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Imidazolidinium-based robust crypt with unique selectivity for fluoride anion†

Bing-guang Zhang,[a] Ping Cai,[a] Chun-ying Duan,*[a] Ren Miao,[a] Long-gen Zhu,[a] Takashi Niitsu*[b] and Hakuai Inoue[b]

[a] *Coordination Chemistry Institute, The State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, P. R. China. E-mail: duancy@nju.edu.cn; Fax: +86 25 8359 4502; Tel: +86 25 8359 7006*

[b] *Department of Bioengineering, Faculty of Engineering, Soka University, Hachioji, Tokyo 192, Japan*

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A new imidazolidinium based receptor exhibiting unique affinity and high selectivity for fluoride anion through steric requirements and the cooperativity of multiple intramolecular binding, has been designed, synthesized and structurally characterized.

In recent decades, supramolecular chemists have devoted considerable effort to developing receptors that only bind a single anion from a collection of putative anion species.[1,2] Receptors for the smallest anion, fluoride, are of special importance due to fluoride's unique properties, compared to its congeners, as a result of its relative size and electronegativity. While a number of compounds that are able to bind fluoride ions with high affinity and selectivity have been reported, challenges in creating unique selectivity for fluoride anion still remain.[3,4] For example, 1,4,7,10,13,16,21,24-octaazabicyclo[8.8.8]hexacosane, **1**, is well known to display an incredible affinity for fluoride anion[5] ($\log K_s$ values of 10.70 and 11.18 in aqueous solution reported under slightly different conditions), however, further studies also provide evidence that the selectivity patterns can change dramatically as a function of pH, due to the inherent flexibility of these systems.[6] As a continuance of our research work on the tri(2-aminoethyl)amine based crypts,[7] we report here a new positively charged receptor **2**, by introducing robust imidazolidinium groups into the arms of crypt **1** (Scheme 1). The selectivity of the crypt is controlled by the steric requirement of the host: the small fluoride anion is able to enter the cavity, whereas larger anions are efficiently blocked. Since the radius of the fluoride ion is significantly shorter than that of other anions, a highly specific receptor for fluoride is expected.

When compound **1** was treated with triethylorthoformate at 120 °C in dry xylene, a white solid was readily formed. Elemental analysis and spectroscopic characterization suggest the formation of the new imidazolidinium-linked compound **2**·3ClO_4·H_2O. An X-ray crystallographic study‡ has unequivocally confirmed the existence of a tricationic imidazolidinium. In compound **2**, the tricationic crypt was empty and had a pseudo-C_3 symmetry (Fig. 1) with the apical N···N separation *ca.* 5.43 Å (shorter than 6.37 Å for compound **1**).[8] The M [center of the crypt] and the electron deficient carbon atoms were separated by about 2.3 Å. Such a small size of the crypt **2** means it is only capable of binding F^- inside, considering the ionic radius of F^- (1.33 Å) and Cl^- (1.81 Å).

The unique selection of F^- was further supported by the ^{1}H NMR titration (Fig. 2). While the ^{1}H NMR signals for all the hydrogen atoms did not vary obviously in the presence of excess chlorine anion (10 times the number of moles of host), significant downfield shifts of the imidazolidinium rings H_α resonance[9] (shifted from 6.20 to 7.15 ppm) were observed until 1 molar equivalent of NaF was added. Further addition of fluoride anion resulted in saturation of the chemical shift changes, indicating that the receptor **2** formed a stable 1 : 1 stoichiometric complex with the fluoride anion. Similar downfield shifts were also found for the other hydrogen atoms attached to the CH_2 atoms, H_β (from 3.25 to 3.92 ppm), H_γ (from 2.75 to 3.28 ppm) and H_δ (from 1.76 to 2.25 ppm), suggesting the strong ancillary interactions of the F^- with the CH_2 protons. The association constant of **2** with fluoride anion was determined ($\log K_s$ = 12.5) using a competition ^{1}H NMR titration instead of conventional NMR titration method.

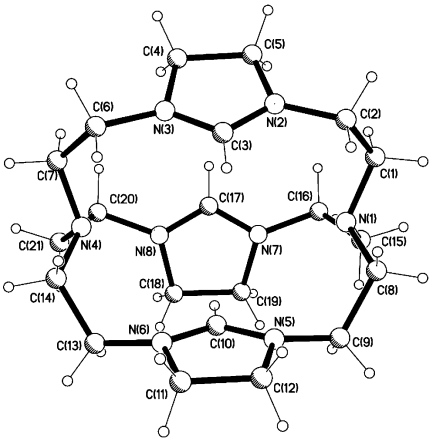
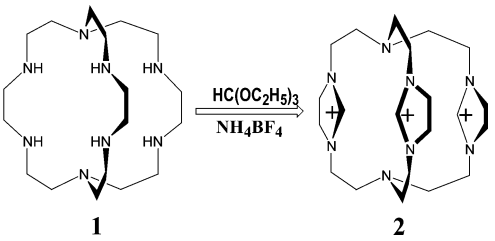


Fig. 1 Perspective views of the free crypt **2**.



Scheme 1

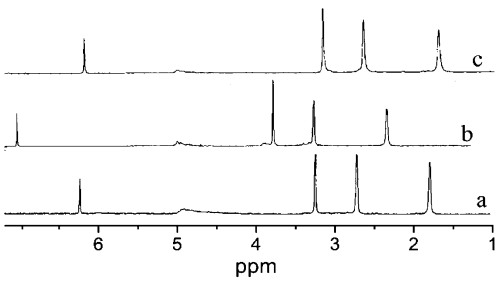


Fig. 2 ^{1}H NMR spectra of compound at pD = 1.0, a: free crypt **2**, b: in the presence of NaF, c: in the presence of NaCl.

