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Molecular Manipulation Technologies Using an Electric Field and Application to Organic Nanoelectronics

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SUMMARY To realize a single or several molecule device, the following are necessary: (1) an electrical wiring method that is not destructive to the molecular aggregates and does not affect the electronic state of the molecules, (2) noncontact and controllable molecular manipulation technology, (3) oriented growth techniques especially to prepare a nanodevice employing an anisotropic molecular system. In this paper, recently developed electric-field assisted growth and its application to molecular device fabrication are presented.

key words: *molecular manipulation, crystal growth under an electric field, organic nanoelectronics, organic nanotransistor, organic nanowire*

1. Introduction

Organic and inorganic nanostructures, such as nanodots and nanorods, have been fabricated by bottom-up or self-organization methods [1]–[5]. However, it is sometimes difficult to fabricate wiring onto a nanostructure using conductive wires for measurement of the electrical properties due to the technical limits of nanofabrication methods. An interface double layer and depletion layer are generally formed at the interface of an organic material and metal; however, no universal solution to restrain or avoid this phenomenon has been established. These phenomena cause contact resistance with respect to the macroscopic electrical properties, and this is not negligible for short channel devices. For single or several-molecular size devices, the electronic state of the nanostructure is affected by such phenomena and becomes fully modulated, because the size of the device is less than that of the depletion layer. Therefore, it is a concern that the electrodes and wires used to measure the electrical properties of such systems will affect the electronic states for a molecular size device.

Another technical issue for molecular-size devices is identification or control of the orientation of organic nanocrystals, which generally exhibit anisotropic optical and electronic properties, and is due to the planar π-electron system and its arrangement in the crystal structure. Basic physical properties, such as the ionization potential, are dependent on various crystal surfaces or directions, although this has yet to be clarified. However, in reality, even basic physical measurements such as X-ray diffraction are impractical for several-molecule-sized crystals. Several single-molecule devices have been realized [6]–[13]; however, identification of the molecular orientation is difficult except for special cases [12]–[14]. In addition, although many macroscopic and microscopic scale orientation control methods have been proposed [15]–[25], the development of universally suitable techniques for molecular scale fabrication is required.

We have investigated the effects of an electric field on the crystal growth of organic crystals and determined that the field-induced effect is useful for molecular manipulation, such as orientation control and selective growth. Moreover, we have reported the self-aligned connection of organic conductive wires [26] and disconnection by Joule heating. Moderate and controlled Joule heating enables not only a destructive disconnection, but also adjustment of the electrical properties of a nanotransistor [27] and molecular break junction (included in this paper). Although part of our results had been experimentally demonstrated at the microscopic level, principle of the crystal growth under an electric field are suitable for nanoscopic level.

We present crystal growth and device fabrication techniques that employ static and dynamic, uniform and nonuniform electric fields. Field-induced selective growth offers a solution for the wiring of organic nanocrystals and fabrication of nanocircuits. Field-induced oriented growth also offers a solution for the orientation control of anisotropic organic nanocrystals. Moreover, field-induced self-aligned growth and related techniques offer a model case for molecular wiring and the fabrication of spontaneously wired nanotransistors in which the constructed molecular wire does not affect the electronic state of the organic nanodevice.

2. Molecular Manipulation with an External Electric Field

2.1 Effects of Electric Field on Charged Molecules

The effects of an electric field on charged molecules are clearly understood. The first possible effect for charged molecules are coulombic force under a electric field which cause spatial modulation of the molecular population and affect nucleation probability, which can lead to selective growth. The second effect is oriented growth along electric lines of force. At first, we will explain the field-induced modulation of the spatial distribution of molecules diffusing on a substrate surface. A charged molecule receives coulombic forces from an electric field. The ori-

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gin of the charged molecules is explained by the temporal formation of a tetrathiafulvalene-tetracyanoquinodimethane ($TTF^{0.59+}$-$TCNQ^{0.59-}$ charge transfer complex and subsequent thermal dissociation into positively charged $TTF^{\delta+}$ ($\delta \leq 0.59$) and negatively charged $TCNQ^{\delta-}$. The evidence for the presence of charged molecules was experimentally confirmed by monitoring the ion current during growth. The ion current was linked to the shutter-controlled incidental molecular flux of TCNQ onto the substrate surface, and the steady ion current was proportional to the electric field strength. As a result of this ionization process, $TCNQ^{\delta-}$ is concentrated by the electric field around the anode. In contrast, TCNQ is depleted around the cathode. Therefore, ionization results in longer TTF-TCNQ crystal growth from the anode, because TCNQ nucleation and growth limits TTF-TCNQ growth [26]. This scheme was merely speculative, because we could not observe the crystal during the growth. However, recently we have successfully observed the *in situ* growth of TTF-TCNQ and clearly demonstrated field-induced selective growth that is due to the spatial modulation of the molecular population by a static electric field. Nucleation and growth was most active at the anode side and high electric field area. Many reported results for TTF-TCNQ growth [26]–[31] can also be consistently explained by this scheme.

