

# DFT studies of binding of fluoride anions with silyl-fluorescein derivatives

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## Abstract

Fluoride is abundantly used in dental healthcare and pharmaceutical industry, it is harmful if it is found over certain concentration in drinking water and in soil. It is therefore essential to develop portable tools to detect fluoride. Fluorescence sensing can be used as a simple and sensitive tool to detect fluoride anions. Fluorescent detection of anions is less widely studied compared to metal cation and neutral organic small molecules. As such, the interactions between F<sup>-</sup> anion and two silyl-fluorescein based sensors were studied here using density functional theory (DFT). Chemical shifts and electronic properties of the free sensor and the sensors in the presence of different number of fluoride anions were obtained and compared. The DFT results show that strong binding responses can be found as a function of fluoride concentration. The change in UV-Vis spectra due to the presence of fluoride indicates they are promising sensor candidates for fluoride detection and further studies on fluorescence response of these sensors are worthwhile.

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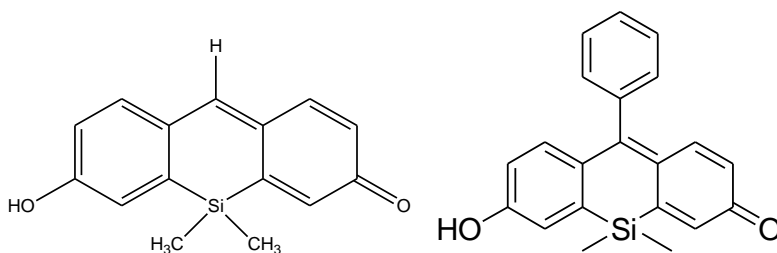
## 1. Introduction

Fluoride has been routinely used in dental healthcare and abundantly used in pharmaceutical industry. However, if the fluoride concentration is above certain threshold in drinking water,<sup>1</sup> many diseases, such as dental fluorosis and skeletal fluorosis, can arise. Therefore, recognition and sensing of fluoride is critical. Like many anions, their recognition and detection are mostly utilize mass spectrometry, atomic absorption spectrophotometry, and other methods that rely on costly and bulky instruments. The ability to detect and quantify it using low-cost and portable sensors is urgently needed for rapid detection. In this regard, developing fluorescent sensors to detect fluoride is an important research towards achieving its rapid and simple detection.

Fluorescent sensors<sup>2-19</sup> has been widely used to detect organic small molecules,<sup>20-25</sup> DNA,<sup>26-30</sup> or metal ions,<sup>31-42</sup> such as Pt,<sup>43</sup> Pb,<sup>44-50</sup> and Zn.<sup>51-55</sup> These fluorescence sensors are mostly organic small molecule based. As such, studies of organic small molecules<sup>56-67</sup> and various aggregates<sup>68-86</sup> have been a very active research area coupled with their applications in energy related applications, such as solar cell research. Syntheses of these molecules,<sup>87-97</sup> including catalysis,<sup>98-107</sup> have been an everlasting research topic in chemistry research. In addition to the traditional organic small molecule based fluorescence sensors, CRISPR<sup>108-110</sup> and nucleic acids<sup>111-116</sup> have been used in the development of fluorescence sensors. Research in biosensing using has also become very active.<sup>117-139</sup> A review of fluorescent sensors for detecting fluoride ion<sup>140</sup> was provided by Chen and Bao by taking advantage of strong F-Si interaction in the development of F<sup>-</sup> sensors.

Fluorescein<sup>12,141-146</sup> has been widely used as fluorescence sensors. In the recent work, we replacing O by Si to developed a Si-fluorescein sensor, 13-hydroxy-2,2-dimethyl-2-silatricyclohexadeca-1(14),3,6,8,10,12-hexaen-5-one (denoted as molecule **1** and shown in Figure 1) to extend the absorption to longer wavelength.<sup>147</sup> As it contains Si, we speculate that it may be

used to selectively detect  $F^-$  due to the strong Si-F interaction. To further expand the sensor candidate pool and to understand the impact of certain functionalizations, we also studied molecule **2** (also shown in Figure 1), i.e. 13-hydroxy-2,2-dimethyl-9-phenyl-2-silatricyclohexadeca-1(14),3,6,8,10,12-hexaen-5-one.

