Electronic structure of Li$^+$@C$_{60}$:

Photoelectron spectroscopies of the Li$^+$@C$_{60}$[PF$_6^-$] salt and STM of the single Li$^+$@C$_{60}$ molecules on Cu(111)

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We report first STM observation of the Li+ ion endohedral C_{60}, prepared by means of evaporation of high-purity $Li^+@C_{60}[PF_6^-]$ salt. The electronic state of $Li^+@C_{60}$ in the $Li^+@C_{60}[PF_6^-]$ salt was also precisely determined by photoemission spectroscopy (PES), X-ray absorption spectroscopy (XAS) and density functional theory (DFT) calculations. In the salt, it is shown that Li and PF_6 have nearly single positive and negative charge, respectively, and the C_{60} cage is nearly neutral. The salt decomposes easily in UHV by heating up to 400 ℃ because of the weak electrostatic interactions between $Li^+@C_{60}$ and PF_6^-, which enables us to selectively deposit $Li^+@C_{60}$ on Cu(111) surface. Although secondary-ion mass spectroscopy (SIMS) of the deposited $Li^+@C_{60}$ film showed decrease in the Li content to 1/3-1/6 of the original salt during evaporation, we were able to distinguish $Li^+@C_{60}$ in the monolayer in STM. DFT calculation of $Li^+@C_{60}$ on Cu(111) suggested that the endohedral Li inside the C_{60} cage singly charged and that the location of Li^+ ion is displaced upward from the center, altering the local density of state at the top parts of C_{60}, especially that of LUMO+2. These calculated results are mostly in fair agreement with the bias-dependent STM and dI/dV images.

1. Introduction

The endohedral doping of fullerenes has been one of the central issues of the physics and chemistry of fullerenes, because it can cause an emergence of the novel electronic properties without altering the shape of fullerene cage [1–3]. However, the small yield in the synthesizing process together with the enhanced reactivity of the endohedral fullerenes has been hampered a large-amount production and sufficient purification of endohedral fullerenes. This has been especially the case of a metal-endohedral C_{60}[1–3], including the pioneering investigation of Li@C_{60}[4]. Recently, a new family of the endohedral C_{60}, namely, *metal-ion* endohedral C_{60} (M^+@C_{60}) has been emerged, and an industrial technique of large-quantity synthesis of M^+@C_{60} utilizing the low-energy ion irradiation has been developed. A stable compound containing high-purity Li^+-endohedral C_{60} (Li^+@C_{60}) up to more than 99 % has been successfully synthesized by utilizing the ion implantation technique and by forming the salt with counter anions such as $SbCl_6^-$ and PF_6^-[5–7] . The crystallographic structure determination of the Li^+@C_{60}[PF_6^-] salt has already been done by synchrotron X-ray diffraction as depicted in Fig. 1(a), and several works have already deduced unique features of the salts of Li^+@C_{60} such as the high ionic conductivity of the solutions, unique optical properties and enhanced chemical reactions[8–11]. One of the important natures of Li^+@C_{60}, which makes it a promising material for applications in the organic electronics, is the fact that the orbital energy levels of C_{60} are largely stabilized due to presence of the Li^+-ion, enhancing the electron-accepting character even compared to pristine C_{60} which is known as one of the few organic semiconductors showing a strong electron accepting

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(n-type) property[7]. Indeed, the electron-accepting characteristics of $Li^+@C_{60}$ have already been utilized recently in developing the dye-sensitized solar cells with high efficiency[12–15]. This is in contrast to the case of $Li@C_{60}$ where significant charge transfer to the C_{60} cage from Li is expected, resulting in smaller ionization potential[16]. Another important aspect of $M^+@C_{60}$ is the application as a molecular switch[17–19]. It has been shown that the fractions (approximately 25%) of the external electric field can penetrate into the C_{60} cage, in spite of the efficient screening due to π electrons[20]. This field can alter the state of endohedral atoms and molecules, provided they are charged or polarized[1–3,17–19]. Therefore, there are two-fold importance in the detailed understandings of the electronic states of $Li^+@C_{60}$ on the substrate surfaces; in order to control the carrier injection and transport properties as an organic electronic devices and to exploring further functionalization such as switching.

