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EDGE ARTICLE

Acid/base controlled size modulation of capsular phosphates, hydroxide encapsulation, quantitative and clean extraction of sulfate with carbonate capsules of a tripodal urea receptor†

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A simple tris-(2-aminoethyl) amine based pentafluorophenyl substituted tripodal urea receptor **L** has been extensively studied as a versatile receptor for various anions. Combined ^{1}H-NMR, Isothermal Titration Calorimetry (ITC) and single crystal X-ray diffraction studies reveal that mononegative anions like F^-, OH^- and $H_2PO_4^-$ are encapsulated into the pseudocapsular dimeric assemblies of **L** with 1 : 1 stoichiometry whereas dinegative anions like CO_3^{2-}, SO_4^{2-} and HPO_4^{2-} form tight capsular dimeric assemblies of **L** with 1 : 2 stoichiometries. Single crystal X-ray diffraction study clearly depicts that the size of the dimer of $H_2PO_4^-$ encapsulated pseudocapsule is 13.8 Å whereas the size of the tight HPO_4^{2-} encapsulated capsular assembly is only 9.9 Å. The charge dependent anion encapsulated capsular size modulation of phosphates has been demonstrated by simple acid/base treatment *via* solution state ^{31}P-NMR and single crystal X-ray diffraction studies. **L** is also capable of encapsulating hydroxide in its $\mathbf{C_{3v}}$-symmetric cavity that is achieved upon treating a DMSO solution of **L** with tetrabutylammonium (TBA) cyanide and characterized by single crystal X-ray diffraction study. To the best of our knowledge this is the first report on the encapsulation of hydroxide in a neutral synthetic receptor. The excellent property of **L** to quantitatively capture aerial CO_2 in the form of CO_3^{2-} capsules $[\mathbf{L}_2(CO_3)][N(n\text{-}Bu)_4]_2$ in basic DMSO solution has been utilized to study the liquid–liquid extraction of SO_4^{2-} from water *via* anion exchange. Almost quantitative and clean extraction of SO_4^{2-} from water (99% from extracted pure mass and >95% shown gravimetrically) has been unambiguously demonstrated by NMR, FT-IR, EDX, XRD and PXRD studies. Selective SO_4^{2-} extraction is also demonstrated even in the presence of $H_2PO_4^-$ and NO_3^-. On the other hand the mixtures of **L** and TBACl (to solubilize **L** in $CHCl_3$) results impure sulfate extraction even when 1 : 1 **L**/TBACl is used. Similar impure SO_4^{2-} extraction is also observed when organic layers containing $[\mathbf{L}(Cl)][N(n\text{-}Bu)_4]$ are used as the extractant, obtained upon precipitating SO_4^{2-} from the extracted mass, $[\mathbf{L}_2(SO_4)][N(n\text{-}Bu)_4]_2$ in the carbonate capsules method using aqueous $BaCl_2$ solution.

Introduction

Capsular assembly of a receptor creates a distinct microenvironment that isolates the guest from the bulk of the solvent media.[1–4] When two or more receptors with interior anion binding sites create an assembly; there is a possibility to satisfy the higher coordination numbers required for the binding of oxyanions[5–7] and hydrated anions.[8–10] Recognition of tetrahedral oxyanions like inorganic phosphates and sulfates are of considerable current interest due to their biological and environmental importance.[11–14] Phosphates are the most important ingredients for fertilizer as plants need phosphorus for growth, though phosphate is often regarded as the main culprit in cases of eutrophication in lakes and river water. It has been shown that the amount of phosphates lost to surface water increases linearly with the amount of phosphorus in the soil. Thus much of the nutrient loading in soil eventually makes its way into water.[15–17] In such situations, the slow release of phosphates to the soil from a capsular assembly as fertilizer and its separation *via* encapsulation would be a better approach in agriculture. Generally, inorganic phosphates exist in three different forms $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} depending upon the pH of the solution which

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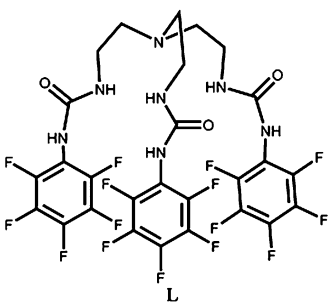
† Electronic supplementary information (ESI) available: Synthesis and characterization of the complex **5** and complex **6**, details of ITC experiment conditions, binding isotherms with thermodynamic and kinetic parameters, details about the X-ray structure determination, details about the X-ray crystal structures, ^{1}H, ^{13}C, ^{19}F and ^{31}P-NMR spectra, stack plots of the ^{1}H NMR, FT-IR and EDX-analysis. CCDC reference numbers 861094 & 861095. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2sc00021k

complicates their recognition chemistry.[18–20] Again the separation of sulfate from nitrate-rich mixtures in order to get rid of it from nuclear wastes and the removal of sulfate from hard water are of immense importance. Thus, different synthetic receptors and approaches have been developed in recent times.[21–24] Liquid–liquid extraction is an important and popular technique to researchers since it provides a means for the selective removal of sulfate anions by transporting it from aqueous phase into organic phase. However, the extremely large hydration energy of sulfate ($\Delta G_h = -1080$ kJ mol^{-1} for hydrophilic sulfate *vs.* $\Delta G_h = -300$ kJ mol^{-1} for hydrophobic nitrate)[25] makes the transport of this anion across the interface more challenging, according to Hofmeister bias.[26] To overcome the Hofmeister bias, which disfavours the separation of the extremely hydrophilic sulfate ion from water, the receptor must have both excellent affinity and selectivity for sulfate ion.