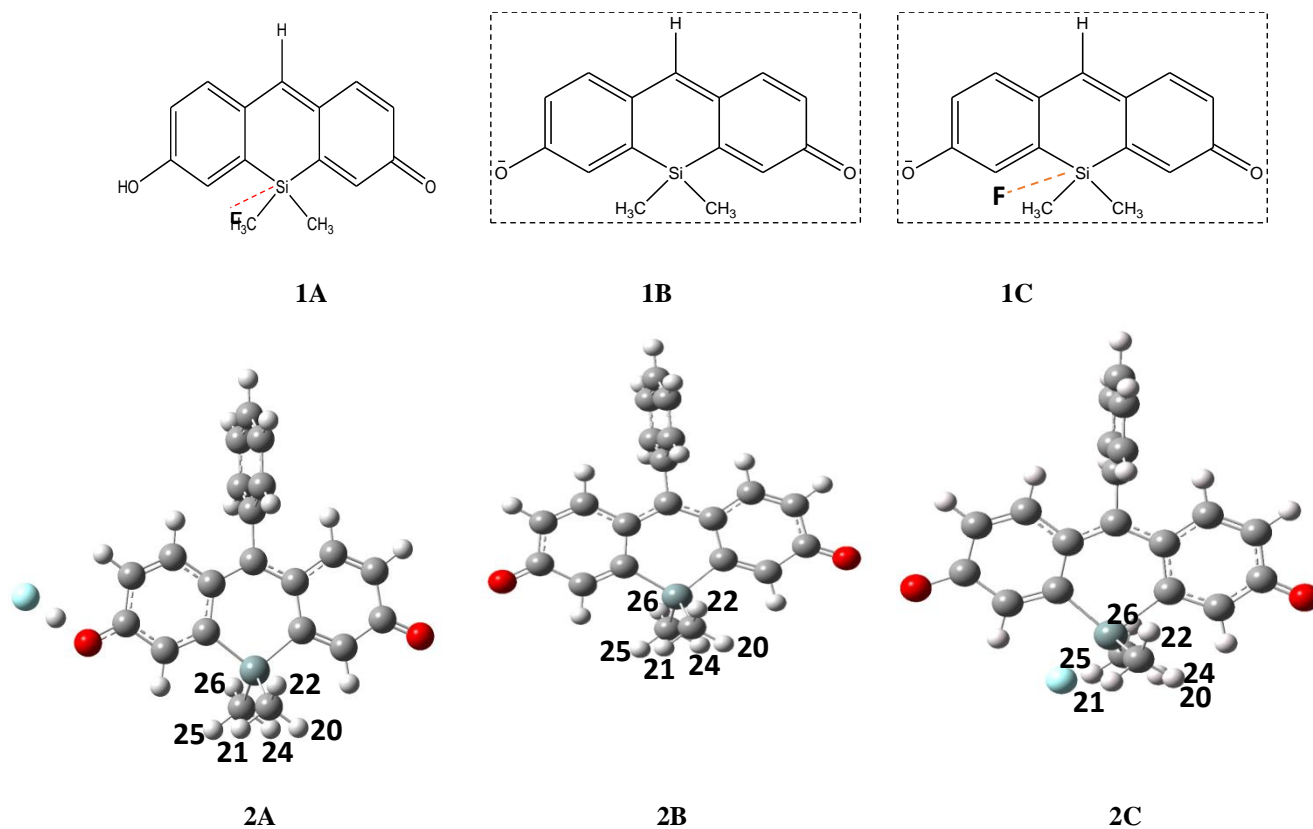


**Figure 1.** Si based fluorescein molecule **1** (left) and molecule **2** (right)

To understand the impact of phenyl replacement on the sensor electronic properties and the binding of fluoride with these sensors, we performed extensive DFT calculations. In section 2, the computational details are given. The results and discussion are presented in section 3. Finally, the conclusion is summarized in section 4.

## 2. Computational details

To study the binding between the sensor and analyte, i.e.  $F^-$ , and explore its impact on various properties of the sensor, we performed DFT calculations on free sensor, molecule **2**, and binding complexes of both molecule **1** and molecules **2**. In addition to the free neutral sensor molecules shown in Figure 1, we also calculated three forms of sensing complexes in the presence of  $F^-$  anions for each sensor with the general structures presented in Figure 2.



