



# Implications of hydrogen/halogen-bond in the stabilization of confined water and anion-water clusters by a cationic receptor



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## ABSTRACT

Anion complexation of benzene capped flexible tripodal receptor and solid state stabilization of discrete hybrid anion-water or infinite water clusters by various supramolecular interactions are reported here. The crystal structure of the receptor in protonated states shows all the three arms projected in one direction. We structurally demonstrate discrete fluoride-water cluster  $[F_2-H_2O]^{2-}$  and square shaped chloride-water cluster  $[Cl_2-(H_2O)_2]^{2-}$  inside the cationic channel of the receptor. Structural analysis also reveals that these clusters are stabilized inside the channel through active participation of N/C/Ow'H...Ow, N/C/Ow'H...X<sup>-</sup> (X<sup>-</sup> = F<sup>-</sup>, Cl<sup>-</sup> and I<sup>-</sup>) H-bonds and electrostatic interactions. Moreover, C-H... $\pi$  and  $\pi$ ... $\pi$  types weak intermolecular interactions appear to play crucial role in supramolecular assembly of receptor. Additionally, on treatment with hydroiodic acid (HI) **L** resulted zwitterionic iodide complex. Crystal structure reveals the presence of S...I halogen bonded dimer, I<sub>2</sub>...I halogen bond, 1D infinite water chain and neutral iodine molecules. It is comprehensible that ligand basal structure (benzene capped and N-bridge head in two tripodal) play crucial roles in the formation of diverse halide-water cluster. All structures were well examined by different techniques such as NMR, IR, TGA, DSC, PXRD and XRD.

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## 1. Introduction

The most essential water molecule has been matter of intense research because of its important function in several biological and chemical processes [1–4]. Role of water molecule mostly remains unexplained. Hence an intensive research has been done to explore key role in protein folding [5], stabilization of biomolecules [6] and protein crystallization [7]. Moreover, structural study of small water cluster indeed exploited towards understanding of chemical insight into the bulk water [8,9], complex ice structure [10], their anomalous property and elusive array of water molecules in hydration shell [11]. Therefore, interpretation on diverse morphology of water clusters has dominated the recent research [12–19] which includes 1D chain, 2D sheets structure and 3D network with discrete to infinite structural motif. These results help to elucidate mysterious H-bonding pattern, self-aggregated structure and various interactions with host molecule in confined synthetic systems.

Aggregation of solvated anions have been focused recently owing to various imperative role such as ion translocation in water membrane interface [20,21], diffusion of ion across bilayer membrane [22,23], electrical phenomena in troposphere and ionosphere [24–27] and mobility of ions in ion channel [28–31]. Hence characterization of various topology of anion-water cluster in restricted environment is also important to evolve complex H-bonding network around hydrated anion. Compared to water assemblies the hybrid anion-water assemblies are not adequately known. However, some recent structural reports on anion-water clusters [32–37] has given an understanding on anion-water structure. Among the inorganic anions, halide ions particularly are special interest due its natural occurrence and key role in several biological processes [38–45]. These are the intriguing factors to study H-bonding network of water and anion-water cluster in confined environment. In the course of our current research, we have already established aggregation of anion-water clusters and their structure directing role in various supramolecular hosts [46–55]. Herein we have chosen mercaptobenzimidazole substituted benzene capped flexible tripodal receptor which successfully described confinement of fluoride-water cluster  $[F_2-H_2O]^{2-}$  and square shaped chloride-water cluster  $[Cl_2-(H_2O)_2]^{2-}$  inside its cationic channel. It

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is worth to mention that iodide complex of **L** is found to stabilize neutral iodine and 1D infinite water chain  $[\text{H}_2\text{O}]_\infty$  by  $\text{I}\cdots\text{Ow}$  H-bond and  $\text{I}_2\cdots\text{I}$  halogen bond.