Here, molecular-resolution STM measurements reveal the electronic structure of the adsorbed $Li^+@C_{60}$ on a metal surface, Cu(111), utilizing the temperature-dependent evaporation of the $Li^+@C_{60}[PF_6^-]$ salt in ultra-high vacuum (UHV). Prior to the STM studies, we also precisely characterized the electronic structures of $Li^+@C_{60}$ in the salt. The photoemission and photoabsorption spectroscopy measurements together with DFT calculations of the $Li^+@C_{60}[PF_6^-]$ salt deduced a charge distribution in the salt, where Li and the counter anion are positively and negatively charged, respectively, leaving the C_{60} cage almost neutral. These observations unambiguity showed that $Li^+@C_{60}$ in the salt retains its original electronic structure such as the large ionization potential, and this is because the fact that the interaction between $Li^+@C_{60}$ and PF_6^- in the salt is weak.

This weak interaction allows us to separately evaporate the $Li^+@C_{60}$ molecules from the salt by heating in UHV. We were able to identify small amount of $Li^+@C_{60}$ molecules in the monolayer and its electronic structure was in fair agreement with the DFT calculations. Besides the fair agreement between theory and experiments, there still remained a quantitative discrepancies and they may be originated from the electric field-induced phenomena such as the polarization of the π electrons at the cage or the displacement of Li+ ion in the cage.

2. Experimental and Computational Methods

$Li^+@C_{60}[PF_6^-]$ salt with a purity of >99% were produced by Idea international Inc. For the measurements of ultraviolet photoemission spectroscopy (UPS) and X-ray photoabsorption spectroscopy (XAS), the powder of the $Li^+@C_{60}[PF_6^-]$ salt was loaded on a clean Ag foil. The measurements were performed in the synchrotron radiation facility of the Photon Factory (BL-13B and BL-7B) and UVSOR (BL2B). XAS at the Li K edge was performed in the SR-center of Ritsumeikan Univ (BL-8). The vacuum evaporation of the $Li^+@C_{60}[PF_6^-]$ salt was done with a homemade Knudsen-cell, which is equipped with a thermocouple to read the cell temperature, installed in the room-temperature UHV-STM system (UNISOKU). The evaporation rate was monitored by a quartz microbalance (QCM). In the SIMS measurements (CAMECA, IMS-7f), an evaporated film of approximately 10 nm thickness on a gold film was used as a specimen and a O^{2+} ion beam of 1.2 nA was used as the primal ion beam for analysis. The dI/dV images are obtained with the lock-in detection method with the additional AC bias modulation voltage of ±80meV with 2 kHz.

Density functional theory (DFT) within the projector augmented wave (PAW) method[21] and GGA exchange-correlation functional in the form proposed by Perdew, Burke and Ernzerhof (PBE)[22] were used as implemented in the VASP [23,24] code. The empirical D3 Grimme corrections[25] and periodic boundary conditions (PBC) were employed. The Brillouin zone reciprocal space was sampled by 6×6×1 and 9×9×1 k-points using the Monkhorst-Pack scheme[26] for a geometry optimization and electronic structure calculations of Li@C_{60}/Cu(111), respectively. In the case of $Li^+@C_{60}[PF_6^-]$

salt the Brillouin zone was $5\times5\times5$ k-points. The kinetic energy cutoff for the plane-wave basis set was equal to 450 eV. The vacuum region was set to be >12 Å for all Li@C_{60}/Cu(111) calculations. The theoretical STM images were generated using the Hive program[27].

