

From Organic Conductor to “Epigenetic” Molecular Circuit

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Abstract– various non-linear conducting behaviors, such as higher order I - V characteristics, hysteretic behavior, rectification, gradual increase/decrease, are observed and induced in organic crystalline conductors, conducting polymers, and thin-film semiconductors.

1. Introduction

Chemists have developed various kinds of useful materials through imitating natural products such as medicines, fibers, dyes, etc. Furthermore, electric conductors, semiconductors, superconductors, and ferromagnets have been constructed only with organic molecules through imitating the electronic structure of corresponding inorganic materials, and the resulted knowledge became the basis of emerging organic electronics. One of the next frontiers of chemistry should be the information system. Since molecule is the smallest functional object, molecule-based integrated circuits consist of single molecule devices are expected to overcome the silicon-based technology especially in terms of the device density per volume. Actually, electric characteristics of single molecule have been investigated in various ways and deep knowledge has been accumulated. However, it would not be good idea to use single molecule devices as the substituting components of recent silicon-based integrated circuits because so many kinds and numbers of molecular devices are necessary and should be perfectly positioned and wired on the wafer avoiding any defect.

Another possible strategy would be an artificial neural network consists of organic molecules having non-linear conducting properties. Organic conductor often shows various non-Ohmic conducting properties, such as higher order I - V characteristics, hysteretic behavior, rectification, gradual increase/decrease, etc. These non-linear conducting properties could be attributed to the internal freedom of molecular structures and packing structures of molecular assemblies. In this paper, non-linear conducting properties and their mechanism in organic crystalline conductor, conducting polymer, and organic thin-film transistor, are described and discussed in terms of the “epigenetic” functional circuit formation related to the artificial neural network.

2. Non-linear Conducting Behavior in Organic Systems

2.1. Conductivity Change in Crystalline Molecular Conductor through Structural Change of Molecular Structure [1]

An ion-radical salt of a TTF-based dimeric donor with a cross-cyclophane-skeleton (Figure 1) was prepared and found that the conductivity of the salt was enhanced abruptly under the application of the external voltage, e.g. 340 V at 170 K as shown in Figure 2. Since this process has relatively large hysteresis, the ion-radical salt was converted to a low-resistance “phase” under the application of high voltage. We succeeded an X-ray crystallographic analysis of the salt under applying the external current and revealed that the disproportionation of charge along the donor stack in the crystal became uniform during the current application in terms of the bond lengths of each donor unit. This result is interpreted that the class I mixed-valence state of the cation–radical salt of the dimeric donor was converted into the class III state by the application of the large current.

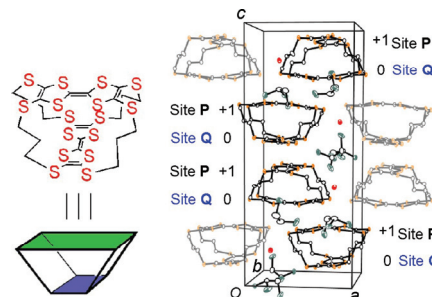


Fig.1 Molecular structure of cyclophane-type donor CPTD and the crystal structure of its ion-radical salt CPTD·Br(TCE)₂.

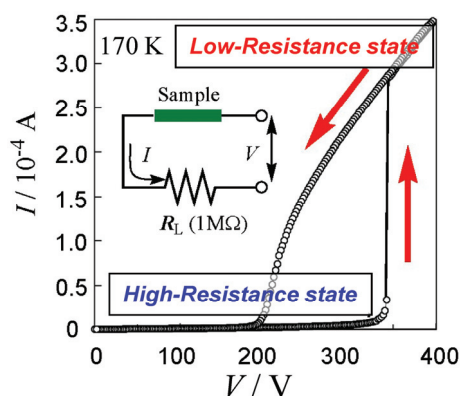


Fig.2 I - V Characteristic of CPTD·Br(TCE)₂ at 170 K.

