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Encapsulation of $[F_4(H_2O)_{10}]^{4-}$ in a dimeric assembly of an unidirectional arene based hexapodal amide receptor[†]

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An unidirectional orientation of all six arms of an arene based hexapodal amide receptor shows dimeric capsular assembly templated by a $[F_4(H_2O)_{10}]^{4-}$ cluster.

Recognition of anions has attracted a great deal of attention in the recent past due to their diverse functions in health and the environment.¹ In particular, recognition and sensing of fluoride is an area of immense research interest to the supramolecular chemist due to its role in chemistry, industry, food and toxicity.² Fluoride exists as various types of fluoride-water clusters in water or even in the presence of moisture and its recognition is a challenging task owing to its small size, high electronegativity, and high hydration enthalpy. Thus, recent studies indicate that the receptor for anions such as fluoride should target the hydrated ions rather than the naked ions.³ Numerous theoretical calculations have predicted the existence of a range of fluoride-water clusters.⁴ On the other hand, selfassembled supramolecular capsules or dimeric assemblies that provide an isolated nano-cavity have attracted much attention in recent years for unusual guest encapsulation.⁵ One of the most fascinating features of these assemblies is their ability to isolate the encapsulated guests from the bulk.⁶ The hydrogen bond motif has been applied successfully for the construction of supramolecular assembly capable of engulfing suitable guests. Within the area of self-assembly driven by hydrogen bonding, Rebek, Atwood, and Steed et al. have independently constructed molecular capsules by the self-assembly of various subunits.⁷ The anion or hydrated anion assisted formation of capsular assembly are important in the area of molecular recognition and self-assembly.^{3b-c,8} Herein, we demonstrate $[F_4(H_2O)_{10}]^{4-}$ cluster encapsulation inside the dimeric capsular assembly of a newly synthesized arene based hexapodal amide receptor, L (Scheme 1), where all six arms are projected in one direction (an unfavorable conformation) along with the binding of other anions in solution and solid states.

The hexasubstituted amide receptor, L was synthesized from hexakis(aminomethyl)benzene9 in good yield and the anion binding ability of L in solution was validated by ¹H NMR experiments in DMSO- d_6 at 2 °C in the presence of tetrabutylammoniun (TBA) salts of different anions. In qualitative ¹H NMR studies, F⁻, AcO⁻ and H₂PO₄⁻ showed huge changes in the NMR spectral pattern. (Fig. S9, ESI[†]). These studies indicated the solution state binding of F⁻, AcO⁻ and H₂PO₄⁻ with L. For detailed solution state binding of these ions, we carried out ¹H-NMR titration experiments in DMSO- d_6 at 25 °C which showed the existence of multiple equilibriums in the solution state (See ESI[†]). In the case of F⁻, the arvl-CH (singlet) signal is monitored for Job's plot analysis. The Job's plot for L with F⁻ showed host-guest stoichiometry 1:2 (Fig. 1b). In addition to the parent signals, a set of new signals are generated after the addition of two equivalents of F^- (Fig. 1).

The fluoride complex, 1, is isolated by adding TBAF, $[(CH_3(CH_2)_3)_4NF \cdot xH_2O]$, to the dioxane solution of L, whereas the acetate complex 2 is obtained from acetone solution upon charging TBA-OAc, $[(CH_3(CH_2)_3)_4N \cdot OAc]$. The single-crystal X-ray structure of complexes 1 and 2 confirm the versatility of L as an anion receptor.‡The solid state structure of 1 revealed the encapsulation of an unusual fluoride-water cluster, $[F_4(H_2O)_{10}]^{4-}$ inside the dimer of L with the highly unfavourable *aaaaaa* conformation of the hexapodal bowl (Fig. 2). Hexapodal molecules generally adopt a conformation in which the arms alternate in positions above and below the plane of the central benzene ring.¹⁰



Scheme 1 (a) Molecular structure of L and (b) pictorial representation showing the encapsulation of $[F_4(H_2O)_{10}]^{4-}$ inside the dimeric assembly of L.

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, 2A & 2B Raja S. C. Mullick Road, Kolkata 700 032, India. E-mail: icpg@iacs.res.in; Fax: +91 33-2473-2805 † Electronic supplementary information (ESI) available: Synthetic procedures, Copies of the ¹H NMR, ¹³C NMR, HRMS (ESI-MS) characterization data and ¹H NMR titration data. CCDC 812289–812290. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc10742a



Fig. 1 (a) ¹H-NMR spectral changes of L with added TBA-F ([L] is varied from 5.18 mM to 3.84 mM by the addition of aliquots of 100.03 mM TBAF). Ratio of concentration $[L]/[F^-]$: (i) 0, (ii) 0.62, (iii) 1.04, (iv) 1.45, (v) 2.08, (vi) 2.49, (vii) 3.12, (viii) 3.53, (ix) 3.95, and (x) 6.02. (b) Job's plot for L with TBAF.



