Inverse spin crossover in fluorinated Fe(1,10-phenanthroline)$_2$(NCS)$_2$ adsorbed on Cu (001) surface

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Abstract

Density functional theory (DFT) including van der Waals weak interaction in conjunction with the so called rotational invariant DFT+U, where $U$ is the Hubbard interaction of the iron site, is used to show that the fluorinated spin crossover Fe(phen)$_2$(NCS)$_2$ molecule whether in the gas phase or adsorbed on Cu(001) surface switches from the original low spin state to the high spin state. Using Bader electron density analysis, this inversion of the spin-crossover is explained in terms of electron doping of the Fe-octahedron cage which led to an increase of the Fe-N bond lengths. Consequently, the ligand-field splitting is drastically reduced, making the high-spin ground state more stable than the low-spin state. The calculated scanning tunneling microscopy (STM) images in the Tersoff-Hamann approximation show a clear distinction between the fluorinated and the unfluorinated molecule. This theoretical prediction is awaiting future STM experimental confirmation.

Graphical TOC Entry

Keywords

spin crossover, spin polarization, magnetism, density functional theory, scanning tunneling microscopy
Introduction

The interest in spin crossover (SCO) molecules is due to their ability to switch from the $^1A_1$ low spin (LS) state at low temperatures to the $^5T_2$ high spin (HS) state at higher temperatures. The transition between these two states is accompanied with a change in their structural, electronic and magnetic properties. The ease and multitude ways leading to the spin crossover, such as the variation in temperature, light, pressure, magnetic field, or electric field, make these molecules potential candidates for applications in spintronics and magnetic recording. However the high sensitivity of the SCO molecules to their environment makes their control challenging, especially when they are in interaction with a substrate, where recent experiments showed a fragmentation and distortion of many of these molecules. However, recently the principle of electrical detection of the light-induced spin transition in SCO/graphene heterostructures was demonstrated and even room temperature optoelectronic device operating with spin crossover nanoparticles.

The SCO molecules are composed essentially of a transition element ion complex, like iron (II), surrounded by ligands. When the ligands take an octahedral or tetrahedral conformation around the metallic element, they generate a field called "ligand field $\Delta$" operating on the $d$ orbitals of the metallic ion. This causes a partial lifting of degeneracy in the $d$-orbitals leading to the splitting of the $e_g$ and $t_{2g}$ energy levels by $\Delta$. The electronic configuration of these two levels and hence the SCO ground state depends on the competition between the ligand field $\Delta$ and the Coulomb electronic repulsion $U$ between the $d$ electrons. If $\Delta$ is smaller than $U$ the high-spin state is favored, on the other hand if $\Delta$ is larger than $U$ the low spin-state is favored.

One of the most interesting challenges is to confirm whether these spin-crossover molecules can maintain their LS-HS spin-crossover when deposited on a metallic substrate. Previous experimental works on individual Fe(phen)$_2$(NCS)$_2$ molecules (labeled Fephen) on Cu(001) or Au(111) identified both magnetic conformations when the surface is scanned by scanning tunneling microscopy (STM), showing two different sizes of the double phen lobes
corresponding respectively to the HS and LS states. Distinction between the spin state of each conformation was done by scanning tunneling spectroscopy (STS), observing a Kondo peak in the high-spin (HS) state whereas only a low electric conductivity was obtained in the LS state. The screening of the iron spin magnetic moment was attributed to the interface conduction electrons. However, unsuccessful efforts have been made to switch the molecules on the surface by applying an electric field, high tunneling voltage or high current density. It was concluded that the molecules are trapped in their magnetic states, LS or HS, due to the strong interaction between the two NCS groups of the molecule and the metallic substrate via the sulfur atoms. However, the introduction of a monolayer of CuN between the molecule and the copper surface led to a reversible electrical switching of the Fephen molecule from the LS to the HS state. This is corroborated by theoretical results, which showed a significant reduction of the difference of the adsorption energy between the two magnetic states of the Fephen molecule adsorbed on a CuN(100) substrate.