Tris(2-aminoethyl)-amine, tren, is an important building block in tripodal receptor systems for anions that have been studied by different groups.[27–40] The binding ability of tren-based acyclic tripodal urea receptors towards anions like sulfate and phosphates *etc.* varies with the attached moiety to the tren (N4) unit, since functional groups modify the hydrogen bonding capability.[35] We have shown pentafluorophenyl-substituted tren-based tris-urea, **L** (see Scheme 1), as an effective receptor for $H_2PO_4^-$, SO_4^{2-}, CO_3^{2-} and F^- in the cavity of its dimeric capsular assemblies.[38–40] Very recently, Gale *et al.* have extensively studied the transmembrane transport abilities of a series of similar tren-based tris-ureas and tris-thioureas which provided an insight into the relationship between the structure, anion affinity, lipophilicity and anion transport ability of the fluorinated and unfluorinated tripodal urea/thiourea receptors.[41] On the other hand, the first observation of facilitated sulfate ion transfer by neutral receptors across the interface of two immiscible electrolyte solutions (water/1,2-dichloroethane) is observed in late 1990's by Teramae and co-workers.[42] Later, on the basis of liquid–liquid anion exchange technology, Plieger *et al.* showed the extraction of sulfate from water with a series of salen compounds.[43–46] Recently Sessler *et al.* with protonated cyclo[8] pyrroles and Moyer and co-worker with two types of calixpyrroles have demonstrated the liquid–liquid extraction of sulfate from water.[47–49] However, in most of the cases high concentrations, about 10–1000 times SO_4^{2-} to the receptor, are needed to ensure applicable extraction. Very recently Wu and coworkers have reported a mixture of second generation tripodal hexaurea and TBACl salt in excess as an extractant for sulfate extraction from aqueous solution.[50]



Scheme 1 Tren-based pentafluorophenyl-substituted urea receptor **L**.

Herein we demonstrate the anionic charge dependent dimeric capsular size modulation of phosphates encapsulated by **L** by simple acid/base treatment where dianionic species show tight capsular and monoanionic species show pseudocapsular dimeric assemblies. We also present a serendipity result on encapsulation of hydroxide in the cavity of **L**. To the best of our knowledge this represents the first report on encapsulation of hydroxide in any synthetic neutral receptor. Further we demonstrate a very efficient, pure and almost quantitative liquid–liquid extraction of SO_4^{2-} ion (99%) by the carbonate complex of **L** from aqueous solution (where SO_4^{2-}: $[\mathbf{L}_2(CO_3)][N(n\text{-}Bu)_4]_2 = 1:1$) even in presence of NO_3^- and $H_2PO_4^-$ *via* the anion exchange strategy.

Results and discussion

Solution state ITC studies

The detailed binding studies of **L** with different anions like F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, CH_3COO^-, NO_3^-, ClO_4^-, SO_4^{2-}, CO_3^{2-} by NMR and single crystal X-ray diffraction are shown that monoanionic guests generally form dimeric pseudocapsular assemblies with 1 : 1 stoichiometry whereas dianionic guests like SO_4^{2-} and CO_3^{2-} form tight capsular assemblies (1 : 2 stoichiometry) which have been reported earlier.[38–40] Herein we have undertaken a detailed isothermal titration calorimetric (ITC) study to evaluate the thermodynamic and kinetic parameters upon the binding of **L** with the above mentioned anions (as tetrabutylammonium (TBA) salts, except HCO_3^- as a tetraethylammonium (TEA) salt) in dry dimethylsulfoxide (DMSO) (Fig. 1–3, Supporting Information†, Figures 1S–4S). All the thermodynamic parameters are tabulated in Table 1.

ITC studies are provided the thermodynamic finger prints of the binding processes of these anions with **L**, which served as a starting point for unravelling the different contributions to the

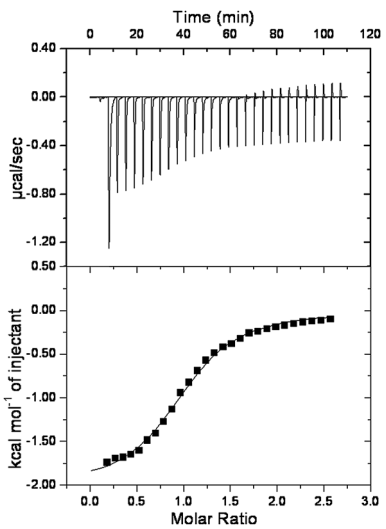


Fig. 1 ITC profile of fluoride (0.104 mM) binding to host **L** (1.248 mM) in dry DMSO at 298 K. The upper panel shows the heat pulses experimentally observed in each titration step. The lower panel reports the respective time integrals translating as the heat absorbed for each aliquot and its coherence to a 1 : 1 binding model. Model: one sites, χ^2/DoF = 217.4, $n = 1.01 \pm 0.011$, $K = 4.49 \times 10^4 \pm 3.06 \times 10^3$ M^{-1}, $\Delta H = -979.8 \pm 16.04$ cal mol^{-1}, $\Delta S = +18.0$ cal mol^{-1} deg^{-1}.

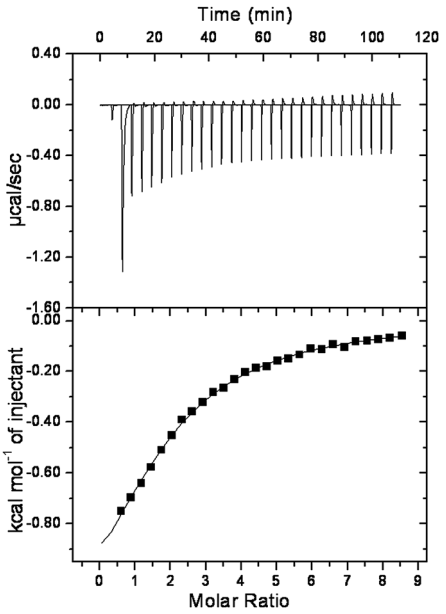


Fig. 2 ITC profile of dihydrogenphosphate (0.028 mM) binding to host **L** (1.245 mM) in dry DMSO at 298 K. The upper panel shows the heat pulses experimentally observed in each titration step. The lower panel reports the respective time integrals translating as the heat absorbed for each aliquot and its coherence to a 1 : 1 binding model. Model: one sites, χ^2/DoF = 202.7, $n = 1.01 \pm 0.009$, $K = 1.16 \times 10^5 \pm 2.08 \times 10^3$ M^{-1}, $\Delta H = -8374 \pm 92.58$ cal mol^{-1}, $\Delta S = -4.91$ cal mol^{-1} deg^{-1}.