3. Results and discussion

Firstly, we argue the electronic states of $Li^+@C_{60}$ in the $Li^+@C_{60}[PF_6^-]$ salts. The ultraviolet photoemission (UPS) spectra and the X-ray absorption (XAS) spectra of the $Li^+@C_{60}[PF_6^-]$ salt, exhibiting the information of the frontier orbitals, are shown in Fig. 1(b) and (c) together with those of pristine C_{60}. In Fig. 1(b), the binding energy from the vacuum level was determined based on the high-binding-energy cut-off positions of the spectra. The UPS spectra exhibit well-defined occupied molecular orbitals (HOMO and HOMO-1) of C_{60} for both samples. It is observed that the HOMO level of $Li^+@C_{60}$ in the salt is lowered by 0.6 eV compared with that of pristine C_{60}, indicating a larger ionization potential (IP) of $Li^+@C_{60}$ as expected[5,10]. It is important to note that the small peak at 6.8 eV in the spectrum of the $Li^+@C_{60}[PF_6^-]$ salt should be due to impurities such as non-endohedral Li atoms, because the intensity of this feature depends on the sample and the corresponding states were not reproducible by DFT calculations as discussed in the followings, while this peak has been assigned to the charge transfer state of the C_{60} cage[28].

The C K edge XAS spectra of $Li^+@C_{60}[PF_6^-]$ (Fig. 1(c)) showed that the energy positions of the lowest unoccupied molecular orbitals (LUMOs) of $Li^+@C_{60}$ are located approximately at the same position of those of pristine C_{60}, while the line shape of LUMO becomes slightly broadened. These facts suggest that the change in the HOMO-LUMO gap of $Li^+@C_{60}$ is small, as expected from ref. [10] and our theoretical calculations (Fig. 2b). Therefore, the charge transfer to the LUMO of $Li^+@C_{60}$ is negligible. We also confirmed that the line shape of the C1s photoelectron spectrum of

$Li^+@C_{60}[PF_6^-]$ in Fig. 1 (d) remains nearly unchanged from that of C_{60}, also suggesting that the modification of the molecular orbitals of C_{60} cage due to the charge transfer is indeed subtle. The charge state of the Li^+ ion in the salt was examined by observing the Li K edge XAS spectrum as shown in Fig. 1(e). Although the signal intensity is weak due to small Li content, a clear and reproducible XAS spectrum was obtained. The Li K edge XAS spectrum exhibited a characteristic step at 61 eV and a peak at 71 eV. These spectral features are known to be characteristic for singly charged Li^+ ion[29,30].

These experimental observations are in good agreement with the DFT calculations of the $Li^+@C_{60}[PF_6^-]$ salt. Fig. 2(b) shows calculated density of state (DOS) of $Li^+@C_{60}[PF_6^-]$ together with that of pristine C_{60}. The Fermi level in Fig.2 (b) is set at the top of the HOMO. It is seen that the structure of the frontier orbitals of $Li^+@C_{60}[PF_6^-]$ is almost unchanged from those of pristine C_{60}, indicating a negligible charge transfer to the C_{60} cage as well as the small modification of the C_{60} electronic structure. The calculations clearly show that the charge at Li is +0.99e and at PF_6 is -1.00e, leaving the C_{60} cage almost neutral (+0.01e), as shown in Fig. 2(a). We can also see a small overlapping between the Li^+ ion and the C_{60} cage and resulting little modification of the DOS shape of C_{60}. The overlapping between Li-derived vacant states and LUMO+2 orbital of the C_{60} cage is most significant. This overlapping may be the cause of the broadening of the unoccupied states found in the XAS spectra (Fig. 1(c)). The energy-gain due to the overlapping between Li and C_{60} displaces the most stable position of Li^+ ion in the C_{60} cage from the center by 1.28Å, in near agreement with the recent report[31].