2.2. Switchable Resistance in Organic Ion-radical Salt Having Hydrogen-bonded Counter Ion Network [2]

Electro-crystallization of **BEDT-TTF**, which is one of the most well-investigated organic conducting donor, in the presence of chloride ion and the droplets of H_2O in a mixed solvent of 1,1,1-trichloroethane (1,1,1-TCE) and dichloromethane (DCM) afforded needle-like black crystal of $(\text{BEDT-TTF})_2\cdot\text{Cl}(\text{H}_2\text{O})_4$. This ion-radical salt was found to show the characteristic conducting property as shown in Figure 3. The resistance of the sample changes up to 20% by changing the direction of the applied current. However, since this resistance change takes place gradually and needs very long time (~ 10 min), it could not be attributed to the rectification due to the PN junction or Schottky barrier.

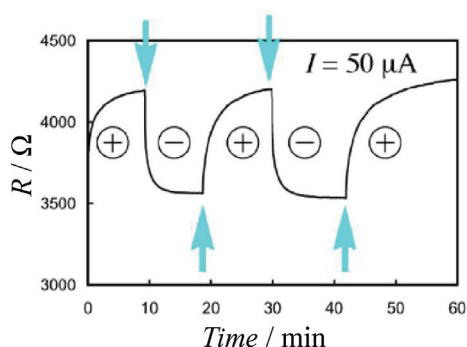


Fig.3 Gradual conductivity switching in $(\text{BEDT-TTF})_2\cdot\text{Cl}(\text{H}_2\text{O})_4$. The direction of the loaded current was changed at the arrows.

Figure 4 shows the crystal structure of $(\text{BEDT-TTF})_2\cdot\text{Cl}(\text{H}_2\text{O})_4$. In this crystal, both donors and counter ions form two dimensional layers in ab plane. Interesting point is that the counter ions (chloride ion, Cl^-) and water molecules form infinite hydrogen-bonding network parallel to the long axis of this needle-like crystal. Judging from the crystal structure, the mechanism of the gradual increase/decrease of resistance in this crystal could be estimated as shown in Figure 5.

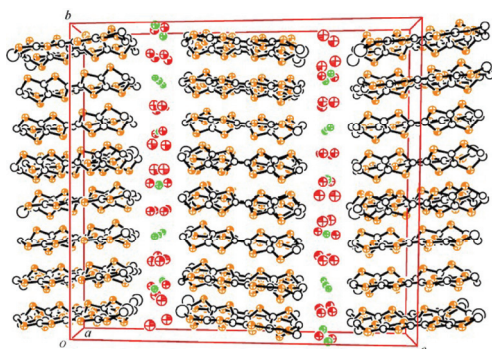


Fig.4 Molecular packing in $(\text{BEDT-TTF})_2\cdot\text{Cl}(\text{H}_2\text{O})_4$ Crystal. Counter ions (Cl^-) and water molecules forms infinite hydrogen-bonding network in ab plane.

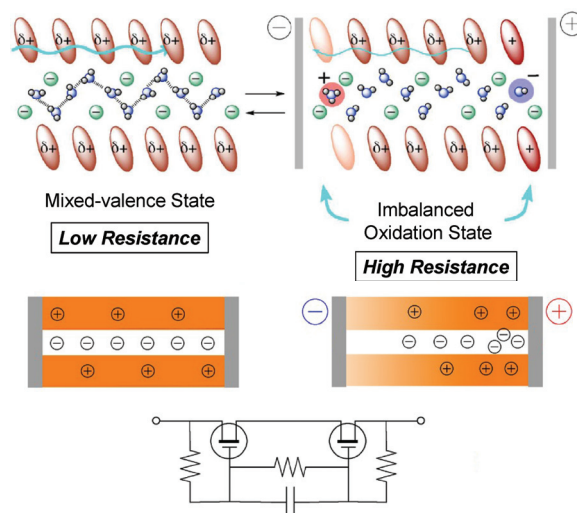


Fig.5 Schematic drawings of the plausible mechanism and an expected equivalent circuit diagram of the gradual conductivity switching in $(\text{BEDT-TTF})_2\cdot\text{Cl}(\text{H}_2\text{O})_4$ crystal.

