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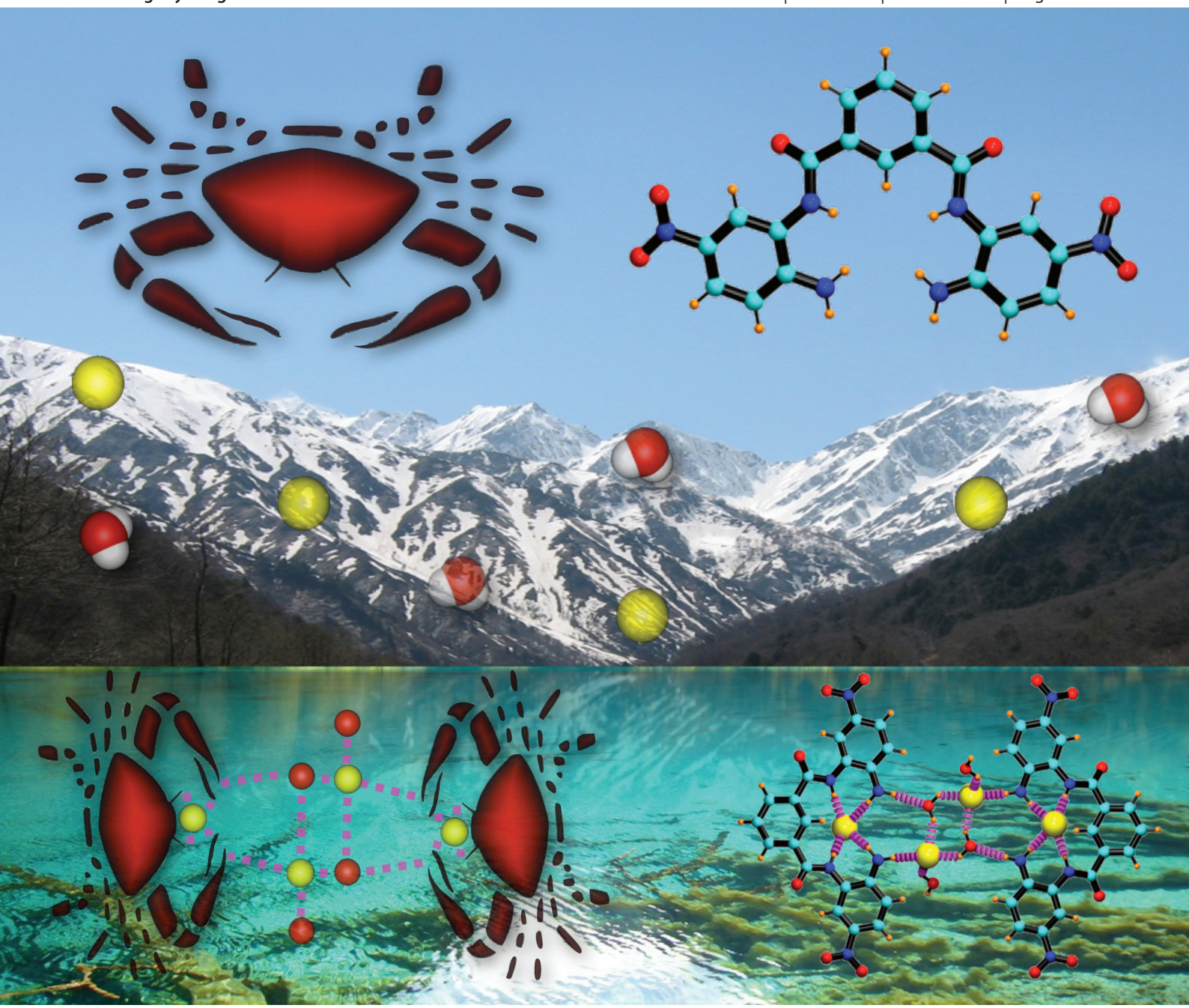

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Akhtarul Alam, Guchhait *et al.*

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COMMUNICATION

An efficient size-selective anion binding cleft-shaped receptor: A novel $[F_2(H_2O)_3]^{2-}$ cluster with pseudo-encapsulated F^- ion†

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A cleft-shaped receptor 1 was synthesized and its anion binding properties have been investigated. Receptor 1 can selectively recognize fluoride ion by naked-eye color change and UV-vis spectral changes in aqueous-acetonitrile solvent. The single crystal X-ray analysis of 1 with fluoride ion shows that there are two types of fluoride ions in the unit cell, one of which is *pseudoencapsulated* within the cleft-shaped cavity and the other type forms a dimer through $[F_2(H_2O)_3]^{2-}$ *fluoride-water cluster*.

