STM/STS observation of ferrocene derivative adduct to C_{60} on HOPG

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Abstract

The C_{60}ONCF_{n} cycloadduct (Fn=ferrocene) was prepared in the reaction between C_{60} and ferrocene oxime, the ferrocene derivative was bound to C_{60} at the 6–6 bond by a heterocyclic oxygen–nitrogen–carbon ring; the compound was stable in air. The compound dissolved in dichloroethane was deposited on HOPG and observed by UHV STM/STS methods. The molecules of C_{60}ONCF_{n} formed several-microns-long straight chains with clearly visible adducted groups pointing to one side of the chain. The STM/STS observations are discussed within the terms of semiempirical quantum chemical molecular modeling.

Keywords: Fullerene adducts; Conformation; Scanning tunneling microscopy; Scanning tunneling spectroscopy

1. Introduction

Scanning tunneling microscopy (STM) allows to investigate molecules like C_{60} and other organic molecules with open HOMO–LUMO gap that are insulating in their bulk structure as well as self-assembled monolayers of molecules or dense layers of organic adsorbates. Previous studies have been carried out on fullerenes on HOPG [1–4], Si(111)–(7×7) [5], Pd(110) [6] or even on a fullerite crystal C_{60}(111) [7].

Despite the spherical shape of free C_{60}, fullerenes on some substrates are not mobile because they lose icosahedral symmetry though they maintain their electronic identity that allows their precise imaging and identification of molecular orbitals. Furthermore, the tip of the scanning tunneling microscope (STM) was used to position individual C_{60} molecules on a Si(111) surface [8]. The negative differential-resistance exhibited by two C_{60} molecules joined using the STM tip suggested that fullerenes could be used to build molecular electronic devices [9]. The electronic properties of fullerenes and their interactions...
with substrates may be modified by adducting functional groups to fullerenes, e.g. phenylated \( C_{60} \) on Si(111)-(7\times7) was found to diffuse and rotate due to the presence of the phenyl groups until ordered layers were formed [10]. Intense research in the area of the chemistry of fullerenes has been carried out since the discovery of a method of producing fullerenes in large amounts [11,12]. To the first compounds adducted to \( C_{60} \) belong organometallic compounds containing palladium [13], and osmium oxide with organic ligands [14]. The organometallic compounds may form charge transfer complexes with \( C_{60} \) as, e.g., cobaltocene-(\( C_{60} \))\(_{1.3}\) (cobaltocene=\( C_{2}H_{4}CoC_{2}H_{4} \)) [15,16] or be cycloadducted to \( C_{60} \) at the 6–6 bond and the compounds may also be used to introduce metals with high melting temperatures into fullerite sandwich compounds such as ferrocene.

Pure \( C_{60} \) deposited on HOPG was previously observed, e.g. Refs. [1–4], and high-resolution images of individual \( C_{60} \) molecules were obtained suggesting that fullerenes strongly interacted with the HOPG substrate. Our experiments were specifically aimed at the observations of both parts of the complex \( C_{60} \)-adduct molecules in order to determine whether recognition of orientation of the adduct is possible. The STM topographic and tunneling spectroscopy experiments presented here were performed on \( C_{60} \)ONCFn complexes consisting of ferrocene (Fn, \( C_{5}H_{4}FeC_{2}H_{4} \)) bound to \( C_{60} \) at the 6–6 bond by a heterocyclic ring. The cyclopentadienyl ring (cp=\( C_{5}H_{4} \)) and heterocyclic ring may be either parallel or perpendicular to each other. The heat of formation of the complexes in the two structures is the same but the states are separated by a low energy barrier. The purpose of this study was to find out what kind of structures the \( C_{60} \)ONCFn complexes form on highly oriented pyrolitic graphite (HOPG) at low coverage, whether the dense arrangement of the complexes hides the Fn fragments and if whether molecule–molecule and molecule–substrate interactions lead to the stabilization of one of the conformations and change the molecular energy spectrum. An interesting question arises whether the orientations of the detected Fn groups could be determined and modified by the STM tip.

