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Fluoride Recognition of Amide- and Pyrrole-Based Receptors: A Theoretical Study

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ABSTRACT

The novel amide-based receptors, *N*-(anthracen-1-yl)-1*H*-pyrrole-2-carboxamide (**1**) and *N*-(8-(1*H*-pyrrole-2-carboxamido) anthracen-1-yl)-1*H*-pyrrole-2-carboxamide (**2**) have been designed and investigated for their halide ion recognition using the density functional theory calculations in gas and solvent phases. Electronic and thermodynamic properties of halide ion binding complexes of receptors were investigated. Intermolecular interactions in all the studied complexes occurring via hydrogen bonding are found. The designed receptors **1** and **2** are found to be excellent selectivity for fluoride ion in both gas and solvent phases.

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1. Introduction

Anions especially halide ions play an important role in several fields such as biology, the environment, catalysis and potential medical application. The development of anion receptors is one of the most attractive fields of supramolecular chemistry (Steed & Atwood, 2000). To achieve this goal, the anion binding part may consist of urea/thiourea (Jose *et al.*, 2007) (Wanno *et al.*, 2009) (Amendola *et al.* 2006), amides (Bondy & Loeb, 2003) or pyrrole (Zhang *et al.*, 2007) because the NH units are known to interact strongly with anions. Amide-

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and pyrrole-based anion receptors have been used more extensively for anion recognition. Recently, pyrrole-2-carboxamide based compound was synthesized and tested for its anion recognition using spectroscopic methods. The results reveal that it is good for fluoride recognition (Yin *et al.*, 2004). Investigation of binding property of amide- and pyrrole-based receptors toward several halide ion guests using molecular modeling should probably yield useful information for further experimental researches.

In this work, two novel amide- and pyrrole-based receptors, *N*-(anthracen-1-yl)-1*H*-pyrrole-2-carboxamide (**1**) and *N*-(8-(1*H*-pyrrole-2-carboxamido) anthracen-1-yl)-1*H*-pyrrole-2-carboxamide (**2**) which employ pyrrole-2-carboxamide as a binding site connected with anthracene unit have been designed. The interaction of receptors **1** and **2** with spherical shape halide ions i.e. F^-, Cl^-, Br^- and I^- was theoretically investigated using the density functional theory (DFT) method. Electronic and thermodynamic properties for both receptors and their complexes with the halide ions were also determined.

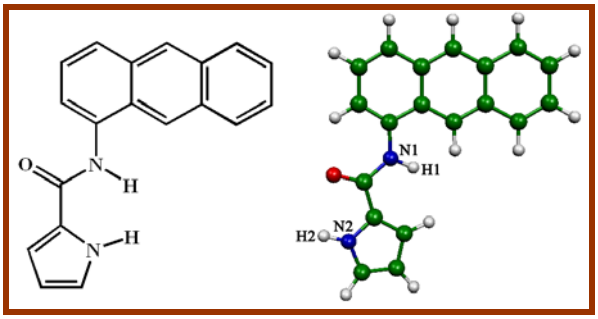

Figure 1: The chemical and optimized structures of the receptor **1**.

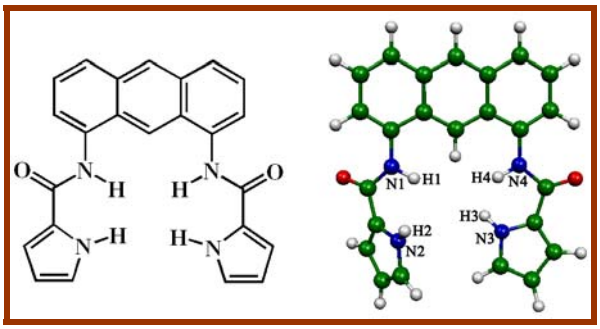

Figure 2: The chemical and optimized structures of the receptor **2**.