To control the HS-LS transition of the SCO molecules on metallic surfaces, it is desirable to find a way to control or tune the ligand field and hence the spin crossover energy barrier. In this work our aim is therefore to perform such a tuning of the ligand field by fluorination of the molecule, and thus creating a perturbation on the octahedral ligands. We can therefore monitor the evolution of the ligand field and the energy barrier between the two magnetic states of the molecule as a function of this perturbation. To this end, we computed the minimum energy path (MEP) between the two HS and LS ground states when the iron ligands of the spin-crossover molecule were modified by fluorination. We show that fluorination can invert the molecule spin state, i.e., making the HS state lower in energy than the natural low temperature LS state of the molecule. Thus our results demonstrate that the HS and LS adsorption energy can be tuned by choosing an appropriate dopant to the molecule. To make the calculation, we have chosen the Fe(Phen)$_2$(NCS)$_2$ molecule (Phen = 1,10-phenanthroline) (see Fig. 1) and substituted all the hydrogen atoms by fluorine atoms. Using Bader analysis, we show that the difference of electro-negativity between fluorine and
carbon leads to a reorganization of electrons around the iron octahedron which modifies its ensuing physical properties. For simplicity, we label H-Fephen the unfluorinated molecule, and F-Fephen the fluorinated molecule.

The paper is organized as follows. In the second section we provide our method of calculation and give the most relevant parameters needed to perform the electronic structure and compute the total energy. In the third section we describe the effect of fluorination on the spin crossover molecule, analyze the electron distribution using Bader analyses and show its effect on inversion of the spin crossover. We then analyze the iron density of states in terms of a simple ligand-field charge model for both the unfluorinated and the fluorinated molecule. In the fourth section we compute the minimal energy path by constrained minimization and the so called nudged elastic band method (NEB) and in the fifth section we report and analyze the constant current STM images.

Effect of fluorination on the spin-crossover molecule

Adsorption of F-Fephen on Cu (001)

The H-Fephen molecule is one of the most interesting iron (II) spin crossover molecules, discovered by Baker in 1964. In this molecule, the iron(II) atom is surrounded by 6 nitrogen atoms forming an octahedral shape. The HS-LS transition in this molecule leads essentially to the variation of the bond lengths and bond angles between the iron and nitrogen atoms and we observe a significant increase of these bond lengths in the HS state compared to the LS state.

By substituting hydrogen by fluorine, we obtain the fluorinated molecule (labeled F-Fephen). After atomic relaxations, except for some elongation in the iron-nitrogen bond lengths, the global geometry of the structure of the molecule for the two magnetic states remain similar to those of the unfluorinated molecule. However, we will show that these elongations are of crucial importance, as they lead to an inversion in the total energy of the
two magnetic states of the molecule, i.e., the high-spin state (HS) is now the most stable state. We report in table 1 the energies and magnetic moments obtained for the relaxed free unfluorinated and fluorinated molecule in the two LS and HS magnetic states and the difference of the total in kJ/mole which shows this inversion.

The F-Fephen molecule adsorbed on copper surface shows the same behavior as the unfluorinated molecule. Figure 1 shows the relaxed structure of the two LS and HS magnetic states. The equilibrium position is the same as the unfluorinated molecule, i.e.; the sulfur atom is in the bridge position and is 1.97 Å away from the substrate in the LS state, compared to 1.95 Å in the high-spin state in agreement with the results of Ref. 10.

Figure 1: Relaxed LS (left) and HS (right) structures of the F-Fephen molecule on Cu(001) substrate.