In the resistance measurements, direction of the current flow was parallel to the long axis of the needle-like crystal shape. This direction is also parallel to the 2D conducting plane of the donor assembly and the hydrogen-bonded counter ion network. Since the formal charge of each donor molecule in this crystal is $+0.5$, the donor layer is in the mixed-valence state and the resistance should be minimum for this structure. However, if the charge distribution of donor units has deviation, some part will be less than $+0.5$ and some other part will be higher than $+0.5$, and the resistance will be higher than the expected value for the uniform charge distribution. In usual ion-radical salt, cationic charges of donors are compensated by anion and the distribution of both components and charges should be uniform in the crystal. On the other hand, counter ions have infinite hydrogen-bonding network parallel to the conducting path (2D donor layer) in this crystal, and the charge distribution could be changed through the formation of H_3O^+ ions and OH^- ions at the electrode surface resulted by the application of bias voltage assisted with proton-relay along the hydrogen-bonding network as shown in Figure 5. This charge distribution could be controlled by loading current and the accumulated charge could be cancelled by loading current of opposite direction. This change of charge distribution in anionic layer should take effect in the donor layer and its total resistance. Although the proton-relay across the crystal should need relatively large potential gradient and such large electric field could not be obtained in usual bulk conductor, this crystal has high resistivity and can involve reasonably high electric field to drive the counter ions. The utilization of the field effect of counter ion is considered to be the key for developing bistability in conducting molecular materials.

2.3. Various Non-linear Behaviors in Electro-polymerized Organic Conducting Polymer and Its “Epigenetic” Preparation [3]

In the former section, non-linear conducting property in a crystalline organic conductor was discussed in terms of the dynamics of its counter ion system. To demonstrate its generality, the conducting properties of a typical conducting polymer was then investigated because electro-polymerized conducting polymers have various degrees of freedom, such as conformational variety of polymer main chain, degree of charge doping, position of counter ions, and incorporated solvent molecules. As the result, various kinds of non-linear I - V characteristics were observed on small strips of electro-polymerized poly(3-ethylthiophene) although these samples were divided from the same film (Figure 6). Since these non-linear characteristics were not observed with 4-probe method, these non-linear characteristics could be attributed to the contact interface between the sample and the electrodes. Furthermore, some of non-linear character was obviously suppressed with increasing the speed of voltage sweeping.

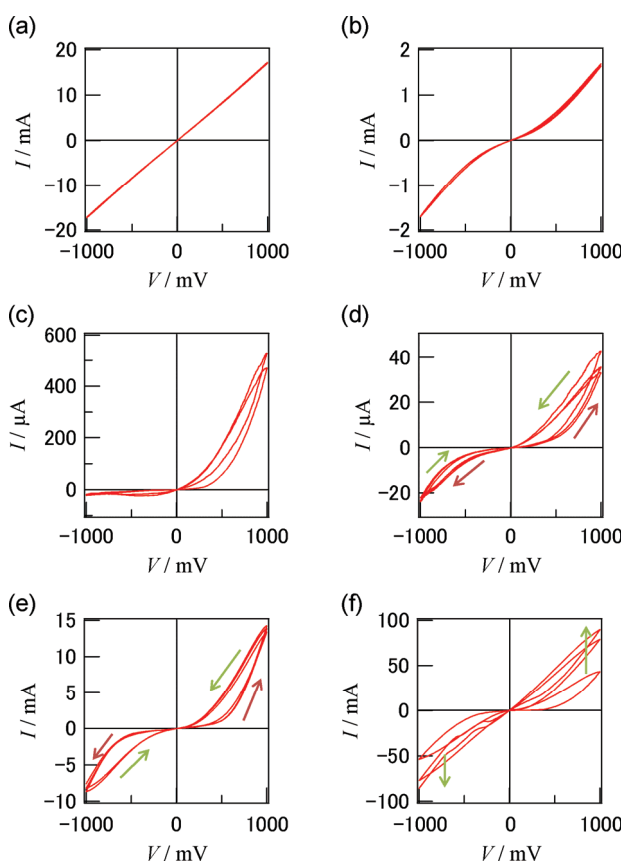


Fig.6 Various I - V characteristics observed on poly(3-ethylthiophene) films [3]. The polymer was prepared by electro-polymerization of 3-ethylthiophene in 0.1 mol · L⁻¹ tetrabutylammonium tetrafluorophosphate / nitrobenzene solution with a pair of SUS304 plate electrode.