2. Computational Methods

The density functional theory has been applied to optimize the structures of amide- and pyrrole-based receptors **1, 2** and their complexes with F^-, Cl^-, Br^- and I^- ions. All DFT calculations have been performed using the Becke's three-parameter exchange functional with the Lee–Yang–Parr correlation functional (B3LYP) (Becke, 1988) (Lee *et al*., 1988). The 6-311G(d,p) basis set was used for all complexation studies except for iodide ion complexation, the 6-31G(d) basis set was used. Stationary points have been fully optimized and characterized by vibrational frequency calculations at 298.15 K and 1 atmosphere, which also provided zero point vibrational correction energy (ΔE_{ZPE}), standard enthalpy (ΔH) and Gibbs free energy changes (ΔG) of the complexations (Ochterski, 2000). The highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (ELUMO) energies were derived from the same level of theory.

For the computations in DMSO, the solvent effect using the conductor-like polarizable continuum model (CPCM) (Barone *et al*., 1998) (Cossi & Barone, 1998) with UAKS cavity model (Frisch *et al*., 2008) was carried out. The natural bond orbital (NBO) analysis implemented in GAUSSIAN 03 program was applied throughout a series of intermolecular interactions under the above system to evaluate the NBO charges. All calculations were performed with the GAUSSIAN 03 program (Frisch *et al*., 2008). The molecular graphics of all related species were generated with the MOLEKEL 4.3 program (Flükiger et al., 2000).

3. Results and Discussion

3.1 Molecular structures and interaction configurations

The geometrical structures of free amide- and pyrrole-based receptors **1**, **2** and their complexes with halide ions F^-, Cl^-, Br^- and I^- computed by full optimization without any constrains are obtained. The chemical and optimized structures of receptors **1** and **2** are displayed in Figures 1 and 2, respectively. The optimized structures of halide ions complexes with the receptors **1** and **2** and their selected geometrical parameters and Gibbs free energy changes are displayed in Figures 2 and 3, respectively. It is found that the molecular symmetries of the receptor **1** complexes with F^-, Cl^-, Br^- and I^- ions are C_1 point group. The molecular symmetries of the receptor **2** complexes with Cl^-, Br^- and I^- ions are C_2 point group whereas the molecular symmetry of the receptor **2** complexes with F^-, is C_S point group. Moreover, from the optimized structures, it is confirmed that halides and receptors **1** and **2**

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can form the stable complexes through hydrogen bond interactions, in which the F^- ion is found to locate at the cavity centers of receptors, the same plane of anthracene unit, whereas Cl^-, Br^- and I^- ions locate at the top of the cavity centers of receptors or above the plane of anthracene unit (see Figures 3 and 4). The complexes between the receptor **1** and halide ions occur via two hydrogen bonds. The average hydrogen bond distances of complexes of F^-, Cl^-, Br^- and I^- are 1.518, 2.424, 2.598 and 3.006 Å, respectively. On the other hand, the halide ions form four hydrogen bonds with all NH protons of the receptor **2** and the hydrogen bond distances of complexes of F^-, Cl^-, Br^- and I^- are 1.735, 2.311, 2.479 and 2.762 Å, respectively. It should be noted here that the hydrogen bond characteristics of receptors complexes with the halide ions bonds are NH---X (X= F^-, Cl^-, Br^- or I^-) types and F^- ion complexes with receptors **1** and **2** are the shortest hydrogen bond distances at the center of receptor cavities. This behavior may be caused by the smallest size of F^- ion.

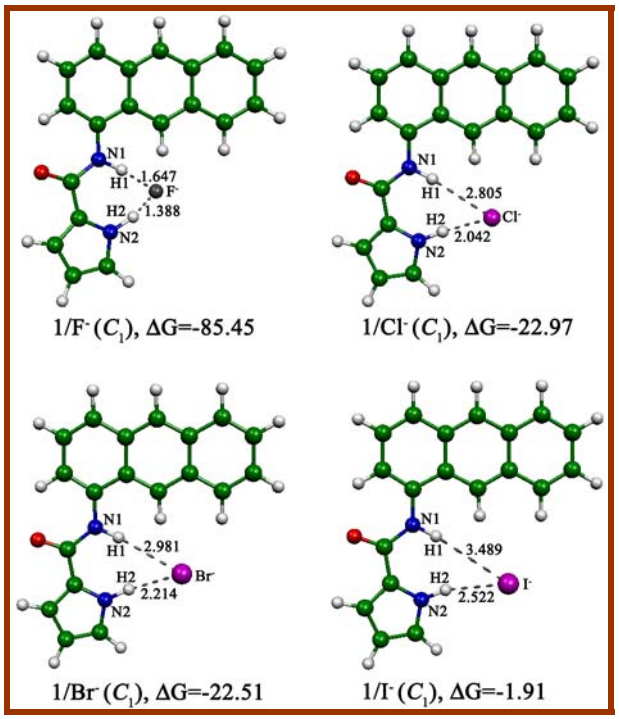

Figure 3: The optimized structures of the receptor **1** complexes with anions, the binding free energies are in kcal/mol and the hydrogen bond distances are in Å.

