RESEARCH ACTIVITIES IX

Research Center for Molecular-Scale Nanoscience

IX-A Nano-Science and Nano-Technology toward Molecular Scale Electronics

Molecular electronics is a fairly new and fascinating area of research that is firing the imagination of scientists. However, most single organic molecules are not conductive in a classical sense, long range electronic transport through single molecules can not be so effective to realize practical electronic circuits. Our group is interested in (1) construction of nano-structures made from conductive materials such as carbon nanotubes, metal particles or rods, with functional organic molecules, (2) measurements of electric or photonic properties of individual nano-structures while observing their nanometric images, and (3) conductance change of single molecules by external stimulation such as electric field, photon irradiation or chemical species.

IX-A-1 Photo Precursor for Pentacene

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[*Tetrahedron Lett.* **46**, 1981–1983 (2005)]

Pentacene is one of the most sensational polycyclic hydrocarbons, which draws attention from many fields due to its high electron mobility. Many efforts have been focused on the device preparation of not only pentacene itself but also its derivatives. For the application of pentacene and its derivatives, one of the biggest problem is the low solubility in common solvents. Difficulties are often encountered in the puriffication of its derivatives, and several manipulations of a high vacuum sublimation are required. In the final stage of pentacene based devices, the vapor deposition technique under high vacuum is usually employed. In order to overcome the problem, precursors, which give pentacene or its derivatives by thermal decomposition, namely retro Diels-Alder reaction, were developed and their applications for field effect transistors (FET) and organic thin film transistors (OTFT) were recently reported. In these cases, retro Diels-Alder reaction of the precursors was designed to proceed at rather low temperatures by extrusion of tetrachlorobenzene and *N*-sulfinylacetamide. The requisite for such leaving molecules is sufficiently small and inert not to affect the property of pentacene devices. For these precursor methods, there is an inevitable drawback that the high vacuum sublimation technique, one of the most reliable and successful device preparation methods, cannot be applied, because the trigger of the precursors to pentacene is heat. We thought that not only this shortcoming of the precursor method but also property of the leaving molecules can be dramatically improved if the alternative physical decomposition method, namely light, is applied. In this communication, we report preparation of the first photo-convertible precursor to pentacene and its fundamental properties.

IX-A-2 Synthesis and Self-Assembly of Novel Porphyrin Molecular Wires

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[*Thin Solid Films* in press (2005)]

Sub-micrometer long butadiyne-linked porphyrin wires were synthesized by oxidative coupling of diethynylporphyrin. The porphyrin wires were analyzed by analytical gel permeation chromatography, absorption spectroscopy and matrix-assisted laser desorption/ionization time of flight mass spectroscopy. Observations of the wire were performed by atomic force microscopy. Self-assembled structures of the wires were observed on highly oriented pyrolytic graphite. Self-assembling features of the porphyrin wires depended on the length of the porphyrin wires and the concentration of the depositing solution.

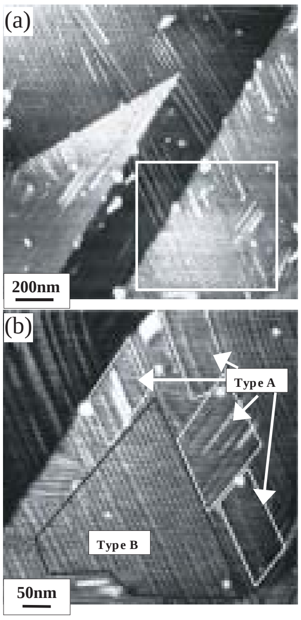

Figure 1.

IX-A-3 Molecular Junctions Composed of Oligothiophene Dithiol Bridged Gold Nanoparticles Exhibiting Photoresponsive Properties

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[*Chem. Eur. J.* **12**, 607 (2006)]

Three oligothiophene dithiols with different number of thiophene rings (3, 6 or 9) were synthesized and characterized. X-ray single crystal structures of compounds 3’,4’-dibutyl-5’5’’-dithiocyano-2,2’:5’,2’’-terthiophene (**2**) and 5,5’’’’’-dithiocyano-tetrabutyl-2,2’:5’,2’’:5’’,2’’’:5’’’,2’’’’:5’’’’,2’’’’’-hexathiophene (**5**) were involved herein to show the exact molecular lengths as well as the difference between their UV-vis spectra arising from the different packing modes. These dithiols with different chain lengths were then treated with *t*-dodecanethiol protected active gold nano-particles (Au-NPs) *via* in situ thiol-to-thiol ligand exchange in the presence of 1 μm gap Au-electrodes. Thus the molecular junctions composed of self-assembled films were prepared, where oligothiophene dithiol bridged Au-NPs were attached to two electrodes by means of Au–S bonded contacts. The morphologies and *I-V* characteristics of these films were studied by SEM and AFM approaches, which suggest the thickness of the films varied within the size of one isolated Au-NPs and typical distance dependent semiconductor properties could be observed. Current-voltage (*I-V*) measurements for these devices were performed where the films served as active elements in the temperature range 6 ~ 300 K and classical Arrhenius plots and their linear fittings were carried out to give the activation energies (ΔE). Furthermore, preliminary studies on the photoresponsive properties of these junctions were explored at 80, 160 and 300 K, respectively. Physical and photochemical mechanisms were used to explain the possible processes. To the best of our knowledge, this is the first report where oligothiophene dithiols act as bridging units to link Au-NPs, and also the first report about functionalized Au-NPs exhibiting photo response properties in the solid state.