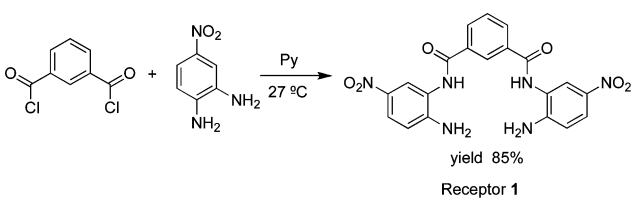
The recognition and sensing of anions have attracted considerable attention in the past decades because of the important roles played by anions in biological, industrial, and environmental processes.[1–3] In particular, the selective sensing of fluoride ion has gained tremendous attention due to its significance in clinical treatment for osteoporosis and fluorosis.[4,5] In this regard, the development of chemosensors for fluoride ion detection in aqueous medium is one of the most challenging targets for anion recognition due to its small size, high electronegativity, and high hydration enthalpy.[6] Thus, the fluoride ion detection limit is restricted in organic solvent.[7] However, during crystallization fluoride ion combines with a water molecule and forms a fluorine water cluster.[8]

In this regard, here, we report a cleft-shape molecular receptor **1** having amide and amine binding sites with an electron withdrawing nitro group, namely; signaling unit, can selectively detect fluoride ion through the naked eye color change as well as UV-vis spectral changes in aqueous-acetonitrile medium. Furthermore, the single crystal X-ray analysis of **1** with fluoride ions shows that there are two types of fluoride ion in the unit cell, one of which is ***pseudoencapsulated*** within the cleft-shape cavity and the other fluoride ion takes part in dimer formation through a $[F_2(H_2O)_3]^{2-}$ ***fluoride-water cluster***. To the best of our knowledge this is the first example where a single anion receptor contains both non-hydrated[9] and hydrated fluoride ions.[8]

The cleft-shaped receptor **1** was synthesized by reacting isophthaloyl chloride with two equivalents of 4-nitro-*o*-phenylenediamine in the presence of pyridine (Scheme 1).[10] The compound **1** was characterized by ^1H and ^{13}C NMR and IR spectra (ESI, Fig. S1 and S2†). The anion sensing capability and binding affinity of **1** was studied by absorption spectral changes in the presence of various anions such as F^-, $H_2PO_4^-$, AcO^-, Cl^-, Br^-, I^-, NO_2^-, NO_3^-, ClO_4^-, HSO_3^- and HSO_4^- in aqueous-acetonitrile medium (CH_3CN, H_2O and DMSO v/v 95 : 4 : 1).

Visual color change of receptor **1** (1.0×10^{-5} M) was investigated in aqueous-acetonitrile medium. Upon addition of two equivalents of F^- ion to the solution of **1**, a detectable naked-eye color change was observed from colorless to intense yellow color (Fig. S3†). However, under similar experimental conditions, addition of $H_2PO_4^-$ and AcO^- ions exhibit only a faint yellow color. Other ions, such as Cl^-, Br^-, I^-, NO_2^-, NO_3^-, ClO_4^-, HSO_3^- and HSO_4^- did not exhibit any detectable naked-eye color change.

To get a better insight into the cause of colorimetric detection of anions by receptor **1**, we have investigated the UV–vis spectral changes upon addition of different anions. Receptor **1** in the absence of any anionic guest shows an absorption band at ~278 (sh) nm and ~364 nm (Fig. 1). The higher energy band at ~278 nm corresponds to the π–π^* transition of the aromatic system and the lower energy broad band at ~364 nm arises due to charge transfer processes occurring in the entire molecular unit. However, upon adding increasing amounts of F^- ion to the aqueous-acetonitrile solution of receptor **1**, the peak at 364 nm gradually decreases in its intensity with a gradual appearance of a new absorption band at 395 nm (Fig. S4, ESI†). Interestingly, two distinct isosbestic points at 377 and 325 nm were observed during the titration process indicating the existence of a host–guest H-bonding complexation equilibrium between the bare



Scheme 1 Synthetic route of receptor **1**.

