogen bonding interactions. Capsular size of $HPO_4^{2-}\subset\mathbf{12_2}$ is measured as 9.92 Å higher than CO_3^{2-} and SO_4^{2-} encapsulated capsules. Interestingly, $H_2PO_4^-$ pseudo-capsule of **12** can be regenerated upon simple acid treatment of the $HPO_4^{2-}\subset\mathbf{12_2}$ capsule (Chart 5).

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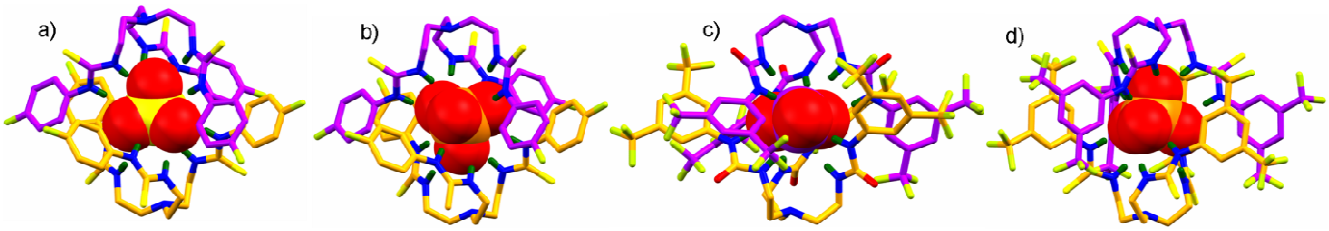

Fig. 4 View of X-ray crystallographic structures of a) $SO_4^{2-}\subset\mathbf{7}_2$, b) $PO_4^{3-}\subset\mathbf{7}_2$, c) $CO_3^{2-}\subset\mathbf{10}_2$ and d) $PO_4^{3-}\subset\mathbf{11}_2$ showing anion templated formation of dimeric capsular assemblies of the receptors. Non-bonding hydrogens, countercations and solvents are omitted for clarity.

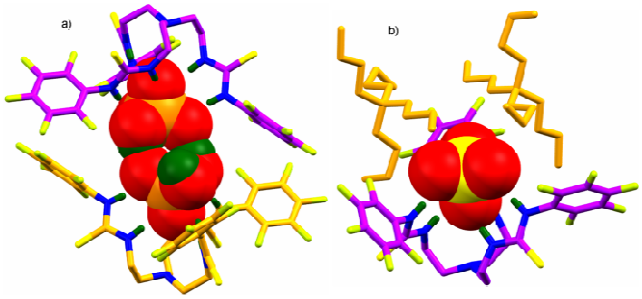

Fig. 5 X-ray structures of a) $(H_2PO_4)_2^{2-}\subset\mathbf{13}_2$ and b) $TBA_2SO_4\subset\mathbf{13}_2$. Non-bonding hydrogens and countercations are omitted for clarity.

Capsular transformation of the phosphate capsules are corroborated by ^{31}P-NMR in DMSO-d_6. $H_2PO_4^-$ complexation of **12** is demonstrated by 8.33 ppm (Δδ) downfield shift in ^{31}P resonance *w.r.t* the signal of free $TBAH_2PO_4$; whereas upon addition of **12** to 1:1 mixture of TBAOH and $TBAH_2PO_4$ results a downfield shift of 3.55 ppm (Δδ) *w.r.t* 1:1 mixture of TBAOH and $TBAH_2PO_4$. Finally, the addition of perchloric acid to the above mixture shows regeneration of $[H_2PO_4]_2^{2-}\subset\mathbf{12}_2$ as revealed by ^{31}P-NMR signal. We have also shown the first report of hydroxide (OH^-) encapsulation by tris-urea **12** upon reaction with TBACN. Hydroxide (OH^-) encapsulation in the dimeric pseudo-assembly of **12** is achieved by six N-H···O interactions in 2:2 (host/guest) stoichiometry (Fig. 6a). We have reasoned possible deprotonation of the acidic –NH proton by CN^- followed by the encapsulation of a H_2O molecule in the tris-urea cavity of **12**. Finally, *in situ* generation and the encapsulation of OH^- are explained by protonation of deprotonated **12** with H_2O molecule. Kinetic and thermodynamic parameters of anion binding properties of **12** with different anions are demonstrated by ITC study in DMSO, which closely resemble with the ^{1}H-NMR titration data.

Recently, we have explored tris-urea **12** towards the binding of environmentally relevant and toxic arsenate[51] in aqueous medium. Hydrogenarsenate ($HAsO_4^{2-}$) and hydrogenphosphate (HPO_4^{2-}) have remarkable similarity in terms of charge, thermodynamic radii, pKa values, and binding modes.[52] $HAsO_4^{2-}$ encapsulated complex of the tris-urea **12** is isolated by the reaction of **12**, TBAI and Na_2HAsO_4 in DMSO/5%H_2O solvent mixture. $HAsO_4^{2-}$ is found to be encapsulated in the dimeric capsular assembly of **12** *via* eleven N-H···O and one O-H···O interactions (Fig. 6c).[53] Capsular dimension of $HAsO_4^{2-}\subset\mathbf{12}_2$ is similar to that of the $HPO_4^{2-}\subset\mathbf{12}_2$ capsule but higher than that of $SO_4^{2-}\subset\mathbf{12}_2$ and $CO_3^{2--}\subset\mathbf{12}_2$. $HAsO_4^{2-}\subset\mathbf{12}_2$ capsule represents the first example of the structural evidence of arsenate binding by any synthetic neutral anion receptor. Solution state selectivity of **12** towards $HAsO_4^{2-}$ is observed over HPO_4^{2-}, SO_4^{2-} and CO_3^{2-} in semi-aqueous solvent mixture [DMSO-d_6/D_2O (9:1, v/v)]. Thus, a general trend of dimeric pseudo-capsular *vs* capsular assembly formation is established for tris-urea **12** *via* uni-negative *vs* dinegative anion encapsulation respectively (Fig. 7).

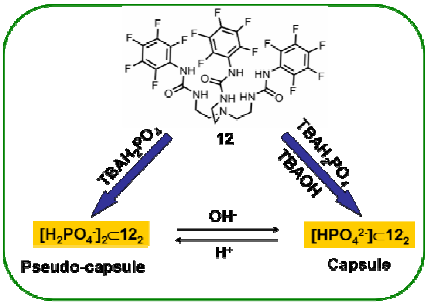

Chart 5 Schematic representation of formation and acid-base controllable transformation between $(H_2PO_4^-)_2^{2-}\subset\mathbf{12}_2$ and $HPO_4^{2-}\subset\mathbf{12}_2$.

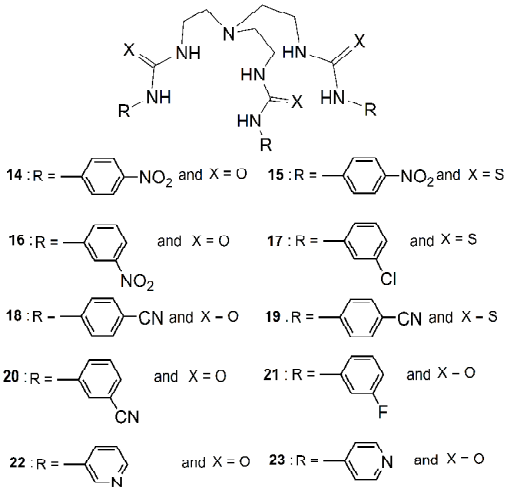

Chart 6

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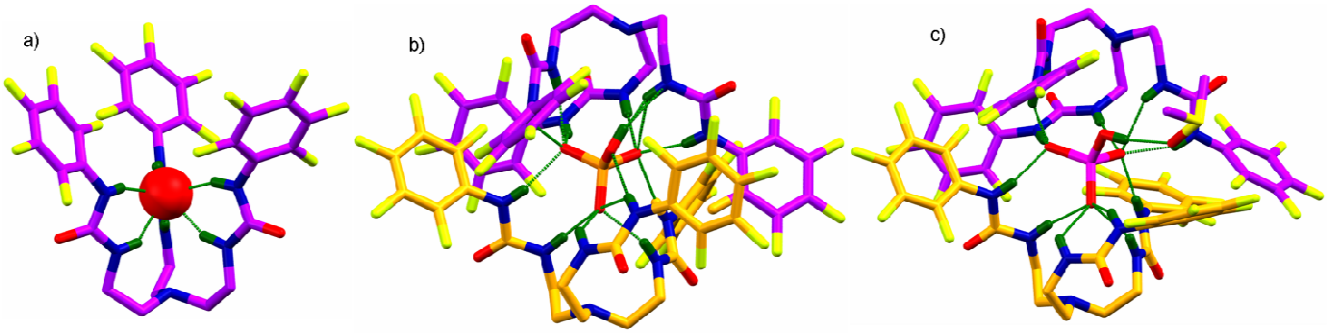

Fig. 6 View of X-ray crystal structures of a) $OH^-\subset$**12**, b) $HPO_4^{2-}\subset$**12**$_2$ and c) $HAsO_4^{2-}\subset$**12**$_2$. Non-bonding hydrogens and countercations are omitted for clarity.

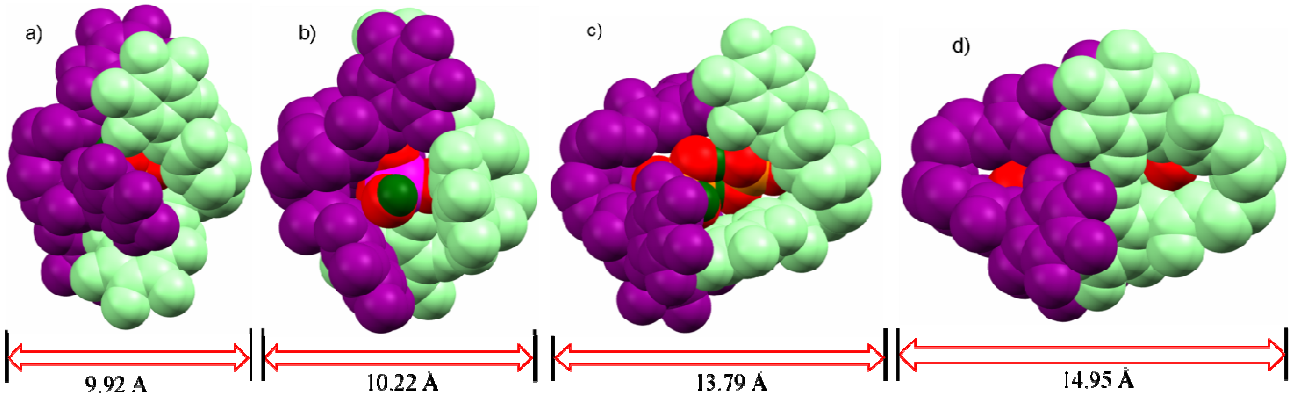

Fig. 7 Space-fill view showing capsular size of the dimeric capsular assemblies of a) $HPO_4^{2-}\subset$**12**$_2$, b) $HAsO_4^{2-}\subset$**12**$_2$, c) $(H_2PO_4)_2^{2-}\subset$**12**$_2$ and d) $(OH)_2^{2-}\subset$**12**$_2$.