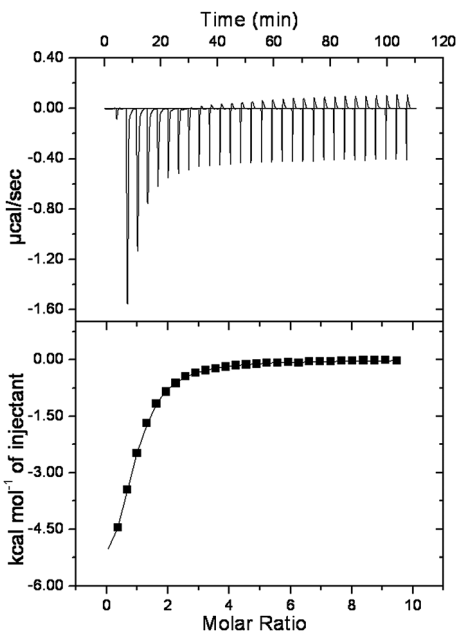


Fig. 3 ITC profile of carbonate (0.051 mM) binding to host **L** (2.046 mM) in dry DMSO at 298 K. The upper panel shows the heat pulses experimentally observed in each titration step. The lower panel reports the respective time integrals translating as the heat absorbed for each aliquot and its coherence to a 1 : 1 binding model. Model: one sites, χ^2/DoF = 58.47, $n = 1.86 \pm 0.086$, $K = 1.19 \times 10^4 \pm 635$ M^{-1}, $\Delta H = -1666 \pm 94$ cal mol^{-1}, $\Delta S = +13.1$ cal mol^{-1} deg^{-1}.

free energy of anion binding. For all anionic species, we are invariably found strong exothermic binding, indicating that the exclusive cause for binding. The ITC profiles indicate the presence of single equilibrium in the solution corresponding to the formation of 1 : 1 (host: guest) adduct for F^-, Cl^-, Br^-, CH_3COO^-, and $H_2PO_4^-$ which is evident from the stoichiometries $n = 1.01$, 0.96, 1.04, 1.03 and 1.01 respectively, whereas 2 : 1 adduct is observed for sulfate and carbonate with $n = 2.06$ and 1.86 respectively. In cases of NO_3^- and ClO_4^- no appreciable heat change is observed during ITC experiments *i.e.* these anions do not show any sign of complexation in dry DMSO. In the case of I^- no reliable fit to 1 : 1 binding isotherm is observed. It has been shown that for low binding constant ($<10^2$), ITC could not provide reliable values for 1 : 1 binding, probably the cause in the case of I^-.[51]

For the values of the thermodynamic parameters, Table 1 clearly shows that the binding of halides (F^-, Cl^- and Br^-) are strongly entropy driven which can be attributed to their willingness to enter and fit in the host cavity *via* suitable hydrogen-bonds. In cases of dihydrogen phosphate and acetate, highly negative enthalpy values easily compensate the slight unfavorable negative entropy values in their binding process, probably due to their larger size and higher solvation in DMSO which acts as a hydrogen bond acceptor.[52] The binding of sulfate is a high enthalpy and moderate entropy driven process whereas in the case of carbonate binding process is highly entropically and moderately enthalpically driven. Table 1 also clearly depicts that the highest negative free energy value for dihydrogen phosphate translates to the highest binding constant in DMSO as observed in the ^{1}H-NMR titration study. The solution state data obtained from ITC is corroborated with the previously reported solution states binding of **L** with different anions by ^{1}H-NMR titration experiments in DMSO-d_6 shown in Table 1. Stoichiometry and binding constant values obtained from both these methods closely resemble each other, except for bromide. The ^{1}H-NMR titration data gave a relatively low binding constant value compared to the value obtained by ITC measurement.

Single crystal X-ray diffraction studies

In our previous study we have reported single crystal X-ray structural evidence for the binding of **L** with $H_2PO_4^-$, F^-, SO_4^{2-} and CO_3^{2-} as $[\mathbf{L}(H_2PO_4)][N(n\text{-}Bu)_4]$ (**1**), $[\mathbf{L}(F)][N(n\text{-}Bu)_4]$ (**2**), $[\mathbf{L}_2(SO_4)][N(n\text{-}Bu)_4]_2$ (**3**) and $[\mathbf{L}_2(CO_3)][N(n\text{-}Bu)_4]_2$ (**4**) respectively. Herein we report the single crystal X-ray structures of two new complexes of **L** with HPO_4^{2-} and OH^- as $[\mathbf{L}_2(HPO_4)][N(n\text{-}Bu)_4]_2$ (**5**) and $[\mathbf{L}(OH)][N(n\text{-}Bu)_4]$ (**6**) respectively. The single crystal of complex **5** is obtained by the reaction of **L** with $n\text{-}Bu_4N^+H_2PO_4^-$ and $n\text{-}Bu_4N^+OH^-$ in DMSO. In complex **5** two molecules of **L** form a cavity that encapsulates a mono-hydrogenphosphate (HPO_4^{2-}) in its centre *via* hydrogen bonding to the six urea groups (Fig. 4). There are in total fifteen hydrogen bonding interactions between the twelve NH groups of the two **L** moieties and four O atoms of HPO_4^{2-} (Fig. 4). Three oxygen atoms, O2, O3 and O4, accept four hydrogen bonds each and the other oxygen atom (O1) containing a hydrogen atom accepts two hydrogen bonds from the urea proton of **L** and donates a hydrogen bond to the urea NH group, giving overall fifteen hydrogen bonds between two urea receptors and the

Table 1 Thermodynamic parameters for binding of different anions (as TBA salts, except CO_3^{2-} as a TEA salt) with **L** in dry DMSO at 298 K and binding constant of different anion from NMR titration carried out in DMSO (d_6) at 298 K

Guest	n	$T\Delta S$ [kcal mol^{-1}]	ΔH [kcal mol^{-1}]	ΔG [kcal mol^{-1}]	log K (ITC)	log K (NMR)[a]
SO_4^{2-}	2.06	1.42	−4.96	−6.38	4.67	4.73
$H_2PO_4^-$	1.01	−1.46	−8.37	−6.91	5.06	5.52
CO_3^{2-}	1.86	3.90	−1.67	−5.57	4.07	4.04
$CH_3CO_2^-$	1.03	−0.20	−6.22	−6.01	4.41	4.45
F^-	1.01	5.36	−0.98	−6.34	4.65	4.06
Cl^-	0.96	4.53	−1.05	−5.58	4.08	3.42
Br^-	1.04	4.77	−0.57	−5.35	3.92	1.27

[a] Previously reported data (ref. 38–40).