## 2. Experimental section

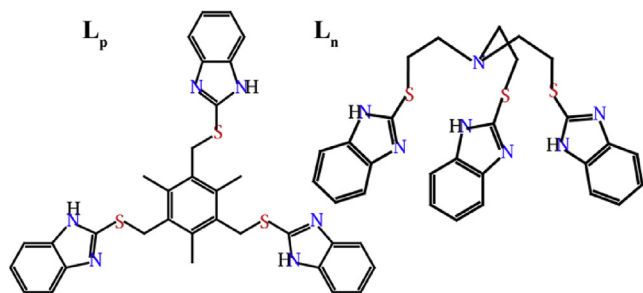
### 2.1. Materials and methods

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian FT-600 MHz spectrometer in  $d_6$ -DMSO at 298 K. The IR spectra were recorded on a Perkin–Elmer–Spectrum One FT-IR spectrometer with KBr disks in the range 4000–500  $\text{cm}^{-1}$ . The starting materials triethanol amine, thionyl chloride and mercaptobenzimidazole (**L**) were purchased from Sigma–Aldrich, USA and were used as received and 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene [56] and tripodal receptor presented here (**L<sub>p</sub>**) [57] were prepared through the modification of previously reported procedure. Solvents were purchased from Spectrochem Ltd., India. Chemical shifts for  $^1\text{H}$  and  $^{13}\text{C}$  NMR were reported in parts per million (ppm), calibrated to the residual solvent peak set. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a TA Instruments Q20 differential scanning calorimeter and SDT Q600 analyzer under nitrogen atmosphere with a heating rate of 2  $^\circ\text{C}/\text{min}$ .

### 2.2. Synthesis and characterization

#### 2.2.1. Synthesis of tripodal receptor **L<sub>p</sub>** (**1**)

The planar benzene capped tripodal receptor **L<sub>p</sub>** (Scheme 1) was synthesized by following procedure (Scheme S1). To a solution of 2-mercaptobenzimidazole **L** (0.900 g, 6.0 mmol) in 30 ml acetone:ethanol (3:1) crushed NaOH (0.240 g, 6.0 mmol) was added, and the solution was refluxed for 1 h. A 20 ml acetone containing 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (0.800 g, 2.0 mmol) was added at once, and the reaction mixture was further refluxed for another 24 h at 80  $^\circ\text{C}$ . After completion of reaction the white precipitate was filtered off and washed several times with cold water followed by acetone-ethanol (3:1) mixture. The white mass then dried under vacuum. The characterization was done by using crystalline materials of **L<sub>p</sub>** (see note). Yield = 65%, M. P: 345  $^\circ\text{C}$ .  $^1\text{H}$  NMR (600 MHz,  $d_6$ -DMSO)  $\delta$  (ppm): 7.457 (d 1H, C–H<sub>ar</sub>), 7.130 (dd 2H, C–H<sub>ar</sub>), 4.643 (s 2H, C–H<sub>alp</sub>), 4.587 (s 1H, N–H), 2.479 (s 3H, C–H<sub>alp</sub>).  $^{13}\text{C}$  NMR (150 MHz,  $d_6$ -DMSO)  $\delta$  (ppm): 16.53, 32.24, 109.44, 121.48, 123.25, 132.87, 136.87 and 149.62. IR spectra (KBr pellet): 2962  $\text{cm}^{-1}$  vs(C–H), 1500  $\text{cm}^{-1}$  vb(C=N), 1445  $\text{cm}^{-1}$  vs(C=C), 1268  $\text{cm}^{-1}$ , 1231  $\text{cm}^{-1}$ . ESI-mass in methanol: m/z 607.23 in positive mode.



**Scheme 1.** Illustration of benzene capped and apical N-atom based tripodal receptors **L<sub>p</sub>** and **L<sub>n</sub>** respectively.

### 2.3. Crystallographic refinement details

The crystallographic data and details of data collection of all compounds are given in Table 1. In each case, a crystal of suitable size was selected from the mother liquor and immersed into silicone oil, then mounted on the tip of a glass fiber and cemented using epoxy resin. Intensity data for the all crystals were collected Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 298 K, with increasing  $\omega$  (width of 0.3 $^\circ$  per frame) at a scan speed of 6 s/frame on a Bruker SMART APEX diffractometer equipped with CCD area detector. The data integration and reduction were processed with SAINT software [58]. An empirical absorption correction was applied to the collected reflections with SADABS [59]. The structures were solved by direct methods using SHELXTL [60] and were refined on  $F^2$  by the full-matrix least-squares technique using the SHELXL-97 program package [61]. Graphics are generated using MERCURY 2.3 [62]. In all cases, non-hydrogen atoms are treated anisotropically. Wherever possible, the hydrogen atoms are located on a difference Fourier map and refined. As an example hydrogen atoms associated with water molecules in complexes **3**, **4** and **5** were located in the Fourier map and were isotropically refined. In other cases, the hydrogen atoms are geometrically fixed. All the imidazole hydrogen atoms in **2**, **3**, **4** and **5** are geometrically fixed.