Presence of non fluorinated electron-withdrawing groups can also provide suitable anion receptors for capsular recognition of anions (Chart 6).[54,55] Nitro-substituted urea/thiourea receptors on tren scaffold are reported for the encapsulation of various tetrahedral oxyanions. Thiourea receptor **15** is found to encapsulate PO_4^{3-} inside the π-stacked dimeric capsular assembly of **15** (Fig. 8a) *via* twelve strong hydrogen bonding interactions.[56] Planar oxyanion CO_3^{2-} also assists the formation of dimeric assembly of **15** (Fig. 8b) assembled by intermolecular C-H···O and C-H···S interactions. On the other hand, F^- and SO_4^{2-} lead to the formation of unimolecular capsules of **15** *via* the participation of external solvent/countercation, which will be discussed later.[57] Interestingly, selective formation of $PO_4^{3-}\subset$**15**$_2$ capsule is demonstrated in the presence of excess HSO_4^-, HCO_3^-, NO_3^-, CH_3COO^-, F^- and Cl^- by ^{1}H and ^{31}P-NMR studies. ^{1}H-NMR titration study of **15** with $H_2PO_4^-$ shows switching of the equilibrium from 1:2 to 2:1 (host/guest) stoichiometry upon gradual addition of $H_2PO_4^-$. Chemical shift values of NH protons at 2:1 equilibrium closely resemble the ^{1}H-NMR spectrum of $PO_4^{3-}\subset$**15**$_2$, which confirms the formation of $PO_4^{3-}\subset$**15**$_2$ capsule in solution. Similarly, 2:1 (host/guest) stoichiometry is observed for HSO_4^-. Both F^-/Cl^- binds in 1:1 stoichiometry, whereas 1:2 binding pattern is observed of CH_3COO^-. ^{1}H-NMR titration studies result the following trend of binding affinity: $H_2PO_4^-$ >CH_3COO^->F^->HSO_4^->Cl^-.

3-nitro substituted urea receptor **16** also forms dimeric capsular assembly upon CO_3^{2-}, SO_4^{2-} and HPO_4^{2-} encapsulation (Fig. 8c,d).[58,59] CO_3^{2-} complexation study through the fixation of aerial CO_2 will be discussed later. ^{1}H-NMR titration studies have shown 1:1 binding of **16** with all the anions in DMSO-d_6 with the selectivity towards SO_4^{2-}. Further, oxyanion encapsulation by **16** is confirmed by 2D NOESY NMR. First example of thiosulfate ($S_2O_3^{2-}$) encapsulation in the dimeric capsular assembly of a trisurea receptor **17** (Fig. 9a) have been reported by Das *et al.*[60] Dimeric capsular assembly is also observed for the SO_4^{2-} complex of **17** (Fig. 9b). Solution state ^{1}H-NMR study of **17** shows selectivity for SO_4^{2-} over $S_2O_3^{2-}$ in 1:1 (host/guest) stoichiometry.

On the other hand, cyano terminal tris-urea receptor **18** fails to encapsulate anions as evident from the solid state structure from Cl^-, Br^- and HSO_4^- complexes of $[$**H18**$]^+$.[61] However, tris-urea **18** shows 1:1 binding with all the anions in DMSO-d_6 with high binding affinities for F^- (4.51) and SO_4^{2-} (4.70). We have established thiourea analogue, **19** towards efficient encapsulation of anions as determined by solid and solution state studies.[62]

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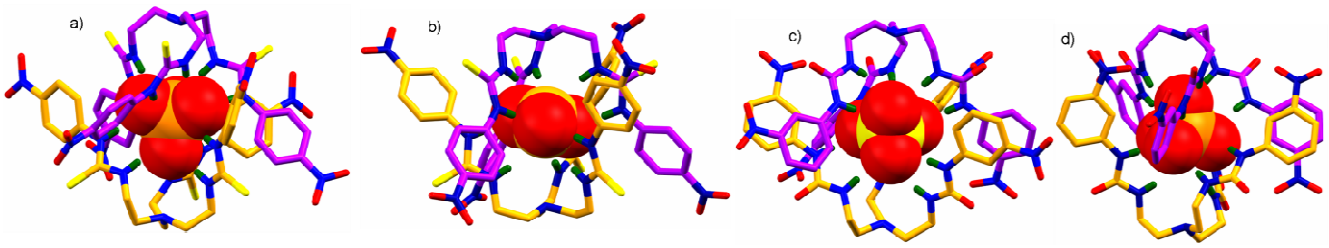

Fig. 8 X-ray crystal structures of dimeric capsules a) $PO_4^{3-}\subset$**15**$_2$, b) $CO_3^{2-}\subset$**15**$_2$, c) $SO_4^{2-}\subset$**16**$_2$ and d) $HPO_4^{2-}\subset$**16**$_2$. Non-bonding hydrogens and countercations are omitted for clarity.

Solution state binding of **19** towards anions by ITC measurement in acetonitrile shows the selectivity towards F^- which is well supported by ^{1}H-NMR titration study in DMSO-d_6. Structural characterisation of SO_4^{2-} and CO_3^{2-} complexes reveal anion assisted dimeric assemblies of **19** with capsular and sandwich modes respectively (Fig. 10a). On the other hand, monotopic encapsulation of spherical F^- is observed by **19** *via* six N-H···F interactions (Fig. 10b). Structural features of SO_4^{2-} complex and the liquid-liquid extraction of SO_4^{2-} by **19** will be discussed in section 5.2.

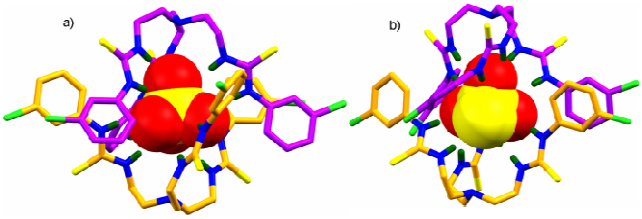

Fig. 9 View of crystal structures of a) $SO_4^{2-}\subset$**17**$_2$ and b) $S_2O_3^{2-}\subset$**17**$_2$. Non-bonding hydrogens and countercations are omitted for clarity.

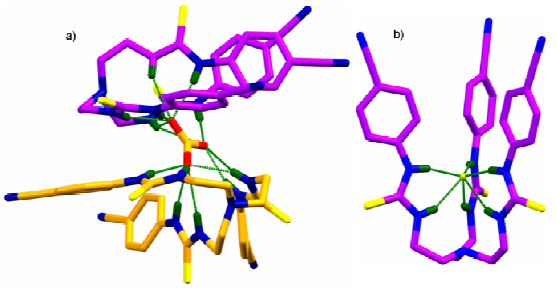

Fig. 10 Crystal structures of a) sandwich type assembly of $CO_3^{2-}\subset$**19**$_2$ and b) $F^-\subset$**19.** Non-bonding hydrogens and countercations are omitted for clarity.

Recently, we have structurally demonstrated an interesting example of conformer discrimination of oxalate by two structurally analogous urea receptors **20** and **21**.[63] Oxalate ($C_2O_4^{2-}$) complexes of tris-urea **20** and **21** obtained from DMSO/5% H_2O solvent show $C_2O_4^{2-}$ assisted dimeric capsular assembly of the receptors in 2:1 (host/guest) stoichiomtery. $C_2O_4^{2-}$ encapsulation in both $C_2O_4^{2-}\subset$**20**$_2$ and $C_2O_4^{2-}\subset$**21**$_2$ are facilitated by twelve N-H···O interactions (Fig. 11 and 12). The geometry of the encapsulated $C_2O_4^{2-}$ marks their conformational differences in the $C_2O_4^{2-}$ capsules. Simplest dicarboxyalate, $C_2O_4^{2-}$ exists in two different conformer namely planar and staggered conformers with 2-6 kcal/mol rotational energy barriers.[64] Although, staggered conformer is stable in solution, most of the structural reports reveal isolation of planar conformer. Receptor **20** shows encapsulation of staggered $C_2O_4^{2-}$ conformer with 68.8° torsion angle in $C_2O_4^{2-}\subset$**20**$_2$, whereas in $C_2O_4^{2-}\subset$**21**$_2$, **21** encapsulates planar $C_2O_4^{2-}$ conformer with 0.02° torsion angle (Fig. 11 and 12). Thus, by simply tuning the receptor functionality from –CN (**20**) to –F (**21**), discrimination of two $C_2O_4^{2-}$ conformers is possible in the molecular capsular assembly. However, in solution 1:1 association is observed between **20**/**21** and $C_2O_4^{2-}$ with high binding affinities (~10^4) in DMSO-d_6/D_2O (9:1, v/v) solvent.

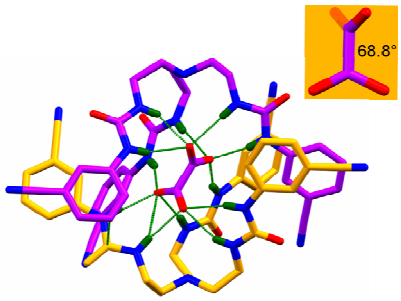

Fig. 11 View of staggered $C_2O_4^{2-}$ encapsulation in the dimeric capsule $C_2O_4^{2-}\subset$**21**$_2$. Non-bonding hydrogens and countercations are omitted for clarity.

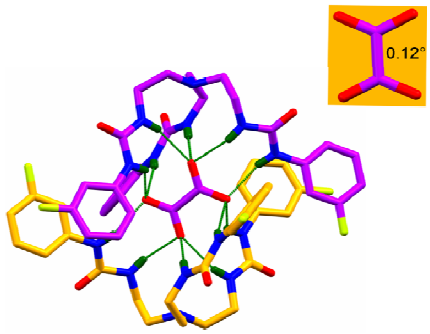

Fig. 12 View of planar $C_2O_4^{2-}$ encapsulation in the dimeric capsule $C_2O_4^{2-}\subset$**22**$_2$. Non-bonding hydrogens and countercations are omitted for clarity.