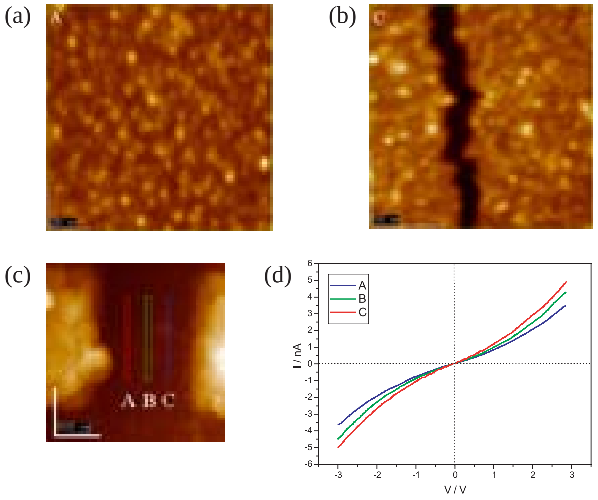

Figure 1. (a) and (b) Tapping mode AFM topographies of the self-assembled film of **14** on the micro-gap gold electrodes corresponding to the areas marked in (c). (d) *I-V* curves with different separations between cantilever and brass substrate by using contacting mode AFM.

IX-A-4 Simple Preparation Method for Supramolecular Porphyrin Arrays on Mica Using Air/Water Interface

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[*Jpn. J. Appl. Phys.* in press (2005)]

The fabrication of supramolecular porphyrin arrays on the surface of a mica substrate is demonstrated. The supramolecular structures are prepared at the air/water interface from a dilute solution of porphyrin dimer and bidentate ligand and then transferred to mica by using the conventional Langmuir-Blodgett method. Isolated wire-like structures and networks of structures are observed by atomic force microscopy. From the analysis of the height histogram and average width, these structures are considered to be side-by-side arrangements of supramolecular chains of porphyrin dimer and bidentate ligand. By changing the ligand molecule, we demonstrate that the configuration of the supramolecular structure can be controlled.

IX-A-5 Novel Photochemical Synthesis of Pentacene and Its Derivatives

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[*Chem. Eur. J.* **11**, 6212 (2005)]

A novel -diketone precursor of pentacene, 6,13-dihydro-6,13-ethanopentacene- 15,16-dione, was prepared and converted successfully to pentacene in 74% yield by photolysis of the precursor in toluene: Irradiation of the diketone solution in toluene with light of 460 nm under an Ar atmosphere caused the solution to change from yellow to fluorescent orange-pink within a few minutes, after which, purple precipitates appeared. After 35 min, the solution changed to colorless and the purple precipitates were filtered to give pentacene in 74% yield. By contrast, in the presence of oxygen, the color of the solution changed from yellow to pale yellow, and only 6,13-endoperoxide of pentacene was quantitatively obtained. The rate of the reaction upon photolysis was measured by observing the decay of n-* absorption of the precursor at 460 nm, and was found to be similar in both the presence and absence of oxygen. Therefore, the photoreaction of the -diketone precursor seemed to occur *via* the singlet excited state. Because the T-T absorption of pentacene was observed upon photolysis of the precursor in the nanosecond transient absorption measurement under an Ar atmosphere, the excited triplet state of the pentacene generated singlet oxygen by sensitization, and it reacted with the ground-state pentacene to give the 6,13-endoperoxide. The -diketone deposited on glass was also converted successfully to pentacene film by photoirradiation. In addition, diketone precursors of a mixture of 2,8- and 2,9-dibromopentacene and 2,6-trianthrylene were also prepared and their photoconversion was performed.