As in the free molecule case, the global molecular structure remains similar and the fluorination causes an elongation in the iron-nitrogen bonds length. We report in Figure 2 the superposition of the H-Fephen and F-Fephen molecule at the octahedral and NCS level, LS left and HS right. We observe that the fluorination causes significant structural alterations of the octahedral environment of the molecule. The average root mean square deviations (RMSD) of the bond lengths show that this structural deformation is more important in the HS state. The two magnetic states are still conserved when the molecule is adsorbed in the substrate, however, similar to the free molecule, the total energy is lower for the HS state. We report in table 1 the total energies and total magnetic moment for the molecule adsorbed on Cu(001) for the two LS and HS magnetic states. However, it is important to mention that the fluorination without relaxation of the molecule did not cause the spin crossover inversion. Indeed, although the HS-LS difference of total energy is significantly
reduced from 55.3 kJ/mole in the unfluorinated case to 20.4 kJ/mole, it is only when the atoms of the molecule are allowed to relax that this difference becomes negative as shown in table [1]. This underlines the importance of atomic relaxation influenced by the relatively strong electronegativity of the fluorine atom compared to that of hydrogen. The effect of fluorination on the atomic relaxation will be further studied in the next subsection by analyzing the electronic distribution on each atom by means of Bader analysis.

Table 1: Total energy ($E_T$) in eV and iron magnetic moment ($\mu_{Fe}$) in Bohr magneton ($\mu_B$) for the high spin (HS) and low spin (LS) states of the unfluorinated and fluorinated Fephen molecule adsorbed on the Cu(001) substrate (the values for the free molecule are between parenthesis). The last column shows the total energy difference $\Delta E = E_{T}^{HS} - E_{T}^{LS}$ in kJ/mole.

|                | LS                  | HS                  | $\Delta E$ (kJ/mole) |
|----------------|---------------------|---------------------|----------------------|
| Unfluorinated  |                     |                     |                      |
| $E_T$ (eV)     | -749.57 (-359.726)  | -749.00 (-359.517)  | 55.3 (20.3)          |
| $\mu_{Fe}$ ($\mu_B$) | 0.00 (0.00)       | 3.60 (3.72)        |                      |
| Fluorinated    |                     |                     |                      |
| $E_T$ (eV)     | -887.407 (361.701)  | -887.609 (361.977)  | -19.6 (-26.8)        |
| $\mu_{Fe}$ ($\mu_B$) | 0.00 (0.00)       | 3.25 (3.72)        |                      |

Figure 2: Superposition on the iron atom of the octahedral and (NCS) groups of the relaxed H-Fephen and F-Fephen molecules on the substrate in the two magnetic state (LS-left, HS-right), in color for the F-Fephen, and transparent for the H-Fephen.

Electron distribution analysis.

It is important to determine the effect of the distortion of the iron octahedron on the electronic levels of the molecule due to fluorination. Using Bader analysis, we focus on the electron distribution for each atom and its variation as we pass from the H-Fephen to F-Fephen. Fig. shows the Bader valence electron difference for each atom of the H-Fephen
and F-Fephen molecule adsorbed on Cu(001) surface. Due to the relative symmetry of the Fe(Phen)$_2$(NCS)$_2$ molecule, we consider only one phen group. We then obtain for each atom the number of valence electrons before (pink dots) and after fluorination (green squares). To show the electron transfer caused by fluorination, we calculated the electron difference in each site between the H and F-Fephen. This is shown by a red triangles in Fig. 3 for each magnetic state.

The electron transfer occurs mainly in the carbon atoms which have a direct bond with fluorine. This transfer is in general uniform for those atoms except for the C2 and C11, with 1.14 to 1.28 electron in the LS state and 1.24 to 1.23 electron in the HS state. Indeed we notice an additional transfer from the two atoms. This excess of electrons is captured by the two nitrogen N2 and N3, and this situation is observed in the two magnetic states. The excess electrons on the two nitrogen atoms of the phenyl group increases the electrostatic repulsion with the iron site. This repulsion leads to the elongation of the bond length between the central iron and the neighboring nitrogen atoms, especially in the phen group. The bonding energy being lower in the HS state compared to the LS state, the former is subject to more distortion in the octahedral environment as it was already seen in the previous subsection.