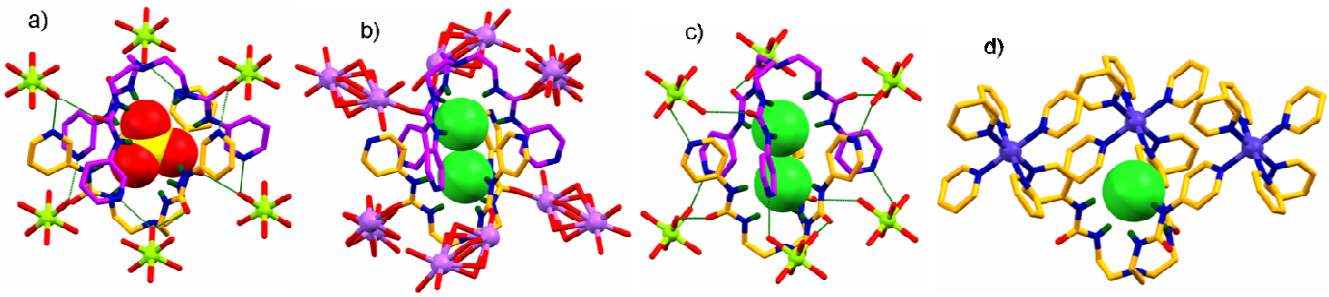

Fig. 13 X-ray crystal structures of a) $SO_4^{2-}\subset\mathbf{22_2}$ capsule having $[Mg(H_2O)_6]^{2+}$ cations, b) $Cl_2^{2-}\subset\mathbf{23_2}$ capsule having $[Na_2(H_2O)_6]^{2+}$ cations, c) $Cl_2^{2-}\subset\mathbf{23_2}$ capsule having $[Mg(H_2O)_6]^{2+}$ cations and d) $Cl^-\subset\mathbf{23}$ having $[Co(N^{Py})_6]^{2+}$ cations. Non-bonding hydrogens are omitted for clarity.

Custelcean and Wu *et al.* have independently explored tren based 3-pyridyl urea, **22** towards SO_4^{2-} recognition and separation studies *via* crystalline capsule formation in aqueous medium.[65,66] Very recently, Wu *et al.* have exploited 4-pyridyl urea receptor, **23** for capsular binding of SO_4^{2-} and Cl^- in aqueous medium.[67,68] Crystallization of **23** with $MgSO_4$ in 1:1 MeOH/H_2O solvent yields the crystals of composition $[MgSO_4{\cdot}\mathbf{23_2}{\cdot}(H_2O)_6]$. Two molecules of **23** encapsulates SO_4^{2-} in its dimeric capsular assembly, where the $[Mg(H_2O)_6]^{2+}$ countercation holds the crystalline capsule by second sphere coordination, like in the case of **22**. Capsular dimension of $[SO_4^{2-}\subset\mathbf{23_2}]$ capsule is slightly higher than that of the $[SO_4^{2-}\subset\mathbf{22_2}]$. However, differences are found in the number of hydrogen bonding interactions present for SO_4^{2-} encapsulation. In case of $SO_4^{2-}\subset\mathbf{23_2}$ capsule, SO_4^{2-} is involved in nine strong N-H···O interactions compared to the eleven strong N-H···O interactions in $SO_4^{2-}\subset\mathbf{22_2}$. Apart from the tetrahedral SO_4^{2-} anion, tris-urea **23** is also found to encapsulate $Cl^-/F^-/CO_3^{2-}$ in its dimeric capsular assemblies. Complexation of **23** with metal chlorides such as NaCl and KCl yield 2:2 anion complexes $[Cl\subset\mathbf{23}]_2^{2-}$ (Fig. 13b), where Cl^- is trapped in the cavity of **23** *via* multiple N-H···Cl interactions. $[Cl\subset\mathbf{23}]_2^{2-}$ capsule is surrounded by six $[M_2(H_2O)_6]^{2+}$ [M = Na^+/K^+] units to form a pseudo-octahedral arrangement. Capsular dimension of $[Cl\subset\mathbf{23}]_2^{2-}$ capsule [M = Na^+] is measured as 11.18 Å, which is reasonably higher than the dimension of $[SO_4^{2-}\subset\mathbf{23_2}]$ capsule. Similar Cl^- encapsulation in the form of $[Cl\subset\mathbf{23}]_2^{2-}$ capsule is observed for **23** during crystallization with $MgCl_2$, $CaCl_2$ (Fig. 13c), where the $[M(H_2O)_6]^{2+}$ [M = Mg, Ca] countercations assist capsule formation *via* second sphere coordination. On the other hand, direct coordination of pyridyl group to metal ion leads to the monotopic encapsulation of Cl^- (Fig. 13d) during complexation of **23** with chloride salts of Co^{2+} and Mn^{2+} cations. Importantly, rigidity of the capsular assembly predominates over the countercation effect for the chloride capsules as evident from the similarity in capsular dimensions. Sodium/potassium salts of carbonate also form 2:1 (host/guest) complex with CO_3^{2-} encapsulation in the dimeric capsule $CO_3^{2-}\subset\mathbf{23_2}$. Again the Na^+/K^+ counteractions are directly coordinated by two pyridyl groups of **23**. Thus, profound effects of countercations on anion complexation stoichiometry for **23** are observed. ^{1}H-NMR titration data shows 1:1 association between **23** and Cl^-/SO_4^{2-} in DMSO-d_6 solvent with comparable binding affinity (~10^3).

2.2 Tripodal anion receptors with rigid platforms

Apart from the flexible tren platform, rigid platforms like 1,3,5 trilalkyl benzene, triazene and cyanuric acid scaffolds are also emerging in the rapidly growing field of anion coordination chemistry. Anion assisted capsular assemblies of benzene based tripodal and hexapodal receptors till 2011 are discussed thoroughly in our previous article.[20] In the next section, we will discuss the current reports on anion-induced capsular assemblies of systems based on such rigid platforms.

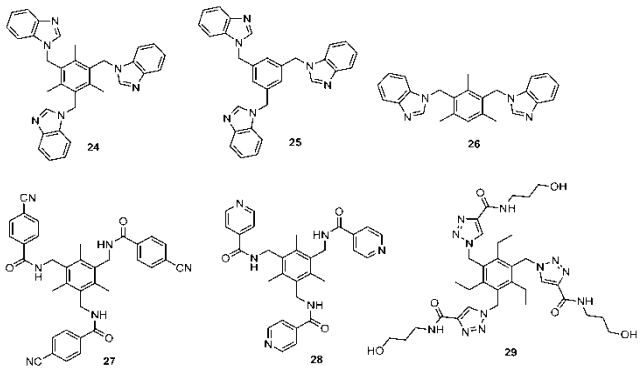

Chart 7

2.2.1 Tripodal receptors phenyl bridgehead

Anion assisted capsular assembly and disassembly processes of benzene platform based protonated benzimidazole receptors **24-26** (Chart 7) are reported by our group.[69] Dimeric capsular assembly of triprotonated **24** is previously observed via encapsulation of nitrate-water cluster.[70] Variation in anion dimensionality and the receptor functionality result the formation of different supramolecular architectures. Triprotonated receptor **24** forms a discrete staggered dimeric capsular assembly, templated by four CF_3COO^- and two water molecules *via* multiple N-H···O and C-H···O interactions (Fig. 14b). Similarly, trisprotonated form of **24** shows discrete dimeric capsular assembly stitched by six ClO_4^- and two encapsulated water molecules (Fig. 14a). Capsular dimension of the dimeric capsular assemblies of $[(H_6\mathbf{24_2}){\cdot}(CF_3COO)_4{\cdot}(H_2O)_2]^{2+}$ and $[(H_6\mathbf{24_2}){\cdot}(ClO_4)_6{\cdot}(H_2O)_2]$ are measured as 11.5 and 11.0 Å respectively. It is worth mentioning that $[H_3\mathbf{24}]^{3+}$ forms six nitrate-two water zipped discrete dimeric capsular assembly of dimension 11.14 Å. On the other hand, triporotonated receptor **25** shows polymeric assembly with NO_3^-, ClO_4^- and I^-, thus establish

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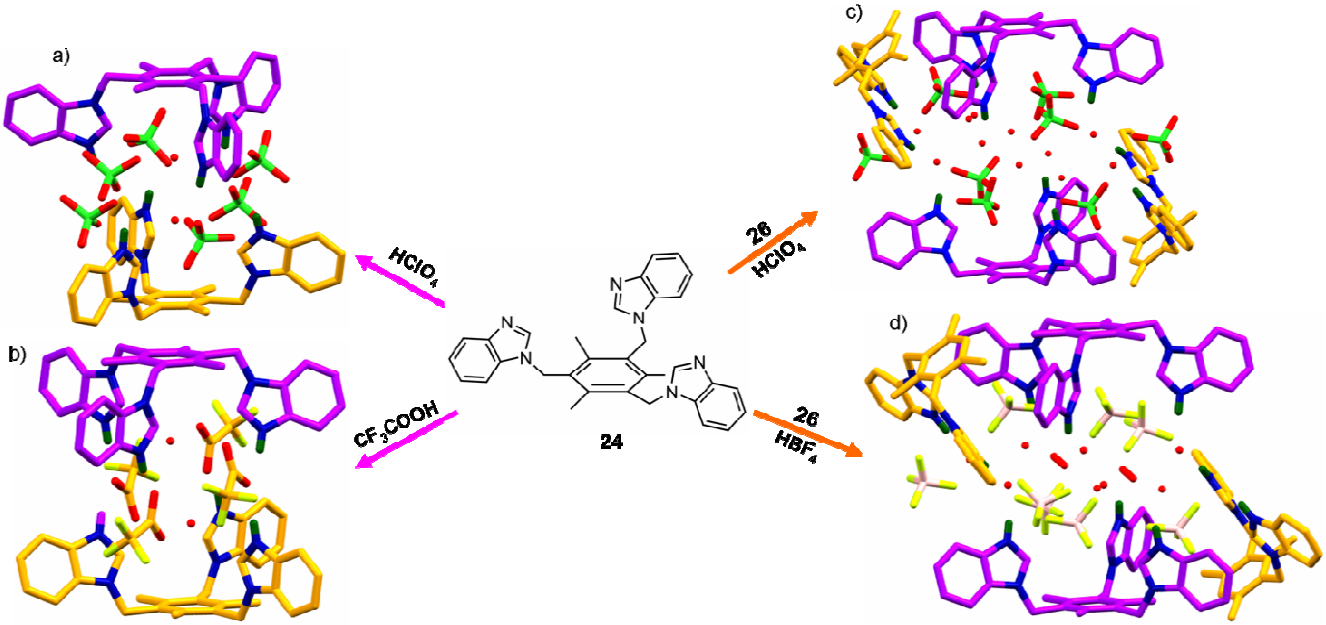

Fig. 14 Scheme showing a) ClO_4^-, b) CF_3COO^- assisted dimeric capsular assemblies of $[H_3\mathbf{24}]^{3+}$ and c) ClO_4^-, d) BF_4^- assisted heterotetrameric capsular assemblies of $[H_3\mathbf{24}]^{3+}$ and $[H_2\mathbf{26}]^{2+}$. Non-bonding hydrogens and lattice solvents are omitted for clarity.

the necessity of alkyl substitution on the benzene platform. Interestingly, when a mixture of tripodal receptor **24** and analogous dipodal receptor **26** are protonated with $HClO_4$, a new assembly $\mathbf{24}\cdot\mathbf{26}_2\cdot\mathbf{24}$ is formed *via* encapsulation of eight ClO_4^- and fourteen water molecules. ClO_4^- templated dimeric assembly of $[H_3\mathbf{24}]^{3+}$ is formed where two $[H_2\mathbf{26}]^{2+}$ units also share their ClO_4^- counteranions and thus forms a heterotetrameric assembly (Fig. 14c). The cooperative self-assembly of two molecules of $[H_3\mathbf{24}]^{3+}$ and two molecules of $[H_2\mathbf{26}]^{2+}$ in the presence of ClO_4^- anions form a near spherical assembly. Similar heterotetrameric assembly is formed for $[H_3\mathbf{24}]^{3+}$ and $[H_2\mathbf{26}]^{2+}$ templated by eight BF_4^- anions and water molecules (Fig. 14d). Capsular dimensions of the heterotetrameric assemblies are similar (~13 Å) which is higher than the homodimeric assembly of **24** (~11 Å).