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† Electronic supplementary information (ESI) available: Experimental details, Synthesis, ^1H, ^{13}C NMR, Naked-eye color change, UV-vis spectra ORTEP diagram and crystallographic tables. CCDC reference number 842781. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce06286k

‡ Responsible for X-ray crystal analysis.

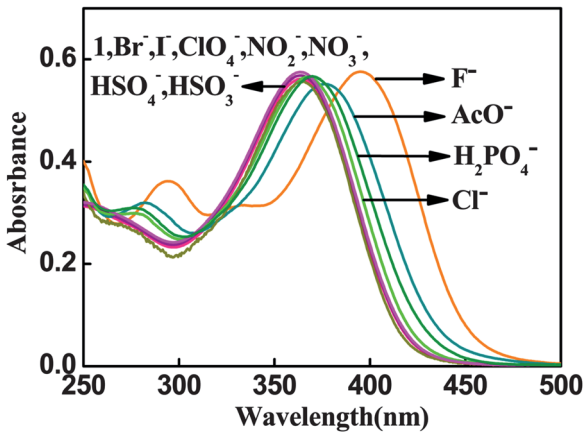

Fig. 1 UV-vis spectral changes of **1** in the presence of various anions in aqueous-acetonitrile solvent.

receptor **1** and fluoride ion. The Benesi–Hildebrand (B–H) plot[11] of $1/[A - A_0]$ *vs.* $1/[F^-]^2$ for the titration of **1** and F^- ion provides a straight line (Fig S5†), indicating 1 : 2 complex formation with association constant (K) 4.7×10^8 M^{-2}. The cause of these visual color changes and UV-vis spectral changes might be due to the hydrogen bonding interaction between the amide/amine proton and F^- ion. The H-bonding interaction of the amide/amine moiety caused a significant increase in the charge density on the amide/amine nitrogen and an internal charge transfer (ICT) occurred between the amide/amine group (donor) to the electron withdrawing nitro group (acceptor), resulting in bathochromic shifting in the absorption spectra.

On the other hand, under similar experimental conditions, upon adding increasing amounts of AcO^-, $H_2PO_4^-$ and Cl^- ions, the peak at 364 nm of receptor **1** is shifted gradually to the higher wavelengths at 380, 370 and 366 nm, respectively (Fig. 1, S6–S8†). However, on addition of other competitive anions such as Br^-, I^-, NO_2^-, NO_3^-, ClO_4^-, HSO_3^- and HSO_4^-, there are hardly any notable spectral or color changes observed, indicating no interaction or complexation of such anions with receptor **1**.

To get further evidence for the H-bonding interaction between **1** and F^- ion in solution, we have performed ^1H NMR titrations in DMSO-d_6 solvent (Fig. 2). Upon addition of 0.5–2.0 equiv. F^- ion, the peaks at 9.87 and 6.59 ppm, which were assigned to the amide (–CONH) and amine ($–NH_2$) protons, respectively shifted to downfield with spectral broadening, indicating the formation of a H-bonding complex between **1** and F^- ion. On further addition of F^- ion, the amide and amine proton peaks completely disappeared and this might be due to deprotonation of the respective protons. Interestingly, the aryl $–CH_b$ proton also exhibits a downfield shift.[9] These observed phenomena indicates a structural alteration of **1** that could influence both the amide, amine and aryl $–CH_b$ protons due to pseudo-encapsulation of the fluoride ion. However, in the case of other anions no appreciable changes in the chemical shift were observed, suggesting the non-interacting nature or very weak interactions of the respective anions with receptor **1**.

Although the basicity of the anions play an important role for selective binding through strong hydrogen bonding interaction with the receptor, however, in the present studies the size and structure of the anion play the pivotal role. Receptor **1** displayed the strongest binding affinity towards F^- ion which might be due to its highest electronegativity and the optimal shape complementarities between spherical F^- and cleft shaped receptor **1**.

