

Chemical Approach Toward Molecular Electronic Device

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An attempt to actualize high-speed information processing system with molecular electronic devices is a fascinating approach within several other possible ideas for practical use of organic molecules for electronic devices. In order to fabricate the high-speed molecular electronic device, we need molecules of sub-micrometer size with rigid structure and high functionality. We have prepared several "molecular wires" based on porphyrin and related compounds, and studied their electronic properties by using gold nano particles and gold nano-gap electrodes.

Key words: molecular electronic device, organic synthesis, porphyrin, nano-gap electrode

1. INTRODUCTION

Present silicon rectifiers have been fabricated based on the potential difference at the interface of *n*- and *p*-type silicon semiconductor, which were made by doping of other elements than silicon. As the minitization of the electronic circuit progresses, the size of one functional unit will consist of countable number of atoms. In such small structures doped silicon can not be used as the functional unit, because the doping level can not be controlled in such a small number of atoms. If one unit consists of 100 silicon atoms, 0.1% doping means that 0.1 phosphorus atom should be mixed with 99.9 atoms of silicon. Of course it is impossible to treat decimal number of atoms and the doping can not be used for such ultimately small devices. The molecular electronic device was first proposed by

Aviram in 1974 as a "molecular rectifier" to overcome such limitations of the silicon device systems for minitization.^[1] His proposal was to realize rectifying functionality by using a dyad molecule made from a donor part (higher frontier orbitals) and an acceptor part (lower frontier orbitals). In this idea, the rectifying functionality is actualized by the difference of intrinsic orbital levels of each molecular part, and the difficulty observed in the doped silicon for atomic scale structure can be overcome. Since then, plenty of studies and proposals have been reported. However the practical molecular electronic device has not been realized yet. In these several years, progresses of scanning probe microscopy (SPM), physical theory, and synthetic organic chemistry have made it a realistic scientific target, and a lot of scientific projects have

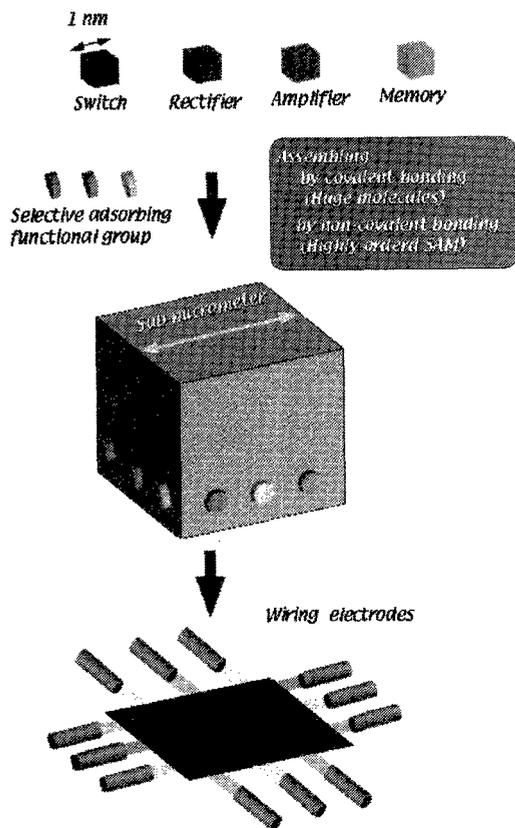


Figure 1. Sub-micrometer molecular “integrated circuit” which has been fabricated from singly functional molecular parts.

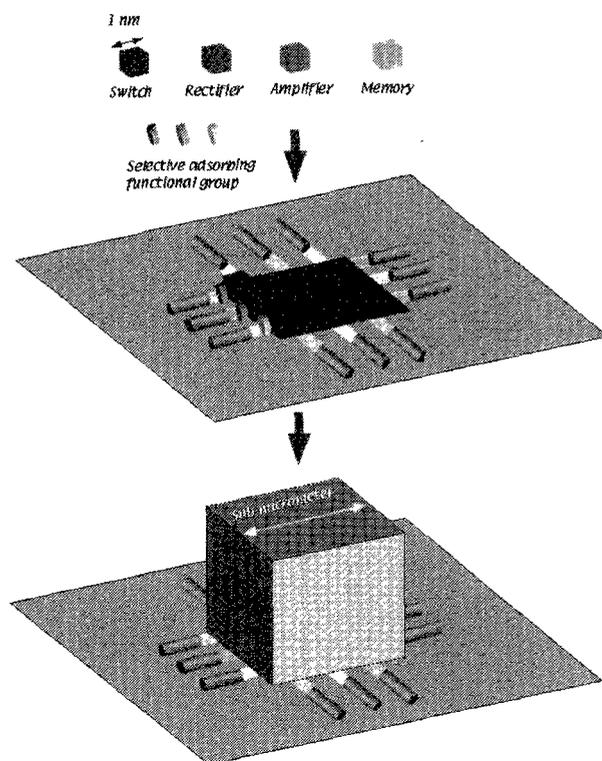


Figure 2. Sub-micrometer molecular system prepared by bottom up method

emerged all over the world.^[2,3]