The \( C_{60} \)ONCFn compound was selected for the experiments because its large density of states localized at similar energies on \( C_{60} \) and the Fn fragment enables the STM observations. Large molecules with a high degree of degeneracy of molecular states are also interesting because of the possibility of relatively easy observations of negative differential resistance. The compound is stable in air and soluble in organic solvent, which facilitates the preparation of the samples.

The experimental results obtained are compared with calculations using semiempirical quantum chemical models based on neglecting the diatomic differential overlap approximation. The calculations were performed within the terms of the PM3 model where the Slater type atomic orbitals were used and the electron–electron interaction was accounted for by the self-consistent field method. The model was parametrized to reproduce the structure and heat of formation of organic and organometallic complexes. The model also reproduces well the structure of fullerenes.

2. Experimental

2.1. Synthesis of \( C_{60} \) adduct

The adduct was prepared using commercially available \( C_{60} \) and ferrocenecarboxaldehyde (FnCHO) as the reagents. At first, the ferrocenecarboxaldehyde was transformed to ferrocenecarboxaldehyde oxime (FnCH=NOH). For this purpose FnCHO and hydrochloride hydroxylamine (\( \text{NH}_2\text{OH.HCl} \)) were dissolved in ethanol and sodium hydroxide (NaOH) was successively added to the solution maintained at boiling temperature for 2 h. Next, the solution was cooled and water was added to cause partial precipitation of the reaction products, the reaction product needed for further process: ferrocenecarboxaldehyde oxime remained in the solution. Subsequently the solution was dried and the obtained FnCH=NOH was dissolved in chloride methylene (\( \text{CH}_2\text{Cl}_2 \)) and was reacted with \( N \)-chloromide succinic acid (\( C_6\text{H}_2\text{O}_2\text{NCl} \)) to produce nitrile oxide (FnC=N=O \). The final cycloaddition reaction between FnC=N=O \ and \( C_{60} \) took place in toluene solution of \( C_{60} \) at reflux in the presence of triethylamine (\( C_3\text{H}_4\text{N} \)). The molar ratio of the main substrates \( C_{60}/(\text{FnCH}=\text{NOH}) \) was equal to 1/4. The
product C_{60}ONCFn was separated by chromatography using a silica gel column with toluene as the eluent.

The \(^1\)H and \(^{13}\)C NMRs and absorption in visible light were used to identify the product (C_{60}ONCFn). The \(^1\)H NMR exhibited one resonance line with the chemical shift \(\delta = 4.20\) ppm and two lines with \(\delta = 4.53\) and \(5.20\) ppm, the ratio of the intensity of the lines equalled 5:2:2. The number of lines and the intensity ratio corresponded to the number of various hydrogen atom positions at one non-substituted cp ring where all five protons are equivalent and to the singly substituted ring where four hydrogen atom sites split in two different types. The \(^{13}\)C NMR spectrum consisted of resonance lines at \(\delta = 68.1, 69.7, 69.8\) ppm that can be ascribed to the C_{5}H_{4} ring and at \(\delta = 73.2, 75.4, 102.7\) ppm ascribed to C_{4}H_{4} and to C atoms in isoxazoline ring binding Fn to C_{60}. There were also 28 lines in the range of \(\delta = 135.2–152.4\) ppm ascribed to C_{60} which lost symmetry because of the adduct.

There were only minor differences in the absorption spectra of the C_{60}ONCFn cycloadduct dissolved in toluene in comparison to pure C_{60} in the 400–600 nm region. The absorption was stronger at 496 nm, weaker in the ranges of 540 and 600 nm, also observed was the disappearance of the band at 408 nm and appearance of a new one at 430 nm. This band is characteristic for the closed [6,6]-C_{60}-adducts \[17\]. The changes in absorption were caused by the distortion of fullerene, lowering its symmetry that lifted the degeneracy of the electronic levels and activated the orbitally forbidden electronic transitions. The reaction procedure and the properties of the compound have been described in detail in Ref. \[18\].

The STM/STS experiments were performed at room temperature with a VT-STM/AFM system in UHV condition (Omicron). The C_{60}ONCFn samples for the observations were prepared by sonicating for 30 min a few micrograms of the prepared and dried C_{60}ONCFn compound in 2 cm\(^3\) 1.2-dichloroethane and depositing a drop of this solution on the fresh (0001) basal plane of a HOPG. A fresh surface of the HOPG was prepared by cleaving the crystal with adhesive tape. The samples were loaded to the UHV STM chamber. The investigations were performed in the constant current mode, with a typical tunneling current of 0.2–1 nA and the positive sample bias of 0.2–1.2 V. The STM tips were prepared by mechanically cutting the Pt90%–Ir10% alloy wires.