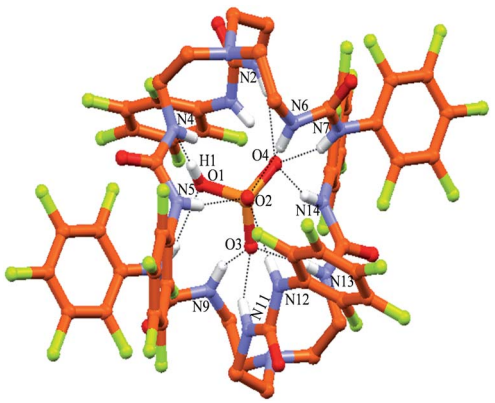


Fig. 4 Binding of HPO_4^{2-} by fifteen hydrogen bonds in the capsule of two **L** molecules in **5**; non-acidic hydrogens are omitted for clarity.

encapsulated HPO_4^{2-} anion (Supporting Information†, Table 2S). A correlation of N–H···O angle *vs.* H···O distance (Fig. 5) shows that in the strong hydrogen bonding region (*i.e.*, $d_{H\cdots O}$ < 2.5 Å and $d_{N\cdots O}$ < 3.2 Å) there are fourteen contacts. Out of fourteen contacts only three contacts have an N–H···O angle smaller than 140°, which are N4–H4···O1, N4–H4···O2 and N3–H3···O4 with N–H···O angles 137°, 136° and 138° respectively, but $d_{N\cdots O}$ values are 3.074 Å, 3.175 Å and 2.833 Å respectively. One hydrogen bonding interaction N10–H10···O3 falls in the weak interaction zone (2.5 < $d_{H\cdots O}$ < 2.8 Å) where the angle is 132° and $d_{N\cdots O}$ is 3.193 Å.

Complex [**L**(OH)][N(*n*-Bu)$_4$] (**6**) is isolated as a crystal suitable for single crystal X-ray study when **L** is treated with *n*-$Bu_4N^+CN^-$ in moist DMSO as a serendipitous result. The crystal structure of compound **6** (Fig. 6) reveals that the hydroxide anion is encapsulated in the tripodal cavity, with hydrogen bonds to all six urea protons. Structural analysis shows that encapsulation of OH^- inside the receptor cavity is governed by six intramolecular N–H···OH^- interactions from three urea moieties of the tripodal receptor (Table 2 and Fig. 6). A correlation of the N–H···O angle *vs.* H···O distance (Supporting Information†, Figure 5S) shows that all are in the strong hydrogen bonding interaction region of $d_{H\cdots O}$ < 2.2 Å and $d_{N\cdots O}$ < 3.0 Å. A further two units of hydroxide encapsulated **L** are held together *via* two weak intermolecular π···π interactions having distance 3.88 Å (Fig. 7). In the dimeric pseudo cage of **L** two hydroxide ions are separated at a distance of 8.109 Å whereas distance between the two bridgehead nitrogen centers is 14.952 Å.

It is surprising that for the hydroxide encapsulated pseudocapsule, complex **6** is formed when **L** is treated with *n*-$Bu_4N^+CN^-$ whereas for the carbonate encapsulated capsule, complex **4** is isolated when **L** is treated with *n*-$Bu_4N^+OH^-$ in aerobic condition. In order to know the probable mechanism of hydroxide encapsulation in the cavity of **L**, we carried out the same experiment in anaerobic conditions inside glove box. No crystal is formed even after 2–3 months in anaerobic conditions but a single crystal of complex **6** is isolated within 2–3 days when the above solution is kept outside the glove box in

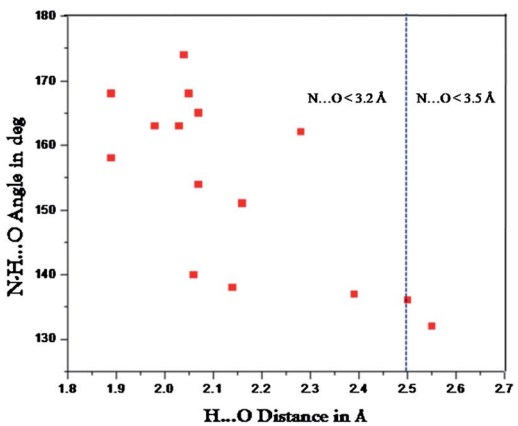


Fig. 5 The scatter plot of N–H···O angle *vs.* H···O distance for the hydrogen bonds in complex **5**.

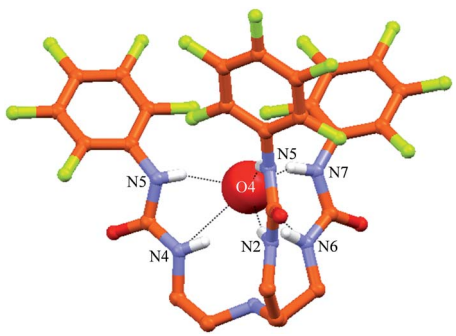


Fig. 6 Binding of OH^- by six hydrogen bonds in the tripodal cavity of **L** in **6**; non-acidic hydrogens are omitted for clarity.