### 2.4. Crystallization of complexes

#### 2.4.1. [ $L_p\text{H}_2\text{-2F-H}_2\text{O}$ ](**2**)

To a methanol solution containing **L<sub>p</sub>** (0.060 g, 1.0 mmol) in plastic container 0.1 ml of hydrofluoric acid (1.2 equiv. 40% HF) was added and stirred for 1 h. The clear solution was left open to atmosphere. After 1–2 weeks solution afforded colorless needle shape X-ray mountable crystals. Yield = 70%, M. P: 360  $^\circ\text{C}$ .  $^1\text{H}$  NMR (600 MHz,  $d_6$ -DMSO)  $\delta$  (ppm): 7.567 (d 1H, C–H<sub>ar</sub>), 7.264 (dd 2H, C–H<sub>ar</sub>), 4.726 (s 2H, C–H<sub>alp</sub>), 3.687 (broad 1H, N–H), 2.549 (s 3H, C–H<sub>alp</sub>). IR spectra (KBr pellet): broad band at 3202  $\text{cm}^{-1}$  vs(O–H), 2965  $\text{cm}^{-1}$  vs(C–H), 1503  $\text{cm}^{-1}$  vb(C=N), 1435  $\text{cm}^{-1}$  vs(C=C), 1270  $\text{cm}^{-1}$ , 1222  $\text{cm}^{-1}$ .

#### 2.4.2. [ $L_p\text{H}_2\text{-2Cl-2H}_2\text{O}$ ](**3**)

Preparation of complex **3** was identical to that of complex **2**, except that hydrochloric acid (1.2 equiv. 37% HCl) was added in place of HF acid. After one-week solution afforded colorless needle shape X-ray mountable crystals. Yield = 80%, M. P: 381  $^\circ\text{C}$ .  $^1\text{H}$  NMR (600 MHz,  $d_6$ -DMSO)  $\delta$  (ppm): 7.565 (d 1H, C–H<sub>ar</sub>), 7.252 (dd 2H, C–H<sub>ar</sub>), 4.714 (s 2H, C–H<sub>alp</sub>), 3.587 (broad 1H, N–H), 2.537 (s 3H, C–H<sub>alp</sub>). IR spectra (KBr pellet): broad band at 3205  $\text{cm}^{-1}$  vs(O–H), 2972  $\text{cm}^{-1}$  vs(C–H), 1508  $\text{cm}^{-1}$  vb(C=N), 1440  $\text{cm}^{-1}$  vs(C=C), 1265  $\text{cm}^{-1}$ , 1222  $\text{cm}^{-1}$ .

#### 2.4.3. [ $L_l\text{-0.5I}_2\text{-H}_2\text{O}$ ](**4**)

Preparation of complex **4** was identical to that of complex **2**, except that hydroiodic acid (1.2 equiv. 55% HI) and **L** were mixed in place of HF acid and **L<sub>p</sub>** respectively. After 1–2 weeks solution afforded dark red needle shape X-ray mountable crystals. Yield = 75%, M. P: 211  $^\circ\text{C}$ .  $^1\text{H}$  NMR (600 MHz,  $d_6$ -DMSO)  $\delta$  (ppm): 7.680 (dd 2H, C–H<sub>ar</sub>), 7.409 (d 1H, C–H<sub>ar</sub>), 4.017 (broad 1H, N–H).  $^{13}\text{C}$  NMR (150 MHz,  $d_6$ -DMSO)  $\delta$  (ppm): 87.80, 113.54, 124.01 and 138.22. IR spectra (KBr pellet): broad band at 3407  $\text{cm}^{-1}$  vs(O–H), 3042  $\text{cm}^{-1}$  vs(C–H), 2964  $\text{cm}^{-1}$  vs(C–H), 2916  $\text{cm}^{-1}$ , 2861  $\text{cm}^{-1}$ , 1620  $\text{cm}^{-1}$ , 1509  $\text{cm}^{-1}$  vb(C=N), 1450  $\text{cm}^{-1}$  vs(C=C), 1222  $\text{cm}^{-1}$ .

#### 2.4.4. [ $L_n\text{H}_3\text{-3Br-4H}_2\text{O}$ ](**5**)

Preparation of complex **5** was identical to that of previously reported chloride complex except that hydrobromic acid was added in place of HCl acid [50]. Methanolic solution of **L<sub>n</sub>** was acidified to

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