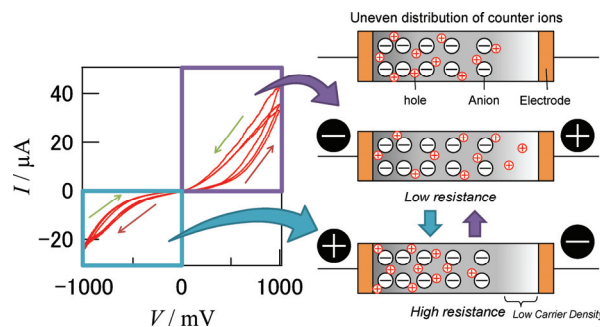


Fig.7 Plausible mechanism for the non-linear I - V characteristics in electro-polymerized poly(3-ethylthiophene).

These results suggest that the dynamics of counter ions near the electrode surface is the key of the non-linear conductivity. In this kind of semiconducting material, applied voltage will drive not only electron (or hole) but also the counter ions incorporated as dopant as discussed in the former section. If the distribution of counter ions and doping level of the semiconducting polymer film was not uniform, it will be a cause of the rectifying I - V characteristics. If the distribution of counter ions was changed under the applied electric field, the conductivity will be enhanced or depressed, and it will be the cause of hysteric behavior as shown in Figure 7. Gradual increase and decrease of the conductivity could be also explained in the same manner. In this mechanism, the non-linear character is governed by the distribution and the dynamics of the counter ions in the polymer film, which is incorporated in the electro-polymerization process. To control this situation, we tried to induce the non-linearity after the preparation of the polymer film. As shown in Figure 8, a piece of polymer film was added a drop of electrolyte solution and swollen. Then current was applied on the film to induce the distribution change of counter ions in the film. After drying the film, obvious rectifying I - V characteristic was successfully observed as we expected. Although these experiments were carried out in the millimeter sizes of samples, this mechanism would be applicable for any scale of devices, if the incorporated counter ions have appropriate degree of freedom.

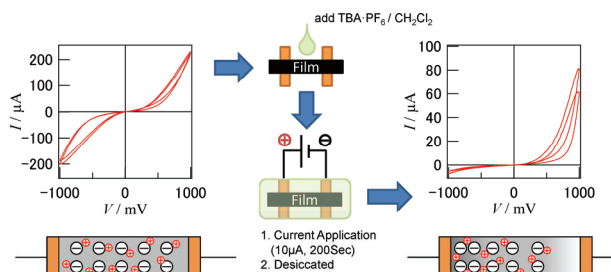


Fig.8 “Epigenetic” induction of non-linear I - V characteristics in an electro-polymerized poly(3-ethylthiophene) film.

2.5. “Epigenetic” Device Preparation in Ambipolar Organic Semiconductor Thin Film [4]

In recent years, electrostatic doping utilizing field-effect transistor (FET) device structure has been studied intensively in terms of organic electronics. One of the advantages of this method is that various valence states (degree of charge doping) could be set seamlessly as the function of gate voltage (V_G) without any chemical and structural change of the semiconductor material. On the other hand, the introduced charge carrier will leave the material when the V_G was released. However, the introduced charge is often stabilized in semiconductor material, the relaxation time can be in mS range, and the resulted current between Source and Drain electrodes (I_{SD}) become weaker. The phenomena, that the channel current in FET device become weaker under the applied gate voltage is known as “Bias-stress Effect”. The above mechanism could be one of the explanations of “Bias-stress Effect”. We found that the “Bias-stress Effect” of organic FET device is well suppressed at low temperature, typically below 100 K. This result could be explained in terms of the suppression of the structural relaxation of molecules in solid state. Then, we tried to decrease temperature of organic FET device under applying constant V_G . After getting low temperature, typically at 100K, the device characteristic was investigated. As the result, the device showed the shifted threshold voltage, almost the same to the applied V_G during decreasing temperature. It becomes clearer when an ambipolar semiconducting material was used as shown in Figure 9. This result could be interpreted as the fixation of introduced charge carrier. At room temperature, the introduced charge will be stabilized gradually, and immobilized in the semiconducting layer. If the applied voltage was released, the immobilized charge will be also released gradually, and the neutral state will be recovered.