3.2 Electronic properties

Frontier molecular orbital energies and NBO charges

The highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}) energies, frontier molecular orbital energy gaps (ΔE_{H-L}), of receptors **1**, **2** and

their halide ion complexes are presented in Table 1. The ΔE_{H-L} of all halide ion complexes are slightly different and range between 3.118-3.374 eV for receptor **1** and 3.220-3.272 eV for receptor **2**. The energy gaps of complexes are not much different from their corresponding free receptors. The HOMO and LUMO orbitals of receptors **1** and **2** including their complexes presented over iso-surface value of 0.03 au are displayed in Figures 5 and 6. The HOMO and LUMO orbitals of free receptors **1**, **2** and the LUMO orbitals of all complexes are located over the anthracence unit while for Br^- and I^- ion complexes, their HOMO orbitals are found to locate at both the anthracence unit and Br and I atoms.

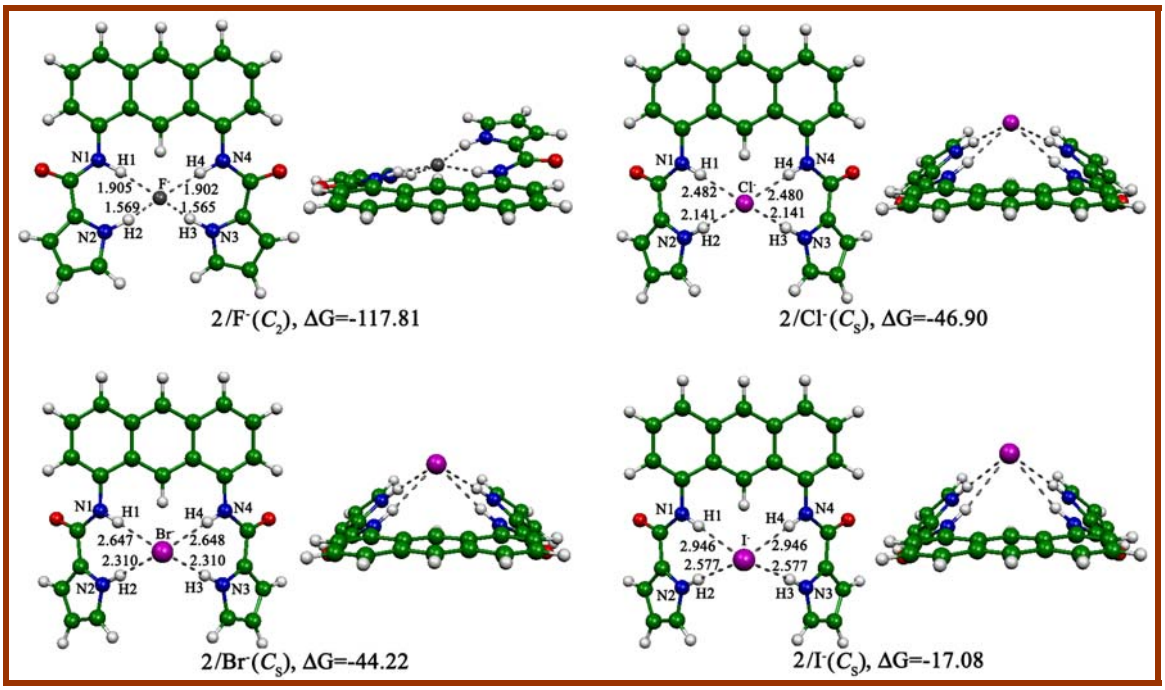

Figure 4: Top and side views of optimized structures of the receptor **2** complexes with halide ions, the binding free energies are in kcal/mol and the hydrogen bond distances are in Å.