In this paper, I would like to describe what should be done to materialize the “molecular electronic devices” and what has been done up to the present time, from the view point of a synthetic organic chemist.

2. PERSPECTIVE OF THE TARGET

Several different ideas are possible for the term of “molecular electronic device”. The first one is the original idea of Aviram to utilize molecules as the ultimately small electronic parts in order to scale down and speed up to the maximum. The device should run at several THz (10^{12} - 10^{13}) frequency, and consequently single process should be performed at several pico seconds (10^{-12} sec) or less than that. Since only electron or photon can move in this time range, these

particles are the only possible media to transmit the information with this high speed. The molecules work only as the potential field for these fundamental particles, and movement of the molecules will cause detrimental noise. To avoid the molecular movement they should be completely rigid and no conformational isomers can be allowed.

Even if one functionality such as rectifying or switching function could be realized in one molecule, it would be nonsense if you should wire to each singly functional molecules. This is because such wiring need metal wires with the width of less than 1nm, and such thin metal will not work as “metal” any more. Such high speed molecular electronic devices will become practical when we can make highly integrated molecular systems in which a large number of

functionalities are incorporated to make a huge molecular system; the size will be several hundreds nm³ and they will have higher level functionality such as a logic gate or an operating amplifier. To these molecular systems, several wiring will be made by using contemporary lithographic technology. The idea is graphically illustrated in Figures 1 and 2. If the molecular system is prepared by covalent bonding it will be a synthesis of a huge molecule, and if it is fabricated by non-covalent bonding it will be a highly ordered molecular assembling. At the present time, it is not easy to realize such huge molecular systems with highly ordered manner, and these will be a fascinating target for both synthetic organic chemists and supramolecular chemists. Actually, as will be described below, a 100nm long porphyrin wire, which has distinct structure, has already been synthesized.

The second idea for the molecular electronic device is to utilize the properties of molecules more positively. The most distinctive difference of organic molecules from inorganic nano structures such as silicon island is that they have more freedom in movement. For example, most double bonding compounds (R-C=C-R) have *cis* and *trans* isomers and each isomers can be converted to another by photo and/or thermal reactions reversibly. The similar isomerization can be done by electrochemical reactions in some compounds. Such isomerization can be utilized for high-density memory; actually it has already been realized by using SPM technique with self assembled monolayer of isomerizable organic molecules. These processes are naturally slow since they require molecular movement which are generally more than 1000 times slower than electronic movement.

In the brains, each neuron works with rather slow speed, sometimes it requires milliseconds for one process. However, as a whole the performance of the brains sum up to be quite high. The same strategy may be adopted for molecular processing; by using large amounts of slow molecular processors in a parallel way, the total performance can be enhanced. Although the

mechanism of the brain system has not yet been fully clarified, there are several proposed models for parallel processing. Most promising model for the (slow) molecular computing could be cellular automaton, in which no addressing to each functional unit is required. However, the present cellular automaton models need substantial modifications to be adopted for molecular systems. All the present mathematical models proposed so far for them ignore the consumption of energy during information processing, and interactions of each cell should be decisive. However, in the real physical systems we should find ways to supply energy to the system, and the interactions of each cells are probabilistic and dependent on space-time of each cells. We need further mathematical and physical discussions to materialize the molecular cellular automaton.

There are several other ideas for the (slow) molecular computing; DNA computing, molecular computing in solution, and molecular mechanical analogue computing. Although these ideas seems to be very attractive, no concrete way for practical use has been proposed for them yet within our knowledge. Thus, for the present time, only the current silicon devices can be the sole actual model for molecular electronic devices.

