Molecular-Scale Size Tuning of Covalently Bound Assembly of C$_{60}$ Molecules

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ABSTRACT The creation of a molecular-scale covalently bound assembly of fullerene C$_{60}$ molecules has been precisely controlled in ultrathin multilayer films of C$_{60}$ molecules. When a negative sample bias voltage is applied to a tunneling junction between the C$_{60}$ film and the tip of a scanning tunneling microscope (STM), a C$_{60}$ molecule beneath the tip covalently bonds to an adjacent molecule in the underneath layer. We show that such a chemical reaction is not necessarily limited to the top and second layers of the C$_{60}$ film and that the resulting C$_{60}$ oligomer can be tuned to form a dimer, trimer, tetramer, or pentamer; the number of interconnected C$_{60}$ molecules increases one by one upon increasing the magnitude of the local electric field under the STM tip. The created oligomers are linear chains of C$_{60}$ molecules starting from the top layer and aligned toward the interface layer in the multilayer C$_{60}$ films. We consider that the electrostatic negative ionization of C$_{60}$ molecules and its spatial distribution in the multilayer C$_{60}$ film are critical factors in achieving size-tunable oligomerization.

KEYWORDS: molecular chemistry · oligomer · C$_{60}$ · intermolecular reaction · molecular device · scanning tunneling microscopy · nanostructure

Realizing molecular nanoarchitectures with finely controlled properties and geometries is one of the ultimate tasks of molecular science and technology.[1−3] The creation of molecular-scale assemblies of fullerene C$_{60}$ molecules[4] connected with each other *via* covalent intermolecular bonds, *i.e.*, oligomers of several C$_{60}$ molecules, is a promising route toward achieving the above goal, because the electronic,[5−8] electrical,[9,10] magnetic,[11] and optical[12] properties of C$_{60}$ molecules are controllable through molecular interconnection. It is also known that the electronic structures of π-conjugated polymeric molecular materials strongly depend on their size,[13−16] suggesting that precisely controlling the number of molecules involved in polymeric materials would be substantially important. To date, one-, two-, and three-dimensional oligomers of C$_{60}$ molecules cross-linked *via* [2+2] cycloadditive four-membered rings (referred to as [2+2] bonds hereafter) have been created in C$_{60}$ solid crystals on the basis of various methodologies such as photoirradiation,[17] pressure application at high temperatures,[18] and alkali-metal doping.[19] However, it is not easy to control the size of C$_{60}$ oligomers with single-molecule-level precision using these conventional methods. Although the recent progress in chemical molecular synthesis and purification technologies has made the production of size-controlled C$_{60}$ oligomers feasible, it is essentially difficult to form them at designated positions on solid surfaces. To address this issue, we have recently developed a new method for selecting the creation or annihilation of [2+2] bonds at designated positions in a thin film of C$_{60}$ molecules at room temperature (RT).[20,21] This is performed *via* the electrostatic ionizations and electronic excitations of C$_{60}$ molecules using a strong electric field

and a tunneling current generated in a tunneling junction between the C$_{60}$ film and the metal tip of a scanning tunneling microscope (STM). Although this method has provided a way of creating C$_{60}$ dimers and trimers at designated positions at the single-molecule level in ultrathin films of C$_{60}$ molecules, the ability to tune the size of the oligomer has not yet been established.

