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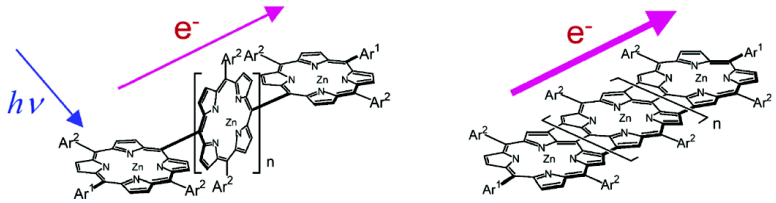

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Electrical Conduction through Linear Porphyrin Arrays

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Abstract: Electrical conduction measurements were made on two extreme types of directly linked porphyrin arrays by using nanoelectrodes. One type is the directly linked Zn(II)porphyrin arrays, consisting of 48 Zn(II)porphyrin moieties (Z48), and the other type is the completely flat, tape-shaped Zn(II)porphyrin arrays, consisting of eight Zn(II)porphyrin units (T8). The $I-V$ curve for Z48 exhibits the diode-like behavior and the hysteresis depending on the voltage sweep direction presumably due to the conformational heterogeneity arising from the dihedral angle distribution in Z48. On the other hand, the $I-V$ curve for T8 is nearly symmetric without any hysteresis, leading to the higher conductivity and the smaller band gap. These results illustrate that the stronger π-electron conjugation in T8, as compared with that of Z48, results in better electrical conduction.

Porphyrin-based molecular systems have received considerable attention as models for natural photosynthetic systems[1] and as enzyme mimics.[2] Besides, since directly linked porphyrin arrays without using any linkers[3] exhibit versatile physical properties and have the long and rigid molecular shapes, they are of interest in the field of molecular electronic devices. Several electrical transport experiments[4,5] have been made on porphyrin films and optoelectric memory devices,[4] and light-emitting diodes[5] based on porphyrin films have been demonstrated. However, the electrical transport properties of individual porphyrin molecules which should be characterized for the application as molecular-scale devices have not yet, to our knowledge, been reported. Thus, we have performed the electrical transport measurements through single or, at most, a few porphyrin arrays and report the results in this communication.

The electronic structure of porphyrin arrays is closely related to the electronic overlap between π-conjugated systems.[6] In this regard, we have prepared two extreme types of porphyrin arrays to investigate the influence of electronic interactions between the adjacent porphyrin molecules on the electrical transport properties. One is directly *meso*−*meso*-linked Zn(II)porphyrin arrays consisting of 48 Zn(II)porphyrin moieties (Z48).[7] These linear porphyrin arrays have an orthogonal conformation between the neighboring porphyrin units (orthogonal porphyrin array). The other one is completely flat, tape-shaped Zn(II)-porphyrin arrays consisting of 8 porphyrin units (T8) in which

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(7) The directly linked orthogonal porphyrin arrays up to 128 Zn(II)porphyrins connected together can be prepared. But because of the relatively low solubility and the possibility of aggregation of longer arrays such as **Z64** and **Z128**, **Z48** was employed for electrical measurement in this study. For fused porphyrin arrays, Zn(II)porphyrin moieties can be fused up to 12 units (**T12**). But since the longer fused array is more vulnerable to oxidation reaction, **T8** was employed in our measurements.

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the constituent porphyrin macrocycles are triply linked at *meso*−*meso*, *β*−*β*, *β*−*β* positions (fused porphyrin array).[7] The electronic *π*-conjugation over the fused porphyrin array is much more enhanced than that of the orthogonal porphyrin array. The details of the synthetic and purification procedures of these two types of porphyrin arrays were described elsewhere.[8]

To measure the electrical transport properties of porphyrin arrays directly, two kinds of Au/Ti nanoelectrodes were prepared. For the orthogonal porphyrin array with the length of about 40 nm, nanoelectrodes with a spacing of about 20−30 nm were fabricated by electron-beam lithography and a double-angle evaporation technique onto degenerately doped silicon substrate with a top SiO_2 layer of 0.5 μm. On the other hand, for the fused porphyrin array with about 7 nm in its length, the Au/Ti nanoelectrodes with a spacing of less than 7 nm were prepared by utilizing the electromigration-induced break-junction technique.[9] Electrical contact between porphyrin arrays and metal electrodes was made by using the electrostatic trapping method.[10] A drop of porphyrin solution (3 nmol) was positioned on the top of the electrode gap. Then, a voltage of up to 5 V was applied to the electrodes. After the porphyrin array was trapped between the electrodes, the sample was dried under nitrogen purging and characterized using a semiconductor characterization system (Keithley 4200). All electrical transport measurements were performed in a vacuum to eliminate the effect of water on the conductance.