Fig. 1. C_{60}ONCFn molecule in parallel conformation.
should be close to 1 nm as in fullerite crystals. However, if complexes were aligned with the adducts along the chains then the separation between C_{60}ONCFn complexes in rows should not be larger than 1.8 nm since the largest distance between C and H atoms in the adduct is ~1.5 nm. Because the observed spacing is different than expected, we suppose that here not all complexes constituting the rows are visible as the bright spots and the rows contain solvent molecules that are invisible in the experiment but play a role in arranging the molecules. The structure of other chains less densely packed may be analysed in more detail.

3. STM observations

We observed C_{60}ONCFn complexes arranged in long parallel chains of the type shown in Fig. 2 though there were also clusters of the sizes corresponding to single and several molecules that did not show any particular structures. We suppose that the central, brightest, i.e. highest, feature in Fig. 2 consists of two layers of complexes and side rows of single linearly arranged complexes.

The average distance between the rows consisting of single molecules and the separation between the bright spots within the rows are observed to be ~2.2 nm. If the distance between the bright spots, i.e. centers of fullerenes, within the single molecular rows was determined by the size of C_{60} then it

Fig. 3. Details of the single molecular chains structure. (a) 2-D topography of a 23×23 nm² fragment which shows four well-separated chains built of the C_{60}ONCFn complexes; recorded at: U=0.2 V and I=0.1 nA. (b) Enlarged fragment of the rightmost chain scanned at U=0.05 V and I=0.06 nA. (c) Probable layout of C_{60}ONCFn in a chain. (d) Z-profile across a single molecule measured along the arrow shown in the image (b).
occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO, LUMO). Thus at low scanning voltages applied in topographic experiments, only the electronic states of a conducting substrate may participate in the tunnelling process. According to molecular modelling performed for C\textsubscript{60}ONCF\textsubscript{n} placed 0.3 nm above the substrate graphene sheet, the substrate states extend perpendicularly to a larger distance in the area where the molecule resides rather than in other regions. Because these states do not envelop the whole complex, the apparent height of the molecule is smaller than expected.

The periodicity of the bright objects along the chains neither in Fig. 3 nor in Fig. 2 corresponds to the size of the complexes and the observed slightly varying contrast suggests that all visible molecules along the chains have comparable density of states. It may be explained assuming different orientation of every other molecule in the chains. One of the possible arrangements of complexes is shown in Fig. 3c. For the construction of the diagram, the structure of C\textsubscript{60}ONCF\textsubscript{n} dimer with the molecule’s electric dipoles oriented anti-parallel \(\uparrow\downarrow\) was optimized using the PM3 model. The maximal heat of formation was found with C\textsubscript{60}ONCF\textsubscript{n} molecules tilted relatively as shown in Fig. 3c; then the charge distribution around the dimer was calculated to simulate an effective diameter of C\textsubscript{60} equals 1 nm and finally the dimers were placed at proper distances to reconstruct the STM image. Similarly reconstructed STM images may be obtained for both possible conformations of the C\textsubscript{60}ONCF\textsubscript{n} molecule. Although there is no experimental proof of this particular orientation of the complexes within the dimers, such arrangement explains the characteristic distances and the fine steps along the chains shown in Fig. 3a and b. There are evident differences in shape of the part of the image tentatively ascribed to the Fn adducted group. However we are not able to unambiguously determine what is the conformation of the individual fragment.

4. STS measurements

The molecular chains were conducting at any voltage in the range of applied \(\pm 2\) V allowed by the experimental set-up even though the energy gap between HOMO and LUMO of the isolated molecule is relatively large. The current increased monotonically with the applied voltage observed in the \(I(V)\) characteristics. The current increase results from the tunnelling of the electrons to density of states (DOS) of the conducting substrate continuously distributed in the energy scale.