Benzene platform based neutral amide receptors have shown their potential towards capsular recognition of nitrate, hydrated halides in the capsular cavity.[71,72] Recently, we have shown NO_3^- encapsulation in the half capsule **27** (Chart 7) decorated with cyano substituted aryl terminal.[73] Two such half capsules intercalate to form a staggered dimeric capsular assembly, that encapsulates two NO_3^- anions (Fig. 15a). Very recently, we have designed tripodal amide receptor **28** with 4-pyridyl terminal to impart aqueous solubility, and the possibility of anion binding in aqueous medium.[74] Interestingly, F^- and Cl^- complexes of **28** are isolated from acetone/water (1:1) solvent mixture in good yields. The isolated F^- complex shows the formation of 1D-polymeric chain of dimeric assembly of **28** zipped by fluoride-water cluster $[(F)_2(H_2O)_4]^{2-}$ (Fig. 15b). The dimeric assembly of **28** encapsulates a cyclic $[F_2(H_2O)_2]^{2-}$ unit *via* multiple N-H···F, O-H···F and N-H···O interactions. The other two water molecules of $[F_2(H_2O)_4]^{2-}$ unit help to propagate the cluster in 1D-polymeric form. Similarly, the formation of $[Cl_2(H_2O)_4]^{2-}$ cluster is observed in case of Cl^- complex where dimeric assembly of **28** encapsulates $[Cl_2(H_2O)_2]^{2-}$ cluster (Fig. 15c). The capsular dimension is slightly higher for $[Cl_2\cdot(H_2O)_4\cdot 28_2]^{2-}$ (9.62 Å) than that of $[F_2\cdot(H_2O)_4\cdot 28_2]^{2-}$ (9.41 Å). Furthermore, the complexation of **28** with F^- in dioxane/water solvent results the formation of SiF_6^{2-} encapsulated dimeric assembly of **28** (Fig. 15d). However, in solution 1:3 (host/guest) sioichiometry is observed from ^{1}H-NMR titration study in acetone-d_6/5%D_2O solvent, as opposed to 1:1 binding in the solid state. ^{1}H-NMR titration data reveals comparable binding affinity of **28** towards halides, whereas slightly higher binding constants are calculated for HSO_4^- and NO_3^-. Another benzene platform based tripodal receptor **29**, (Chart 7) having amide-triazole recognition element shows encapsulation of SO_4^{2-} in its cavity *via* eleven hydrogen bonding interactions.[75] In solution 1:1 (host/guest) stoichiometry is observed with high association constant (>10^5).

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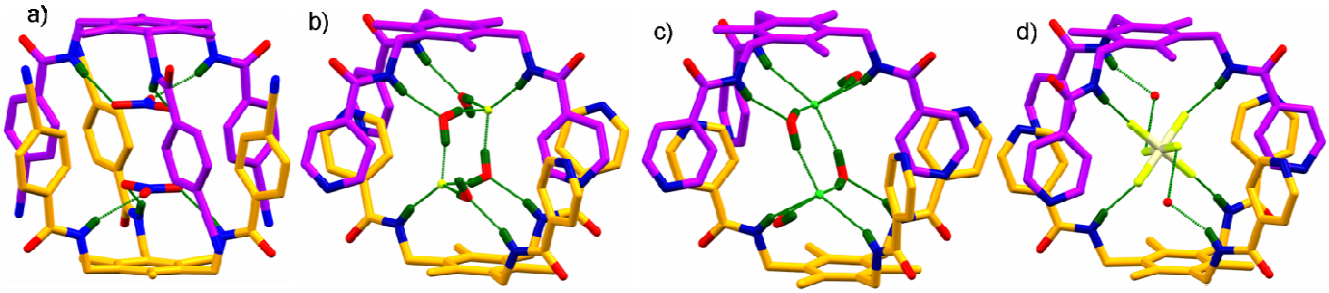

Fig. 15 X-ray crystal structures of a) $(NO_3)_2^{2-}\subset\mathbf{27_2}$, b) $[F_2(H_2O)_4]^{2-}\subset\mathbf{28_2}$, c) $[Cl_2(H_2O)_4]^{2-}\subset\mathbf{28_2}$ and d) $[SiF_6(H_2O)_2]^{2-}\subset\mathbf{28_2}$. Non-bonding hydrogens, countercations and lattice solvents are omitted for clarity.

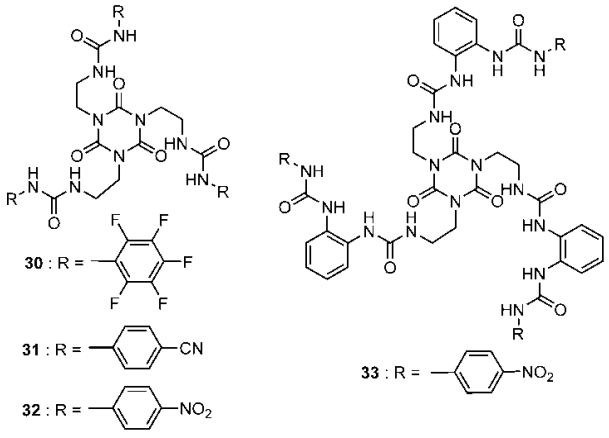

Chart 8

2.2.2 Tripodal receptors with cyanuric acid platform

Cyanuric acid platform is a hybrid system having the rigidity in platform like benzene and flexibility in side arms like tren. However, it is poorly explored unlike the other platforms.[76,77] We have shown selective monotopic recognition of F^- in the C_{3v}-symmetric cleft of a cyanuric acid platform based tris-amide receptor.[78] On the other hand, urea-functionalization (Chart 8) on cyanuric acid platform prefers tetrahedral SO_4^{2-} anion which is established for tris-urea **30** *via* SO_4^{2-} encapsulated unimolecular capsule formation.[79] Recently, we have shown SO_4^{2-} encapsulation in the staggered dimeric capsular assembly of cyano terminal tris-urea **31** (Fig. 16) *via* twelve N-H···O interactions.[80] Thus, higher coordination number of SO_4^{2-} is furnished by either coordination from countercations in case of **30** or dimeric assembly of the receptor for **31**. This observation encourages us to develop second generation hexaurea receptor **33** with six chelating urea groups, which eventually shows monotopic SO_4^{2-} encapsulation in its cavity by ten N-H···O interactions.

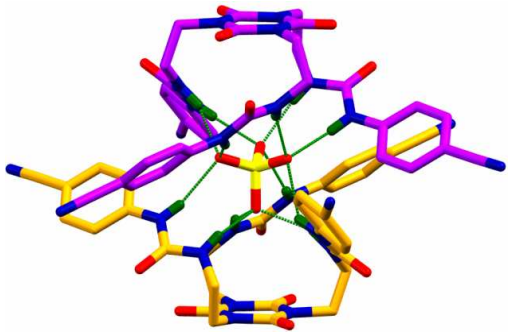

Fig. 16 View of SO_4^{2-} encapsulation in dimeric capsular assembly of **31**. Non-bonding hydrogens, solvent and countercations are omitted for clarity.

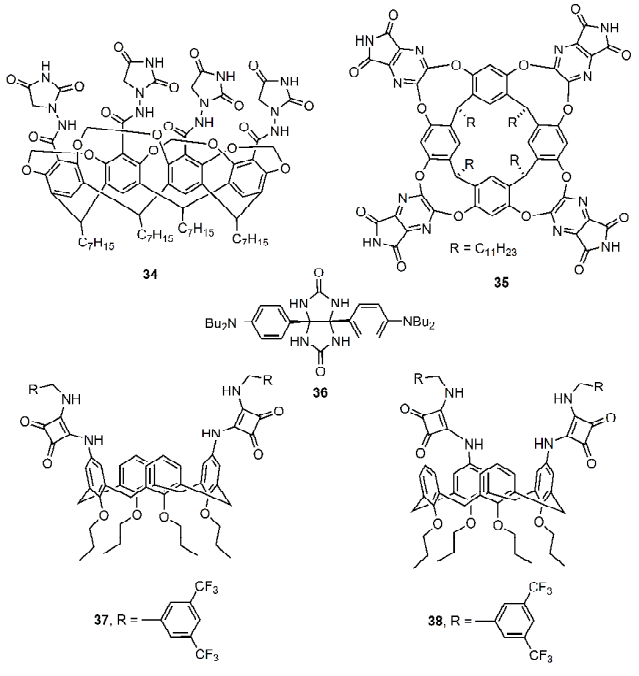

Chart 9

2.3 Receptors with macrocyclic platforms

Macrocyclic platform based receptors such as resorcin[4]arenes are suitable for capsular recognition of anions, cations and also neutral molecules due to the presence of bowl-shape cavity and phenolic functions. In 2011, Paek and co-workers have reported synthesis of resorcin[4]arenes modified tetra-amidocavitand **34** (Chart 9) and studied the solution state dimeric capsular assembly with suitable anionic guests.[81] Two monomeric units of **34** forms dimeric capsular assembly upon encapsulation of $CH_3OSO_3^-$ and BF_4^-, as evident from ^{1}H-NMR study in $C_2D_2Cl_4$ solvent. Monomeric unit of **34** in $2CH_3OSO_3^-/BF_4^-\subset$**34$_2$** capsules are held together by multiple intermolecular and intramolecular N-H···O interactions, as suggested by molecular modelling study. ^{1}H-NMR and 2D-DOSY NMR studies in $C_2D_2Cl_4$ with $CH_3OSO_3^-$ and BF_4^- guests show slow guest exchange and encapsulation of two anionic guests in the dimeric capsular assembly, which is confirmed by diffusion coefficient value of the capsule. Dissociation of the capsule in CD_3OD and non-capsular pattern with carboxylates, halides, PF_6^- validate the necessity of proper solvent choice and host/guest complementarity towards dimeric capsule formation.