In this study, we show that the size of C$_{60}$ oligomers is controllable in an ultrathin C$_{60}$ multilayer film at RT. When negative sample bias voltages are applied between an STM tip and the C$_{60}$ multilayer film, linear C$_{60}$ oligomers (*e.g.*, dimers, trimers, tetramers, and pentamers in pentalayer films) are created *via* a [2+2] cycloaddition reaction. The number of interconnected C$_{60}$ molecules increases one by one upon increasing the magnitude of the electric field in the tunneling gap, which is mainly controlled by changing the magnitude of the tunneling current. We consider that the spatial distribution of negatively ionized C$_{60}$ molecules in the thin film is a critical factor for
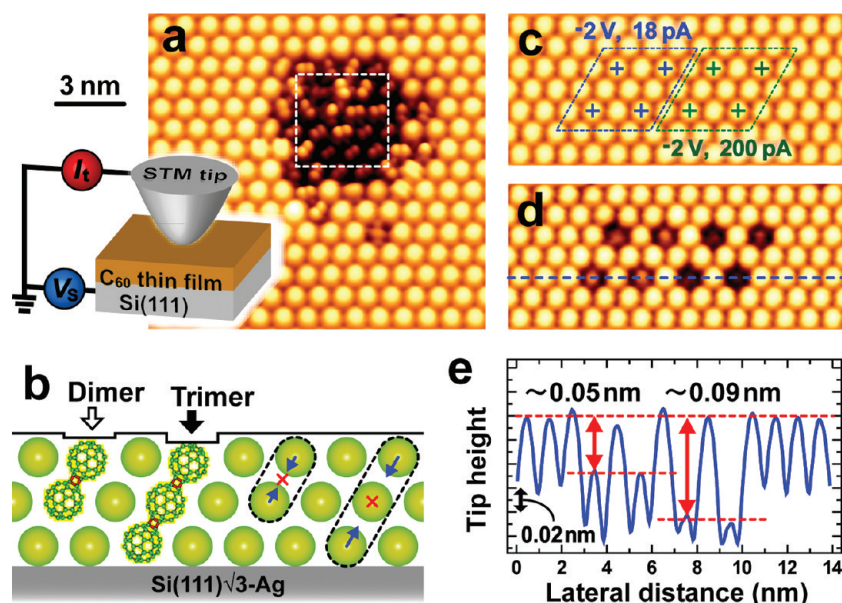
Figure 1. (a) STM image of a group of C_{60} oligomers (dimers and trimers) in a C_{60} trilayer film. (b) Schematic side view of C_{60} dimer and trimer in a trilayer film. (c and d) STM images of a C_{60} trilayer film taken before and after creating an array of single C_{60} oligomers, respectively. Two values of I_t, 18 and 200 pA, were used to induce the oligomerization. (e) Cross-sectional line profile taken along the dashed line in (d) at $V_s = 1.0$ V and $I_t = 30$ pA. All STM images were taken at $V_s = 1.0$ V and $I_t = 30$ pA.

determining the size of the C_{60} oligomer. In addition, we also demonstrate that the selective decomposition of C_{60} dimers into monomers using the STM tip is possible in a local region of the C_{60} film including both dimers and linear trimers, for example. This corresponds to a primitive purification of longer C_{60} oligomers at designated positions.

RESULTS AND DISCUSSION

Ultrathin films of pristine C_{60} molecules were grown on Si(111)$\sqrt{3}\times\sqrt{3}R30°$-Ag [referred to as Si(111) $\sqrt{3}$-Ag] surfaces (see Experimental Methods). The weak interaction between the substrate surface and C_{60} molecules enables the formation of a C_{60} film with a well-ordered molecular arrangement from the early stages of growth.[22] Figure 1a shows an STM image of a C_{60} trilayer film taken under typical imaging conditions of a sample bias voltage (V_s) of $+1.0$ V and a tunneling current (I_t) of 30 pA after creating oligomers of C_{60} molecules. The oligomerization was induced by applying $V_s = -3.5$ V at $I_t = 80$ pA during a scan of the STM tip over the region indicated by the dashed square in Figure 1a. In the scanned region, all C_{60} molecules exhibit internal structures and a darker image contrast as compared with the molecules away from the square region. The former feature indicates that the free rotation of C_{60} molecules at RT[23] is inhibited because of covalent bonding with their neighbors. The latter feature originates from the downward displacement of surface molecules bonding with a neighbor in the underlying molecular layer,[21,24] as schematically shown in Figure 1b. Although the dark contrast in the STM image may also be caused by a decrease in the

electronic density of states (DOS), scanning tunneling spectroscopy measurements indicate that the change in the DOS of C_{60} molecules due to oligomerization under the imaging condition of $V_s = 1.0$ V is negligible (see Supporting Information). This consideration is also supported by the fact that, in the STM image taken at $V_s = 1.0$ V, no obvious difference in the image contrast is observed among C_{60} monomers, dimers, and trimers created in the C_{60} monolayer film,[20,25] where the displacement of C_{60} molecules via [2+2] cross-linking occurs only in the in-plane direction of the film (see Supporting Information).