Table 2 Hydrogen bonding interactions of encapsulated hydroxide in the cavity of **L** in complex **6**[a]

D-H···A	*d*(H···A) Å	*d*(D···A) Å	∠DHA (°)
N2–H2···O4	2.01(4)	2.8775(5)	156(4)
N3–H3···O4	1.99(5)	2.760(5)	155(4)
N4–H4···O4	2.12(4)	2.841(3)	145(4)
N5–H5···O4	2.09(4)	2.766(5)	159(4)
N6–H6···O4	2.00(4)	2.779(4)	158(4)
N7–H7···O4	2.05(4)	2.830(5)	150(4)
Mean	2.04(0.05)	2.81(0.05)	153.8(5.3)

[a] Symmetry operations: *x*, *y*, *z*.

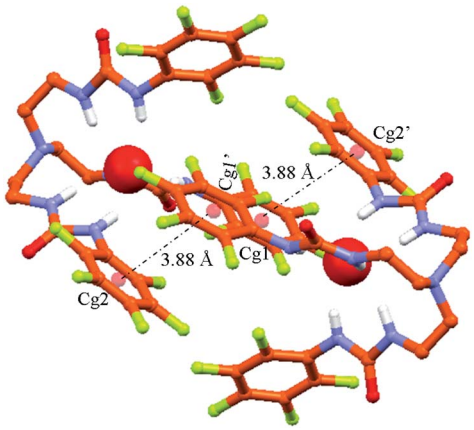
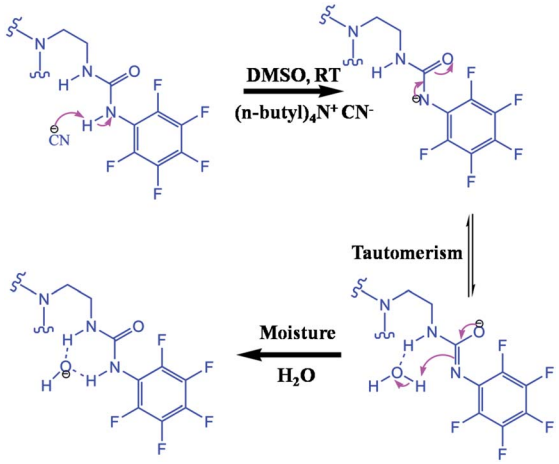


Fig. 7 Binding of two OH- in the cavity of pseudocapsule of 2**L** *via* π···π interaction, non-acidic hydrogens are omitted for clarity.

aerobic conditions. Similarly no crystal formed when *n*-$Bu_4N^+OH^-$ is added to the DMSO solution of **L** in anaerobic conditions. No crystal formation in anaerobic conditions in the cases of CN^- and OH^- clearly indicates that these anions could not enter in the cavity of **L** from the outside environment. Thus OH^- encapsulation must be taking place due to *in situ* generated OH^- inside the cavity of **L** and atmospheric moisture must be playing the role behind the encapsulation of hydroxide in presence of TBACN. Based on this the probable mechanism for hydroxide encapsulation is shown in Scheme 2. Cyanide is a good enough base to abstract one of the six highly acidic urea N–H protons of **L**. The highly electron withdrawing pentafluorophenyl moiety undoubtedly enhances the acidic nature of the urea N–H proton. Deprotonated **L** can easily be stabilized in terms of two different tautomeric forms in solution. This species probably encapsulates a molecule of H_2O in the cavity *via* formation of a six membered ring intermediate followed by protonation of the deprotonated **L** and captures *in situ* generated OH^- by six hydrogen bonds from the three urea moieties as obtained from single crystal X-ray diffraction study. Another plausible mechanism for hydroxide encapsulation in **L** in the presence of CN^- could be explained based on simple proton transfer from the receptor bound acidic H_2O molecule to CN^-. This is similar to the work demonstrated by Gale *et al.* in the case of proton transfer from bound $H_2PO_4^-$ to unbound $H_2PO_4^-$ in the formation of monohydrogenphosphate complex.[53]



Scheme 2 Probable mechanism for hydroxide encapsulation.

Acid/base controlled size modulation of capsular phosphates

Fig. 8 summarizes the type of dimeric assemblies of **L** assisted by various anions of different charges. It is clear from the Figure that the mono negative anions like F^-, $H_2PO_4^-$ and OH^- encapsulate into the pseudocapsular dimeric assemblies of **L** with 1 : 1 stoichiometry having capsular size (*i.e.* the bridge head N distance of two **L**) of 19.82 Å, 13.97 Å and 14.59 Å respectively whereas dinegative anions like HPO_4^{2-}, SO_4^{2-} and CO_3^{2-} form tight capsular dimeric assemblies of **L** having much smaller capsular sizes of 9.92 Å, 9.18 Å and 9.17 Å respectively. In cases of mono negative anions $H_2PO_4^-$ and OH^- capsular sizes are quite comparable whereas F^- shows a larger size. This could be due to the anion–anion repulsion of the high negative charge density of F^-. On the other hand sizes of tight capsular assemblies with HPO_4^{2-}, SO_4^{2-} and CO_3^{2-} are comparable. Inorganic phosphates and their derivatives can exist in the forms of $H_2PO_4^-$ and HPO_4^{2-} at or near pH 7.2. Thus **L** can provide a suitable environment in complexes **1** and **5** to encapsulate both these phosphates *via* different binding modes. In the case of $H_2PO_4^-$ the dimer of $H_2PO_4^-$ forms a pseudocapsule of 13.79 Å, whereas in the case of HPO_4^{2-} that size is measured to be 9.92 Å. The acid/

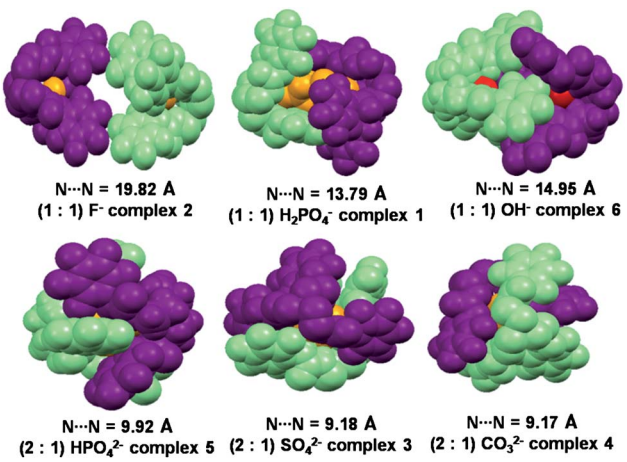


Fig. 8 Representation of capsular size in the space filling X-ray structure of different encapsulated anions in the cavity of **L**.