**Figure 2.** Complexes formed with molecule **1** (top) and with molecule **2** (bottom)

All DFT calculations were performed using the Becke's three-parameter exchange functional with the Lee-Yang-Parr correlation functional (B3LYP) with a 6-31+G(d,p) basis set. Ethanol was used as solvent and was treated in DFT calculations using polarized continuum model (PCM). For each system, three types of DFT calculations were carried out: geometry optimization, frequency, and time-dependent DFT (TDDFT) calculations. In the TDDFT calculations, six states were used to obtain excitation energies. All default convergence criteria were adopted, i.e. the self-consistent field (SCF) convergence was  $10^{-8}$  a.u., the gradient and energy convergence were  $10^{-4}$  a.u. and  $10^{-5}$  a.u., respectively. Once the optimization structure was obtained, frequency calculation was then conducted and inspected for imaginary frequencies to ensure the optimized geometry (structure) was indeed at an energetic minimum. When the structure is confirmed to be at its minimum, i.e.

there were no imaginary frequencies, TDDFT calculation was then performed to obtain information on the electronic excitation. The above procedure was used in our previous studies of organic small molecules.<sup>148,149</sup>

Mullikan charges of key atoms of a system were compared and the frontier molecular orbital and their energies were also provided. To correlate with experimental measurements on binding strength, we calculated NMR chemical shifts using the Gauge-Independent Atomic Orbital (GIAO) method.<sup>150</sup>

### **3. Results**

To understand the functionality impact on free sensor, we performed DFT calculations on molecule **2** and compared the changes in chemical shifts and electronic properties, which are presented in 3.1. The results of binding of fluoride with the two sensors are presented in 3.2 for binding with one fluoride and in 3.2 for binding with two fluorides.

#### **3.1 Free sensors**

To understand the effect of functionalization, we provided charge density of the atoms of dimethyl silyl groups in both sensor molecules in Table 1. Two observations can be obtained through the comparison. The most significant change in charge density is Si atom. When the H atom is replaced by a phenyl group as shown in Figure 1, the charge density of Si in molecule **2** becomes more positive, which would increase the interaction between Si and fluoride anion. Additionally, the C atom of the dimethyl group is more negatively charged with the six H atoms are least affected.

**Table 1.** Mullikan charge density of Si and the methyl atoms (in Figure 2) in molecules **1** and **2**.

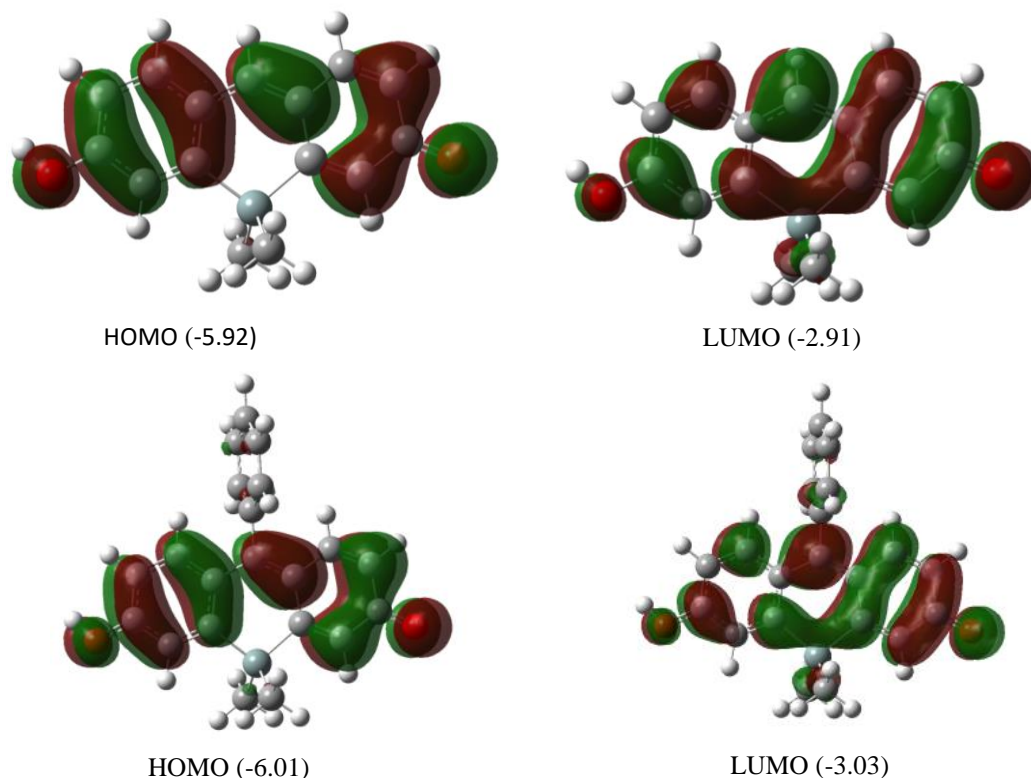
Atom	Molecule <b>1</b>	Molecule <b>2</b>
Si	0.957	1.131
C	-0.594	-0.641
<sup>22/26</sup> H	0.178	0.174
<sup>21/25</sup> H	0.178	0.174
<sup>20/24</sup> H	0.175	0.174