For better understanding of interaction between receptor and its halide ion, the NBO atomic charges were computed for consideration of the charge transfer behavior of complexation. Tables 2 and 3 display the selected NBO atomic charges for the optimized structures of free receptors **1** and **2** and their complexes with halide ions. The results show that the highest charge transfer is found in both F^- ion complexes. This indicates that fluoride electron easily transfers to amide and pyrrole protons.

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Table 1: The computed orbital energies (E_{LUMO}), (E_{HOMO}) and frontier molecular orbital energy gap (ΔE_{H-L}) of the receptors **1, 2** and their complexes with anions.

Halide ions	**1**			**2**		
	E_{LUMO}[a]	E_{HOMO}[a]	E_{H-L}[a]	E_{LUMO}[a]	E_{HOMO}[a]	ΔE_{H-L}[a]
None	-2.010	-5.384	3.374	-2.221	-5.486	3.265
F^-	0.978	-2.197	3.175	0.752	-2.520	3.272
Cl^-	0.749	-2.584	3.333	0.522	-2.725	3.248
Br^-	0.706	-2.558	3.264	0.435	-2.785	3.220
I^-	0.863	-2.256	3.118	0.705	-2.542	3.248

[a] In eV.

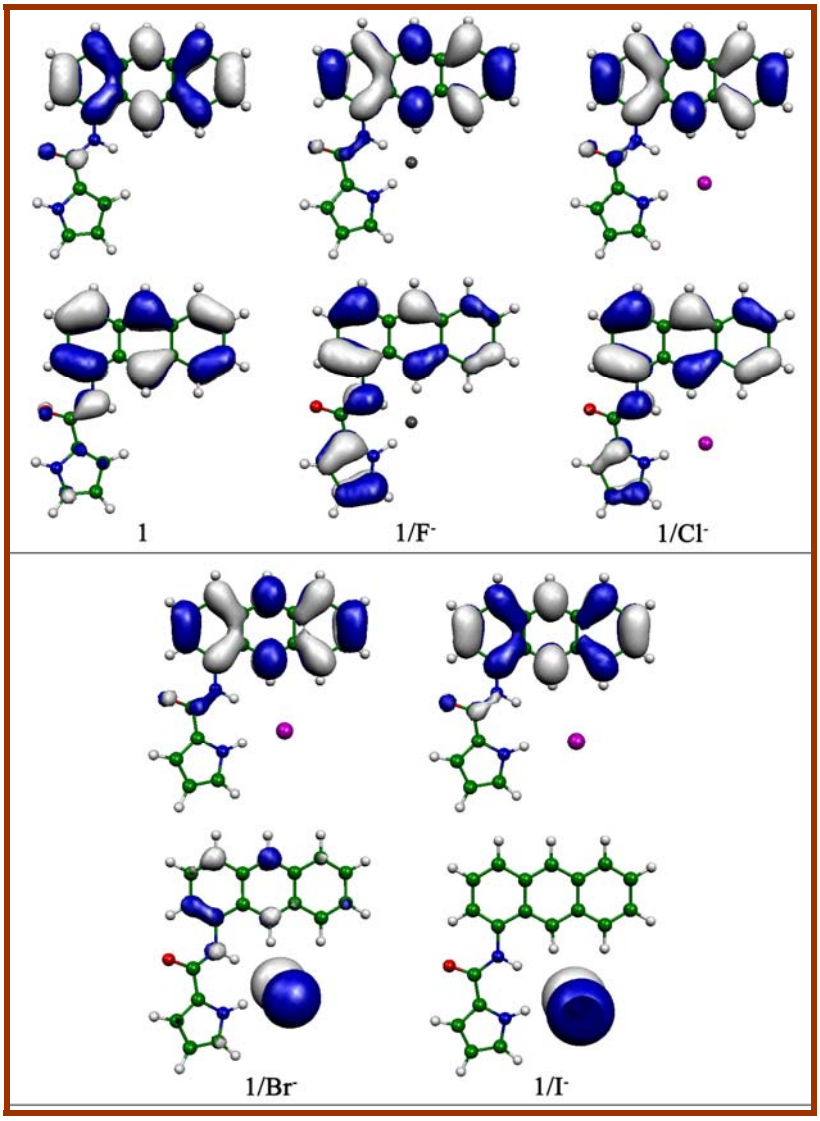

Figure 5: Plots of the LUMO (top) and HOMO (bottom) orbitals of the free forms of **1**, **1**/F^- **1**/Cl^-, **1**/Br^- and **1**/I^- at iso-surface value of 0.03 au.