base controlled charge dependent binding of $H_2PO_4^-$ and HPO_4^{2-} to **L** can also be easily demonstrated using solid state single crystal X-ray diffraction studies and solution state ^{31}P-NMR experiments. The addition of 2 equivalents TBAOH in to the DMSO solution of complex **1** results in single crystals suitable for X-ray diffraction studies. The structural parameters of the crystals obtained from the above solution is the same as that of the HPO_4^{2-} encapsulated crystal structure of complex **5**. Again the addition of **L** to a solution of *n*-$Bu_4NH_2PO_4$ in DMSO-d_6 showed a significant downfield shift ($\Delta\delta$ = 8.33 ppm) in the ^{31}P resonances of the $H_2PO_4^-$ with respect to the anion in the absence of **L** (Fig. 9), indicating the formation of a strong complex between $H_2PO_4^-$ and the urea groups of **L**. On the other hand when **L** is added to the solution of *n*-$Bu_4NH_2PO_4$/*n*-Bu_4NOH (1 : 1) in DMSO-d_6 it showed a downfield shift ($\Delta\delta$) of 3.55 ppm in the ^{31}P resonances with respect to a mixture of *n*-$Bu_4NH_2PO_4$ and *n*-Bu_4NOH. Upon addition of perchloric acid in to the above solution the ^{31}P-NMR experiment shows the characteristic P-signal exactly matches with the value obtained in the case of **L** in the presence of $H_2PO_4^-$. Thus simple acid/base treatment can easily modulate the anionic charge dependent capsular assemblies.

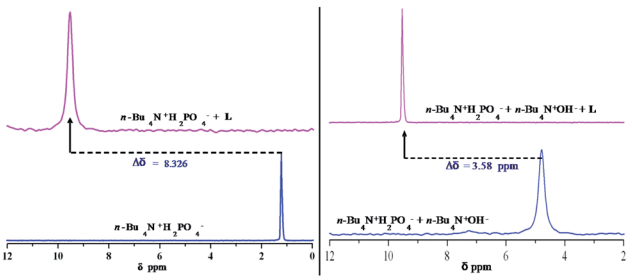


Fig. 9 Partial ^{31}P NMR spectra (500 MHz, DMSO-d_6, 298 K) of *n*-$Bu_4NH_2PO_4$ and *n*-$Bu_4NH_2PO_4$ + *n*-Bu_4NOH and their downfield shift of ^{31}P resonance upon addition of **L**.

Highly efficient and clean extraction of sulfate

One of the most important difficulties in liquid–liquid extraction of sulfate by synthetic urea receptors is the solubility of these extractants in water immiscible apolar organic solvents like CH_2Cl_2 and $CHCl_3$ *etc.* A recent report shows that the addition of excess of TBACl can solubilize receptors with multiple urea moieties in the above mentioned solvents in a liquid–liquid extraction process.[50] Our attempt to extract SO_4^{2-} from water using **L** and excess TBACl is unsuccessful. In a typical experiment, 1 mmol of **L** is dissolved in 10 ml of $CHCl_3$ in the presence of 2 equivalents or even excess (>2 equivalents) of TBACl. Distilled water containing 1 mmol of K_2SO_4 is added to the $CHCl_3$ solution containing **L** with excess equivalents of TBACl. The mixture is stirred vigorously at room temperature for 3 h for extraction of SO_4^{2-} from water to $CHCl_3$ layers. ^{1}H-NMR study on the extracted mass clearly indicates no binding of SO_4^{2-} with **L** which is evident from the unaltered –NH peak positions of **L** in presence of TBACl (Supporting Information†, Figure 6S). This is further confirmed by FT-IR analysis which shows no characteristic peak of SO_4^{2-} at 1100 cm^{-1} (symmetric stretching frequencies of sulfate) (Supporting Information†, Figure 7S). This could be due to the higher concentration of Cl^- which does not allow SO_4^{2-} to transfer into the organic layer in the present case. When **L** is dissolved in 10 ml of $CHCl_3$ by careful addition of exactly 1 equivalent of TBACl and subjected to SO_4^{2-} extraction from 1 equivalent of K_2SO_4 in water, it shows impure extraction of SO_4^{2-} from water. The ^{1}H-NMR spectrum of the extracted mass shows the characteristic urea –NH^a peak position at 8.55 ppm which is in between 8.38 ppm and 8.69 ppm, obtained from **L** in the presence of excess TBACl and the sulfate encapsulated complex of **L**, **3**, respectively (Supporting Information†, Figure 8S). This observation indicates that the exchange of SO_4^{2-} for Cl^- is not clean. Energy-Dispersion X-ray (EDX) analysis (Supporting Information†, Figure 9S) confirmed the presence of Cl (from TBACl) along with S (from extracted SO_4^{2-}) in addition to C, N, F and O.

In our recent communication, we have shown an efficient method for fixation of aerial carbon dioxide of carbonate capsules by **L** in presence of TBAOH in DMSO in the form of single crystals as carbonate encapsulated molecular capsule **4** in almost quantitative yield.[40] Gunnlaugsson *et al.* and Gale *et al.* have reported early examples of the isolation of carbonate complexes from hydroxide solutions.[54,55] The carbonate complex **4** has high solubility in $CHCl_3$ and CH_2Cl_2. A further higher association constant of **L** for SO_4^{2-} (4.73 from NMR and 4.67 from ITC) over CO_3^{2-} (4.04 from NMR and 4.07 from ITC) and comparably lower hydration energy for SO_4^{2-} ($\Delta G_h = -1080$ kJ mol^{-1})[25] than CO_3^{2-} ($\Delta G_h = -1315$ kJ mol^{-1})[25] led us to select single crystals of **4** as a probable extractant for liquid–liquid extraction of SO_4^{2-} from water. In a typical experiment 1 mmol of **4** is dissolved in 10 ml of $CHCl_3$ is used to extract SO_4^{2-} from an aqueous solution containing 1 mmol of K_2SO_4 in 10 ml of distilled water. Then the organic layer is separated after 3 h of stirring at room temperature and evaporated under vacuum to yield the colorless solid in 99% yield. The addition of phenolphthalein indicator to the aqueous layer shows a dark pink color supports its basic nature (Supporting Information†, Figure 10S) due to the exchange of carbonate anions from the organic layer to the aqueous layer and simultaneous transport of sulfate anions from the aqueous to the organic layer.