Moreover, it was demonstrated that the TTF-TCNQ organic conductive crystal that begins to grow from the electrode grows along the lines of electrical force (Fig. 1) [26]. The principle of the field-induced oriented growth is explained by an anisotropic electrostatic energy of the uniaxial TTF-TCNQ crystal in the early stage of nucleation. In the early stage of nucleation, small aggregates composed of several molecules are repeatedly formed and are thermally dissociated in the quasi-thermal equilibrium condition. If there is no external electric field, each early nucleus can diminish in an equal probability regardless of their direction. However, under an electric field, an anisotropic electrostatic energy makes a free energy difference according to the relative direction between the principal axis of the crystal and electric field vector. If the difference in the free energy exceeds the thermal energy, then stable nuclei can reach the critical radius and continue to grow. On the other hand, other unstable nuclei cannot exceed the critical radius and they finally diminish.

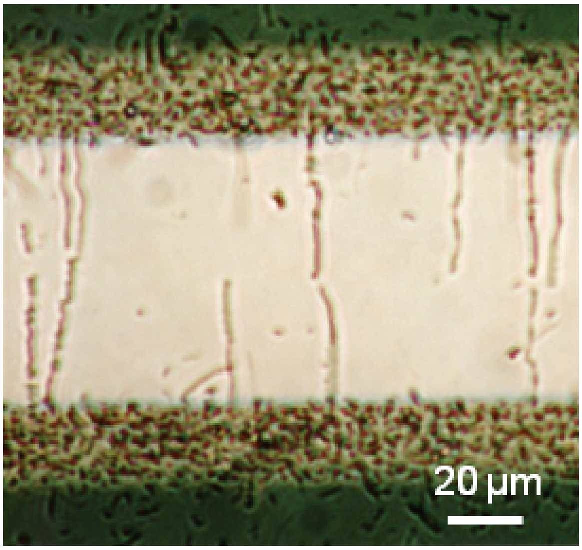

Fig. 1 Optical micrograph of TTF-TCNQ crystals grown under a static electric field and quasi-thermal equilibrium conditions. The self-aligned growth of needle-like crystals along electric lines of force results in a tip-to-tip connection of two individually grown TTF-TCNQ crystals. See Ref. [26] for details.

In addition, for the TTF-TCNQ organic conductor, the self-aligned connection of two TTF-TCNQ crystals has been observed due to the metallic nature of TTF-TCNQ (Fig. 1) [26]. The self-aligned growth is a direct result of field-induced oriented growth. The electric field is concentrated at the growth tip of the TTF-TCNQ crystal because TTF-TCNQ crystals are highly conductive. As the crystals grow, the electric field strength increases between the growth tips of two TTF-TCNQ crystals. The direction of growth from the tip is along the concentrated electric field toward the opposite TTF-TCNQ tip. Therefore, two spontaneously grown TTF-TCNQ crystals make a connection at their tips. This technology is very useful for the fabrication of organic microcircuits, nanocircuits, and nanodevices. An example of the fabrication of an organic nanotransistor is presented later.

2.2 Effects of an Electric Field for Neutral Molecules

The effect of an electric field on neutral molecules is understandable when the molecular dipole moment and quadrupole moments are considered. The effect of the coulombic force on a neutral molecule under a uniform electric field is, in principle, zero. However, in a nonuniform electric field, the molecular dipole moment and molecular quadrupole moment are attracted by a static electric field. The potential energy of a single charge is proportional to the electrical potential (ϕ); therefore, the potential energy of the molecular dipole moment and molecular quadrupole moment are proportional to the first and second derivative of ϕ, respectively. A typical case is observed in the vapor phase growth of lead phthalocyanine (PbPc) crystals under an electric field and quasi-thermal equilibrium conditions. A metallophthalocyanine molecule is composed of a Pc ring and a metal ion in the center of the Pc ring. For example, CuPc is a planar molecule that has a Cu ion in the barycenter of the Pc ring. However, the Pb ion in PbPc has a slight displacement from the center of the Pc ring due to the large ion radius of the Pb ion. As a result, PbPc has both a molecular dipole moment and quadrupole moment. Although CuPc also has a molecular quadrupole moment, the net charge of the Cu ion (+0.33) is smaller than that of the Pb ion (+0.45); therefore, the effect of the molecular quadrupole moment is relatively weak in CuPc.