The changes in charge density can be reflected in chemical shifts and should be measured using NMR technique. The calculated chemical shifts of the atoms are shown in Table 2. The changes in chemical shifts are significant for Si and C. We expect that <sup>29</sup>Si NMR, <sup>13</sup>C NMR, and <sup>1</sup>H NMR will all be useful to detect the differences in the sensor molecules.

**Table 2.** Chemical shifts (in ppm) of Si and the methyl atoms (in Figure 2) in molecules **1** and **2** calculated using GIAO-B3LYP/6-31+G(d,p).

Atom	Molecule <b>1</b>	Molecule <b>2</b>
Si	-87.81	-11.98
C	-10.15	1.35
<sup>22/26</sup> H	0.45	0.28
<sup>21/25</sup> H	0.45	0.50
<sup>20/24</sup> H	0.75	0.40

In addition to the changes in Milliken charge and chemical shifts, we expect the functionalization of molecule **1** will alter the molecular orbitals. Therefore, the frontier molecular orbitals of these molecules with the corresponding energies are depicted in Figure 3. These frontier orbitals in Figure 3 are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).



**Figure 3.** Molecular orbitals of molecule **1** (top) and with molecule **2** (bottom). The unit of energy is given in eV.

As the picture and data shown in Figure 3, the changes in molecular orbital contours are less noticeable than the other two properties described above. However, the energy levels are lowered slightly in molecule **2** with respect to molecule **1** for both HOMO and LUMO. We also note that the above calculations do not include the dynamics where atoms undergo vibrational changes. In this case, dynamics studies<sup>151</sup> will be needed to account for the changes.

### 3.2 Sensors binding with one F<sup>-</sup> anion

The binding of fluoride anions to the sensor is directly reflected in the change in chemical shifts. We therefore summarized the results of binding complexes of sensor **1** in Table 3. The Si and the protons on the dimethyl silyl groups shifted up-field in the presence of fluoride anions, which demonstrates a shielding effect on those protons.

**Table 3.** Chemical shifts relative to free sensor **1** (in ppm) of Si and the methyl atoms (in Figure 2) when it binds with fluorides.

Atom	<b>1A</b>	<b>1B</b>	<b>1C</b>
Si	-73.25	-1.62	-71.78
C	8.61	0.26	-9.49
<sup>22/26</sup> H	-0.75	-0.11	-0.71
<sup>21/25</sup> H	-0.75	-0.11	-0.71
<sup>20/24</sup> H	-0.40	-0.10	-0.50

