

# F<sup>-</sup> Preference of Polyamide Cryptand to Cl<sup>-</sup>

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**Abstract** The variations in geometry structure, IR spectra, as well as the molecular orbitals upon anion recognition for polyamide cryptand are explored with the hybrid density functional theory. The cavity generated by six amide NH groups shrinks upon F<sup>-</sup> recognition because of the strong hydrogen bonds between the amide protons and F<sup>-</sup>, while the cavity expands upon Cl<sup>-</sup> binding because of the strong electron repulsion between the *p* electron of Cl<sup>-</sup> and the lone pair electrons of the nitrogen atom of the pyridine moieties. The “electropositive field space” ...Cl<sup>-</sup> coupling exists when Cl<sup>-</sup> is recognized. The strong anion binding energy with F<sup>-</sup> indicates that the polyamide cryptand prefers F<sup>-</sup> to Cl<sup>-</sup>.

**Keywords** Anion recognition · Host–guest interaction · Polyamide cryptand · IR spectra · Hydrogen bonding · Amine

## Introduction

Molecular recognition refers to the specific coupling between host and guest through noncovalent bonding, such as hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces,  $\pi$ – $\pi$  interactions, electrostatic and/or electromagnetic effects. The synthetic organic chemistry has been significantly affected by the architectural design of various multidimensional and multitopic supramolecular hosts [1–7]. Considerable focus has been put on the robust amides as anion receptors for selective targeting of anions. In this context, a series of amide-based macrocycles and cryptands have been designed and synthesized for anion recognition owing to their amenability to functional applications such as ion-selective electrodes and separations [8–13]. In these systematic reports, acyclic, monocyclic, and bicyclic receptors were synthesized; the structural and binding characteristics with anions are investigated; the influence of hydrogen bonding, dimensionality, as well as charge on structure and selectivity in anion binding were explored.

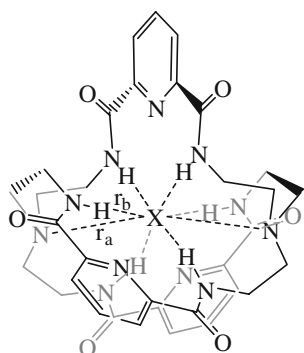
The NMR spectra of these polyamide cryptands as well as the complexes generated after binding with the anions have been determined, while most of the other properties for this kind of cryptands are still pendent. The origin of anion selectivity, the coupling characteristics between host and guest molecules, the role of amide and amine group in molecular recognition processes are all quite worthy of further investigations. It has been reported that the tren-based amide cryptand, **Host**, (Scheme 1) displays high affinity for F<sup>-</sup> than Cl<sup>-</sup> [10]. This result is concluded only from the NMR titration experiments and no related analyses about the other properties are reported yet. Here, the emphasis of this work is put on the geometry structure, IR spectra, binding energy, and the molecular orbital

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**Host** X=Dummy Atom  
**Host-F** X=F<sup>-</sup>  
**Host-Cl** X=Cl<sup>-</sup>

**Scheme 1** Structures of the trenbased amide cryptand (**Host**) and its F<sup>-</sup> and Cl<sup>-</sup> complexes

differences of tren-based amide cryptand during the recognition processes for F<sup>-</sup> and Cl<sup>-</sup> anions.

### Computational methods

The hybrid density functional theory calculations using the nonlocal density function of Becke's three parameters employing the Lee-Yang-Parr functional (B3LYP) with 6-31G(d) basis set has been successfully applied on anion recognition in supramolecular systems [14–17]. Here, all calculations on anion, host, and complexes are carried out employing the B3LYP/6-31G(d) basis set implemented with a suit of Gaussian 03 program [18]. The vibrational frequency analysis is performed for every configuration at the same level to verify whether the optimized structures correspond to true local minima on the global potential energy surface (PES). The obtained zero-point energy is utilized as the correction for anion binding energy,  $E_{AB}$ , which is used generally to denote the capability of the host to recognize the anion.

### Results and discussion

#### Geometry structure

The primary geometry parameters optimized for tren-based polyamide cryptand (**Host**), fluoride complex (**Host-F**), and chloride complex (**Host-Cl**) at B3LYP/6-31G(d) basis set are collected in Table 1. It is impossible to keep the symmetry in experiment owing to the different environment around the system. Therefore, the symmetry of the system is not fixed during the optimization.