Rebek and co-workers have reported the encapsulation of a pair of ion-pair in a self assembled molecular capsule of fourteen components.[82] Previously, neutral cylindrical capsule **35$_2$** (Chart 9) has reported for the encapsulation of two neutral molecule of picoline.[83] Interestingly, upon addition of trifluoroacetic acid (TFA) and glycouril **36** (Chart 9) to the above assembly generates the extended assembly with composition **35·36$_8$·35**. ^{1}H-NMR analysis of the assembly reveals significant downfield shift of the acidic proton (18.7 ppm), which actually suggests protonation of picoline nitrogen with TFA and thus, concomitant encapsulation of picoline-TFA ion pair. Further, ^{1}H/^{19}F-DOSY NMR studies confirm guest encapsulated capsular assembly.

Very recently, hybrid squaramide-calix[4]arene regioisomers **37** and **38** (Chart 9) are reported for capsular dimerization assisted by spherical anion encapsulation.[84] Both the distal isomer **37** and proximal isomer **38** form dimeric capsular assemblies with spherical Br^- and Cl^- anion as suggested by ^{1}H-NMR, ESI-MS and molecular modelling studies. In addition, **38** shows dimeric capsular assemblies with planar oxyanions like nitrate and benzoate unlike **37**. Presence of favourable intramolecular H-bonding interactions and greater complimentarity with planar guests facilitate the formation of dimeric capsules with nitrate and benzoate in case of **38**.

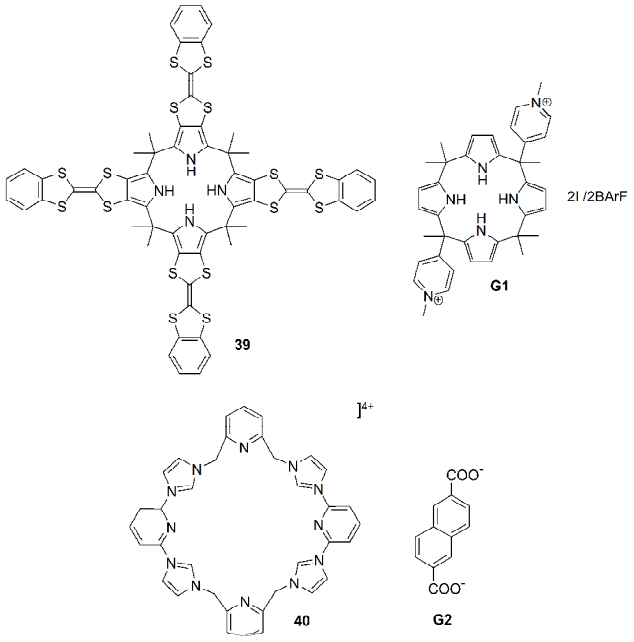

Chart 10

Electron rich tetrathiofulvalene-functionalised fluxional calix[4]pyrrole macrocycles are known to adopt unidirectional cone structure from thermodynamically stable 1,3-alternate conformation during anion complexation.[85] Further, anion directed cone conformation can accommodate a cationic guest of suitable size. Based on this concept, Sessler *et al.* have demonstrated iodide (as TBA salt) assisted dimeric assembly of cone conformer of **39** (Chart 10), which completely encapsulates a bismethylpyridinium-functionalized calix[4]pyrrole (**G1**) cationic guest (Fig. 17).[86] The self-assembled system functions as NAND logic gate, where the logic operations are triggered *via* changing the countercation inputs. Varying the countercation from TBA to TEA, dimeric assembly of **39** rearranges to a TEA encapsulated monomeric unit. Further, changing the anion from iodide to non coordinating tetrakis[bis(3,5-trifluoromethyl)phenyl]borate, formation of 1,3 alternate conformation of **39** with encapsulated **G1** is observed. Further, the logic operations are nicely corroborated by UV-Vis spectral data.

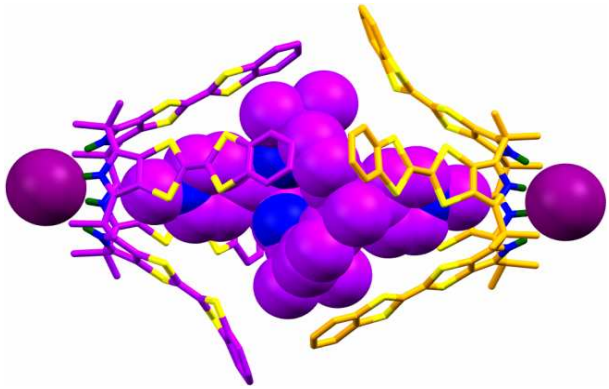

Fig. 17 View of encapsulation of two **G1** molecules in the dimeric capsular assembly of [I·**39**]$^-$. Non-bonding hydrogens and lattice solvents are omitted for clarity.

Sessler *et al.* have reported construction of anion directed formation of supramolecular architectures with tetracationic imidazolium macrocycles.[87] Complexation of **40** with dicarboxylate **G2** (Chart 10) reveals stepwise formation of 1:1 (host/guest) complex to 2:3 (host/guest) adducts.[88] This stepwise host/guest complexation is supported by job's plot analysis of ^{1}H-NMR titration data in DMSO-d_6. Structural analysis shows the formation of a dimeric capsular assembly of the flexible macrocycle **40** with one encapsulated **G2** (Fig. 18), while the remaining **G2** binds outside. Although, the dimeric assembly is more like a pseudo-capsular assembly rather than a capsule.

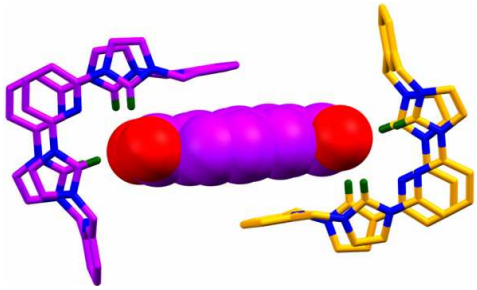

Fig. 18 View of crystal structure of **G2**⊂**38**$_2$. Non-bonding hydrogens and outside **G2** molecules are omitted for clarity.

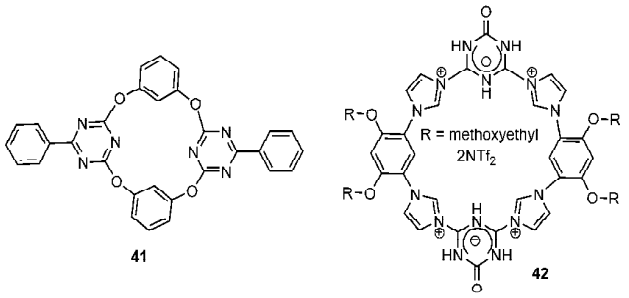

Chart 11

Wang *et al.* have reported an interesting example of anion directed self-assembly of a oxacalix[2]arene[2]triazine receptor **41** (Chart 11) *via* anion-π interaction.[89] Two molecules of **41** forms a dimeric assembly that encapsulates one $[Cl_2(H_2O)_2]^{2-}$ rectangular cluster *via* $Cl^-\cdots\pi$ (triazene), $\pi\cdots$O-H (H_2O) and $Cl^-\cdots$H-O (H_2O) interactions (Fig. 19a). Anion binding properties of **41** are monitored by fluorescence quenching emission upon addition of anion in acetonitrile. All the anions show 1:1 binding stoichiometry in solution. ^{1}H-NMR studies with anions induce no noticeable changes, which further confirm binding mode *via* anion$\cdots\pi$ interactions. Recently, synthesis of a triazinonide based shape persistent tetrakisimidazolium macrocycle **42** (Chart 11) is described for anion recognition in water *via* fluorescence output.[90] Fluorescence titration *via* emission enhancement results the selective binding of SO_4^{2-} in water with very high binding constant (~10^9). Structural analysis of the crystals grown from a mixture of **42** and excess Na_2SO_4 shows trapping of SO_4^{2-} in the sandwich type dimeric assembly of **42** (Fig. 19b) *via* charge assisted strong C-H$\cdots$O interactions. Further, the receptors in the sandwich assembly are held together *via* π-π stacking between the phenyl and the triazinonide rings.

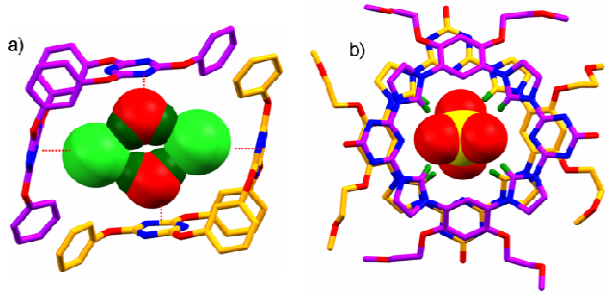

Fig. 19 Crystal structures of a) $[Cl_2(H_2O)]^{2-}$⊂**41**$_2$ and b) SO_4^{2-}⊂**42**$_2$. Non-bonding hydrogens and countercations are omitted for clarity.

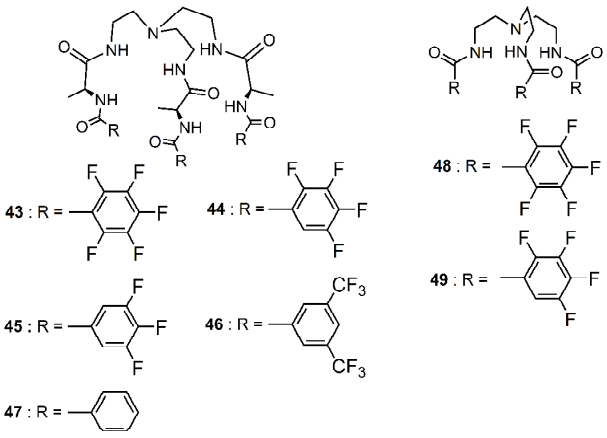

Chart 12

3. Anion binding in unimolecular capsules

Construction of unimolecular capsule from a single receptor can be achieved by i) sealing the receptor cavity with anion, ii) binding of anion followed by intramolecular hydrogen bonding within the receptor, iii) stoppering the anion encapsulated receptor with cation/solvent. Literature examples of above classes of unimolecular capsules reported by Atwood, Steed and our group are discussed in our previous article.[20] Some recent reports of such single molecule capsules, aiming towards recognition of anion, mainly covers the last category of the above mentioned strategies.