The main observed effect on CuPc was a large area of oriented crystal growth. The field-induced growth con-

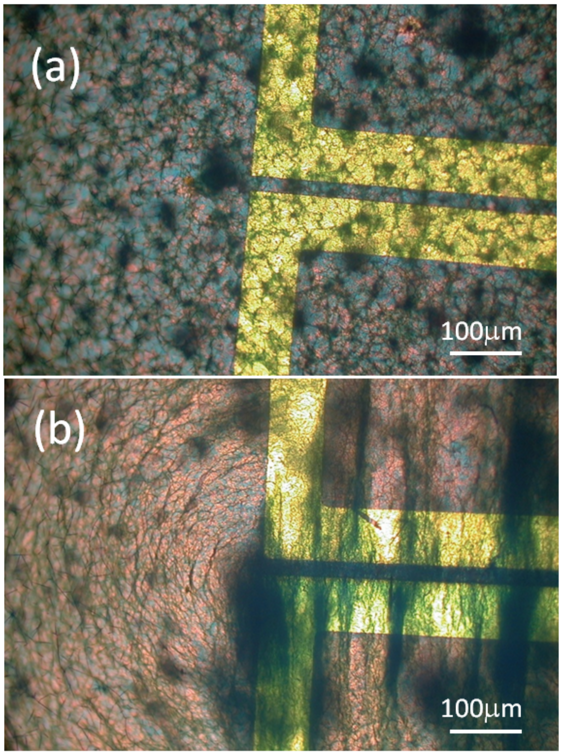

Fig. 2 Optical micrographs of CuPc crystals grown under a static electric field and quasi-thermal equilibrium conditions. The oriented growth of needle-like crystals along lines of electrical force is evident over a wide area. (a) Under zero electric field. (b) Electrical potential difference of 50 V DC was applied between two electrodes. See Ref. [32] for details.

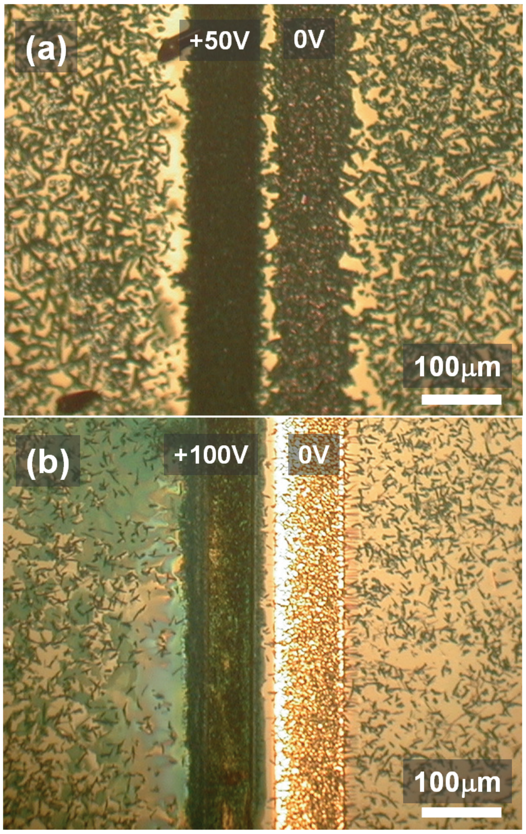

Fig. 3 Optical micrographs of PbPc crystals grown under a static electric field and quasi-thermal equilibrium conditions. The crystal distribution is modulated by the electric field. The difference in crystal distribution is clearly dependent on the applied electric field strength. See Ref. [35] for details.