As a result of the elongation of the Fe-N bonds, the octahedral ligand field is reduced and the Coulomb repulsion among the iron $d$ electrons becomes larger because of the reduced ligand screening. This leads to the stabilization of the high-spin over the LS state in comparison to the unfluorinated case.

**Iron density of states and ligand-field analysis.**

It is now interesting to see how the substitution of the hydrogen atoms by fluorine atoms affects the iron density of states. Figure 4 shows how the $e_g$ and $t_{2g}$ ligand-field splitting is modified by fluorination. For the unfluorinated molecule the ligand-field splitting in the low-spin state is 3.50 eV compared to 1.55 eV in the high-spin state. For the F-Fephen, the ligand field in both spin states is significantly reduced to 3.1 eV in the LS state and 0.77 eV in
Figure 3: From left to right: (1) Valence Bader electrons (VBE) per atom for H-Fephen (pink dots), F-Fephen (green squares), (2) LS VBE difference between H-Fephen and F-Fephen (red triangles) for each site, (3) and (4) are respectively same as for (1) and (2) but for HS state. The labels of atoms are as shown on the top picture of the moiety of the molecule.

In the LS state, this reduction is due to the shift of the $e_g$ level towards lower energies, and in the HS state to the shift of the $t_{2g}$ towards high energies. As stated earlier, this reduction of ligand-field splitting and the increase of the pairing Coulomb energy among the $t_{2g}$ electrons lead to the stabilization of the high-spin over the LS state. The ligand-field theory helps describe the splitting of the electron energy states of Fe in the Fephen molecule, in the presence of a Coulomb potential generated essentially by the first neighbor nitrogen atoms. This model has been very successful in explaining the spin-crossover phenomenon, where the ligand-field energy can be of the order of the pairing energy between electrons.

In the case of an octahedral environment, the electrons of the nitrogen are closer to the the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals of Fe and away from the $d_{xy}$, $d_{yz}$, and $d_{xz}$ orbitals. The strong
electrostatic between the atoms of nitrogen and iron would lead to a splitting of the five
$d$ orbitals into two subshells, called $t_{2g}$, consisting of the $d_{xy}$, $d_{yz}$, and $d_{xz}$ orbitals, and $e_g$
consisting of the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals, with the former being lower in energy due to a lower
electron repulsion compared to the latter. Two important details should be pointed out here:

Figure 4: LS (left), HS (right) iron $d$-DOS for the Fe(Phen)$_2$(NCS)$_2$ molecule on Cu(001)
surface, H-Fephen (top) and F-Fephen(bottom). The $e_g$ states are shown in brown and filled
green and $t_{2g}$ states in green. The red vertical dotted lines show the alignments of states and
the reduction of the ligand field. The Fermi energy level is at zero energy.

First, that the $e_g$ and $t_{2g}$ orbitals are described using real spherical harmonics, also known as
cubic harmonics, and second, that these are defined through their $m$ quantum number, i.e.,
the eigenvalue of the $L_z$ operator, and depend on the coordinate system. To obtain the effect
of the ligand field on the $e_g$ and $t_{2g}$ DOS, we need either to rotate the real spherical harmonics
from the global coordinate system to the local one. We have implemented this feature in
VASP, the details are given in Ref. We present below our results for the octahedral cationic
Fe site in Fephen.