To rationalize our experimental results obtained from colorimetric test and spectroscopic (UV-vis and NMR) investigation, we have successfully performed the crystal structure analysis of the **1**-fluoride complex, obtained from slow diffusion of diethyl ether into acetonitrile solution of a 1 : 2 mixture of **1** and Bu_4NF. The compound was crystallized in the space group $P2_1/c$ (Table S1†) with the molecular formula of $[\mathbf{1}\text{-}F_2.(n\text{-}Bu_4N)_2 \cdot 1.5H_2O]$ (Fig. 3). The crystal structure shows that two fluoride ions are in two different positions (Fig. S9†). The F1 atom is situated at the centre of the two amide (–CONH–) groups and two amine ($–NH_2$) groups and are strongly hydrogen bonded with four N atoms (distances F1···N2, F1···N3, F1···N7, F1···N8 are 2.764, 2.780, 2.768, 2.752 Å, respectively, Fig. 4 and Table S2†). Importantly the amide N–H protons are pointing upwards with respect to the amine N–H and the amide C=O groups are pointing downwards with respect to the mean molecular plane. To avoid the steric repulsion between F1 and C–H hydrogen of the phenyl ring (1,3-biscarboxamide), the C–H hydrogen is pointing downwards with a 15° angle of deviation from the molecular plane and weakly H-bonded with the fluoride ion (distance 2.79 Å and ∠ D–H–A 109°). It is noteworthy to mention that the fluoride anion

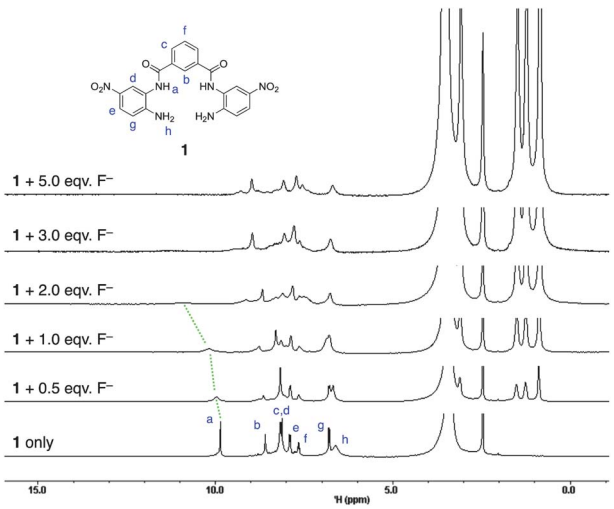

Fig. 2 ^1H NMR spectral shift of **1** in the presence of F^- ion in d_6-DMSO.

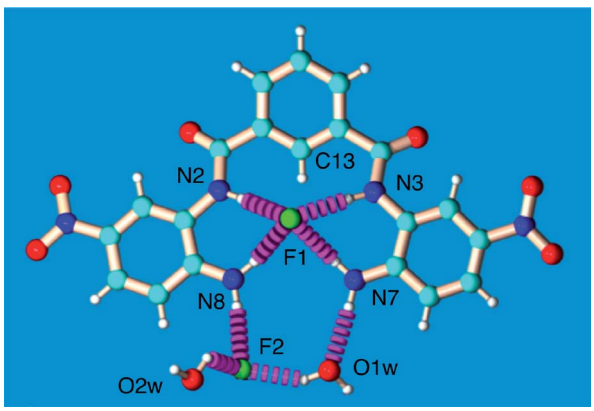

Fig. 3 Molecular structure of **1**.F^- complex. Tetrabutylammonium (n-Bu_4N^+) cations were omitted for clarity.

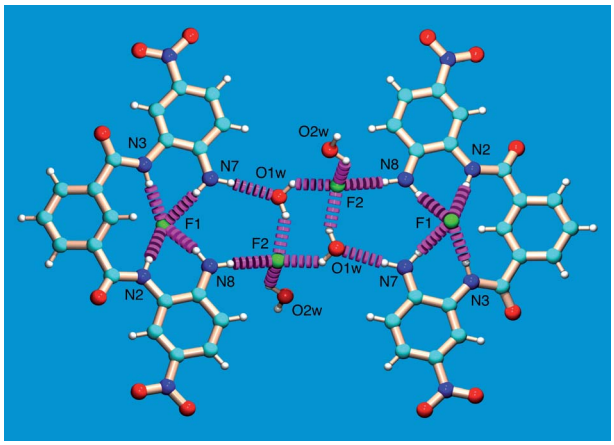

Fig. 4 H-bonding network within the dimeric unit of **1**.F^- complex, *n*-Bu_4N^+ ions were omitted for clarity.