Tren based L-alanine amino acid backboned electron-withdrawing group attached hexa-amide receptors **43**-**47** (Chart 12) are explored by our group towards anion binding.[91] Appreciable binding between receptors and Cl^-, AcO^-, BzO^-, HSO_4^- with 1:1 (host/guest) stoichiometry is revealed by detailed ITC studies. Furthermore, this class of receptors show selectivity towards AcO^- over other investigated anions. Solid state structural evidence of Cl^- complex of the pentafluorophenyl attached receptor **43** shows the formation of Cl^- encapsulated unimolecular capsule (Fig. 20). Cl^- is encapsulated in the C_{3v}-symmetric cleft of **43** by three N-H$\cdots$Cl interactions. One tetrabutylammonium countercation seals the cavity of Cl^-⊂**43** *via* C-H$\cdots$O and C-H$\cdots$F interactions with the receptor, thus, results the formation of an unimolecular capsule. Further the role of countercation in Cl^- binding is verified by solution state ITC experiments, by varying the countercation. In cases of all the hexa-amides higher binding affinity is measured for Cl^- with TBA countercations over TEA and TMA countercations, which further validates the cooperative effect of ion-pairing.

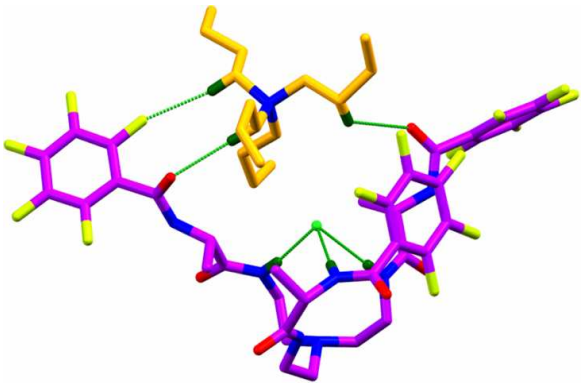

Fig. 20 Crystal structure showing ion-pair recognition in TBACl⊂**43**. Non-bonding hydrogens are omitted for clarity.

Halide recognition properties of tris-amide **48** (Chart 12) have been utilized towards liquid-liquid extraction of potassium fluoride/chloride *via* the formation of halide encapsulated 1D-polymeric assembly.[92] Very recently, we have reported fluoride recognition properties of tris-amides **48** and **49** in solution and solid state structural studies.[93] Structural analysis of both F^- and Cl^- complexes of **48** show the formation of F^-/Cl^- encapsulated unimolecular capsules (Fig. 21), where one chloroform molecule seals the capsular cavity. Encapsulated F^- in F^-⊂**48** is hydrogen bonded by three N-H···F interactions from amides and one C-H···F interactions from $CHCl_3$ (Fig. 21a), whereas the Cl atoms of $CHCl_3$ 'cap' are in short contact with the $-C_6F_5$ ring. Thus, a solvent capped F^- encapsulated single molecule capsule of **48** is described by single crystal X-ray study. Similarly, ditopic recognition of Cl^- and $CHCl_3$ *via* three N-H···Cl and one C-H···Cl interactions *via* unimolecular capsule formation is observed in case of Cl^-⊂**48** (Fig. 21b). Selective recognition of F^- is established for both **48** and **49** in $CDCl_3$ as determined by ^{1}H-NMR titration study.

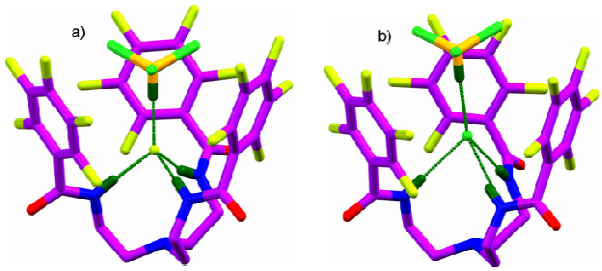

Fig. 21 X-ray crystal structures of unimolecular capsules $[F(CHCl_3)]^-$⊂**48** and $[Cl(CHCl_3)]^-$⊂**48**. Non-bonding hydrogens and countercations are omitted for clarity

Apart from the amide receptors, few urea receptors are also accounted for anion recognition *via* unimolecular capsule formation. Das *et al.* have reported the formation of solvent/cation sealed unimolecular capsule of **15** (Fig. 22) toward the encapsulation of F^- and SO_4^{2-}.[57] PO_4^{3-} and CO_3^{2-} induced dimeric capsular assemblies formation of **15** are already demonstrated in the section 2.1. Monotopic F^- encapsulation in F^-⊂**15** is facilitated by six N-H···F interactions with the urea groups of the tris-urea. Furthermore, one DMSO/CH_3CN solvent seals the cavity *via* C-H···O interactions, leading toward the formation of F^- bound unimolecular capsule (Fig. 22a) in both the cases. SO_4^{2-} encapsulation in **15** is assisted by nine N-H···O interactions with **15** and one C-H···O interaction from the TBA cation. Thus, the TBA cation acts as a stopper of the SO_4^{2-} encapsulated unimolecualr capsule (Fig. 22b).

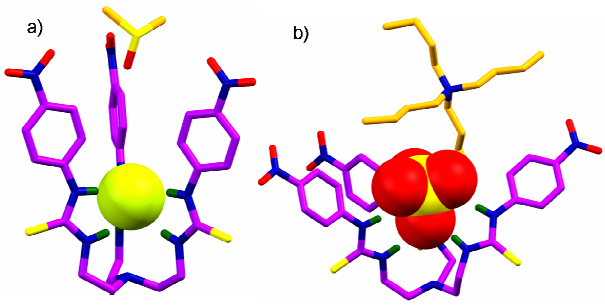

Fig. 22 Crystal structures of unimolecular capsules a) $[F(DMSO)]^-$⊂**15** and b) $(TBASO_4)^-$⊂**15**. Non-acidic hydrogens and countercations are omitted for clarity.

We have reported the formation of SO_4^{2-} encapsulated unimolecular capsule by a cyanuric acid based tris-urea receptor **32**.[80] Crystal structure of SO_4^{2-} complex shows a partial encapsulation of SO_4^{2-} *via* six N-H···O interactions. One TBA countercation seals the cavity of the SO_4^{2-}⊂**32** *via* one C-H···O interaction, thus, generates the unimolecular capsule (Fig. 23). This structure resembles our previously reported two TBA capped SO_4^{2-} encapsulated complex of tris-urea **30**.[79]

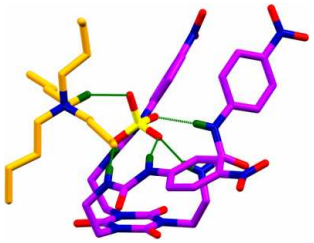

Fig. 23 View of SO_4^{2-} bound TBA capped unimolecular capsule of **32**. Non-bonding hydrogens, solvent and countercations are omitted for clarity.

4. Sizes of dimeric capsular assemblies

Comparative capsular sizes of various anion assisted dimeric capsules are summarized in table 1. Dimeric capsular assemblies reported for tren based receptors are generally formed through 2:1 and 1:1 (host/guest) stoichiometry *via* the encapsulation of one and two anionic guest/(s) respectively. In cases of extended tris-amide **4**, capsular sizes slightly vary from 20.6 to 20.7 Å with the change of encapsulated guest from $[Cl_2(H_2O)_2]^{2-}$ to $[Br_2(H_2O)_2]^{2-}$.[44] Dimeric capsules of tris-urea **12** show significant size variation with anions of different size and shape. Capsular sizes of $HAsO_4^{2-}$⊂$\mathbf{12_2}$ and HPO_4^{2-}⊂$\mathbf{12_2}$ capsules are measured as 10.22 and 9.92 Å respectively, which are reasonably higher than SO_4^{2-}⊂$\mathbf{12_2}$ and CO_3^{2-}⊂$\mathbf{12_2}$ capsules.[50] Pseudo-capsular assembly of **12** with both OH^- and $H_2PO_4^-$ show higher capsular sizes as 14.95 Å and 13.79 Å respectively. Thus, the inherent flexibility of the tren scaffold is reflected in the capsular size of anion complexes of tris-urea **12**. Interestingly monoanionic $H_2PO_4^-$ also induces pseudo-capsular assembly of thiourea **13** with the similar capsular size of 13.44 Å like that of **12**. Similar capsular sizes of ~9.1 Å are measured for carbonate capsules for tris-urea **10**, **12** and **16**. PO_4^{3-} encapsulated dimeric capsules of thiourea **7** and **11** also

show similar capsular size of ~10.1 Å.[47] Thus, size and shape of the anions also contribute to the size variation of the dimeric capsules. Capsular size and anion selectivity relationship is nicely depicted by Custelcean *et al*. in the anion complexes of tris-urea **22**.[65,94] Dimeric capsules formed by encapsulation of anions of different shapes having same countercation show similar capsular size. This feature marked the remarkable rigidity of the capsule despite the inherent flexibility of **22**, which is eventually reflected in the anion selectivity of competitive crystallization. On the other hand, variation in countercations causes size variation of the capsules. Further, minimal variations in capsular sizes are reported for Cl^- complexes of tris-urea **23**.[68] Change in cation from Na^+ to Mg^{2+}, the capsular sizes remain similar ~11.2 Å, which suggest significant rigidity of the capsules by multiple hydrogen bonding interactions.

The heights of the capsules are measured between the centroids of the two receptors in cases of benzene platform based anion receptors. Similarities are found in the capsular sizes of the dimeric capsules formed by $[H_3\mathbf{24}]^{3+}$ with different hydrated anions such as NO_3^- (11.14 Å), ClO_4^- (11.02 Å) and CF_3COO^- (11.51Å).[69,70] The slight differences in the capsular size may be due to the variation of shape of the anion and associated water molecules. In cases of the benzene platform based tris-amide receptors dimeric capsules are generally formed *via* encapsulation of one anionic guest in each half capsule irrespective of the functionality of the receptor. Capsular size of $(NO_3)_2^{2-}\subset\mathbf{27_2}$ capsule is measured as 9.75 Å which resembles the same to the NO_3^- trapped dimeric assembly of *para*-nitro substituted tris-amide receptor (10.01 Å).[72,73] Capsular size of $[F_2(H_2O)_4]^{2-}$ cluster templated diemeric capsules of **28** is measured as 9.41 Å which is remarkably similar to the fluoride-water cluster encapsulating *ortho*-nitro (9.19 Å) and *para*-nitro (9. 45 Å) substituted tris-amide receptors.[71,72,74] Similar trend is also observed in capsular sizes of $[Cl_2(H_2O)_4]^{2-}\subset\mathbf{28_2}$ capsule (9.65 Å) and hydrate-chloride trapped *para*-nitro substituted tris-amide receptor (9.57 Å).[72,74] Thus, inherent rigidity of the benzene based tripodal receptors is revealed by the significant similarities in capsular size of the dimeric capsules despite the differences in substituent and composition of the encapsulated guest.