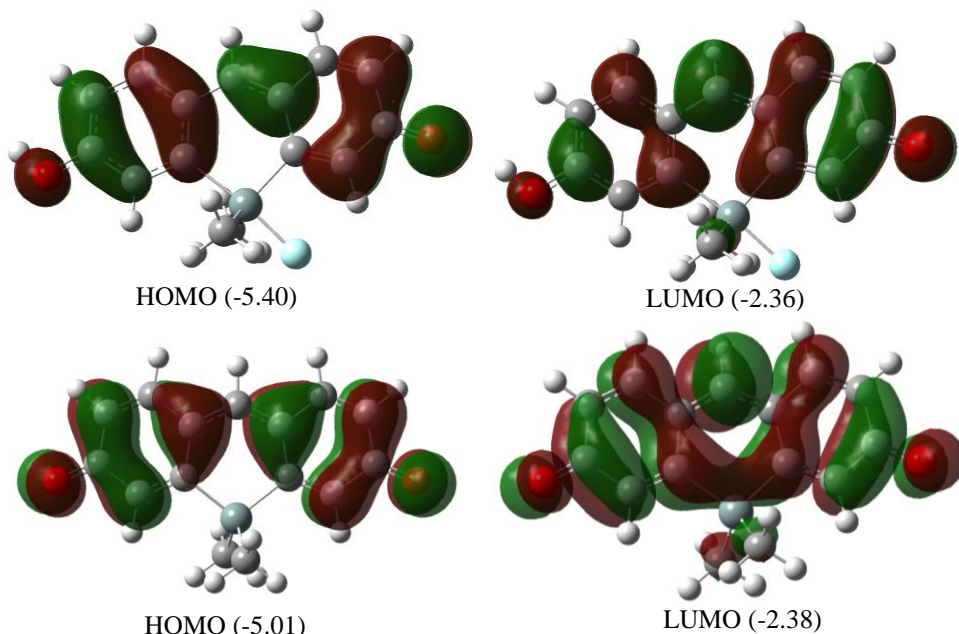
The charge densities of the atoms of the dimethyl silyl group are listed in Table 4, which reflected in general the changes being observed in NMR. It is interesting to mention that complex **1B** and **1C** are slightly different from complex **1A** in that one proton is lost in **1B** and **1C** due to the strong interaction of fluoride anion with proton. We further note that **1B** is most likely being formed than **1A** when a limited number of fluoride anions are present in the solution, as **1A** is less stable than **1B**.

**Table 4.** Mullikan charge density of Si and the methyl atoms (in Figure 2) in molecule **1** when it binds with fluorides.

Atom	<b>1A</b>	<b>1B</b>	<b>1C</b>
Si	1.400	1.003	1.425
C	-0.635	-0.606	-0.630
<sup>22/26</sup> H	0.147	0.168	0.143
<sup>21/25</sup> H	0.147	0.168	0.143
<sup>20/24</sup> H	0.152	0.169	0.145



The changes in the frontier molecular orbitals will be interesting to investigate. As such, Figure 4 plotted the frontier orbitals of two complexes **1A** and **1B**. In the presence of a fluoride anion, both the contour and energy are perturbed. Especially, the strong bonded complex **1B** shows significant decrease in HOMO-LUMO gap, which indicates a longer wavelength absorption.



**Figure 4.** Molecular orbitals of molecule **1A** (top) and with molecule **1B** (bottom). The unit of energy is given in eV.

For sensor molecule **2**, although three binding complexes in Figure 2 were studied, **2A** are not stable and therefore we will not discuss below. Furthermore, the Si-F bond distance in the complex **2C** is 1.881 Å, which is substantially longer than a typical Si-F bond of 1.600 Å. This indicates a significant bonding between the silicon and the fluoride anion. The calculated chemical shifts of two binding complexes relative to the free sensor **2** are provided in Table 5. The Si, C, and the protons on the dimethyl silyl groups shifted up-field in the presence of fluoride anions.

**Table 5.** Chemical shifts relative to free sensor **2** (in ppm) of Si and the methyl atoms (in Figure 2) when it binds with fluorides.