It is also worthy to note that no additional electronic state is formed in the HOMO-LUMO gap of the $Li^+@C_{60}[PF_6^-]$ salt. The DOS originated from PF_6 is also absent from the region of the frontier orbitals. Therefore, the small in-gap states found at 6.8 eV in Fig.1 is indeed likely to be due to impurity rather than the charge-transfer state. The above results confirm that the interaction between $Li^+@C_{60}$ and PF_6^- are weak electrostatic character and thus $Li^+@C_{60}$ in the salt retains its original electronic structure. On the other hand, the weak interactions between $Li^+@C_{60}$ and the surrounding PF_6 anions together with the small interaction with the C_{60} cage and Li+ ion lead to the reduction of the structural symmetry and subtle modification of the electronic state of C_{60}. It is also noted that our calculations are not in full agreement with recent reports on the electronic structure of $Li^+@C_{60}[PF_6^-]$ salt by means of the calculation using the GAUSSIAN code[31], especially the charge state of the elements. The difference should come from the solid-state effect, i.e., weak but sizable interactions from the surroundings, which has not been considered in the calculation of isolated pair of $Li^+@C_{60}[PF_6^-]$.

Next, we examined the deposition of $Li^+@C_{60}$ on the surface of Cu(111) by heating the $Li^+@C_{60}[PF_6^-]$ salt in UHV. It was found that the increase of the temperature of $Li^+@C_{60}[PF_6^-]$ in the Knudsen cell results in a characteristic two step deposition from the salt; the first-step deposition of PF_6^--related species which are evaporated at approximately 220 °C and the following second-step deposition of $Li^+@C_{60}$-related species at approximately 400 °C (S1). We were thus able to deposit $Li^+@C_{60}$ separately from $[PF_6^-]$ anion, by utilizing the second-step deposition after the

completion of the first-step deposition. The Li content in the deposited film was analyzed by SIMS. Table 1 summarizes the relative peak intensities for C^+, Li^+, F^+ and P^+ ions at the charge-to-mass ratio of 12, 7, 19 and 31, respectively, in the SIMS spectrum obtained for the 10 nm thick film deposited on a gold film by the second-step deposition from $Li^+@C_{60}[PF_6^-]$, in comparison with that from the powder sample of the salt. Note that the relative intensities do not represent the atomic composition of the film, due to the matrix effect in the ionization cross section. It was found that the Li content in the deposited film was reduced to 1/3 of that in the $Li^+@C_{60}[PF_6^-]$ salt. This indicates that a significant fraction of Li ions in $Li^+@C_{60}$ are thermally desorbed from the cage upon the evaporation process. Judging from the drastic decrease of the P and F content together with the UPS and XPS of the deposited film, it is reasonably concluded that the deposited film is mainly composed of $Li^+@C_{60}$ and C_{60}.

We then deposited slightly less than one monolayer of $Li^+@C_{60}$ and C_{60} from the second-step deposition on a clean Cu(111) substrate and the film was examined by STM. In order to remove possible contaminations, the sample was annealed at 400 ℃ subsequent to the deposition. Figures 3(a) and 3(b) show the wide range and molecular-resolution STM images of the evaporated film on Cu(111). We confirmed the formation of the monolayer islands of C_{60} with the well-known 4×4 superstructure as shown in the LEED pattern[32,33]. We can see some disordering at the rim of the islands, as seen in Fig. 3(a), which has not been observed in the island formed by depositing pristine C_{60} on Cu(111). The disorders at the rim can be attributed to the aggregation of $Li^+@C_{60}$ with C_{60}, which usually occurs in the production process of $Li^+@C_{60}$, or with