The iron $e_g$ and $t_{2g}$ DOSs are shown respectively in brown and green in Fig.
observe that the occupied 3d states are clearly split, with the \( t_{2g} \) orbitals lower in energy than the \( e_g \), and that the ligand field is much reduced for the fluorinated molecule by 0.4 eV for the LS state and about 0.8 eV for the HS state. Using the ligand-field splitting, it is possible to probe the filling of \( d \) orbitals and understand why the spin magnetic moment of Fe is about \( 4\mu_B \) as shown in the DOS given in Fig. [4]. To understand the splitting in an octahedral environment, a point-charge model was developed, in which the effects of hybridization can be fully neglected. Such a model would help us understand qualitatively the \( e_g \) and \( t_{2g} \) splitting. The electrons in the model can only interact through the Coulomb interaction with the neighboring negatively charged nitrogen ions. With this requirement, we assumed a formal ionic charge of +2 on the central atom and -2 distributed on the nitrogen neighboring atoms forming the octahedron. To maintain consistency between the ab initio calculation and the point-charge model, the octahedron was oriented in the same direction as in the rotated frame of reference, i.e., with the octahedral arms aligned maximally along the axes the reference frame. The Hamiltonian describing the ligand field is given by

\[
\hat{H}_\lambda^\sigma = V + \frac{I_\lambda}{2} \sigma_z, \tag{1}
\]

where, \( \lambda \) is set to the LS or the HS state, \( I_\lambda \) is the an effective Stoner parameter splitting of the spin up and spin down DOS for the HS state and is about 3 eV as given by our ab initio calculation and is zero for the low spin state, and \( \sigma_z \) is the \( z \) component Pauli matrix. The potential \( V \) due to the nitrogen ligands and felt by the central atom is given by

\[
V(r) = \sum_{i=1}^{6} \frac{q_i}{|r - R_i|} = 4\pi \sum_{i=1}^{6} q_i \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} (-1)^m \frac{1}{2\ell + 1} Y_{\ell}^{-m}(\hat{r}) Y_{\ell}^{m}(\hat{R}_i) \frac{r_<}{r_<^{\ell+1}}, \tag{2}
\]

where \( r_< (r_> \) is the smaller (larger) radius between \( r \) and \( R_i \) and where \( q_i = C e^2 \), \( C \) being an effective product of charges in each nitrogen atom and the central iron atom, the \( Y_{\ell}^{m} \) are the spherical harmonics, and \( R_i \) are the distance vectors connecting the central iron atom to the different ligands \( i \). Note that the local reference frame is centered on the iron atom and its
axes are along the ligands if the octahedron is perfect. Since the octahedron is deformed, the local frame is optimized to reduce the angles between $\bm{R}_i$ and the corresponding axis. The spherical angles $\vartheta$ and $\varphi$ of the vector $\bm{R}_i$ are then obtained in this optimized reference frame to compute the spherical harmonics. The results of this point-charge model are shown in

![Figure 5: Ligand-field splittings using the point-charge model for both the LS (a) and HS (b) state and for the unfluorinated (top plots) and the fluorinated (bottom plots) Fephen. The distorted octahedron obtained from ab initio calculation are shown in the insets (the bond lengths are in Å). The color code shows the different symmetries of the eigenvectors.](image)

Fig. 5 for both LS and HS and for the unfluorinated and fluorinated Fephen. The geometries of the octahedron are taken from our ab initio relaxed structures on Cu(001) and are shown in the insets of the figure. The model clearly shows that the unfluorinated molecule has a much higher ligand-field splitting compared to the fluorinated molecule in both the LS and HS states. However, the splittings are much smaller than the ab initio results. The model also shows that due to the distortion of the octahedron, the degeneracies of both the $e_g$ and $t_{2g}$ are lifted as in the ab initio DOSs. The widths of $e_g$ and $t_{2g}$ orbitals are also in qualitative agreement with the ab initio results. However, the octahedron distortion alone shows that the $t_{2g}$ and $e_g$ do not mix as shown by the color code of the eigenvector characters or the five $d$ orbitals, whereas our ab initio DOSs show small mixing. These mixing are due to additional interactions of the iron $d$ states with the other orbitals of the phen atoms.
Finally, according to the model and our ab initio calculation, all spin up $e_g$ and $t_{2g}$ states and the lowest spin down $t_{2g}$ state are occupied, producing an iron magnetic moment of 4$\mu_B$ in good agreement with our ab initio data shown in table 1.