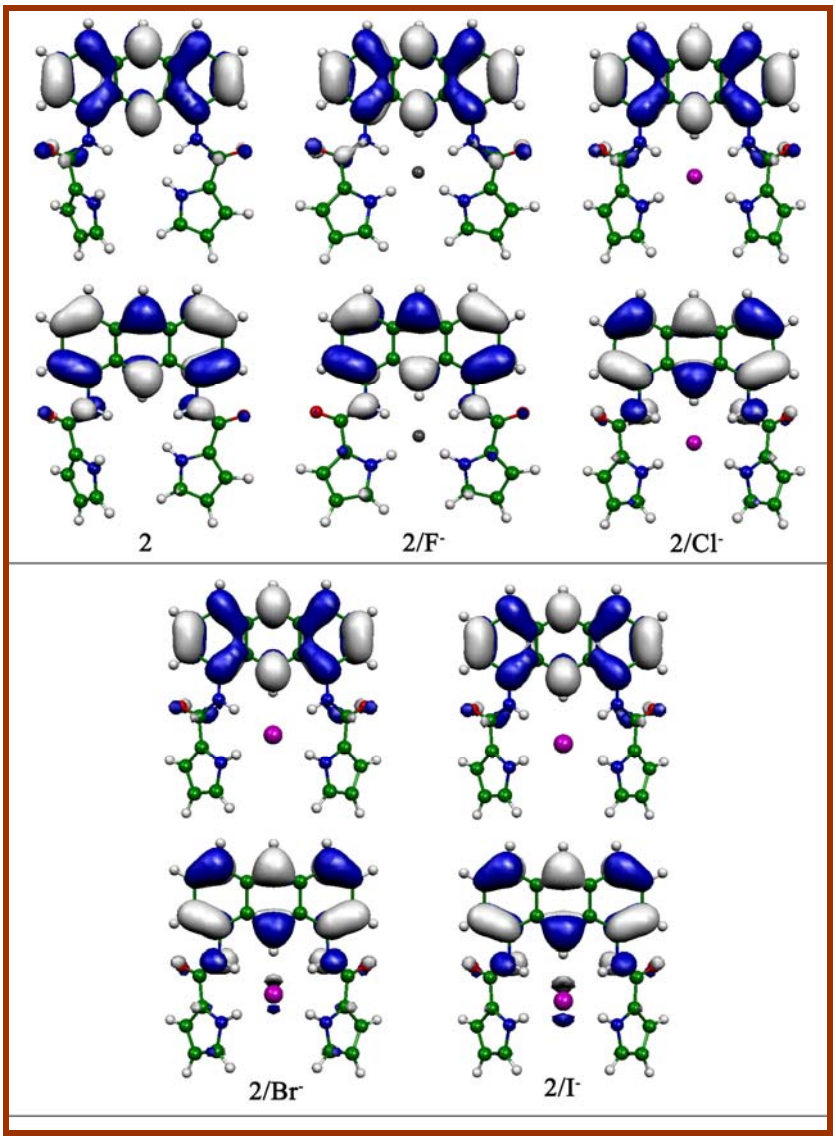

Figure 6: Plots of the LUMO (top) and HOMO (bottom) orbitals of the free forms of **2**, **2**/F^- **2**/Cl^-, **2**/Br^- and **2**/I^- at iso-surface value of 0.03 au.

Table 2 Selected NBO atomic charges (in e) and charge transfer of the optimized structures of the receptor **1** and its complexes with anions.

Receptor/ Halide ions [a]	N1	N2	H1	H2	X[b]	Charge transfer [c]
1	-0.594	-0.494	0.389	0.423	-	-
1/F^-	-0.633	-0.522	0.436	0.454	-0.759	0.241
1/Cl^-	-0.607	-0.528	0.416	0.437	-0.873	0.127
1/Br^-	-0.613	-0.531	0.414	0.433	-0.871	0.129
1/I^-	-0.617	-0.532	0.428	0.433	-0.886	0.114

[a] Atomic labeling is shown in Figure 3.
[b] Where X represents the F^-, Cl^-, Br^- or I^-.
[c] Charge transfer is the charge difference of halide ion before and after complexation.