The contact distance of two amine nitrogens,  $2r_a$ , in **Host** is 7.465 Å. Three methylene groups interact with

**Table 1** Primary parameters for the optimized geometries

	Host	Host-F	Host-Cl
$2r_a^a$	7.465	7.728	7.900
$2r_b$	4.385	3.840	4.650
$E_{AB}$		-142.9	-61.4

<sup>a</sup>  $2r_a$  refers to the contact distance of two amine N atoms of the pyridine moieties;  $2r_b$  denotes the length of two opposite amide protons. Both of them are in Å.  $E_{AB}$  is the binding energy between the **Host** and the anion, which is in kcal/mol

each N atom of the pyridine moieties pointing to the outside the cryptand. The length between two opposite amide protons is denoted by  $2r_b$ , which is about 4.385 in **Host**. Six amide protons generate an octahedral cavity. This cavity should be a good recognition site for the electronegative anions.

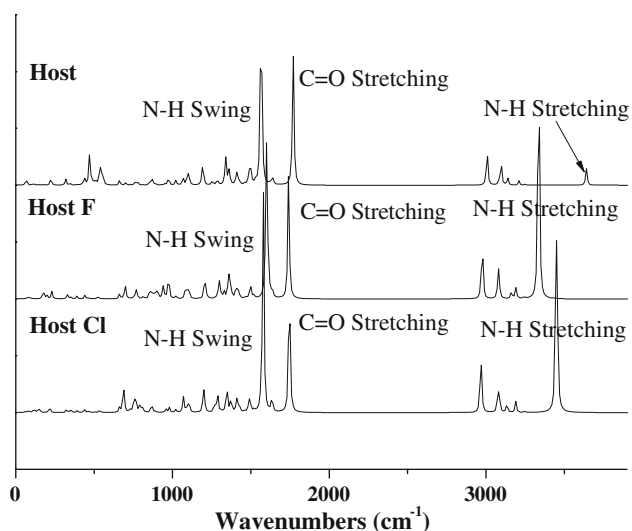
Upon combination with F<sup>-</sup>, the distance of  $2r_a$  increases up to 7.728 Å in **Host-F**. This should be the result of electrostatic repulsion between the recognized F<sup>-</sup> and electronegative amide hydrogen atoms. F<sup>-</sup> locates almost in the center of the system. The hydrogen bonds are formed between the central F<sup>-</sup> and all of the amide protons. The distances between F<sup>-</sup> and the amide protons are about 1.920 Å. Compared with the cavity in **Host**, the octahedral cavity shrinks in binding with F<sup>-</sup>. The anion recognition is mainly accomplished by the synergetic effect of six amide NH groups by forming the hydrogen bonds.

The distance of  $2r_a$  lengthens more significantly when the **Host** recognizes Cl<sup>-</sup>, 7.900 Å. It is a little longer than the case for F<sup>-</sup>. This phenomenon is reasonable with the consideration of their atomic radii. Here, the Cl<sup>-</sup> in **Host-Cl** is also situated in the cavity generated by six amide protons, but only a little apart from the center. Two of the hydrogen bonds are relatively longer than the other four. It is in good agreement with the experimental results [10]. The hydrogen bond lengths between Cl<sup>-</sup> and these amide nitrogens are calculated to be 3.273, 3.277, 3.280, 3.280, 3.288, and 3.293 Å, respectively.

#### Vibrational frequency

The vibrational frequency is generally a useful tool to get some information about the molecular structure in experiment. Therefore, the IR spectra are calculated in this work. The calculated IR spectra for **Host**, **Host-F**, and **Host-Cl** at B3LYP/6-31G\* level are all represented in Fig. 1 with the mode assignment for featured vibrations.

The IR intensity of N–H swing and C=O stretching modes in **Host** are very strong. Around 3,600 cm<sup>-1</sup>, a distinct vibrational mode can be found, which is a typical N–H stretching vibration [19]. In binding with both F<sup>-</sup> and



**Fig. 1** The IR spectra of **Host**, **Host-F**, and **Host-Cl** obtained at B3LYP/6-31G\* basis set level

$\text{Cl}^-$ , the IR intensity of N–H stretching vibration for the **Host** significantly enhances and the frequency is remarkably red-shifted. In binding with  $\text{F}^-$ , the N–H stretching vibrational frequency was red-shifted by about  $300\text{ cm}^{-1}$  owing to the strong interactions between N–H bonds and  $\text{F}^-$  anion. While it was red-shifted by about  $150\text{ cm}^{-1}$  upon the  $\text{Cl}^-$  recognition due to the weaker interactions. Thus, it can be drawn that the combination of **Host** with  $\text{F}^-$  should be stronger than with  $\text{Cl}^-$ . In other words, the **Host** molecule prefers  $\text{F}^-$  to  $\text{Cl}^-$ .

A common phenomenon can be found for all these three systems: several vibrational modes exist around  $3,000\text{ cm}^{-1}$ . These modes are assigned as the combination of C–H stretching on methylene group, which directly interact with the nitrogen atoms of the pyridine moieties. It

is clearly shown in Fig. 1 that the anion recognition has very weak influence on these vibrational modes.