Figure 1c and d show STM images of a C_{60} trilayer film taken before and after creating an array of single C_{60} oligomers, respectively, by applying $V_s = -2.0$ V for 1 s at each tip position (crosses in Figure 1c). The values of I_t were set to 18 and 200 pA at the blue and green crosses, respectively. The different values of I_t resulted in the selective creation of two types of oligomers at designated positions, as shown in Figure 1d. The tip height profile along the dashed line in Figure 1d clearly shows that the surface molecules are displaced downward by ~0.05 and ~0.09 nm after oligomerization at $I_t = 18$ pA and $I_t = 200$ pA, respectively, as shown in Figure 1e. These downward displacements of ~0.05 and ~0.09 nm are the results of dimer and linear trimer formation as explained in the following. It is known that the total lengths of a pair and a linear trio of C_{60} molecules are reduced by ~0.12 and ~0.23 nm upon [2+2] cross-linking,[25] respectively. If such reactions occur in the out-of-surface-plane direction, namely, if interlayer oligomerization occurs, the surface molecules are vertically depressed. Provided that the
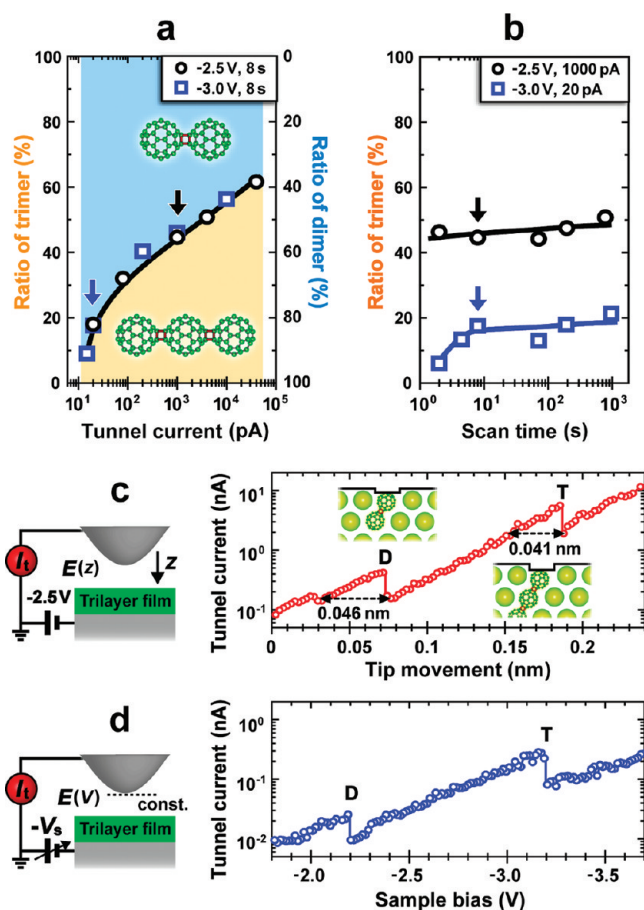
Figure 2. Ratios of trimers and dimers in products created by raster scanning an STM tip over an area of 100 nm^2 in trilayer films at various values of (a) I_t and (b) scan duration t_s. The trimers and dimers were classified from more than 300 products according to their downward displacement. (c and d) Changes in I_t when (c) an STM tip approached a C$_{60}$ trilayer film when V_s was fixed at −2.5 V and (d) when V_s was increased while maintaining a constant tip height.

centers of gravity of the molecular pair and trio are constant, as indicated by red crosses in Figure 1b, the magnitudes of depression are expected to be ∼0.05 and ∼0.09 nm for a dimer and trimer, respectively, in excellent agreement with the experimentally measured values. Note that the present assumption regarding the conservation of the center of gravity in the oligomerization is also supported from the viewpoint of the optimization of the strain energy inevitably generated around the C$_{60}$ oligomer owing to the local change in molecular positions during the oligomerization. The strain energy is optimized by uniformly distributing the strain around the oligomer, which is realized by the present assumption. Although there should be small perturbations in the position of C$_{60}$ oligomers arising from the existence of the interface between the C$_{60}$ film and the substrate, this effect is considered to be negligible in the present case because the binding energy between the C$_{60}$ molecules and the substrate surface with the Si(111)√3-Ag structure is close to that among C$_{60}$ molecules in the multilayer film.[22] In addition to our experimental results, previous tight-binding calculations support the present model; a linear trimer is more stable in terms of

total energy than other geometrically possible trimers such as V-shaped and triangular trimers.[26]

An important finding is that the length of the oligomers is controllable since it depends on the value of I_t. The controllability is demonstrated in Figure 2a, which shows the ratios of trimers (yellow) and dimers (blue) created in C$_{60}$ trilayer films by applying V_s = −2.5 or −3.0 V at various values of I_t. These measurements were performed by scanning an STM tip under the given conditions over the 100 nm^2 region for 8 s. Dimers are predominantly created with a ratio of about 90% when I_t ≈ 15 pA, whereas the ratio of trimers becomes dominant and reaches 60% by increasing the value of I_t up to ∼10 nA. Note that the ratio of trimers can be further increased to as high as ∼90% by the selective decomposition of dimers into monomers, as shown later.