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Table 3 Selected NBO charges (in e) of atoms of the optimized structures of the receptor **2** and its complexes with anions.

Receptor/ Halide ions [a]	N1	N2	N3	N4	H1	H2	H3	H4	X[b]	Charge transfer
2	-0.620	-0.541	-0.539	-0.615	0.376	0.403	0.403	0.379	-	-
2/F^-	-0.620	-0.519	-0.518	-0.623	0.423	0.447	0.447	0.424	-0.771	0.229
2/Cl^-	-0.636	-0.528	-0.528	-0.636	0.422	0.435	0.435	0.422	-0.832	0.168
2/Br^-	-0.640	-0.529	-0.529	-0.640	0.419	0.432	0.432	0.419	-0.824	0.176
2/I^-	-0.645	-0.534	-0.534	-0.645	0.428	0.433	0.433	0.428	-0.822	0.178

[a] Atomic labeling is shown in Figure 3.
[b] Where X represents the F^-, Cl^-, Br^- or I^-.
[c] Charge transfer is the charge difference of halide ion before and after complexation.

Electronic potential surface

Electrostatic potential surfaces of receptors **1**, **2** and their complexes have been generated from the GAUSSIAN output files using the MOLEKEL 4.3 software (Flükiger *et al.*, 2000). The electrostatic potentials (in au) presented over electronic isodensity ρ=0.05 e/Å^3 are illustrated in Figure 7 for receptor **1** and its complexes, and in Figure 8 for receptor **2** and its complexes. The minimum and maximum of electrostatic potentials are presented in the ranges of -0.425 to +0.180 for the free form of receptor **1** and its complexes and -0.480 to +0.085 for the free form of receptor **2** and its complexes. The electronic isodensity surfaces of the receptors **1** and **2** show the strongly positive charge on both amide and pyrrole protons with intense blue. All the halide ion complexes show a decrease of the positive charges of their amide protons as can be seen from the lowering intensity of blue.

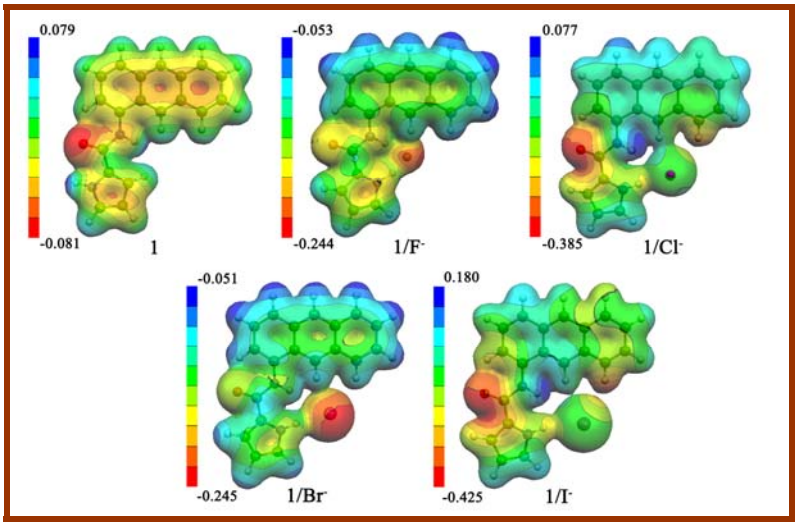

Figure 7: Plots of the molecular electronic potential (in au) presented of **1** and its halide ion complexes.