Table 1. Capsular size of dimeric capsules having various anionic guests.

Receptor	Platform	Guest and capsular size (Å)
1	Tren-amine	SiF_6^{2-} (8.75)
4	Tren-amide	Cl^- (20.62), Br^- (20.75)
7	Tren-thiourea	SO_4^{2-} (10.06), PO_4^{3-} (10.03)
10	Tren-urea	CO_3^{2-} (9.16)
11	Tren-thiourea	PO_4^{3-} (10.13)
12	Tren-urea	$H_2PO_4^-$ (13.79), SO_4^{2-} (9.18), CO_3^{2-} (9.17) HPO_4^{2-} (9.92), $HAsO_4^{2-}$ (10.22), OH^- (14.95)
13	Tren-thiourea	$H_2PO_4^-$ (13.44)
15	Tren-thiourea	PO_4^{3-} (9.59), CO_3^{2-} (7.93)
16	Tren-urea	CO_3^{2-} (9.06), SO_4^{2-} (9.60), HPO_4^{2-} (9.86)
17	Tren-thiourea	SO_4^{2-} (9.33), $S_2O_3^{2-}$ (10.12)
20	Tren-urea	$C_2O_4^{2-}$ (9.81)
21	Tren-urea	$C_2O_4^{2-}$ (10.82)
22	Tren-urea	SO_4^{2-} (9.51)[a], SO_4^{2-} (9.20)[b]
23	Tren-urea	SO_4^{2-} (9.99)[c], Cl^- (11.18)[d], Cl^- (11.24)[e], Cl^- (11.17)[f]
24	Benzene-amine	NO_3^- (11.14), ClO_4^- (11.02), CF_3COO^- (11.51)
27	Benzene-amide	NO_3^- (9.75)
28	Benzene-amide	F^- (9.41), Cl^- (9.65), SiF_6^{2-} (9.31)
29	Cyanuric-urea	SO_4^{2-} (10.39)

a: Na^+, b: K^+, c: Mg^{2+}, d: Na^+, e: K^+, f: Mg^{2+} as countercations

5. Potential applications

5.1 Anion recognition in aqueous media

Synthetic polyamine and polypeptide-based receptors are popular for anion recognition in aqueous medium.[22] However, neutral receptors have also shown their potentiality in this aspect. In fact, tren based first urea/thiourea receptor developed by Morán *et al.* is reported to bind anions in DMSO-water solvent.[46] Recently, tren based urea/thiourea receptors have emerged as effective anion receptor *via* complete encapsulation of anions in aqueous media in their complementary binding site. Fluorinated urea/thiourea receptors reported by Gale *et al.* have shown binding of anions in DMSO-d_6/0.5%D_2O solvent.[47] $HAsO_4^{2-}\subset\mathbf{12_2}$, $C_2O_4^{2-}\subset\mathbf{20_2}$, $C_2O_4^{2-}\subset\mathbf{21_2}$ capsules reported by our group are crystallized from DMSO/5%H_2O solvent and effective binding of anions are estimated even in DMSO-d_6/D_2O (9:1, v/v) solvent.[53,63] Findings of Custelcean and Wu groups reveal the formation of anion encapsulated capsules of **22** and **23** from highly competitive aqueous media.[65,68] On other hand, benzene platform based tris-amide and hexa-amides have shown their interest for recognition of hydrated halides *via* capsule formation.[20] In particular, encapsulation of fluoride-water cluster by tris-amide **28** in highly competitive acetone/water (1:1) solvent confirms functional aspects of molecular capsules.[74] All these results suggest the scope of further exploration of these receptors towards anion separation, transportation etc.

5.2 Anion separation

Custelcean *et al.* have pioneered separation of SO_4^{2-} study by encapsulation of SO_4^{2-} in crystalline capsule.[65] They have extensively employed tren scaffold based 3-pyridyl functionalised tris-urea **22** for the selective SO_4^{2-} encapsulation from a mixture of competitive aqueous solution through size, shape and charge discrimination. Related solid and solution states binding properties are discussed in our previous article.[20] However, SO_4^{2-} separation from highly alkaline aqueous solution is more appealing as it would be a practical solution to the problem of

SO_4^{2-} separation from nuclear waste.[35] In this direction, Custelcean *et al.* have reported SO_4^{2-} encapsulation in two new crystalline capsules self-assembled from tris-urea **22** and Na_2SO_4/K_2SO_4.[95] Crystalline capsules with compositions $[Na_2SO_4(\mathbf{22})_2(H_2O)_4]$ and $[K_2SO_4(\mathbf{22})_2(H_2O)_2]$ are obtained in good yields from aqueous methanol solution. In both cases, SO_4^{2-} encapsulation is found to be assisted *via* twelve complementary hydrogen bonding interactions in the dimeric capsular assemblies of **22** (Fig. 24a,b). However, differences are observed in the coordination environment of countercations. Presence of $[Na_2(H_2O)_4]^{2+}$ *vs* $[K_2(H_2O)_2]^{2+}$ cluster is observed in Na and K-based system respectively, both of which eventually lead to the formation of NaCl-type framework like Mg-based structure of **22**.[35] Capsular dimensions vary from 9.51 Å to 9.20 Å moving from Na to K-based capsule. Interestingly, the SO_4^{2-} encapsulated Na-based system can be selectively crystallized in 90% yield from highly alkaline aqueous solutions (pH = 14) in presence of competitive anions. Further, the **22** can be recycled by simple water-treatment of the capsule that leaves sodium sulfate in solution.

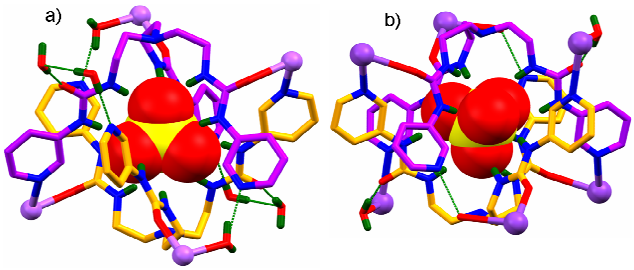

Fig. 24 X-ray crystal structures of $SO_4^{2-}\subset\mathbf{22}_2$ capsules with a) $[Na_2(H_2O)_4]^{2+}$ and b) $[K_2(H_2O)_2]^{2+}$ cluster. Coordination mode and water hydrogen bonding interactions are presented.

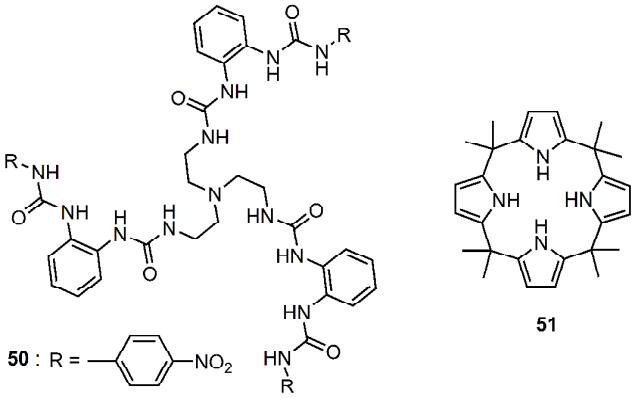

Chart 13

On the other hand, designing of anion receptor aiming toward liquid-liquid extraction of SO_4^{2-} from water is highly challenging due to its large hydration energy.[96,97] Moyer *et al.* have designated a successful extractant, which has solubility in a water-immiscible solvent, water insolubility and a provision for maintaining phase charge neutrality.[35] Due to the importance of SO_4^{2-} separation from nitrate-rich mixtures in the remediation of nuclear waste, several synthetic receptors and different approaches have been developed in recent times. Sessler and Moyer *et al.* have widely utilized dual-host and ion-exchange strategies for SO_4^{2-} extraction.[35,98] Wu *et al.* have demonstrated efficient extraction of SO_4^{2-} from water by a neutral hexa-urea receptor **50** (Chart 13) using tetrabutylammonium chloride as a phase-transfer agent.[99] SO_4^{2-} selectivity pattern of **50** in aqueous medium (DMSO-d_6/10% D_2O) is explored towards liquid-liquid extraction of SO_4^{2-}. Addition of TBACl causes $CHCl_3$ solubility of **50** and possible exchange between Cl^-/SO_4^{2-} in L-L extraction process. Structural analysis of the SO_4^{2-} complex reveals monotopic encapsulation of SO_4^{2-} in the cavity of **50** (Fig. 25) *via* twelve N-H···O interactions.

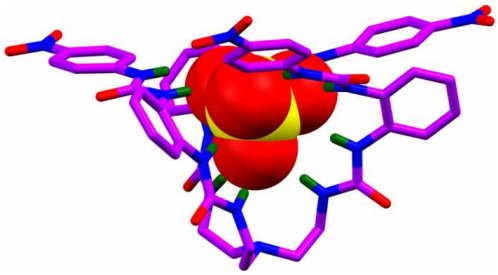

Fig. 25 View of monotopic SO_4^{2-} encapsulation in the cavity of hexa-urea **50**. Non-bonding hydrogens and countercations are omitted for clarity.

We have employed a similar strategy for liquid-liquid extraction of anions by **19** using tetrabutylammonium iodide as phase transfer agent.[62] Solution state F^- selectivity pattern of **19** is established by ^{1}H-NMR and ITC studies. Further, we have shown liquid-liquid extraction of F^- and SO_4^{2-} by **19** *via* anion exchange technique using tetrabutylammonium iodide as phase transfer agent. The $CHCl_3/CH_2Cl_2$ solubility of **19** is achieved by adding TBAI, followed by usual liquid-liquid extraction, which result ~70% and 40% extraction of F^- and SO_4^{2-} respectively. Crystallization of extracted mass shows SO_4^{2-} encapsulation in the dimeric capsular assembly of **19** (Fig. 26) *via* fifteen N-H···O interactions. Capsular dimension of $SO_4^{2-}\subset\mathbf{19}_2$ is measured as 9.51 Å, which is similar to the tren based urea/thiourea capsules. In this context, Moyer *et al.* have demonstrated the role of cations in the liquid-liquid extraction SO_4^{2-} by a calix[4]pyrrole receptor **51** with lipophilic anion exchanger.[100] Superior extraction of SO_4^{2-} is reported with the methyl substituted cations, which is supported by the formation of thermodynamically stable ion-pair complex of SO_4^{2-}.