The extracted mass is subjected to various studies like ^{1}H-NMR, ^{13}C-NMR, FTIR, SEM-EDX, PXRD and single crystal X-ray diffraction to establish superior and pure liquid–liquid extraction of sulfate. ^{1}H-NMR study of complex **3** shows a large downfield chemical shift of both urea –NH signals ($\Delta\delta$ = 0.34 and 0.98 ppm) w.r.t. **L**, indicative of sulfate encapsulation in the cleft of **L** and its strong interactions with the –NH protons (Supporting Information†, Figure 11S). Exactly similar downfield shifts of –NH signals are also observed (Fig. 10b) in the extracted mass, indicating the presence of SO_4^{2-} encapsulated **L** in the extracted products. On the other hand the extractant, $[\mathbf{L}_2(CO_3)][N(n\text{-}Bu)_4]_2$ (**4**) has distinct –NH chemical shifts at 7.61 ppm and 6.91 ppm (Fig. 10a) which are different from **3**. The ^{13}C-NMR analysis of the extracted mass does not show a signal which can be attributed to carbonyl groups of the carbonate, further indicating the absence of the carbonate anion in the extracted mass (Supporting Information†, Figure 24S).

The presence of sulfate and absence of carbonate in the extracted mass is also established by FT-IR study. Fig.11 shows

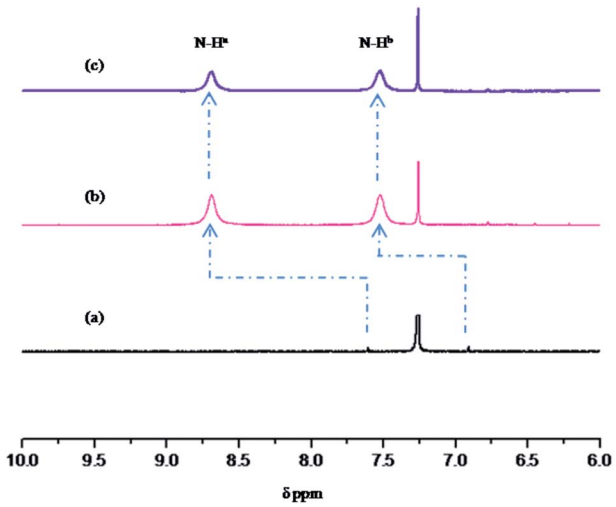


Fig. 10 Partial ^{1}H-NMR spectra of (a) complex **4** (b) extracted mass of sulfate extraction with complex **4** and (c) complex **3** in $CDCl_3$ at 298 K. N–H^a and N–H^b are the two urea N–H protons.

IR spectra of **L** (green), carbonate complex **4** (black) and the extracted mass (red). In the case of the extracted mass the existence of strong new peak is observed at 1100 cm^{-1} (symmetric stretching frequencies of sulfate) and the absence of peak at 1370 cm^{-1} (symmetric stretching frequencies of carbonate) is attributed to the presence and absence of sulfate and carbonate in the extracted mass, respectively. Fig. 12 shows the results obtained from Energy-Dispersion X-ray (EDX) analysis of the extracted mass. The EDX spectrum shows peaks of S from SO_4^{2-} in addition to C, N, F and O.

Single crystals of the extracted mass suitable for X-ray analysis are obtained by the slow evaporation of the acetonitrile solution of the extracted mass and analysis showed formation of the SO_4^{2-} capsular assembly. Thus the X-ray structure confirms the formation of 1 : 2 guest : host complex, encapsulating sulfate in the cavity.[39] In Fig. 13, the experimental powder X-ray patterns of the bulk extracted mass showed similar powder X-ray patterns simulated from the corresponding single crystal X-ray data of the sulfate complex suggesting bulk purity of the extracted mass.

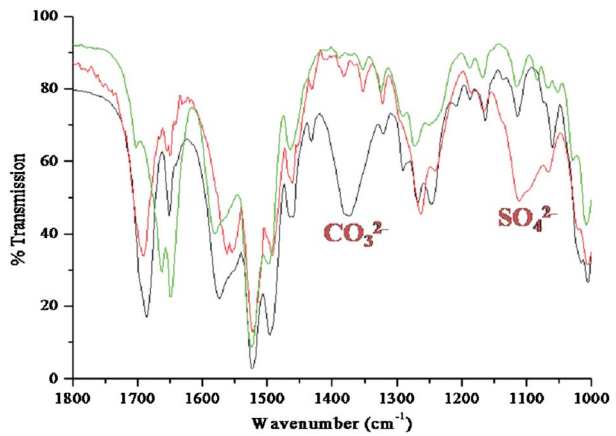


Fig. 11 FT-IR analyses of **L** [green], complex **4** [black] and the extracted mass [red] in KBr discs.

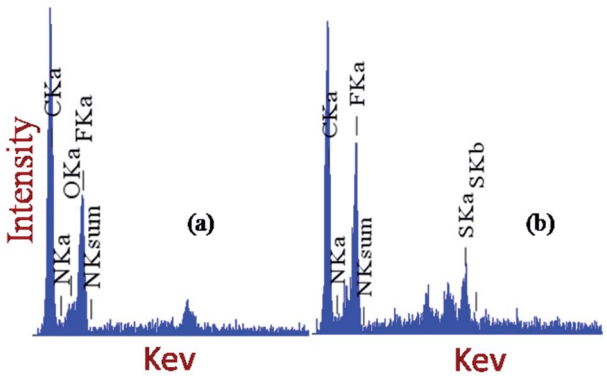


Fig. 12 Energy Dispersive X-ray spectroscopy (EDX) of complex **4** (a) and the extracted mass (b), depicting the presence of sulfur ions.