Fig. 2 (a) Space-filled view of $[F_4(H_2O)_{10}]^{4-}$ cluster inside the dimeric capsule-like assembly of 1, (b) inset showing $[F_4(H_2O)_{10}]^{4-}$ cluster and (c) partial structure showing the hydrogen bonding interactions of $[F_4(H_2O)_{10}]^{4-}$ cluster with L. L has been represented in purple and orange for clarity. (Color code: C—purple and orange; N—Blue; O—Red; F—Yellow; H—Green) TBA counter cations, lattice dioxane and non-bonding hydrogen atoms are omitted for clarity.

Complex 1 possesses [L.(TBA-F)₂·5H₂O·0.5dioxane] in an asymmetric unit. The source of water in the crystal could be from the hydrated TBAF salt and atmospheric moisture. Fig. 2b shows the hydrogen bonding pattern of the $[F_4(H_2O)_{10}]^{4-}$ cluster. The template cluster, $[F_4(H_2O)_{10}]^{4-}$ is formed *via* strong fluoride-water interactions. Five water molecules (O1, O2, O3, O4 and O5), two fluorides (F1 and F2) and half a molecule of disordered dioxane are present in the asymmetric unit. Both hydrogen atoms of O4 and one

hydrogen atom of O5 are not located in the electron fourier map. The cluster contains four, five and six membered rings, constructed by hydrogen bonding interactions. Only two of the five water molecules (O1 and O2) are directly hydrogen bonded to the amide protons of L whereas other three water molecules (O3, O4 and O5) in the asymmetric unit form a symmetry induced cyclic hexameric water cluster with a chair conformation. The symmetry related fused cyclic hexameric unit in the $[F_4(H_2O)_{10}]^{4-}$ cluster are strongly held together by $O{-}H{\cdots}O$ interactions, with $O{\cdots}O$ distances ranging from 2.737 to 2.902 Å (average: 2.823 Å). A fluoride-water dimer is held by strong N–H···F and N–H···O interactions with the half capsule. The fluoride ion, F1 is hydrogen bonded with the amide N-H protons of L designated as N8 and N78 and the fluoride ion F2 is hydrogen bonded with the amide N-H protons of N36 and N50 via N-H···F interactions (Fig. 2c). In addition, F1 and F2 are strongly hydrogen bonded with O1 and O2 via O-H···F interactions with average O···F bond distances of 2.683 Å ranging from 2.628 Å to 2.728 Å. Apart from the hydrogen bonding interactions with F1 and F2, the water molecules O1 and O2 are held strongly with the receptor via N-H···O interactions with the amide hydrogen atoms (N22 and N64) with N···O bond distances 2.868 Å and 2.883 Å respectively. Thus all of the six amide protons are engaged in hydrogen bonding with the encapsulated $[F_4(H_2O)_{10}]^{4-}$ guest (four for fluoride ions and two for two water molecules). Apart from the interactions with the receptor molecule the encapsulated fluoride ions are directly hydrogen bonded to the hexameric water cluster via O-H...F and $O-H \cdots O$ interactions. F1 is held with water hexamer by O-H···F (O3) hydrogen bonding interaction with O···F distance 2.685 Å and $\angle O-H \cdots F = 168.72^{\circ}$ and F2 with $O \cdots F$ (O5) distance 2.783 Å and O–H···F = 167.32° . In addition to the classical hydrogen bonding interactions, the encapsulated $\left[F_4(H_2O)_{10}\right]^{4-}$ cluster is also stabilized by $C\text{--}H\cdots\text{-}F$ and C-H...O interactions with the aryl C-H protons of the receptor bowl. Thus, the encapsulated $[F_4(H_2O)_{10}]^{4-}$ cluster is constructed and stabilized by various hydrogen bonding interactions like N-H...F, N-H...O, O-H...F, O-H...O, $C-H\cdots F$ and $C-H\cdots O$ interactions. In 1, all arms of L are projected unidirectionally to engulf the fluoride-water cluster inside the dimeric assembly of the receptor. Vögtle and Weber reported the unusual cation complexing tendency of an octopuslike hexapodal ligand and its spatial crowding impeded conformational mobility.¹¹ Recently, DFT calculations on a benzene platform based hexanonanamide receptor predicted the existence of a bowl shaped hexapodal receptor with all six substituents intramolecularly H-bonded together on one side of the benzene plane.⁹ A crystal structure of a self-assembled supramolecular complex stabilized by a water decamer $(H_2O)_{10}$ has been reported by Atwood and co-workers.¹² Whilst our recent report showed the encapsulation of $[F_2(H_2O)_6]^{2-}$ inside the dimeric assembly of a benzene based 1,3,5-trisubstituted tripodal triamide receptors.^{3b-c} However, no report on molecular capsule formation by dimeric association of unidirectional hexapodal receptor templated by anion-water cluster has been reported or predicted in the literature.