### Energy

The binding energy is a distinct criterion to judge the molecular recognition capability. The larger the binding energy is, the stronger the capability to recognize the ion should be. The calculated anion binding energy,  $E_{AB}$ , which is corrected with the zero-point vibrational energy, is represented in Table 1.

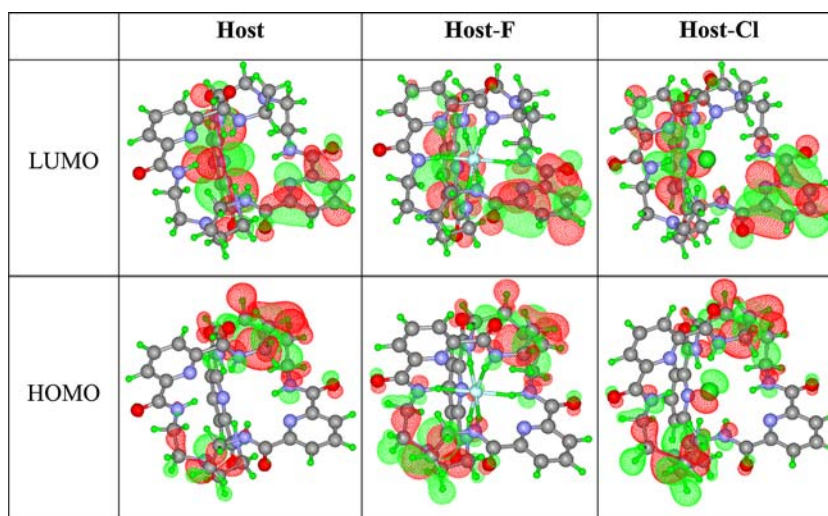
The  $E_{AB}$  of  $\text{F}^-$  is  $-142.9\text{ kcal/mol}$ , while the  $E_{AB}$  of  $\text{Cl}^-$  is only  $-61.4\text{ kcal/mol}$ . This result demonstrates that the binding of **Host** with  $\text{F}^-$  is very strong due to the strong hydrogen bonding interactions. While the coupling between **Host** and  $\text{Cl}^-$  should be the “electropositive field space” ... $\text{Cl}^-$  interaction, which is defined in our previous study [20]. In this system, the electropositive field is generated by six amide NH bonds. The “electropositive field space” ... $\text{Cl}^-$  interaction in **Host-Cl** is a little stronger than the “electropositive field space” ... $\text{F}^-$  coupling in previous systems (ranging from  $-40.9$  to  $-50.1\text{ kcal/mol}$ ). [20] Thus, the strong interaction between the **Host** and  $\text{F}^-$  may be caused by the stronger polarity of N–H bond as compared with that of C–H bond.

### Molecular orbitals

In order to check the influence upon anion recognition, the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of **Host**, **Host-F**, and **Host-Cl** are explored. All the HOMO and LUMO orbitals are shown in Fig. 2.

It can be seen from Fig. 2 that the HOMO electrons of **Host** are populates predominantly on two amine groups

**Fig. 2** The HOMO and LUMO orbitals of **Host**, **Host-F**, and **Host-Cl**



and the linked methylene groups. The lone pair electrons on two amine nitrogen atoms pointing toward the cavity center formed by six amide NH groups. After binding with the anion, the HOMO electrons are still located on two amine groups and the binding methylene groups. The  $p$  electrons on anion ( $F^-$  and/or  $Cl^-$ ) point toward two amine groups. Therefore, the electron repulsion exists between anion and the amine group. This repulsion is obviously stronger between  $Cl^-$  and amine groups as compared to that between  $F^-$  and amine groups. This repulsion should lead to the elongation of  $2r_a$ , the distance of two amine nitrogens. The influence of anion binding on LUMO distribution of **Host** is very weak, as can be seen from the Fig. 2.

## Conclusion

The variations in geometry structure, IR spectra, as well as the molecular orbitals upon anion recognition for polyamide cryptand are explored with the hybrid density functional theory. The electron repulsion between anion and the amine group leads to the elongation of two amine nitrogens. The hydrogen bond interaction between amide NH groups and  $F^-$  is stronger than the “electropositive field space” ... $Cl^-$  coupling between NH groups and  $Cl^-$ . The strong anion binding energy with  $F^-$  indicates that the **Host** prefers  $F^-$  to  $Cl^-$ . The structural changes and the vibrational frequency red-shifts of the **Host** in binding with  $F^-$  and  $Cl^-$  are consistent with the strength of the interaction energies.

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