Figure 1a displays the *I*−*V* curve measured at room temperature for orthogonal porphyrin arrays trapped between two nanoelectrodes. It exhibits the diode-like behavior and the hysteresis, depending on the voltage sweep direction. From the slope of *I*−*V* curves, the room-temperature resistance is estimated to be about ∼125−670 MΩ. We have also measured the *I*−*V* curve under illumination with a red LED (not shown). The conductance was enhanced under illumination. Similar photocurrent effects have been also observed by Liu et al.[4] in porphyrin films. However, the hysteresis was found in both *I*−*V* curves. Although the origin of the observed hysteresis is not clear, we speculate that it is probably attributed to the rotation about the *meso*−*meso* C−C bond in the orthogonal porphyrin array since the theoretical AM1 calculation[11] has shown that the dihedral angle between porphyrin rings varies approximately from 70 to 110° at room temperature and the electrical conductivity is expected to depend on the distribution in the dihedral angle between the adjacent porphyrin rings. We have also measured the *I*−*V* curves as the temperature decreases. The hysteresis was observed to disappear at 200 K, supporting our speculation that the hysteresis is due to the conformational heterogeneity arising from the dihedral angle distribution. In addition, the conductance decreased very rapidly with lowering temperature, and no current was measured in the voltage range from −5 to +5 V even at 180 K.

The observed hysteresis in Figure 1a implies the possibility of application to memory devices, as reported by Reed et al.,[12]

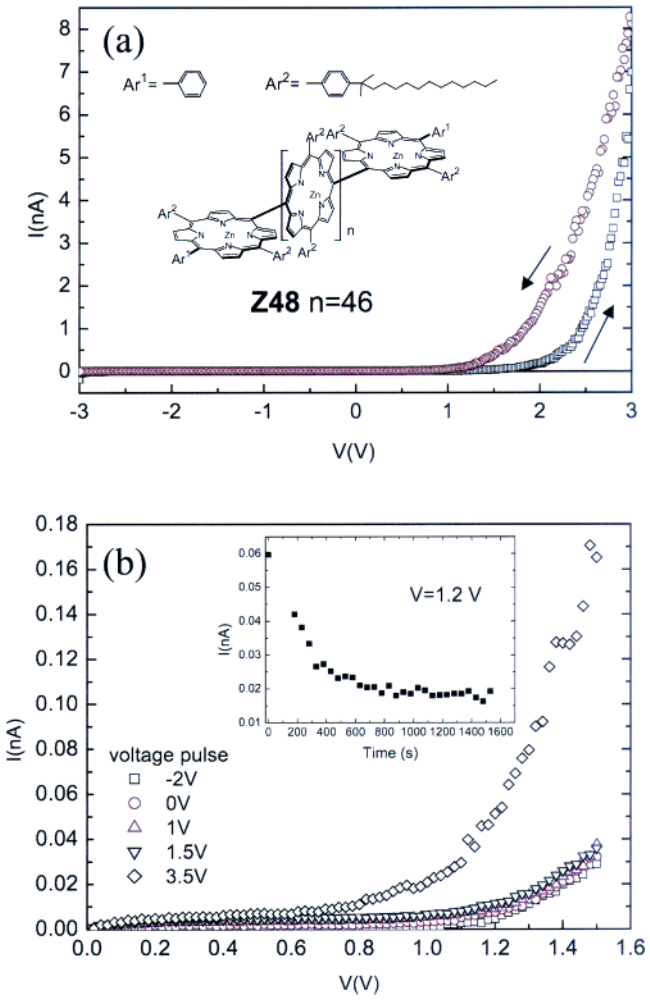

Figure 1. (a) *I*−*V* curves measured at room temperature on orthogonal porphyrin arrays trapped between two metal electrodes. The inset is the molecular structure of the orthogonal porphyrin array (Z48). (b) *I*−*V* curves obtained after applying various voltage pulses. The inset is the time dependence of current measured after applying +3.5 V voltage pulse.