Yield is calculated from the solid mass isolated from chloroform layers. It shows almost quantitative conversion (99%) to sulfate capsules **3**. Further the sulfate extraction was examined by precipitating SO_4^{2-} from the $CHCl_3$ solution of extracted mass as $BaSO_4$ using aqueous $BaCl_2$ solution. Upon stirring, a white suspension is formed due to the formation of $BaSO_4$. The percentage of sulfate extraction is further calculated gravimetrically from the weight of the isolated $BaSO_4$ (see Table 3). The gravimetric analysis also supports almost quantitative extraction of sulfate (yield 96.7 ± 1.6) obtained from the average of three repeated experiments.

After precipitation of sulfate as $BaSO_4$ from the organic layer the resulting $CHCl_3$ solution containing [**L**(Cl)][N(*n*-Bu)$_4$] is further exploited for the extraction of sulfate from a fresh aqueous solution of 1 mmol K_2SO_4. The ^{1}H-NMR study of extracted mass shows impure extraction of SO_4^{2-} as observed in case of **L** with 1 equivalent of TBACl (Fig. 14). Competitive extraction studies are carried out with complex **4** (1 mmol) in $CHCl_3$ and K_2SO_4 (1 mmol) in the presence of an equivalent amount of KH_2PO_4 or KNO_3 in aqueous solution. The ^{1}H-NMR of the extracted masses show exactly the same –NH peak shifts as observed in the case of clean extraction of sulfate only by carbonate capsule **4**. In the case of the K_2SO_4 and KH_2PO_4 mixture, the extracted mass is also subjected to a ^{31}P-NMR study which shows no signal corresponding to phosphorus (Supporting

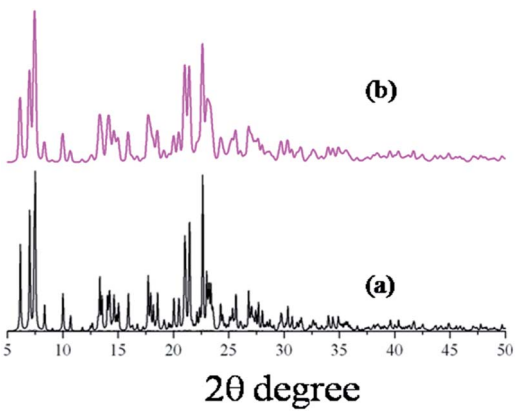


Fig. 13 (a) PXRD pattern of the extracted mass [experimental pattern] and (b) PXRD pattern of complex **3** [simulated].

Table 3 Calculation of percentage of sulfate extracted from both extracted mass and $BaSO_4$ precipitation (gravimetrically)

No. of Expt.[a]	Weight of **4** taken (mg)	Weight of K_2SO_4 taken (mg)	Weight of exted.[a] mass (mg)	% of extn.[a] (from exted. mass)	Weight of $BaSO_4$ (mg)	% of extraction (from $BaSO_4$ mass)
1	21.84	1.95	22.04	99.2	2.32	95.0
2	22.04	1.87	21.95	97.9	2.39	96.9
3	22.38	1.98	22.64	99.4	2.46	98.3

[a] Abbreviations used for Experiment (Expt.), Extracted (Exted.) and Extraction (Extn.).

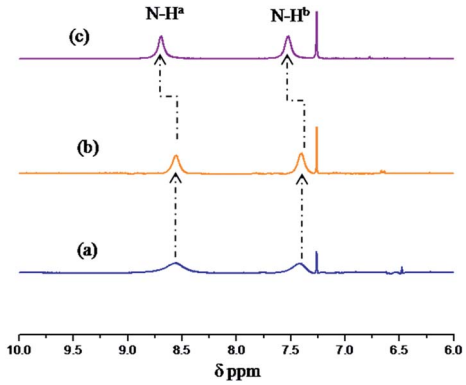


Fig. 14 Partial ^{1}H-NMR spectra of extracted mass of (a) sulfate extraction with Cl^- containing solution after $BaSO_4$ precipitation (b) sulfate extraction with 1eqv. TBACl (c) sulfate extraction with complex **4** in $CDCl_3$ at 298 K. N–H^a and N–H^b are the two urea N–H protons.

Information†, Figure 27S). Thus **4** can extract sulfate selectively from water even in presence of $H_2PO_4^-$ and NO_3^- which is of great environmental significance.

Conclusions

In conclusion, solution state ITC studies on tren-based tripodal urea receptor **L** shows the highest binding affinity towards $H_2PO_4^-$ and the binding affinity order is $H_2PO_4^- > SO_4^{2-} \sim F^- > AcO^- > CO_3^{2-} \sim Cl^- > Br^-$ and no binding is observed with ClO_4^- and NO_3^-. Single crystal X-ray diffraction studies show complete encapsulation of the HPO_4^{2-} and OH^- ion in **L** and supports 2 : 1 and 1 : 1 complex formation respectively. This *in situ* generated hydroxide encapsulation by **L** represents the first example of trapping hydroxide in the pseudocapsular dimeric assembly of a neutral synthetic tripodal urea receptor. The anionic charge dependent dimeric capsular size modulation of $H_2PO_4^-$ and HPO_4^{2-} are confirmed structurally. Further, we demonstrate here a very efficient, pure and almost quantitative liquid–liquid extraction of SO_4^{2-} ion (99%) by the carbonate complex of **L** from aqueous solution (where SO_4^{2-} : $[\mathbf{L}_2(CO_3)][N(n\text{-}Bu)_4]_2 = 1 : 1$) even in the presence of NO_3^- and $H_2PO_4^-$ *via* the anion exchange strategy whereas sulfate extraction with **L** in presence of TBACl demonstrates impure extraction.

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