In general, the value of I_t in an STM junction determines the amount of tunneling carriers injected into a sample and the magnitude of the electric field in a tunneling gap *via* the feedback control of tip−sample distance. To tune the size of a C$_{60}$ oligomer, the former is not considered to be effective because the ratios of dimers and trimers created by raster scanning an STM
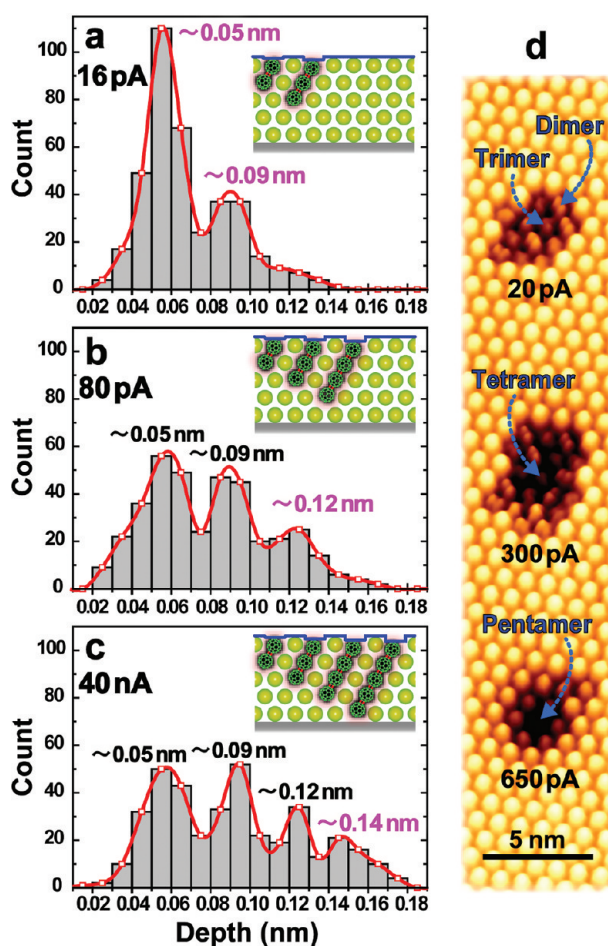
Figure 3. Histograms of downward displacement of surface C_{60} molecules created by oligomerization in pentalayer films. The oligomerizations were induced by the raster scanning of an STM tip over areas of 100 nm² for 8 s at a constant V_s of −2.5 V and I_t of (a) 16 pA, (b) 80 pA, and (c) 40 nA. (d) STM image of C_{60} oligomers induced by applying V_s of −2.5 V at I_t of 20 pA (top), 300 pA (middle), and 650 pA (bottom) after positioning the STM tip on each point in a pentalayer film.

tip do not drastically change even though the total dose of electrons is increased ~10³-fold, as shown in Figure 2b for the cases of I_t = 20 pA and 1 nA. In contrast, Figure 2c and d indicate that the C_{60} trimers are formed under a larger electric field than that required for the formation of the dimers, as follows. Figure 2c shows the change in I_t when an STM tip approaches a C_{60} trilayer film while a constant voltage of V_s = −2.5 V is applied, as illustrated on the left. We recognize two distinct drops in I_t, as indicated by D and T. The magnitudes of the drops at D and T correspond to increases of the tunneling gap distance of 0.046 and 0.041 nm, respectively. Interestingly, these values agree well with the observed displacements of surface molecules *via* dimer formation (0.05 nm downward displacement) and its further oligomerization to a linear trimer (a further downward displacement of 0.04 nm to give 0.09 nm displacement), as shown in Figure 1e. Similar drops in I_t are observed when increasing the value of V_s while maintaining a constant tip height (Figure 2d).