Fig. 4a shows the \(dI/dV(V)\) curve recorded on a pure test graphite sample (graphite which has not been subjected to dichloroethane solvent) where characteristic features are observed at \(\sim 0.5\) eV below and \(0.5\) eV above the Fermi level. They can be attributed to the specific points of the graphite Brillouin zone: \(P_1(\pi)\) and \(P_2(\pi^*)\), respectively [19]. The \(dI/dV(V)\) curve (Fig. 4b) for the graphite uncovered by the molecules is similar with the curve for the pure test graphite sample (Fig. 4a). In both cases the plots are slightly asymmetric, the differential conductance being higher for negative polarization of the sample than for positive voltage of the same value. This type of conductance asymmetry, i.e. LDOS asymmetry, around the Fermi level is typical for pure graphite which proves that dichloroethane solvent evaporated completely. However, in the case of uncovered graphite the \(P_1(\pi)\) and \(P_2(\pi^*)\) states are less visible, especially at the occupied part of the spectra. The atomic structure for the uncovered graphite could be seen away from the molecule chains. However, the 1–2 nm region near the edges of the chains was different from that in the smooth areas on the basal plane. In these regions a superstructure with the periodicity of \((\sqrt{3}\times\sqrt{3})a\ (a = 0.246\) nm) and rotated 30° with respect to the underlying graphite lattice was often observed. Similar structures can be seen on graphite near defects shaped like steps or adsorbed metal particles [20–22].

Different mechanisms were considered to explain the conductivity of the organic molecules observed by STM, like work function modulations [23] or a decrease of the HOMO–LUMO energy gap due to molecule–molecule or molecule–substrate interactions [24]. As it has been previously pointed out, semiempirical quantum chemical models show that substrate states locally extend over molecules making electron tunneling possible. Discontinuous molecular electronic states only slightly modify the total
DOS of the substrate–molecule–STM tip system and thus in most cases they can only be seen on the plots of the $dI/dV$ derivative. The current characteristics $I(V)$ recorded at several sites across the molecular chains revealed no substantial differences in conductance or positions of $dI/dV$ peaks although the amplitudes varied. The $dI/dV$ derivative is shown in Fig. 5 and is compared with the calculated DOS of the C$_{60}$ONCF$_n$ complex. In order to obtain the DOS the complex was optimized using the PM3 model; the energy of molecular orbitals (MO) were calculated within the terms of extended Hückel theory (open and solid dots in the upper panel of Fig. 5); all levels were broadened using Gauss function with the same width and finally the number of states at each energy was found by summing contributions from all broadened MO (lines in the upper panel of Fig. 5).

The calculations were performed for three different level widths looking for a similarity with the experimental plot. The measured $dI/dV(V)$ is shown in the lower panel of Fig. 5 together with the DOS plot calculated for 0.15 eV broadening where best correspondence with the experiment occurred. The line representing the DOS was shifted horizontally to adjust the Fermi energy with the center of the HOMO–LUMO gap. The broadening is much larger than the thermal energy which suggests that tunneling does not occur from single isolated molecules but from dimers or larger clusters with weakly modified energy spectrum. There is a considerable difference in behaviour of the amplitudes of the observed and calculated peaks, for the DOS amplitude of the occupied states increases with lowering of the energy while in the experiment at negative sample bias the amplitude suddenly decreases. It is probably yet another indication that measurements were performed on clusters of C$_{60}$ONCF$_n$ molecules where occupied orbitals originating from the fivefold degenerate $h_x$ and $h_y$ orbitals in isolated C$_{60}$ were close in energy—see Fig. 5—and underwent further splitting in each complex due to the interaction with the substrate or between the complexes. It may produce almost continuous distribution of MO in energy, thus broadened DOS peaks may overlap and obliterate the singularities.

5. Concluding remarks

The C$_{60}$ONCF$_n$ complexes produce well arranged linear forms on HOPG substrates that may be imaged by the STM technique. Typical periodicity observed in the chains may be explained assuming arrangement of C$_{60}$ONCF$_n$ in dimers compensating the
of conductivity ought to be searched in molecular systems extending high above the substrates, like C\textsubscript{60} multi-adducts. To date, we are unable to distinguish parallel conformation of the adduct from the perpendicular one, and also unable to modify any conformation with the STM tip.

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References