In the case of the planar acetate ion, colorless crystals of complex 2 are obtained as single crystals suitable for single



Fig. 3 View of **2** showing the encapsulated acetate ion and water molecule above and below the benzene scaffold of **L**. (Color code: C—orange; N—Blue; O—Red; H—Cyan) TBA counter cations, lattice dioxane and non-bonding hydrogen atoms are omitted for clarity.

crystal X-ray analysis from an acetone–dioxane binary solvent mixture (Fig. 3). Solid state structural analysis revealed 1:2 binding of host to AcO⁻ complexation as observed in the similar hexaamide receptor reported by us recently.¹³ Complex **2** formed two independent tripodal clefts. In **2**, each tripodal cleft encapsulates a single AcO⁻ resulting in two acetate anions encapsulated per receptor molecule. The acetate anion in each cleft is binding with all three of the amide –NH protons *via* strong N–H···O interactions. Detailed hydrogen bonding interactions are as follows: for N7–H7···O1, *d* N7···O1 = 2.755(4) Å and \angle N7–H7···O1 = 153.0°, N21–H21···O1, *d* N21···O1 = 2.838(4) Å and \angle N21–H21···O1 = 168.0° and for N35–H35···O3, *d* N35···O3 = 2.886(4) Å. N35–H35···O3 = 168.5°.

In conclusion, the arene capped hexapodal amide receptor showed an encapsulation of a fluoride-water cluster containing four fluoride and ten water molecules in the cavity of its dimeric capsular type assembly where all six arms of the receptor are unidirectional. The aryl terminals (*m*-nitro phenyl) might have played an important role for its stabilization of the unusual conformation to capture the relatively huge guest, $[F_4(H_2O)_{10}]^{4-}$ whereas pentafluorophenyl terminals with a similar system showed the most favorable conformation upon nitrate ion binding.¹³ Our approach of recognizing different fluoride-water clusters would be useful to develop a new generation of fluoride receptors in their hydrated form.

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Notes and references

‡ Crystallographic parameters of Complex 1: $C_{88}H_{128}F_2N_{14}O_{24}$, M = 1804.04, Crystal dimension 0.22 × 0.18 × 0.16 mm³; T = 120(2) K; Triclinic, space group $P\bar{1}$; a = 15.7347(17), b = 17.1841(18), c = 19.617(2) Å, $\alpha = 101.428^{\circ}$, $\beta = 109.835^{\circ}$, $\gamma = 99.502(3)^{\circ}$, V = 4732.7(9)Å³, Z = 2, $\rho_c = 1.266$ g cm⁻³, $\mu = 0.095$ mm⁻¹, F(000) = 1928, 38 293 reflections collected of which 13 536 were unique, 1211 parameters were refined; Goodness of fit 1.041, $R_1 = 0.0750$, w $R_2 = 0.1985$; max/min. residual electron density 0.770/0.513 e Å⁻³.

Crystallographic parameters of Complex 2: $C_{98}H_{136}N_{14}O_{26}$, M = 1926.21, Crystal dimension $0.18 \times 0.10 \times 0.08 \text{ mm}^3$; T = 100(2) K; Monoclinic, space group $P2_1/n$; a = 13.115(3), b = 27.983(6), c = 13.542(3) A, $\alpha = 90^\circ$, $\beta = 93.325(5)^\circ$, $\gamma = 90^\circ$, V = 4961.8(18) Å³, Z = 2, $\rho_c = 1.289$ g cm⁻³, $\mu = 0.094$ mm⁻¹, F(000) = 2060, 25 345 reflections collected of which 8700 were unique, 627 parameters were refined; Goodness of fit 1.009, $R_1 = 0.0656$, w $R_2 = 0.1634$; max/min. residual electron density 0.456/0.396 e Å⁻³.

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