Much longer oligomers can be created in thicker C_{60} films by controlling I_t. Figure 3a–c show histograms of

tip height differences between pristine C_{60} molecules and oligomers, namely, the depths of oligomers, in a pentalayer film. Oligomerization was induced by applying V_s = −2.5 V at three different I_t of 16 pA, 80 pA, and 40 nA. In the case of I_t = 16 pA (Figure 3a), two peaks are observed, at ~0.05 and ~0.09 nm, in the histogram, which indicates the creation of dimers and linear trimers as previously discussed. Third and fourth peaks additionally appear at ~0.12 and ~0.14 nm in the pentalayer C_{60} film when C_{60} oligomers are created under larger values of I_t, as shown in Figure 3b and c, respectively. They agree well with the expected downward displacements of surface molecules of 0.108 and 0.144 nm caused by the formation of a linear tetramer and a linear pentamer of C_{60} molecules in a pentalayer C_{60} film, respectively, as illustrated in the insets of Figure 3b and c. The displacements are calculated as follows; chains of four and five C_{60} molecules shrink by 0.265 and 0.353 nm in total length upon [2+2] cross-linking,[19] respectively, while keeping constant centers of gravity.

From Figures 2 and 3, it is also clear that the present oligomerization of C_{60} molecules between the topmost
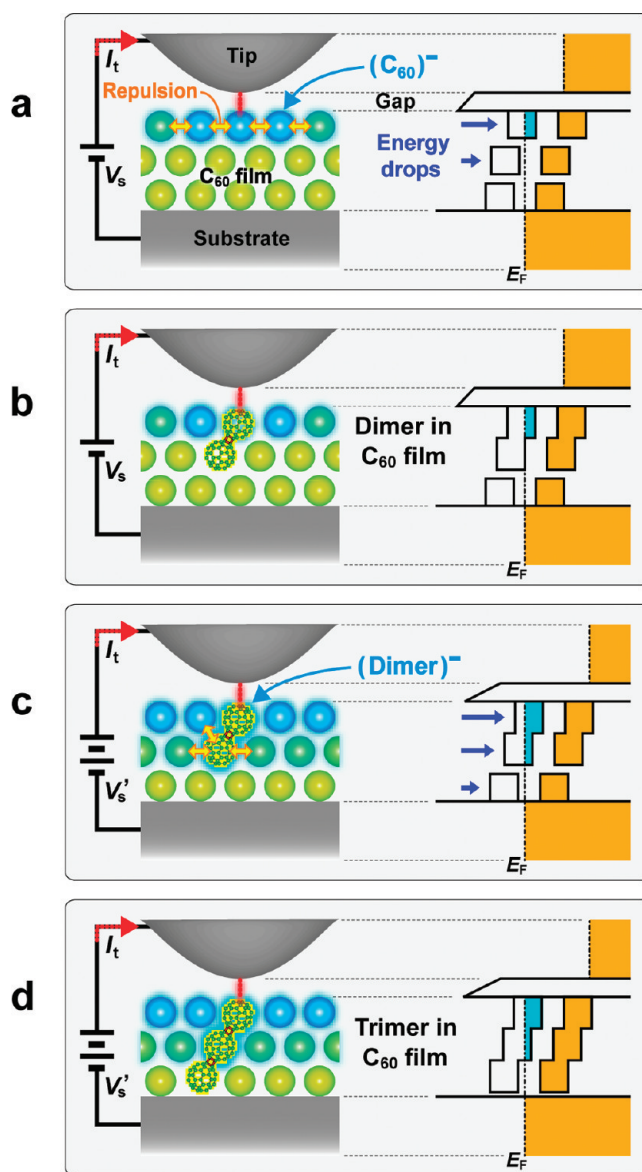
Figure 4. Schematic side views and potential diagrams of tip/gap/C_{60}/substrate when negative values of V_s are applied. (a and b) Situations before and after the formation of a single C_{60} dimer, respectively, under a constant tip height and V_s. In both situations, negatively ionized C_{60} molecules are mainly distributed in the topmost molecular layer. (c and d) Situations before and after trimer formation, respectively, where negatively ionized molecules are distributed in the topmost and second molecular layers under a larger V_s.