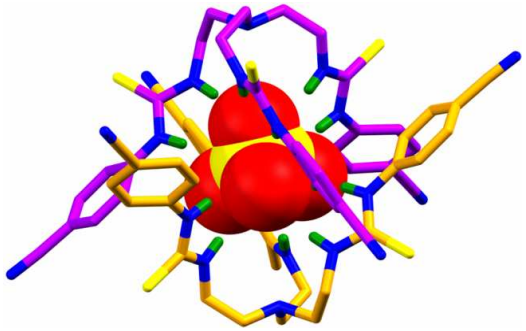

Fig. 26 Single crystal X-ray structure of $SO_4^{2-}\subset\mathbf{19}_2$ dimeric capsule. Non-bonding hydrogens and countercations are omitted for clarity.

Recently, we have demonstrated a rather unique approach for L-L extraction of SO_4^{2-} using the CO_3^{2-} complex of tris-urea **12**. Quantitative formation of carbonate capsules $[\mathbf{12}_2{\cdot}CO_3]^{2-}$ *via* aerial CO_2 fixation and its solubility in water-immiscible solvent like $CHCl_3/CH_2Cl_2$, encourage us to investigate L-L extraction of

SO_4^{2-} by $[\mathbf{12}_2{\cdot}CO_3]^{2-}$.[50] In fact, quantitative (~99%) extraction of SO_4^{2-} as $[\mathbf{12}_2{\cdot}SO_4]^{2-}$ capsule is observed by $[\mathbf{12}_2{\cdot}CO_3]^{2-}$ *via* CO_3^{2-} /SO_4^{2-} exchange process. Further, this anion exchange process in the capsule is clearly visible through the pink colouration of the aqueous phase in presence of phenolphthalein after L-L extraction. Although, use of Cl^- as anion exchanger causes impure extraction of SO_4^{2-} for **12** unlike that of **19** and **51** (Chart 14). Carbonate capsule $[\mathbf{12}_2{\cdot}CO_3]^{2-}$ is an exact (2:1) complex of **12** and CO_3^{2-} which rules out possibility of any excess of CO_3^{2-} (phase transfer agent) in the organic layer in case of **12**.

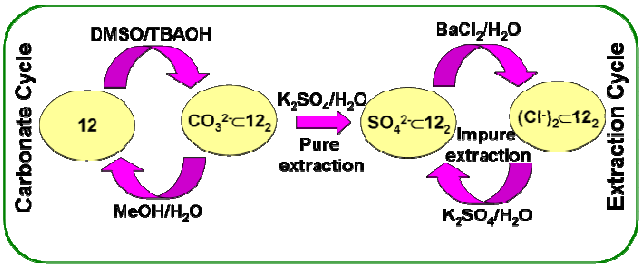

Chart 14 Schematic presentation of CO_2 fixation and SO_4^{2-} extraction cycles of **12** *via* molecular capsule formation.

5.3 Other relevant applications

Synthetic receptors reported for aerial CO_2 fixation by Gunnlaugsson, Gale and our group are generally obtained from basic DMSO solvent.[27-30] Encapsulation of such aerially sequestered CO_2 as CO_3^{2-} in a dimeric capsular assembly is well studied in case of tris-urea **12**.[30] Tren scaffold based 3-nitrophenyl functionalised tris-urea **16** has recently been established as potential system for the fixation of aerial CO_2 as CO_3^{2-} by Das *et al*.[58] Crystallization of **16** with TBAF/TABOH in DMSO yields CO_3^{2-} encapsulated complex of **16** in 90% yield. Structural analysis shows CO_3^{2-} templated formation of dimeric capsular assembly of **16** (Fig. 27). Each oxygen atom of CO_3^{2-} are involved in four N-H···O interactions, thus results a twelve coordinated of CO_3^{2-} complex. ^{1}H-NMR titration study of **16** with HCO_3^- shows 1:1 (host/guest) association in solution as evident from job's plot analysis. Association constant value of HCO_3^- with **16** is estimated to be 4.15, which resembles the same of tris-urea **12** (4.04) in DMSO-d_6.[30]

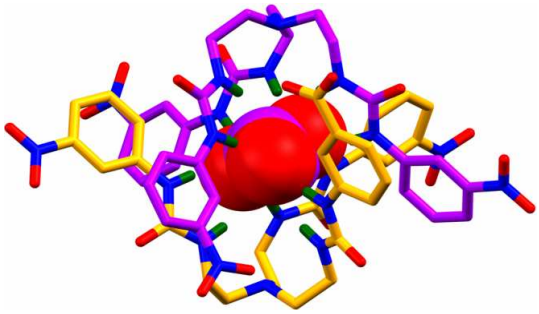

Fig. 27 X-ray crystal structure showing $CO_3^{2-}\subset\mathbf{16}_2$. Non-bonding hydrogens and countercations are omitted for clarity.

Structural evidence of CO_3^{2-} complexes reveals the necessity of higher coordination for CO_3^{2-}. Very recently, Hossain *et al.*

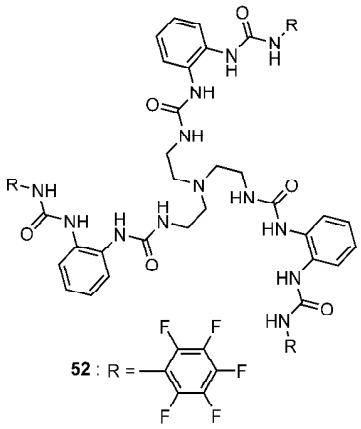

Chart 15

have reported CO_2 fixation as CO_3^{2-} by a tren based tripodal hexa-urea **52** (Chart 15) having chelating urea groups.[101] Attempt to grow crystals from mixture of **52** and TBAF in DMSO generates the CO_3^{2-} complex of **52** in quantitative yield like that of **12**. CO_3^{2-} complex of **52** shows monotopic encapsulation of CO_3^{2-} inside the highly organised cavity of hexa-urea **52** (Fig. 28) *via* twelve N-H···O interactions. However, ^{1}H-NMR titration study shows lower binding affinity for HCO_3^- with hexa-urea **52** (log K = 2.35) with 1:1 binding stoichiometry compared to the CO_3^{2-} encapsulating tris-urea receptors.

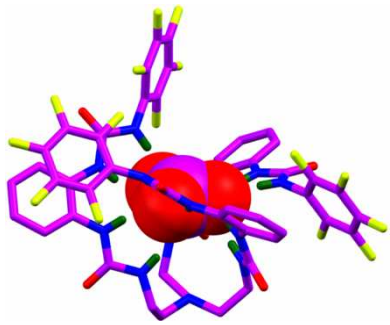

Fig. 28 View of monotopic encapsulation of CO_3^{2-} in the cavity of hexa-urea **52**. Non-bonding hydrogens and countercations are omitted for clarity.

Development of anion receptors for the binding and transportation of anions across lipid membranes has attracted much attention in recent years. Effective transport of bicarbonate by antiport mechanism is demonstrated for tren based phenyl terminal thiourea receptor by Gale *et al.*[102] Encapsulation of CO_3^{2-} is observed in the dimeric capsular assembly of the thiourea in solid state. Fluorinated urea/thiourea receptors (Chart 4) have been reported for better transmembrane transport activity for chloride/nitrate, chloride/sulfate and chloride/bicarbonate antiport over their non-fluorinated analogues due to the high lipophilicity of fluorinated receptors.[47] Capsular recognition of various anions in solid state are observed in cases of this urea/thiourea receptors which are described in section 2.1.

6. Conclusions

This article first covers the recent developments on anion-induced capsular assembly thus establishes necessary foundation for critical insight. Then the discussion is directed towards some

practical application of molecular capsules through anion recognition. Utility of anion binding in molecular capsules can be explored in new directions which are initiated in recent years. Suitable functionality on new platforms have revealed many interesting properties such as capsular size modulation, different halide-water cluster encapsulation, CO_2 fixation, SO_4^{2-} extraction, anion transportation etc. In particular, simple anion receptors have shown efficiency towards aerial CO_2 sequestration as CO_3^{2-} in the molecular capsules. Competitive crystallization and liquid-liquid extraction have emerged as efficient technique to achieve the challenging task of SO_4^{2-} extraction from water in recent years. A vital task for moving towards the practical application is the construction of molecular capsule for the recognition of anions in aqueous media. Encapsulation of toxic $HAsO_4^{2-}$ in the dimeric capsular assembly of a simple tripodal urea receptor in aqueous medium is also demonstrated in recent times. However, selective binding and removal of such toxic anions like $HAsO_4^{2-}$, CrO_4^{2-} from water either by selective crystallization or solvent extraction are yet to be reported. Thus, drinking water purification by removing toxic and hazardous anions using simple anion receptor chemistry is one of the exciting prospects of future work.

Acknowledgements

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Notes and references

[a]*Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, 2A & 2B Raja S. C. Mullick Road, Kolkata 700032, India. E-mail: icpg@iacs.res.in*

Color codes in crystal figures: orange and purple, carbon; blue, nitrogens; red, oxygen; green, hydrogen; yellow, sulfur; yellow-green, fluorine; lime-green, chlorine; arsenic, pink; phosphorous, deep orange.

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Ranjan Dutta obtained his Master's degree in chemistry from Indian Institute of Technology, Kanpur in 2008. He has joined for PhD under the supervision of Professor Pradyut Ghosh in the Department of Inorganic Chemistry, Indian Association for the Cultivation of Science (IACS) in 2008. Recently he has submitted his thesis entitled "Development of Cyanuric Acid Platform Based Anion Receptors: Separation and Extraction Studies Using Relevant Neutral Receptors" to the University of Calcutta. His research interest covers recognition of anions and removal of toxic anions from water.

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 in Chemistry from Indian Institute of Technology, Kanpur, under the direction of Parimal K. Bharadwaj in 1998. He spent two years as a post-doctoral fellow at Texas A&M University with Richard M. Crooks and he was an Alexander von Humboldt Fellow at University of Bonn, Germany, in Fritz Vögtle's group. Upon his return to India, he joined CSMCRI, India, and in 2007 he moved to IACS. His present research interests are recognition, extraction and chemical sensing of ions of environmental and biological relevance, supramolecular aggregation and interlocked molecules.

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Graphical Abstract

Recent developments in anion induced capsular self-assemblies

Ranjan Dutta and Pradyut Ghosh*