IX-A-6 Porphyrin Molecules Working as Nanodevice on Single-Walled Carbon Nanotube Wiring

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[*Adv. Mater.* in press]

For the future development of molecular electronics, we should construct nanosized molecular devices placed on nanowiring. To obtain high-quality devices composed of a few molecules, the wiring and the device should be connected well to maintain a constant interface. For this purpose, a single-walled carbon nanotube (SWNT)/porphyrin complex was prepared and then its electronic property was investigated while observing a topographic image using point-contact current imaging atomic force microscopy (PCI-AFM). Using PCI-AFM, we can measure the current along the long axis of the wiring by which the quality of the device in the circuit can be determined. The *I-V* curves were asymmetric with respect to the origin where an aggregate of several porphyrin molecules was absorbed, while they were symmetric without them. This means the porphyrin aggregation works as a rectification device on SWNT wiring. This is the first study which proves the electron property of a few porphyrin molecules absorbed on SWNT.

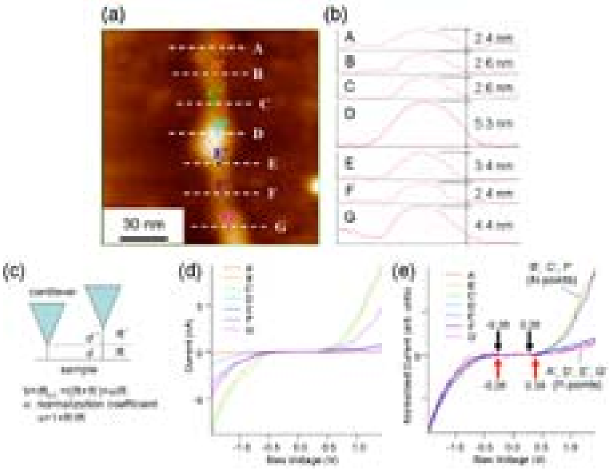

Figure 1. (a) Topographic image of **BPP-Zn** absorbed on SWNT electrode. The *I-V* measurement was performed at points A'-G'. (b) Cross section of each line in (a). (c) Relation between a tunnel resistance and a distance of sample and cantilever. (d) *I-V* curves obtained at each point. (e) The *I-V* curves were normalized at –1.5 V. All curves are coincident below 0 V. *I-V* curves are classified into two types over 0 V. One is symmetrical with respect to the origin where porphyrin is absorbed and another is asymmetrical where no porphyrin is absorbed. Two types of arrow indicate the band edges (BE) of the objects. Black and red arrows indicate the BE of the object for N-points and P-points, respectively.

IX-A-7 Electronic Properties of Single-Walled Carbon Nanotube/Porphyrin Polymer Complex Measured by Point-Contact Current Imaging Atomic Force Microscopy

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[*J. Nanosci. Nanotechnol.* in press]

The electronic properties of a porphyrin polymer wire absorbed on a single-walled carbon nanotube (SWNT) were investigated. Current-voltage (*I-V*) curves were measured simultaneously along with topographic observations using point-contact current imaging atomic force microscopy (PCI-AFM). *I-V* curves taken at the location of porphyrin polymer wire absorption were asymmetric with respect to the origin, while they were symmetric in the absence of a porphyrin polymer wire. The electron conduction mechanism of the porphyrin on the SWNT was similar to the case of SWNT/ 5,15-Bis-pentylporphyrinato zinc(II) complex in our recent work.

IX-A-8 Preparation of Very Reactive Thiol-Protected Gold Nanoparticles: Revisiting the Brust-Schiffrin Method

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[*J. Nanosci. Nanotechnol.* in press]

Metal nanoparticles have attracted great interest in nanoscience and nanotechnology because of the many possibilities envisaged by the bottom-up approach since they possess unique optical, electrical, bonding and catalytic properties. Among them, the gold clusters are the most stable and extensively studied materials, and have been proposed for applications such as in photo-electrochemical devices, drug delivery systems and chemical and immunosensors. In all these cases, the properties of the materials should be adjusted by anchoring molecular species with suitable properties on the surface. In this sense, the availability of easily functionalizable and stable starting materials is an important aspect since there is a myriad of molecular species and other materials that can be combined with for the development of new inorganic-organic hybrid nanomaterials and applications.

The higher stability and possibility to isolate a solid that can be repeatedly isolated and redissolved in common organic solvents without decomposition and the possibility to treat them just as another organic molecular species is very convenient. However, there is a drawback for the widespread use of such a thiol protected materials: the sluggishness of the functionalization reaction by substitution of the protecting species, which can take more than a day to proceed until completion. The use of conventional organic chemistry on ω-functionalized protecting molecules is also tedious and hampers the preparation of organic-inorganic hybrid nanomaterials, for example by coordinative layer-by-layer assembly. Accordingly, we revisited the Brust-Schiffrin method envisaging the preparation of substitutionally reactive but stable enough thiol protected gold nanoparticles to isolate them as a solid.