who demonstrated molecular random access memory cells based on 2′-amino-4-ethynylphenyl-4′-ethynylphenyl-5′-nitro-1-benzenethiolate and 2′-amino-4-ethynylphenyl-4′-ethynylphenyl-1-benzenethiolate. Therefore, we have investigated the memory effect at room temperature. This was achieved by first applying a voltage pulse and then measuring the *I*−*V* curve from 0 to 1.5 V, as shown in Figure 1b. Indeed, the +3.5 V voltage pulse induces the higher conductance, suggesting that a low conductivity state is changed into a high conductivity state upon application of +3.5 V voltage pulse. If a positive voltage pulse larger than +3.5 V induces a change in the dihedral angle, this result may be understood. In the Figure 1b inset, the current measured with the bias voltage of 1.2 V is plotted as a function of time after a +3.5 V voltage pulse has been applied. The current exhibits an exponential decay with a time constant of approximately 300 s.

Figure 2 shows the *I*−*V* curves measured at several temperatures for the fused porphyrin array. In contrast to the orthogonal porphyrin array, it is nearly symmetric without any hysteresis, implying that the rotation about the *meso*−*meso* C−C bond is hindered in the fused porphyrin arrays. Moreover, compared with the orthogonal porphyrin arrays, a higher conductivity[13] and a smaller voltage gap were found. The room-temperature

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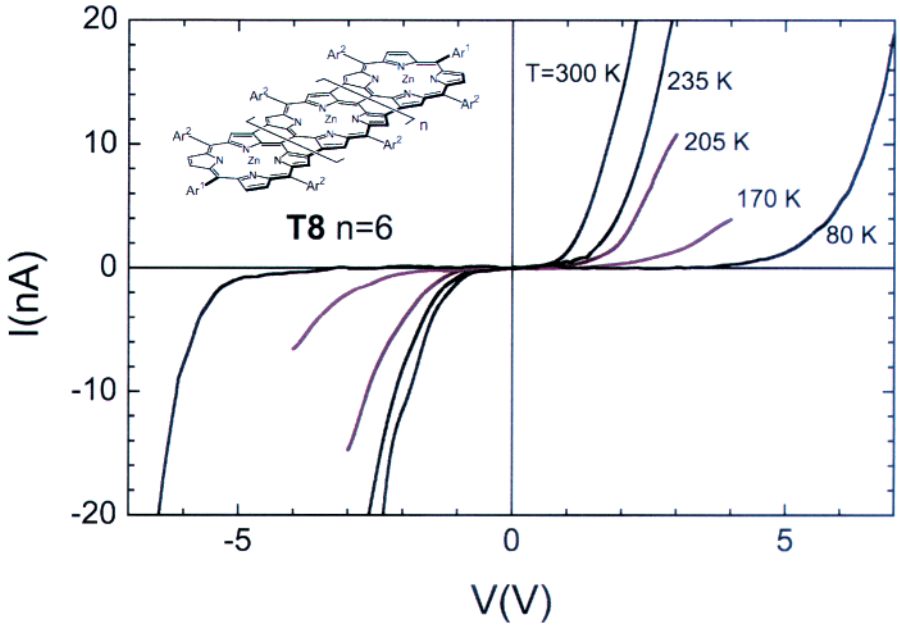

Figure 2. *I*−*V* curves measured at various temperatures on fused porphyrin arrays trapped between two metal electrodes. The inset is the molecular structure of the fused porphyrin array (T8).

resistance estimated from the slope of the *I*−*V* curve is about 50 MΩ, which is smaller than that of the orthogonal porphyrin array. These results indicate that the stronger π-electron conjugation results in better electrical conduction. As the temperature decreases, the conductance decreases and the voltage gap widens. However, it should be noted that the temperature dependence is much slower than that of the orthogonal porphyrin array.

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(13) The current at the voltage of 2.5 V for the fused porphyrin array is higher than that of the orthogonal porphyrin array by about 20 times, while the ratio of the length between the orthogonal and the fused porphyrin arrays is about 7. Consequently, the higher conductivity of the fused porphyrin array is not due to the length difference.

Supporting Information Available: Figures of wavelengths and images of orthogonal porphyr arrays trapped between two metal electrodes and of nanoelectrodes fabricated by the electromigration-induced break-junction technique (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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