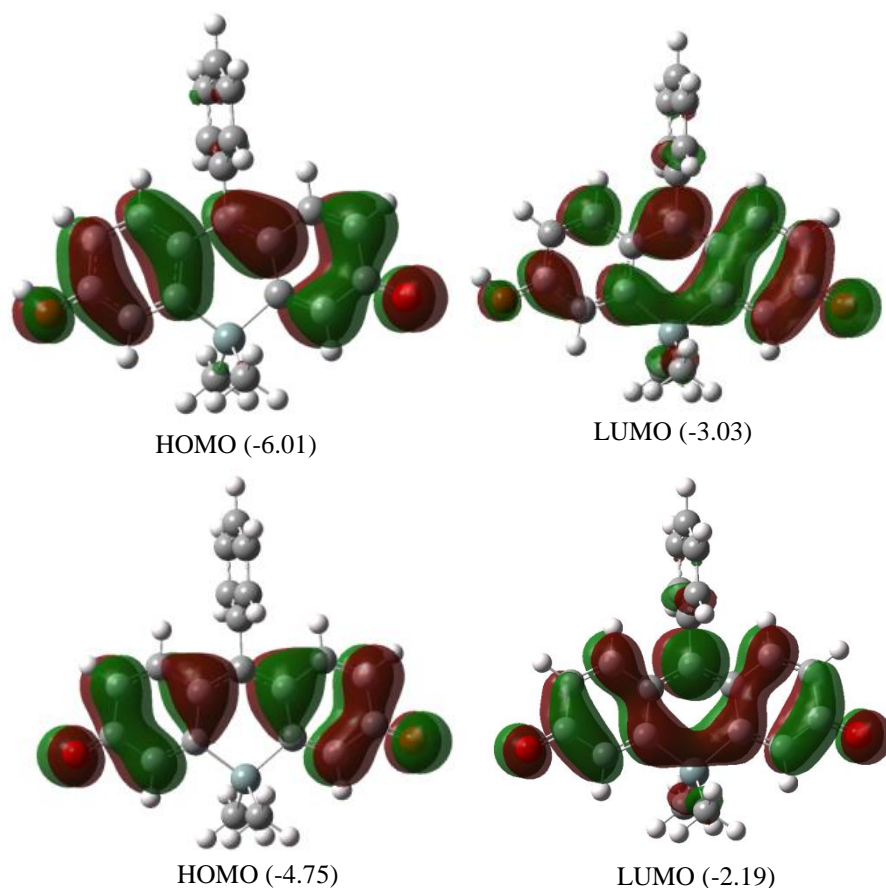
Atom	<b>2B</b>	<b>2C</b>
Si	-0.76	-77.58
C	-0.43	-9.23
<sup>22/26</sup> H	-0.06	-0.34
<sup>21/25</sup> H	-0.06	-0.32
<sup>20/24</sup> H	-0.08	-0.43

The charge densities of the atoms of the dimethyl silyl group in complexes **2B** and **2C** are summarized in Table 6. We note that the charge densities in complex **2B** are slightly different from the free sensor **2** as shown in Table 1. Much of the changes are seen on the other hand in complex **2C** when 2 fluoride anions interact with a sensor molecule. This change with different number of anions indicates the sensor is sensitive not only to the presence of but also to the concentration of the fluoride anions.

**Table 6.** Mullikan charge density of Si and the methyl atoms (in Figure 2) in molecule **2** when it binds with fluorides.

Atom	<b>2B</b>	<b>2C</b>
Si	1.133	1.582
C	-0.645	-0.677
<sup>22/26</sup> H	0.168	0.143
<sup>21/25</sup> H	0.166	0.145
<sup>20/24</sup> H	0.166	0.144

The frontier molecular orbitals of the two complexes are shown in Figure 5. It is clear that the presence of fluoride anion changes the bonding of the sensor, which is reflected by the change in the shape of the molecular orbital contours.