**Energy barrier and minimal energy path.**

To determine the minimal energy path (MEP) between the two magnetic states of the molecule adsorbed on Cu(001), we start by interpolating linearly four images between the coordinates of the HS and LS states. We then used two different methods to search for the MEP. The first one (left in Figure 6), that we call the constrained minimization method (CMM), and the second method (right of Figure 6) is the aforementioned Nudged elastic Band (NEB) method\textsuperscript{14}. The CMM minimizes the total energy of each image independently from the others but constrains the distance $d_{SS}$ between the two sulfur atoms. This distance is interpolated linearly from HS state to the LS state and kept fixed during the atomic relaxation of each image. As a consequence the angle between the two isothiocyanate (NCS) groups is fixed to the interpolated value. This constraint doesn’t allow the molecule to return to its HS or LS ground state and hence gives an estimate of the minimal energy path. We don’t expect that this method will produce the optimal MEP and hence lowest energy barrier but sets a reasonable upper limit. In the second method, shown in dark red, we relaxed the entire molecule using the well known NEB method\textsuperscript{13}. In principle the NEB method will produce the optimal MEP and energy barrier, however in practice it very difficult to converge as the method is CPU very intensive for materials with too many atoms per supercell. For the unfluorinated molecule adsorbed on Cu, the NEB method did not converge well as shown in Fig. 6. It is surprising that for the fluorinated molecule the NEB computed energy barrier of about 0.56 eV is slightly higher than the CMM barrier of 0.49 eV and produced the same spin states $S$ along the path as the CMM. This might also indicate that the NEB results are not fully converged. It is interesting to notice
that for both the fluorinated and unfluorinated molecule the images near the LS state seem to converge better for the two methods compared to images near the HS state. However, as seen in Fig. the CMM results are slightly scattered compared to those obtained using the NEB method. The reason is that each image in the CMM is almost independent whereas in the NEB method the images are connected by spring constants. It is however interesting to notice that these two independent methods provided roughly the same energy barrier.

Figure 6: HS-LS minimal energy path and transition barrier for the unfluorinated (left) and the fluorinated (right) Fephen molecule adsorbed on Cu(001) surface. The constrained minimization method (see text) are in dark green and the NEB method in dark red. The spin state $S$ of each image is also shown. The continuous curves are quadratic interpolations used as guides to the eye.

**Constant current STM images.**

Constant current STM studies of Fephen were conducted experimentally, and results were reported for the H-Fephen molecule on Cu(001). The authors described the images as formed by two types of two oval lobes per molecule. To identify the spin state of each conformation, scanning tunneling spectroscopy (STS) showed a Kondo peak in the HS state (where the lobes of the molecule are well separated). In our work, we used the Tersoff-Hamann model to construct constant current STM images for the fluorinated and unfluorinated molecule adsorbed on Cu(001). To compute the STM images, we integrated the local density of states (LDOS) in a window of 50 meV around the Fermi level. In our approximation a constant intensity will correspond to a given LDOS. To compare the results of HS and LS we have
chosen arbitrarily the highest LDOS at 4 Å of the unfluorinated molecule in its LS state which is $3.88 \times 10^{-5}$ electron/Å² and $2.44 \times 10^{-4}$ electron/Å² for HS state. We have then used these values to scan the molecule in its HS and LS and determine its corrugation over the surface. Using this procedure, we reproduced the general trend of the experimental ob-

Figure 7: H-Fephen (a), F-Fephen (b) constant current STM images on copper substrate. The top panel gives the LS state, and the bottom panel the HS state.

servations for the H-Fephen molecule. We can see in Figure 7 (left) that the two oval lobes corresponding to the phen groups are more separated in the HS state and that the hight in the HS state is much higher than that of LS state as observed in experiment (see Fig 3b of Ref.15). This is because when we scan the surface, the current at the same distance from the molecule (4 Å) is more important in the HS state. For the F-Fephen, the same conformations were observed although the lobes are more expanded in the HS case compared to the unfluorinated molecule.
Conclusion.