3. SHORT TERM TARGET

3-1. Establishment of routine method for molecular conductance measurement

Recent theoretical and experimental works have revealed that electronic conduction through individual molecules is a phenomena of different category from the conduction of bulk materials. In the bulk materials such as powders, polymers, and single crystals, the electronic conduction is dominated by inter-molecular or inter-domain interactions, and crystal structures or supra-molecular structures are important for understanding the conduction characteristics of the materials. In addition, doping is necessary in most cases to generate solitons as the charge carrier.

In the individual molecules, theories predict that the

predominant mechanism of the electronic conduction is tunneling when the Fermi levels of the electrodes do not match with the molecular orbital levels, and the interaction of the electrode with the molecule is not strong.^[4, 5] When the Fermi level of the electrode match with one of the molecular orbitals, resonant tunneling mechanism will work and the conductance is independent on the conduction path length.^[6-8] The conduction mechanism is also affected by the interactions of the electrode with the molecules. According to theoretical calculations, the electronic structure of molecules will become metallic when the interactions are strong.^[9, 10]

For the study of single molecular electronic conduction with high reliability, scanning probe microscopic (SPM) techniques are the most promising method.^[11, 12] However, with the SPM method, both or at least one contact of the target molecule with two electrodes should be physical interaction and can not be made with bonding, since observation of the molecular image is not possible if the SPM tip is bonded covalently to the molecule. Thus with the method, it is impossible to measure the conduction of the molecule which is strongly (= covalently) interacting with the electrodes at both ends.

In this regard, nano-gap electrode method will be a good candidate to measure the conductance of individual molecule which is covalently bonded to both electrodes. A pioneering work by Reed and Tour et al. was reported in 1997, in which they used "break junction technique", and showed that the differential conductance (dI/dV) exhibited peaks at a certain bias voltage.^[13] The result was well reproduced by a theoretical calculation based on the resonance tunneling model.^[8] Park et al. made ca. 1nm gap electrode by electrical migration of gold, and fabricated a C_{60} single electron device, in which the Coulomb blockade by C_{60} was observed.^[14]

However, these methods are not practical for routine measurement of various type of organic molecules. In order to establish the structure - function relationship in molecular conductance, we need a routine way

applicable for diverse organic molecules.

We have made gold electrodes with the gap of 50 to 1500nm by usual photo- or electron beam lithography. The size of molecules in this report ranges from 2 to 3 nm, which are far smaller than the electrode gaps. In order to fill the gap and to connect the molecules to the electrodes covalently, gold nano-particles were used as the molecular bonds. When organic dithiol molecules were mixed with gold nano particles, the thiol group is adsorbed chemically to the gold nano particles, to form three dimensional composites.^[15, 16] We found that when the reaction was performed on the gold nano-gap electrodes, a thin film of the composite was made between the electrodes and the molecular network was made as illustrated in Figure 3. With this method two gold electrodes could be connected by organic molecules covalently in a series by the assist of gold nano-particles.^[17]

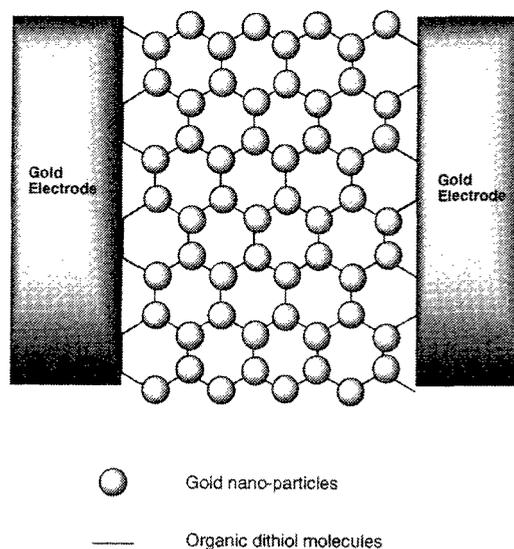


Figure 3. A schematic illustration of the nano-gap electrodes that is connected with the network of organic dithiols and gold nano particles. Shaded circles indicate gold nano-particles, and lines mean organic dithiol molecules.

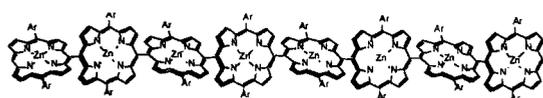
3-2. Preparation of long molecular wires

With the method using gold nano particles and nano-gap electrodes described in section 3-1, there exist more than several hundreds of molecules between the two

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electrodes. Naturally, the interaction between these molecules can not be ignored. In order to connect two electrodes with a single molecule, we need electrodes with a narrower gap and longer molecules. By using electron beam lithography, it is possible to make less than 100 nm gold gap electrodes. If we have the molecule whose size is almost the same of the gap size, direct measurement of a single molecule will become possible with the nano-gap electrodes. However, such huge molecules have generally low solubility in most solvents, which obstruct purification, identification and usage of these molecules. In this context we need huge molecules whose sizes are up to 100nm and their solubility in ordinary organic solvents are reasonable.