trol was conducted using a cylindrical furnace to produce quasi-thermal equilibrium conditions. A Au/Cr electrode pattern was prefabricated by standard vacuum deposition on the glass substrate surface. The substrate was connected to the external voltage supply by the heat-resistant wiring. Figure 2 shows an optical micrograph of the grown CuPc crystals from Ref. [32]. The voltage applied to each electrode is indicated in the figure. Over 500 μm radius of oriented CuPc crystal growth along the lines of electric force is evident. This is the largest scale of oriented growth caused by an electric field known to the authors. The earlier studies of Refs. [33], [34] on orientation control of CuPc crystal growth succeeded in oriented growth by application of an electric field during vacuum evaporation. However, the effect of oriented growth was too weak to be visible in the morphology, but was only observed by X-ray diffraction. An obvious and large area oriented growth was achieved only under quasi-thermal equilibrium conditions. The principle of the oriented growth of CuPc is also explained by the anisotropic electrostatic energy of the needle-like CuPc crystal in the early stage of nucleation, which was described on the field-induced oriented TTF-TCNQ growth in the Sect. 2.1.

The other typical case is PbPc. Figure 3 shows an optical micrograph of PbPc crystals grown under quasi-thermal equilibrium conditions and a static electric field, from Ref. [35]. The voltage applied to each electrode is indicated in the figure. In the case of PbPc, oriented growth is observed only in a limited area on the outer side of the cathode. However, a more visible feature is the spatially nonuniform distribution of the grown PbPc crystals, which was clearly modulated by the electric field. The point in this case is understood by considering the contribution of the molecular dipole and molecular quadrupole moment; a detailed discussion of this is given in Ref. [35]. A higher density of PbPc crystals on the anode than on the cathode is due to the molecular quadrupole moment of PbPc. PbPc consists of a positively charged $\mathrm{Pb}^{+0.45}$ ion and negatively charged Pc ring surrounding the Pb ion, which results in the molecular quadrupole moment. Moreover, the Pb ion has an out-of-plane displacement due to the large radius of the Pb ion, which results in the molecular dipole moment. Both the molecular dipole and quadrupole moments are not attracted by a uniform electric field. However, in a nonuniform electric field, the drift motion of both moments is affected by the electric field. The difference is that the dipole moment is attracted to both the anode and cathode side due to flipping of the dipole direction. In contrast, the quadrupole moment is attracted to only the anode side because the quadrupole moment is not reversible. In addition, the attractive force on the quadrupole moment is rather short-range, in principle, compared with that on the dipole moment.

An electric field is useful for the manipulation of molecules and control of the crystal orientation up to an area of several hundred square micrometers. If a nanotool, such as the conductive cantilever of an atomic force microscope, and designed electrodes are used, then a population of molecules can be manipulated by an electric field to construct a predetermined nanostructure.

3. Application to Organic Nanoelectronics

3.1 Fabrication of Organic Nanotransistors

Electric field-induced oriented growth, selective growth, and self-aligned wiring and nanogap formation are useful elemental technologies to fabricate organic nanodevices without the destruction of organic nanocrystals and modulation of the electronic structure of the organic molecules. Field-induced oriented and selective growth can be used to fabricate an organic nanotransistor in a specific position and orientation. Self-aligned wiring can be used to produce an electrical contact that is not destructive toward the organic material and which is suitable for carrier injection into an organic nanodevice [30]. Satisfactory carrier injection efficiency into TCNQ or pentacene has been reported for the TTF-TCNQ organic conductor [36]–[38].

For example, an organic nanochannel transistor has been fabricated by the spontaneous formation of an active layer [30] or by local Joule heating of connected TTF-TCNQ wires [27]. The spontaneous formation of an active layer is due to the lack of TTF composition at the growth tip during growth [26]. Metallic TTF-TCNQ has a TTF/TCNQ composition ratio of 1; however, due to the high vapor pressure of TTF molecules, TTF molecules cannot form a TTF crystal, but are gradually adsorbed into the TCNQ crystal. Therefore, the TTF/TCNQ ratio at the growth tip is lower than that of the trunk [26], [31]. Therefore, a small area of TCNQ is formed at the junction just after completion of a connection, which was determined to be 500–700 nm by atomic force microscopic potentiometry (AFMP) [39] using a conductive cantilever and high impedance voltage follower. These nanotransistors were experimentally demonstrated and exhibited a maximum electron mobility of 1–3 $\mathrm{cm^2/Vs}$ [30], which is comparable to that for a single crystal TCNQ device [40]. The high performance is mainly due to the high carrier injection efficiency because there is no carrier injection barrier at the TCNQ/TTF-TCNQ interface. The lowest unoccupied molecular orbital (LUMO) band of TCNQ and the TCNQ LUMO band of TTF-TCNQ are common, so that the LUMO band of TTF-TCNQ acts as a carrier reservoir for the TCNQ nanocrystal. The carrier reservoir is generally very effective for an organic nanodevice. However, a disadvantage of this self-aligned connection is that the active material of the field-effect transistor (FET) is limited to TCNQ, of which the channel length is difficult to control, although this method is interesting from the viewpoint of spontaneous formation of an electronic device.