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PF_6^--related residual impurities to form stable clusters. On the other hand, when we focus on the inside of the monolayer island where molecules form a uniformly ordered in the 4×4 phase, as shown in Fig. 3(b), it was found that some of the molecules exhibited a peculiar bias dependence in the apparent height when a positive potential was applied to the sample. These molecules (molecule A), which are indicated by the arrows in the figure, coexist with C_{60} with a normal bias dependence (molecule B) occupying the majority of the molecules. Therefore, the molecule A is likely to be $Li^+@C_{60}$ which was not aggregated at the rim of the island. For both molecules A and B, we can see the characteristic shape of the LUMO in the STM image taken with a positive sample bias voltage of 2 V, indicating that these two kinds of molecules adsorb on Cu(111) with the same molecular orientation (Fig. 3(b)). The different bias-dependence of each molecule, therefore, is not due to the difference in the molecular orientation. The clear LUMO shape of both molecules also suggests that the contrast is not due to impurities adsorbed on the molecules. The bias dependent change of the apparent height of the molecule A and B is summarized in Fig. 3 (c). It is seen that, while the difference between molecule A and B is not obvious in the filled-state imaging, difference in the contrast become clear with increasing the sample potential to the positive side. The difference in the apparent height became as large as 0.8 Å at the bias voltage of 3 eV. Note here that, on metal surfaces including Cu(111), different contrasts of C_{60} molecules in the monolayer have been reported due to the substrate reconstruction [32–34]. The reconstruction of substrate results in significant decrease in the apparent height up to 2 Å, and the apparent height is not much dependent on the bias

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voltage. Therefore, the observed bias-dependent difference in the apparent height is not due to the different adsorption geometry. The difference of the molecule A and B become more obvious in the differential conductance (dI/dV) measurements as shown in Fig.4. The images were taken several characteristic voltages according to the calculated DOS as discussed later. We observed clear dI/dV contrast between two molecules in both bias porality, suggesting that the electronic structures of two molecules are indeed different. Note that, in the dI/dV measurements, we sacrificed the resolution of the images due to large scan area and large modulation bias voltage, in order to enhance the difference of two molecules dispersed in the large area.

In order to determine the origin of two molecules in the STM images with different electronic states, the electronic structure of $Li^+@C_{60}$ on Cu(111) surface were calculated by means of the DFT calculations in comparison with the normal C_{60} on Cu(111). Firstly, we checked the adsorption geometry of $Li^+@C_{60}$ and C_{60} on Cu(111) substrate, and found that the most stable adsorption configuration is C_3 hcp for both C_{60} and $Li^+@C_{60}$ (see S.2), while the adsorption energy of $Li^+@C_{60}$ (2.91 eV) is larger than that of C_{60} (2.24 eV). This result explains the experimental observation that two molecules A and B adsorb in the same molecular orientation in the mixed monolayer, as shown in Fig. 3(b). It is deduced that the LUMO of the $Li^+@C_{60}$/Cu(111) becomes occupied with 1.66 electrons, while normal C_{60} is charged with 0.65 electrons transferred from Cu(111). The equilibrium position of the Li^+ ion is slightly displaced upward from the center by approximately 1.32 Å, as shown in Fig. 5(a). The displacement from center caused by interaction of Li^+ ion with C atoms, as seen in the salt. For the $Li^+@C_{60}$ on

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Cu(111), the electronic state of the bottom C atoms has been largely altered and Li^+ ion tend to interact with top neutral C atoms, resulting in slightly larger upward displacement (S.2(b)). Even though the large amounts of the charge of C_{60} cage in $Li^+@C_{60}$, the charge state at the endohedral Li ion is found to be nearly +1, as in the case of the salt.

The LDOS spectrum of the $Li^+@C_{60}$ on Cu(111) substrate is shown in Fig. 6(a), in comparison with that of the normal C_{60}. It is found that, for both $Li^+@C_{60}$ and C_{60}, the LUMO becomes partially occupied by the transferred charges and molecular states of $Li^+@C_{60}$ on Cu(111) are stabilized by approximately 0.3 eV compared to that of C_{60}/Cu(111) due to the presence of the Li^+ ion. The simulated STM image of the LUMO region of the $Li^+@C_{60}$/Cu(111), shown Fig. 5(b), is quite similar to the shape of LUMO of the pristine C_{60}/Cu(111), suggesting that the spatial distribution of LUMO orbital remains almost unchanged despite the presence of Li+ ion just underneath the top hexagonal ring. This result explains the experimental image of Fig. 3(b) where both A and B molecules are showing the similar LUMO shape. It is also seen that the experimentally obtained DOS contrast in the dI/dV images at the bias voltages indicated in Fig.4, become nearly consistent with the calculated LDOS by assuming that the molecules A and B are $Li^+@C_{60}$ and normal C_{60}, respectively. Therefore, it is confirmed that $Li^+@C_{60}$ are mixed in the monolayer of normal C_{60}, exhibiting the different electronic state. The above assumption of the assignment of the $Li^+@C_{60}$ to the molecule A is further confirmed by comparing the STM image and the calculated LDOS. The calculated LDOS shows only a little difference between $Li^+@C_{60}$ and C_{60} in