One candidate is meso-meso directly linked porphyrin arrays.^[18] We have prepared meso-meso directly linked porphyrin octamer by an electrochemical reaction (chart 1).^[19] Unexpectedly, the compound was highly soluble in ordinary organic solvents. This is probably because the porphyrin planes connect nearly perpendicular to each other due to their sterical requirement, and hence their intermolecular π - π stacking was prevented largely.



Ar = 3,5-Di-tert-butylphenyl

Chart 1. Structure of meso-meso directly linked porphyrin octamer.

Starting from the octamer, we have planned to prepare 128mer of the porphyrin arrays step-by-step; however, a group in Kyoto University has done it earlier than us.^[20] Anyway, molecules with the size exceeding 100nm could be prepared which has distinct size and structure.

As described above, in the meso-meso directly linked porphyrin arrays the porphyrin planes connect nearly perpendicular to each other, and it causes the high solubility of the compound. At the same time, the structure prevents good resonance between the

porphyrin π -systems, and the energy gap (E_g) does not decrease so much even for 128mer. The tunneling resistance through a molecule of length L with an energy gap E_g is roughly estimated as $R \sim (12.9k\Omega) \exp(0.7245) \sqrt{E_g / eV} L / \text{\AA}$.^[5]

According to this equation, the tunneling resistance will be less when E_g of the molecule is smaller. In this sense, the meso-meso linked porphyrin arrays may not be a good molecular "electronic" wire. Another possible method to make long porphyrin wires while keeping both the good resonance and high solubility is to connect them in axial directions.^[21-23] Semi-empirical molecular orbital calculations for the system showed that the resonance between the porphyrin moieties are feasible and E_g of the system steadily decreases when the arrays become longer. Also E_g decreases when the central element becomes heavier.^[24]

Although the arrays of the group 15 element complexes of porphyrins are promising as the molecular wire in this sense, counter anion present in these molecules will disturb the precise analysis of the electronic properties. In the group 15 element porphyrins, the central elements are formally cationic since the porphyrins act as dianionic ligands when complexing. Thus there remains ambiguity in the position of the counter ion in the molecule, which will affect the electronic properties considerably.^[24]

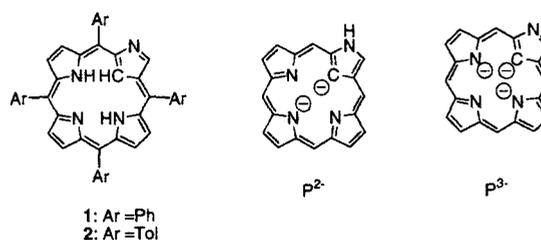


Chart 2. Structure of N-confused porphyrins (NCP)

An "N-confused porphyrin (Chart 2)" is a porphyrin isomer wherein one of the four pyrrole rings is inverted.^[25, 26] The NCPs can behave both as a dianionic ligand (P^{2-}) and as a trianionic ligand (P^{3-}) when complexing with metal ions.^[27] If NCP works

as P^2 for the group 15 element the central element of the product will be cationic, and if it acts as P^3 the central element will be electronically neutral. We have synthesized antimony complex of N-confused tetraarylporphyrins, and studied their structure and properties in the aim to elucidate the possibility to use them as components of highly conductive molecular wires. The neutral structure was confirmed by a single crystal X-ray crystallographic analysis.

The lower energy gap of Sb-NCP compared with Sb-porphyrin was also observed in the absorption spectrum. The λ_{max} of the longest wavelength band of Sb-NCP is 683 nm (1.82 eV) while that of Sb-porphyrin is 610 nm (2.03 eV); the energy difference (0.21 eV) obtained from the absorption spectrum was consistent with the value obtained by voltammetric methods shown above (0.16 eV).^[24]

As described here (1) the size of the molecules has already exceed the gap size of electrodes made by electron beam lithography, (2) molecules of various energy gap and energy levels are available. We are planning to establish routine measurement of electronical behavior of various organic molecules to clarify the structure - functionality relationship after the settlement of some further technical difficulties. These experimental results will be the base for the fundamental physical theories for practical molecular electronic devices.

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