and bottom molecular layers is not a chain reaction[27] but a stepwise [2+2] cycloadditive reaction. The number of C_{60} molecules in an oligomer increases one by one, and, for the reaction to proceed, the electric field in the tunneling gap must be increased, resulting in the addition of a C_{60} molecule in an underlying layer to the oligomer. As we previously reported, an external electric field generated by applying appropriate values of negative V_s induces static electron transfer from the substrate to surface molecules of C_{60} thin films; namely, a negative ionization of C_{60} molecules occurs.[20] This electrostatic negative ionization of C_{60} molecules markedly promotes the [2+2] cycloaddition reaction between C_{60} molecules: In a pair of negatively ionized C_{60} molecules, the lowest unoccupied molecular

orbital (LUMO) with a bonding character between adjacent molecules is statically occupied by electrons and energetically stabilized,[21] leading to an effective lowering of the activation barrier for [2+2] cross-linking.[28] Note that, in the STM-induced oligomerization, the LUMO is considered to be partially occupied by less than two electrons owing to the electric field, as discussed previously.[21] On the other hand, the C_{60} oligomers are created in the nanoscale region beneath the tip, as shown in Figure 3d, even though the external electric field generated by the STM tip laterally extends on the sample surface.[29] This fact suggests that dimers, trimers, tetramers, and pentamers of C_{60} molecules are created because of contributions not only from the electrostatic negative ionization but also from the
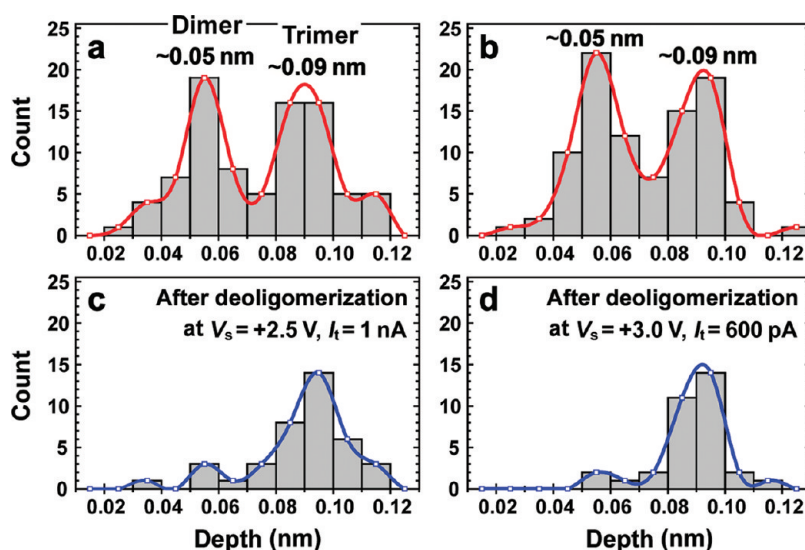
Figure 5. Histograms of downward displacement of surface C_{60} molecules in oligomers (a, b) before and (c, d) after inducing selective deoligomerization of dimers. The oligomers (dimers and trimers) were created by a single raster scan of an STM tip over C_{60} trilayer films at $V_s = -3.5$ V and $I_t = 1.0$ nA. The deoligomerization of the dimers was induced by a single raster scan of the tip over the oligomers at (c) $V_s = +2.5$ V and $I_t = 1.0$ nA and (d) $V_s = +3.0$ V and $I_t = 600$ pA.

electronic excitation of molecules by tunneling carriers locally injected into the C_{60} film.[21,30] In connection with this, we previously found that the reaction probability of the STM-induced oligomerization increases when the energy of tunneling electrons exceeds the energy difference between the highest occupied molecular orbital (HOMO) and LUMO of C_{60} molecules,[21] indicating that oligomerization occurs *via* the HOMO−LUMO excitation of C_{60} molecules.