(F1) is not fully encapsulated inside the cleft-shaped macrocyclic cavity of **1**, but it is placed slightly upwards about 1.01 Å from the mean plane passing through two amide 'N' atoms and two amine 'N' atoms consecutively, producing a distorted square pyramidal like structure where the fluoride ion is at the apex of the pyramid (Fig. 5).

The F2 fluoride ion is hydrogen bonded with the N8 atom of the amine group (distance F2···N8 is 2.895 Å) and 1.5 units of the water molecule (O1w and O2w distances F2···O1w and F2···O2w are 2.709 and 1.992 Å, respectively, Fig. 4 and S10†). On the other hand, the hydrogen atom of another amine group (N7 atom) is strongly hydrogen bonded with the O1w atom of the water molecule (distance O1w···N7 2.931 Å, Fig. 4). Importantly, the water molecule in the crystal might come from the hydrated tetrabutylammonium fluoride salt or solvent or atmospheric moisture.

A lattice diagram shows that one molecular unit of **1** connected with another molecular unit through $[F_2(H_2O)_3]^{2-}$ ***fluoride-water cluster*** and formed a dimer (Fig. 4 and 6). The overall crystal structure description summarized as, the four hydrogen atoms (two from amide groups and two from amine groups) are capable of holding an ***isolated fluoride ion*** and the remaining two extra hydrogen atoms from the two amine groups are responsible for forming a dimer through $[F_2(H_2O)_3]^{2-}$ cluster formation. In other words the ***fluoride-water cluster*** facilitates the formation of the dimer or *vice versa*. All the hydrogen bonding interactions are summarized in Table S2.†

Finally we have tried to get crystals from other anions with receptor **1** but after several attempts we failed to get single crystals with other anions. This might be due to the very small cavity of receptor **1** and hence, it can not accommodate other anions except F^- ion or it might be unable to form such stable crystals as with fluoride ion.

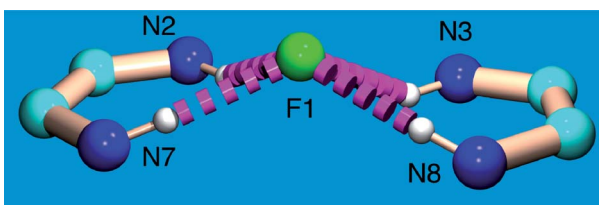

Fig. 5 Pseudo-encapsulated fluoride ion in distorted square pyramidal like structure where the fluoride ion is at the apex of the pyramid.

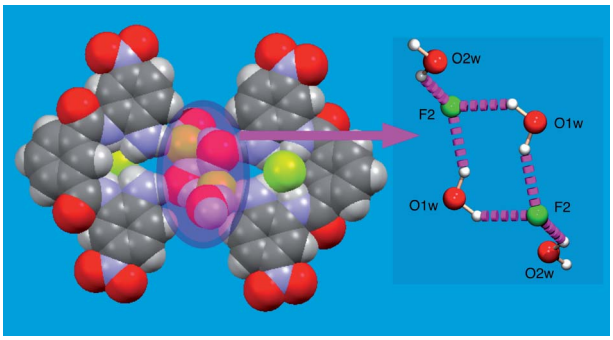

Fig. 6 Space-filling view of dimeric unit (left) and $[F_2(H_2O)_3]^{2-}$ cluster (right).

In summary, a simple cleft-shaped anion receptor **1** containing amide and amine groups as recognition units with a $-NO_2$ signalling group was synthesized using minimal synthetic procedures. Receptor **1** can selectively sense fluoride ion over other competitive anions by naked-eye color change and UV-vis spectroscopic changes in aqueous-acetonitrile medium. The crystal structure analysis shows that receptor **1** binds with two fluoride ions and forms a stable 1 : 2 hydrogen bonded complex. Importantly, one of the fluoride ions is ***pseudoencapsulated*** or ***isolated*** within the cleft-shaped cavity of receptor **1** and the other fluoride ion forms a dimer through $[F_2(H_2O)_3]^{2-}$ ***fluoride-water cluster*** formation. The hydrated fluoride selectivity of receptor **1** has potential application to the selective removal of fluoride ion in its hydrated form in aqueous medium. Presently we are exploring such applications.

Acknowledgements

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