† Electronic supplementary information (ESI) available: synthetic procedures and theoretical calculations. See http://www.rsc.org/suppdata/cc/b4/b407434c/

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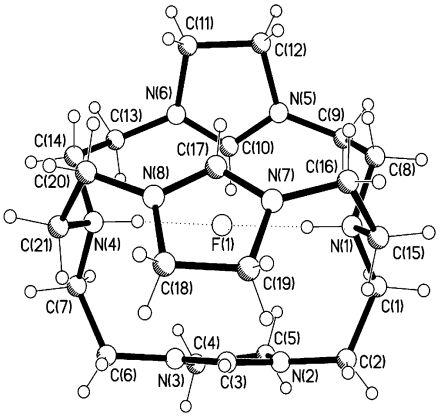

Fig. 3 Perspective views of the imidazolidium contained crypt encapsulating one fluoride anion $F^-\subset\mathbf{2}\cdot H_2$.

The competitive reaction was the comproportionation process of $[ZrF]^{3+}$ ($\log\beta_1 = 8.8$) with constant Zr^{4+} concentration (0.5 M). The ^1H NMR titration measurements clearly indicate that compound **2** is a better receptor for fluoride than **1**, not only in the selectivity, but also for the association constant.

Since the interior compound exhibits higher solubility and the concentration of free F^- is controlled by the pH value due to the dissociation constant of HF in acidic solution, crystals of the interior compound were obtained by maintaining the F^- concentration as constant by using decomposition of BF_4^- in the presence of perchlorate acid.[10] Crystal structure analysis‡ reveals that the crypt in $F^-\subset\mathbf{2}\cdot H_2$ has a pseudo-C_3 symmetry with a F^- ion residing inside (Fig. 3). The F^- is surrounded in a good trigonal bipyramidal geometry with two protonated tertiary bridgehead nitrogen atoms occupied at the axial positions and three planar imidazolidinium rings positioned on the equatorial plane. The N–H···F hydrogen bonds are characterized by average N···F separations of 2.61 Å and N–H···F angles of 176°. The F···C separations of 2.57–2.60 Å corresponding to the electron deficient carbon atoms suggest possible C–H···F hydrogen bonds, however, both the C–H···F angles and H–C···F angles (80° on average) are, surprisingly, too small to support this hypothesis. Not unexpectedly, the cavity is much smaller than that of relative compounds: the apical N···N separation is only *ca.* 5.16 Å, compared to 6.65 Å in the fluoride interior[5] $F^-\subset\mathbf{1}\cdot H_6$ and 6.60 Å for the chloride interior[6] $Cl^-\subset\mathbf{1}\cdot H_6$. This means that the crypt holds the fluoride ion more tightly and displays incredible affinity and high selectivity for fluoride anion.

In summary, we have shown the unique selectivity of the imidazolidinium based robust receptor **2** towards the fluoride anion. Crystal structural analyses and NMR spectra suggest that the steric requirement and the cooperativity of multiple intramolecular binding are important factors controlling the high selectivity and affinity.

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Notes and references

‡ Crystal data of $\mathbf{2}\cdot 3ClO_4\cdot H_2O$, $[(C_{21}H_{39}N_8)(ClO_4)_3(H_2O)]$, $M_r = 719.97$, triclinic, space group $P\bar{1}$, $a = 10.410(2)$ Å, $b = 17.524(4)$ Å, $c = 18.478(4)$ Å, $\alpha = 71.761(4)°$, $\beta = 88.852(4)°$, $\gamma = 88.393(4)°$, $V = 3200.0(12)$ Å^3, $Z = 4$, $D_{calcd} = 1.568$ Mg m^{-3}, 15923 reflections measured of which 11049 ($R_{int} = 0.063$) were independent and all were included in the refinement. For 897 parameters $R_1 = 0.073$ and $wR_2 = 0.144$. CCDC 230608.

Crystal data of $F^-\subset\mathbf{2}\cdot H_2$, $[(C_{21}H_{41}N_8)F](BF_4)_2(ClO_4)_2(H_2O)$, $M_r = 815.15$, triclinic, space group $P\bar{1}$, $a = 18.247(1)$ Å, $b = 19.0596(9)$ Å, $c = 20.798(1)$ Å, $\alpha = 90.150(1)°$, $\beta = 91.850(1)°$, $\gamma = 108.676(1)°$, $V = 6848.0(6)$ Å^3, $Z = 8$, $D_{calcd} = 1.830$ Mg m^{-3}, $F(000) = 6288$. 34252 reflections measured of which 23663 ($R_{int} = 0.060$) were independent and all were included in the refinement. For 2043 parameters $R_1 = 0.073$ and $wR_2 = 0.139$. CCDC 230607.

The structures were solved by direct methods and refined on F^2 using full-matrix least-squares methods using SHELXTL version 5.1. Anisotropic thermal parameters were refined for non-hydrogen atoms. Hydrogen atoms were localized in their calculated positions and refined using a riding model. The perchlorate and the tetrafluoroborate anions were refined as disordered. To assist the refinement, several restraints were applied: (1) all B–F or Cl–O bonds were restrained to be similar; (2) thermal parameters on adjacent atoms in disordered moieties were restrained to be similar. See http://www.rsc.org/suppdata/cc/b4/b407434c/ for crystallographic data in .cif or other electronic format.

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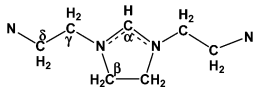

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