A plausible explanation of why size tuning is possible in STM-induced oligomerization is shown in Figure 4. Figure 4a−d show schematic side views and potential energy diagrams of the tip/gap/C_{60}/substrate. When a negative value of V_s is applied to the tunneling junction between a metal tip and a substrate, the potential energy of the C_{60} molecules at the surface of the film shifts downward owing to the electric field beneath the tip, in analogy with the band bending of semiconductor surfaces.[31] As a result, when the LUMO of the surface C_{60} molecules is lowered to below the Fermi level (E_F) of the substrate (Figure 4a), negative ionization of the C_{60} molecules occurs by the transfer of electrons from the substrate, which should promote [2+2] cycloaddition reactions between neighboring C_{60} molecules, as mentioned above. Here, the number of electrons donated to the C_{60} molecules in the second layer should be much smaller than that donated to the surface C_{60} molecules owing to the screening effect of the C_{60} film. As a result, an ionized C_{60} molecule in the topmost layer should preferentially react with a C_{60} molecule in the underlying layer rather than with similarly ionized neighbors in the same layer because of electrostatic repulsion. Thus, C_{60} dimers tend to be created across different molecular layers (Figure 4b). Upon increasing the negative bias voltage,

electrons should also be donated to C_{60} molecules in the second layer because of the larger electric field, as shown in Figure 4c. Therefore, it is reasonable to consider that a [2+2] cycloaddition reaction between a dimer and an adjacent C_{60} molecule in the bottom layer becomes possible, resulting in the creation of a linear trimer (Figure 4d). Much longer oligomers can be created in a stepwise manner by increasing the magnitude of the electric field and the number of layers, as experimentally shown for the case of the pentalayer C_{60} film in Figure 3.

Although the created C_{60} oligomers can be intentionally decomposed into monomers beneath the STM tip by applying a large positive value of V_s such as 4.0 V (see Supporting Information), the stepwise decomposition of a C_{60} oligomer, *e.g.*, deoligomerization from a trimer to a dimer and from a dimer to monomers, is also possible. This is an important feature in the deoligomerization process from the viewpoint of the precise control of the size of C_{60} oligomers. We have preliminarily demonstrated that the selective deoligomerization from dimers to monomers is indeed possible in trilayer films under the conditions of a relatively small positive V_s and large I_t such as 2.5 V and 1 nA, respectively, as shown in Figure 5, which shows histograms of the depth of C_{60} oligomers before (Figure 5a and b) and after (Figure 5c and d) deoligomerization. This finding indicates that the purification of created oligomers may be possible, although further study on this deoligomerization process is required.

CONCLUSION AND PROSPECTS

The size-tunable oligomerization of C_{60} molecules has been reported. Using the tip of an STM, dimers, trimers, tetramers, and pentamers were created *via* a

[2+2] cycloaddition reaction in the interlayer of C_{60} multilayer films. The length of the oligomer was controllable since it depended on the magnitude of the external electric field beneath the tip. We consider that the spatial distribution of ionized C_{60} molecules induced by the electric field is a critical factor for the tunability of the length of oligomers.

An important finding is that we can covalently connect C_{60} molecules in the topmost and bottom molecular layers, which would form a path in the C_{60} film allowing vertical electrical conduction because the increased electronic interaction between C_{60} cages *via*

[2+2] cross-linking improves intermolecular carrier transfer.[10,32] Furthermore, the created oligomers can be completely decomposed into individual C_{60} molecules by simply changing V_s to an appropriate positive value.[21] These results are of interest for realizing novel electronic devices such as molecular-scale two-terminal switches and nonvolatile memories based on the formation and annihilation of conduction paths in multilayer C_{60} films through covalently bound linear assemblies of C_{60} molecules. A novel avenue to the development of molecular nanoelectronics[1−3] may have been made available as a result of this study.

EXPERIMENTAL METHODS

All experiments were carried out in an ultra-high-vacuum chamber with a base pressure of 1.0×10^{-8} Pa. Ultrathin films of pristine C_{60} molecules were grown on Si(111)$\sqrt{3}$-Ag surfaces and were used as samples. The Si(111)$\sqrt{3}$-Ag surfaces were prepared by depositing one monolayer (ML) of Ag atoms onto a Si(111)7×7 surface at 600 °C. C_{60} thin films with thicknesses of two, three, four, and five molecular layers (respectively referred to as bilayer, trilayer, tetralayer, and pentalayer films) were grown by depositing an appropriate amount of C_{60} molecules onto the substrates at RT.[33] C_{60} molecules were deposited by the thermal evaporation of C_{60} powder (purity of 99.95%) from a BN crucible while maintaining a deposition rate of 0.03 ML/min. All the STM experiments were carried out using an electrochemically etched Pt−20%Ir tip at RT.

Supporting Information Available: Origin of the STM image contrast of C_{60} oligomers in multilayer films and the STM-induced deoligomerization of the dimers, trimers, tetramers, and pentamers of C_{60} molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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