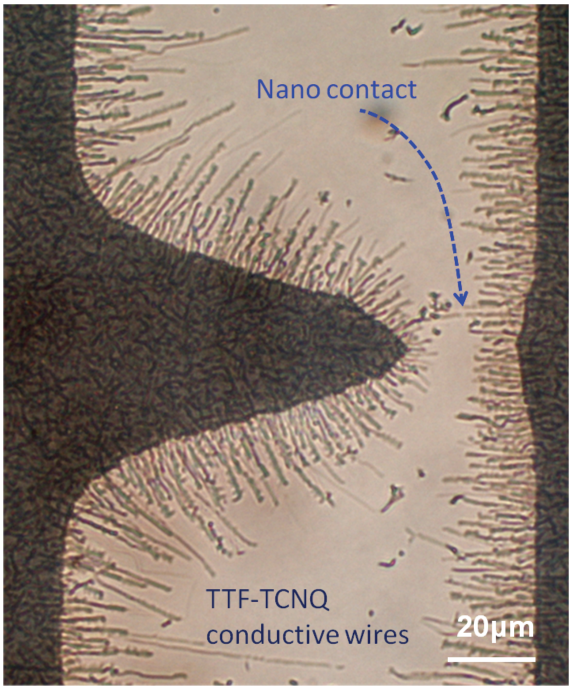

Fig. 4 Optical micrograph of a nanocontact between two TTF-TCNQ conductive wires grown under a static electric field and quasi-thermal equilibrium conditions.

To expand the series of technologies as a more generalized method, the fabrication of nanogap electrodes is expected. Figure 4 shows an optical micrograph of a spontaneously formed nanocontact between two individually grown organic conductive wires. This nanocontact is formed by self-aligned growth just prior to making a connection. If another organic semiconducting material, such as pentacene, is evaporated after making the nanogap, then the nanogap would be filled with the evaporated material. If the length of the nanogap can be observed and controlled, then the channel length of the nanodevice is controllable. However, an organic conductive wire composed of small molecules is easily destroyed by an electron beam; therefore, observation of the nanogap during formation by scanning electron microscopy (SEM) is difficult, although a tunneling current is useful for estimation of the nanogap length. This is another way to fabricate an organic nanodevice.

Another nanofabrication method is self-concentrated Joule heating including a self-termination mechanism [27]. A connected TTF-TCNQ wire has a high electrical resistance point at the junction just after completion of the connection. If an AC or DC electric current is applied, then Joule heat is preferentially generated at the high resistance point. The Joule heat causes TTF desorption from the high resistance part, which results in an increase in the resistance. In this process, the resistance of the initially high resistance point increases and a non-doped semiconducting region is formed at the junction. This semiconductorization process

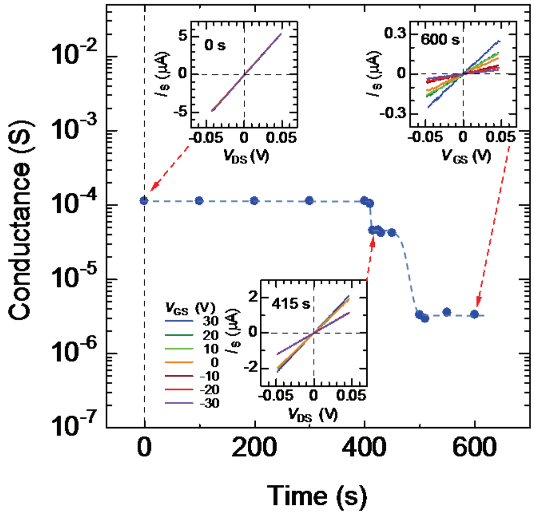

Fig. 5 Time variation of the electrical conductivity for a connected TTF-TCNQ wire. The decrease in conductivity is due to TTF desorption caused by Joule heating. The effect of Joule heating is concentrated in a high resistance area (i.e., junction of two TTF-TCNQ wires) of the connected TTF-TCNQ wire. The TCNQ concentration increases at the junction as a result of TTF desorption; therefore, the n-channel FET characteristics exhibit decreasing conductance (insets). See Ref. [27] for details.