The substitution of hydrogen by fluorine in the spin crossover FePn molecule led to a profound transformation of its electronic structure. It was shown that the fluorination leads to (1) the inversion of the magnetic state for the free and adsorbed molecule on Cu(001) surface, (2) a noticeable modification of the bond lengths and angles between the ligands and the central iron atom - though the overall geometry remains unaffected, (3) the strong reduction of the $e_g$-$t_{2g}$ ligand-field energy splitting, especially in the HS state, and (4) a huge reduction of the HS-LS total energy, and a small reduction of the HS to LS energy barrier.

Finally, the HS and LS STM images of the fluorinated molecule on Cu(001) surface, calculated using the Tersoff and Hamann approximation, are very different from those of the unfluorinated molecule. Those results are of importance since they can be used by future experiments to distinguish the fluorinated molecule from the unfluorinated one and differentiate the HS and LS states.

Methods

To compute the electronic structure and total energy of the SCO molecule adsorbed on a Cu (001) surface, we used the projected augmented wave (PAW) method as implemented in VASP (Vienna Ab initio Simulation Package). The exchange correlation energy is described within the generalized gradient approximation (GGA). The long range Van der Waals interaction between the molecule and the substrate is modeled by means of the Grimme approximation. For the description of the localized $d$ states of iron, we used the rotationally invariant DFT+U method as implemented by Dudarev and coworkers. The values of the Hubbard parameter $U$ and exchange parameter $J$ were set respectively to 3 eV and 0.9 eV. These values are shown to reproduce the iron spin moment and the expected energy difference between the two spin states of Fe(II). The electron analysis on each atom is done with the Bader electron analysis method. The computation of the energy barrier...
and the minimum energy path (MEP) between the high spin and low spin states is done using the nudged elastic band (NEB) method. This method consists in first interpolating many possible transition points, often called images, from the initial to the final states and relaxing them with constraints originating from fictitious spring forces between neighboring images, in order to maintain a constant distance between them along the reaction path. The calculations converge when the MEP is found. But, since we found that this method is difficult to converge and is computationally prohibitive for systems with many atoms per unit cell, we have also used what we called the constrained minimization method (CMM). In this CMM we interpolated linearly the distance between the two sulfur atoms to create different images, we fixed the sulfur-sulfur distance and let all the other atoms relax to find the minimal energy path. Surprisingly, as it can be shown latter, this method led to a slightly smaller energy barrier than the NEB.

The Fephen molecule contains 51 atoms, where the iron atom is surrounded by 6 nitrogen atoms, forming a distorted octahedron. In addition the molecule is composed of 26 carbon atoms and 16 hydrogen atoms, which will be later substituted by 16 fluorine atoms as indicated in Fig. 1. To simulate the substrate we have used three layers of copper grown along the (001) direction, each plane containing 36 (6x6) atoms of copper. Thus we used 159 atoms in the supercell to fully describe the H(F)-Fephen/Cu(001) system. Our calculations were done using a periodic cell of (17.8 × 17.8 × 33.6 Å) for both the gas phase and the molecule adsorbed on the copper substrate.

The total energy is converged to 10^{-5} eV and the plane waves cut-off energy is set at 500 eV. The atoms are allowed to move until the forces are below 10^{-3} eV/Å in each direction of the cell axes. The calculation of the Fermi level is carried with a Gaussian integration method, using a width of 0.1 eV. This electronic entropy is removed when calculating the total energy. Due to the large number of atoms per supercell, we restricted our k-point mesh to the Γ point.
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