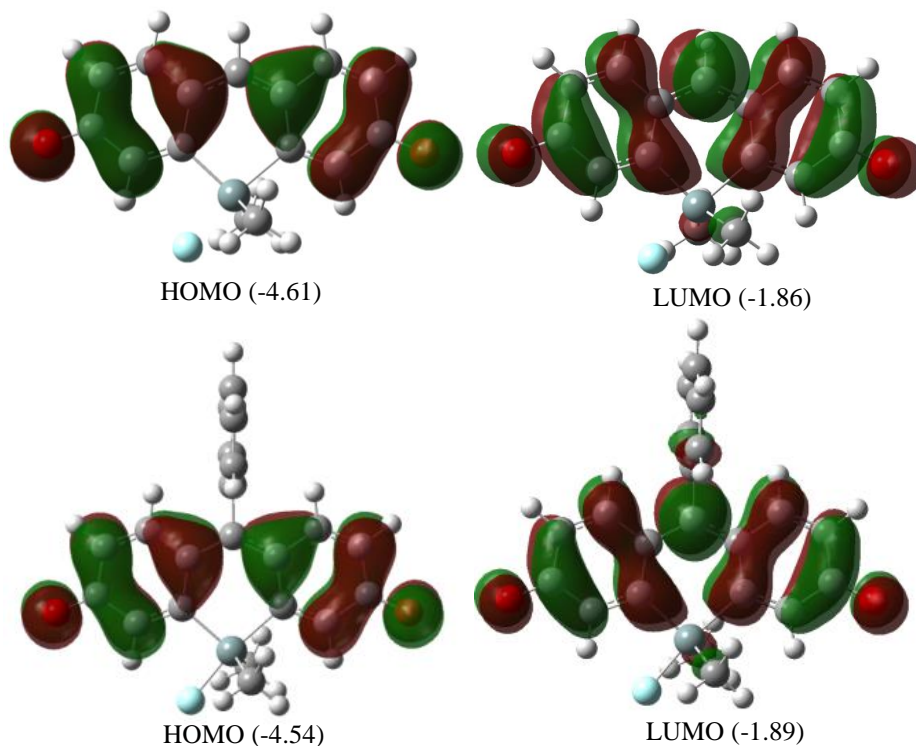
**Figure 5.** Molecular orbitals of molecule **2A** (top) and with molecule **2B** (bottom). The unit of energy is given in eV.

### 3.3 Sensors binding with two F<sup>-</sup> anions

In the previous subsections, we briefly discussed the binding of sensors **1** and **2** with fluoride anions with focus on binding to one fluoride anion. While the presence of one fluoride anion causes the sensor to lose its proton in hydroxyl group, the second fluoride anion binds to the Si atom. The direct binding induces significant changes in <sup>29</sup>Si NMR and should be easily shown in NMR results.

The frontier orbitals of complexes **1C** and **2C** are provided in Figure 6. While the contours of the orbitals are similar, the energies of the HOMO differ by 0.07 eV and those of LUMO by 0.03.

As these energy changes are in different direction, the HOMO-LUMO gap differs by 0.1 eV, which results in UV-Vis absorption wavelength changes.



**Figure 6.** Molecular orbitals of molecule **1C** (top) and with molecule **2C** (bottom). The unit of energy is given in eV.

### 3.4 Discussion

In Table 7 we summarized the UV-Vis absorption properties, i.e. absorption wavelength and intensity, of sensor **1** and its three binding complexes. The results clearly show the change in absorption wavelength and intensity upon the presence of fluoride anions.

**Table 7.** UV-Vis absorption of the free sensor **1** and the three binding complexes.

	<b>1</b>	<b>1A</b>	<b>1B</b>	<b>1C</b>
$\lambda/\text{nm}$	437	428	492	467
f value	0.8440	0.9469	0.9026	1.0542

The DFT results presented above show that both molecules **1** and **2** are promising sensor candidates for detection of fluoride anions. Therefore, it is worthwhile to further study the properties of the excited states,<sup>152</sup> fluorescence,<sup>153</sup> triplet<sup>154-156</sup> and the lifetime<sup>157-159</sup> of the sensor and the binding complexes.

#### **4. Conclusions**

Simple and rapid detection of fluoride is important research towards improving health and environments. Fluorescence sensing is potentially a simple and sensitive tool to detect fluoride anions, though fluorescent detection of anions is less widely studied compared to metal cation and neutral organic small molecules. As such, we studied the interactions between F<sup>-</sup> anion and two silyl-fluorescein based sensors using density functional theory.

Chemical shifts and electronic properties of the free sensor and the sensors in the presence of one or two fluoride anions were obtained and compared. The DFT results show that strong interaction between the fluoride and the phenolic hydrogen and a weaker interaction with Si. Furthermore, strong binding responses can be found in the sensors responding to the number of fluoride anions. The change in UV-Vis spectra due to the presence of fluoride indicates that the proposed Si-fluorescein molecules are promising sensor candidates for fluoride detection and further studies on the response in UV-Vis as well as fluorescence are worthwhile.

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