by Joule heating automatically ceases because the higher resistance (R) limits the electric current. Therefore, the generated heat (V^2/R) decreases with increasing R if an appropriate voltage is selected with constant voltage operation. Figure 5 shows a typical example of the self-concentrated Joule heating process [27]. The initial total conductance of the connected TTF-TCNQ wire is approximately 10^{-4} S. During the first 400 s, the total conductance decreases only slightly and no gate-induced modulation of source current (I_S) is observed at this stage. However, the conductance suddenly drops after 415 s, and a slight gate-induced modulation of I_S appears. Furthermore, another drop of conductance is observed after 500 s of Joule heating. After 600 s of Joule heating, gate-induced modulation is significantly improved, and obvious n-channel FET characteristics are obtained.

In addition, not only nanotransistors or nanowires, but also nanocapacitors and nanoinductors are expected for all-organic nanocircuits. Organic micro- and nanocoils have also been discovered from a series of our investigations. Figure 6 shows a SEM image of grown TTF-TCNQ crystals. These spiral structures are sometimes observed, and the pitch of the spiral and dimensions of the ribbon structure are rich in variety. These spontaneously formed structures are expected to be applicable to organic nanoelectronics in the future.

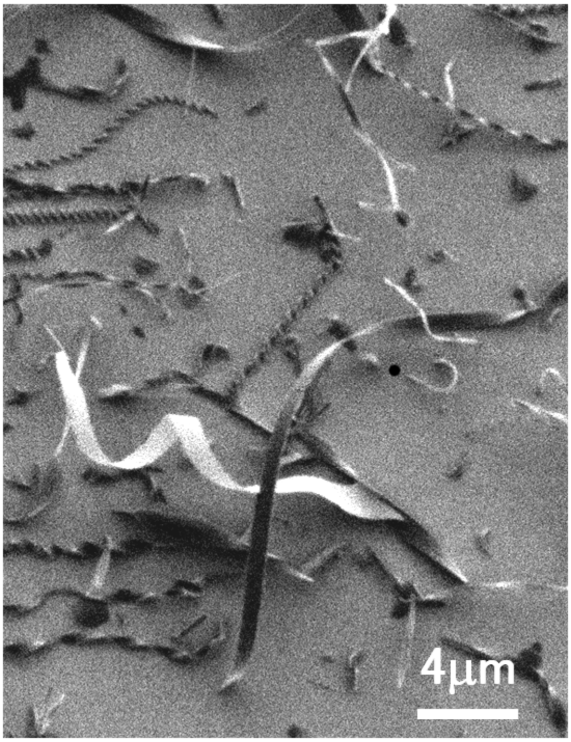

Fig. 6 SEM image of various sized nanoribbons that have a spiral structure. These TTF-TCNQ crystals are similar to solenoids. Spontaneously formed three-dimensional structures are expected to be applicable to organic nanoelectronics in the future.

3.2 Fabrication of Single Molecular Nanogap Electrode or Transistor

An advanced Joule heating method is applicable to the fabrication of molecular-level nanogap electrodes or nanotransistors. This method is essentially the same as that for Joule heating; however, a pulsed electric current provides a more precise and controllable method. A pulsed electric current prevents an accelerated rise of the local temperature. Moreover, if the generated Joule heat pulse energy is slightly lower than the heat necessary for desorption of a single molecule, then several current pulses will cause the desorption of one molecule, which reflects the desorption probability of a single molecule. If the appropriate condition can be identified and maintained, then molecules can be removed one by one. Although such experiments are currently in the early stages, we present preliminary experimental results in Fig. 7. The connected TTF-TCNQ crystals were approximately treated according to that shown in Fig. 5. After the total conductance decreased from an initial value of approximately 10^{-5} to 10^{-9} S, a continuous pulsed electric current was applied. The Joule heat per pulse was controlled and suppressed so as not to cause molecular desorption by only one pulse. The variation in conductance exhibits a step-like decrease, but a step-like increase is also observed as shown in Fig. 7(a). The magnitude of the step-like decrease and increase is approximately 1 pS and its integer multiple, which corresponds to the desorption and adsorption of a single molecule near the contact point. The resolution of this measurement system is 0.22 pS, which is sufficient for detecting these significant conductance steps. This is not a quantum electronic phenomenon, but the connection and disconnection of parallel single molecular bridges, as illustrated