the occupied electronic states, explaining the negligible difference in the STM appearance of $Li^+@C_{60}$ and C_{60} in the occupied states. In the empty states, on the other hand, LDOSs of $Li^+@C_{60}$ and C_{60} on Cu(111) exhibit notable difference in the LUMO+2 state. This is due to the enhanced coupling between Li-derived electronic states and LUMO+2 state of the cage, as seen in Fig.2. The enhanced contrast of $Li^+@C_{60}$ in the STM image with elevated bias voltage is likely due to the alteration of LUMO+2 state. However, the quantitative correspondence between the bias dependent STM images or dI/dV images and the calculated LDOS is not enough satisfactory. Especially, the calculated DOS spectrum suggests that the contrast between $Li^+@C_{60}$ and C_{60} become comparable at the sample bias voltage of 3 V, where we still find enhanced difference. Also, we see that dI/dV contrasts in the empty state are not in good agreement with the calculation.

The discrepancy between theory and the experiment of the in the empty state of the electronic structure of $Li^+@C_{60}$ on Cu(111) indicate the presence of additional factors that are not included in the calculation, and they are most likely to be due to the field-induced phenomena such as the polarization of the π electrons of the C_{60} cage and displacement of the Li^+ ion. Since the Li^+ ion inside the cage locates at the top of C_{60}, it can be rather easily influenced by the strong electric field near the STM tip. Especially at the empty state imaging where the tip is at the negative potential, Li+ ion becomes attracted towards the tip due to Coulomb interaction. This alters the electronic structure of C_{60} significantly because of significant orbital overlapping. However, these effects are very complicated and the simulation is beyond the scope of the present work.

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Further studies are required for understanding the response of the $Li^+@C_{60}$ under high external electric field, in order to explore the possibility of the switching of the electronic states.

Conclusion

In summary, we have determined electronic structure of $Li^+@C_{60}$ in the form of the $Li^+@C_{60}[PF_6^-]$ salt, and the individual $Li^+@C_{60}$ in the evaporated monolayer. In the $Li^+@C_{60}[PF_6^-]$ salt, charges are mainly on the Li atom and PF_6 anion, while the C_{60} cage is almost neutral. The Li inside the cage is approximately singly charged, as observed both experimentally and theoretically. The observations have suggested that the intrasalt bonding between $Li^+@C_{60}$ and PF_6^- is weak enough for $Li^+@C_{60}$ to retain its original electronic structure. We also demonstrated that $Li^+@C_{60}$ can be selectively deposited on the Cu(111) substrate by vacuum evaporation of the $Li^+@C_{60}[PF_6^-]$ salt. During the deposition process, however, the Li content is reduced and we observed that individual $Li^+@C_{60}$ molecules are embedded in the monolayer of normal C_{60} with same orientation. We showed fair agreement with the bias-dependence of the STM images and the dI/dV images of the $Li^+@C_{60}$ and calculated DOS. DFT calculations showed that the Li inside the cage is still singly charged even on the metallic Cu(111) substrate. On the other hand, quantitative agreement with experiment and theory was not enough, especially in the case of empty state imaging where negative potential is applied to the tip. The discrepancy may be originated from the field induced phenomena such as the polarization of the π electrons of the C_{60} cage and the displacement of the Li^+ ion in the cage. Further studies are required for understanding the behavior of Li^+ under external electric field.

Acknowledgments

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