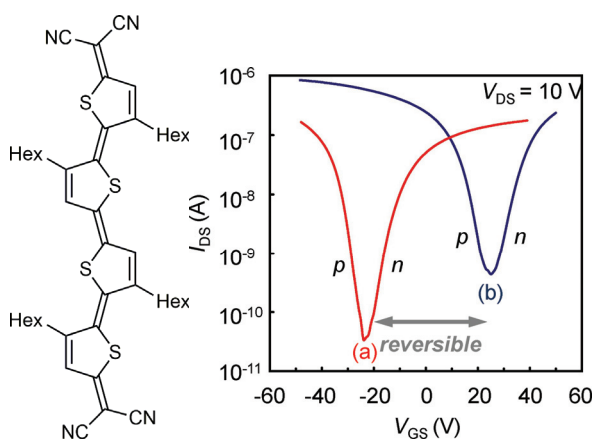


Fig.9 Molecular structure and “Epigenetic” control of the threshold voltage in the field effect transistor device of the molecule. States (a) and (b) were prepared by keeping $V_G = -30$ V and $+30$ V during cooling processes, respectively.

However, if the temperature was decreased with keeping V_G , the immobilized charge is further stabilized and could not be released even when the V_G was released. At this stage, the immobilized “frozen” charge could be regarded as “counter ion” and behaves as the dopant for the opposite sign of charge carrier. Since the semiconducting material has an ambipolar character in this case, both p and n doping could be possible. For a demonstration, we prepared a pn-junction diode within this FET device. In this case, V_{GS} was kept at the half of Drain-Source voltage (V_{DS}) in the cooling process. As the result, rectifying I_{DS} - V_{GS} characteristic was induced and the direction of the rectification could be changed repeatedly by changing the signs of V_{DS} and V_{GS} in the cooling process. Preparation of PNP and NPN transistors would be also possible with this method, if the corresponding charge doping could be controlled in sub-micrometer resolution. Although low temperature for freezing accumulated charge is necessary, this method is applicable for single-component organic semiconductors without any dopant. We will be able to prepare any kinds of devices and circuits on the same molecular semiconductor surface as we intended.

3. Summary

Various non-linear conducting behaviors were observed in organic conductors due to their internal flexibility in molecular structure or molecular assembly. Furthermore, some of non-linearity was induced after the device preparation. These mechanisms for developing non-linearity described in this paper could be generalized for various types of organic conductors. Organic conductors often include relatively big deviation and it brings bad reproducibility. However, there is the chance to find the portion having desired device property in such random molecular assembly. Otherwise, desired property could be induced in selected part of the assembly after device preparation due to the softness of the material. These strategies will be the keys for the “Epigenetic Molecular Integrated Circuit”.

References

- [1] M. M. Matsushita and T. Sugawara, “Current-Induced Low-Resistance State and Its Crystal Structure of a TTF-Based Dimeric Donor Salt”, *J. Am. Chem. Soc.*, vol.127, pp.12450-12451, 2005.
- [2] G. Ono, A. Izuoka, T. Sugawara, and Y. Sugawara, “Unusual Conductive Behavior of (BEDT-TTF)₃Cl₂ Hydrate Salts”, *Mol. Cryst. Liq. Cryst.*, vol.285, pp.63-68, 1996
- [3] M. M. Matsushita, Y. Masui, T. Hayashi, K. Awaga, and T. Sugawara, *to be submitted*.
- [4] T. Sugawara, T. Itoh, K. Suzuki, H. Higuchi, and M. M. Matsushita, “A programmable single-component diode based on an ambipolar organic field-effect transistor (OFET)”, *Pure Appl. Chem.*, Vol.84, pp.979-989, 2012.