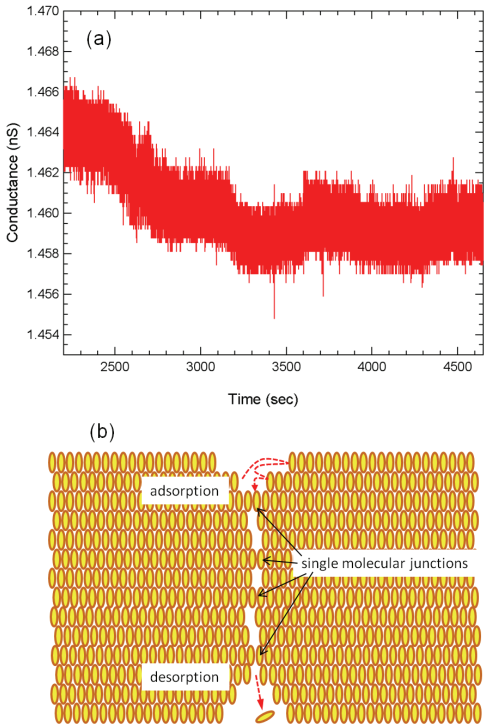

Fig. 7 (a) Time evolution of total conductance for connected TTF-TCNQ wires. Several step-like variations of total conductance are evident in the final stage of the Joule heating. (b) Schematic illustration of single molecular junctions formed at an almost broken junction. Pulsed Joule heat is concentrated around the junction, so that thermal molecular desorption/adsorption occurs dynamically. If a desorbed molecule does not form a new molecular junction, then the conductance decreases. If a desorbed molecule immediately forms a new molecular junction, then the conductance is kept constant. If a molecule not belonging to any molecular junction makes a new junction, then the conductance increases.

in Fig. 7(b). The duration of conductance steps is almost the same, which may reflect the probability of the thermal desorption and adsorption of a single molecule, because the thermal energy per pulsed current is insufficient for a single event of molecular desorption or adsorption; only one step-like change of conductance occurs in approximately 300-400 s. The frequency of Joule heat pulses is 7020 Hz, so that one event occurs in $2.1–2.8 \times 10^6$ pulses, i.e., the probability of one event is $3.6–4.8 \times 10^{-7}$ for an estimated thermal energy of 8×10^{-13} J/pulse. However, this value should be verified by further experimental evidence.

3.3 Additional Interest on Layered Charge Transfer Complexes and Their Nanostructures

In addition to the single molecular devices mentioned, single or several layered structures of organic charge transfer complexes are also of interest [41]–[44]. The minimum unit of the layered structure is a pair of donor and acceptor layers. Novel electronic properties are expected for a nanodevice fabricated using these layered materials [45]. Furthermore, a group of organic charge transfer complexes have been reported that have unique electronic properties, such as the charge ordered state Mott insulators [46]–[49], which are different from simple band semiconductors. Field-induced metal-insulator transition or ferroelectric-like properties are observed in their microscopic FET structure. Nanoscale electronic properties and the applications of such correlated electron systems is an unexplored field in material science, which provides motivation for research into such layered organic charge transfer complexes.

4. Conclusion

Molecular manipulation technologies associated with electric field-assisted growth of anisotropic organic crystals were presented. These field-assisted techniques have previously been recognized as impossible, because the effect of an electric field is so weak that observation of the effects in nonequilibrium processes such as vacuum evaporation is difficult [33], [34]. However, these effects are clearly observable under quasi-thermal equilibrium conditions, which are also useful for the fabrication of single crystal organic devices. Development of these technologies should realize the selective and oriented growth of organic single crystal arrays.

The fabrication of nanotransistors and several molecular scale junctions were also demonstrated. Self-aligned spontaneous formation under an electric field is a model case and the fundamental basis for bottom-up nanodevice fabrication. This process is fully or partially applicable to smaller molecular devices, although verification of oriented molecular device formation is difficult in the present experimental system. Another type of molecular device fabrication was proposed in the one-by-one desorption of molecules from a connected organic wire. This concept will be also widely applicable for molecular size devices.

Acknowledgments

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