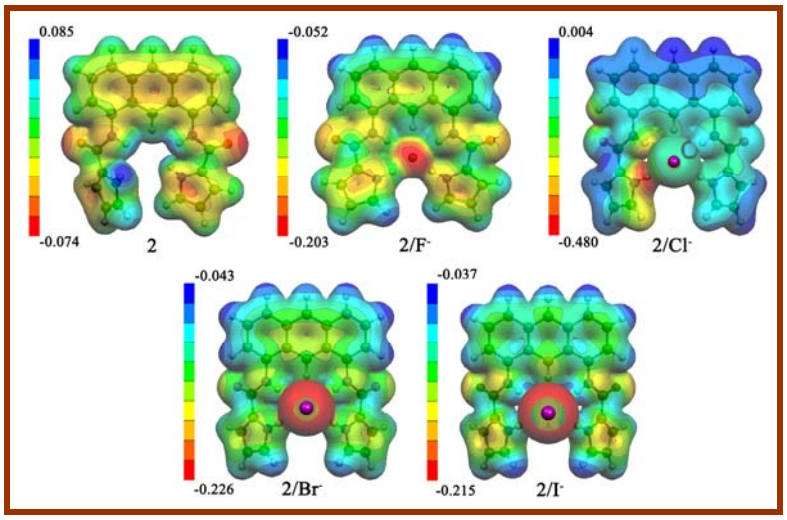

Figure 8: Plots of the molecular electronic potential (in au) presented of **2** and its halide ion complexes.

3.3 Energetic and thermodynamic properties

The zero point vibrational correction energy and enthalpy and Gibbs free energy changes of complexation between receptors **1, 2** and halide ions computed using the DFT methods are presented in Table 4. When considering of thermodynamic property changes of all complexations in gas phase, the negative values of changes indicate that the complexations are thermodynamically favorable. The results show that fluoride complexes of both receptors are the most stable complexes (ΔG of **1**/F^- = -85.45 and **2**/F^- = -117.81 kcal/mol). In addition, receptor **2** forms stronger complexes with halide ions comparing to receptor **1**. This may enable receptor **2** to form the large number of hydrogen bonds with halide ions (Kang *et al.*, 2005). However, the relative stabilities of the complexes of receptors **1** and **2** with halide ions are in the same decreasing order, $F^- > Cl^- > Br^- > I^-$. The Gibbs free energy changes of complexation between receptors **1**, **2** and halide ions in DMSO solvent were also computed using the CPCM model at the same levels and presented in Table 4. Interestingly, fluoride ion also forms the most stable complexes with receptors **1** and **2** in DMSO phase. The Gibbs free energy changes of complexation between receptors and halide ions in gas phase could result in the same order of their binding abilities in DMSO. It should be noted here again that the basicity of anions (F^-, the most basic one) (Wang *et al.*, 2008) could affect the binding to receptor **1** and both cavity of the receptor and basicity of anions could affect the binding to receptor **2**.

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Table 4 The zero point vibrational correction energy (ΔE_{ZPE}) and enthalpy (ΔH), Gibbs free energy (ΔG) changes in gas phase and Gibbs free energy changes in DMSO (ΔG_{DMSO}) phase of complexation between receptors **1, 2** and halide ions.

Halide ions	ΔE_{ZPE} [a]		ΔH [a]		ΔG [a]		ΔG_{DMSO} [a]	
	1	**2**	**1**	**2**	**1**	**2**	**1**	**2**
F^-	-93.81	-127.86	-94.60	-129.37	-85.45	-117.81	-31.44	-55.79
Cl^-	-31.72	-55.77	-32.50	-56.40	-22.97	-46.90	0.57	-7.29
Br^-	-29.49	-53.07	-29.64	-53.52	-22.51	-44.22	1.10	-6.16
I^-	-8.84	-25.54	-8.89	-25.84	-1.91	-17.08	15.64	14.93

[a] In kcal/mol.

4. Conclusion

Halide ion recognitions of the novel amide- and pyrrole-based receptors (*N*-(anthracen-1-yl)-1*H*-pyrrole-2-carboxamide (**1**) and *N*-(8-(1*H*-pyrrole-2-carboxamido) anthracen-1-yl)-1*H*-pyrrole-2-carboxamide (**2**)) and their complexes with F^-, Cl^-, Br^- and I^- were investigated using the DFT-B3LYP computation. The results show that the relative stabilities of the complexes of receptors **1** and **2** with anions are in the same decreasing order: $F^- > Cl^- > Br^- > I^-$. Fluoride ion can form the most stable complexes in both gas and DMSO phases with receptors **1** and **2** with Gibbs free energy changes of -85.45 and -117.81 kcal/mol in gas phase and -31.44 and -55.79 kcal/mol in DMSO, respectively. The receptor **2** shows a stronger interaction with anions than the receptor **1**, because of four hydrogen bonds of the receptor **2** participating in the binding events.

5. Acknowledgements

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