# 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 Synthesis and Self-Assembly of Novel Porphyrin Molecular Wires

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[*Thin Solid Films* **499**, 23–28 (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.

### IX-A-2 Molecular Junctions Composed of Oligothiophene Dithiol Bridged Gold Nanoparticles Exhibiting Photoresponsive Properties

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[*Chem. Eur. J.* **12**, 607–619 (2005)]

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 ($\Delta E$). 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.

### IX-A-3 Simple Preparation Method for Supramolecular Porphyrin Arrays on Mica Using Air/Water Interface

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[*Jpn. J. Appl. Phys.* **45**, 2324–2327 (2006)]

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 thesupramolecular structure can be controlled.

### IX-A-4 Porphyrin Molecular Nanodevices Wired Using Single-Walled Carbon Nanotubes

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[*Adv. Mater.* **18**, 1411–1415 (2006)]

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.

### IX-A-5 Electronic Properties of Single-Walled Carbon Nanotube/150mer-Porphyrin System Measured by Point-Contact Current Imaging Atomic Force Microscopy

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[*J. Nanosci. Nanotechnol.* **6**, 1644–1648 (2006)]

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-Bispentylporphyrinato zinc(II) complex in our recent work.

### IX-A-6 Preparation of Very Reactive Thiol-Protected Gold Nanoparticles: Revisiting the Brust-Schiffrin Method

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[*J. Nanosci. Nanotechnol.* **6**, 708–712 (2006)]

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 photoelectrochemical 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.

### IX-A-7 Spontaneous Resolution of Delta and Gammma Enantiomeric Pair of [Ru(phen)(bpy)$_2$](PF$_6$)$_2$ (phen = 1,10-phenanthroline, bpy = 2,2'-bipyridine) by Racemic Conglomerate Crystallization

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[*Polyhedron* **25**, 1379–1385 (2006)]

Spontaneous resolution study is realized for a Δ and Λ enantiomeric pair of ruthenium(II) complexes obtained by racemic conglomeration from solution, crystalling in $P4_1$ and $P4_3$ space groups. A ligand exchange reaction between phen and bpy ligands is found for these Ru(II) complexes, but racemization is accompanied which has been proved by the single-crystal structure of the product. To extend our research, counter-ion ($BF_4^-$)

and 4,4’-dimethyl-2,2’-bipyridine (dmbpy) are used to synthesize similar six-coordinate Ru(II) complexes. Nevertheless, conglomerate crystallization could not be progressed in these two cases.

### IX-A-8 Structural and Spectroscopic Characterizations of Low-Spin [Fe(4,4-dimethyl-2,2- bipyridine)$_3$] (NCS)$_2$/H$_2$O Prepared from High-Spin Iron(II) Dithiocyanate Tetrapyridine

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[*J. Mol. Struct.* **785**, 21–26 (2006)]

Redetermination of the crystal structure of high-spin iron(II) dithiocyanate tetrapyridine $[Fe(py)_4(NCS)_2]$ (**1**) (pyZpyridine) at 85 and 291 K exhibits different unit cells when compared with that reported in 1967. An elongation in the compressed octahedron coordination environment around central ferrous ion is observed at low temperature, which can be verified by the DFT calculations of energy and dipole moments. **1** was then used as the Fe(II) source to synthesize $[Fe(dmbpy)_3](NCS)_2{\cdot}3H_2O$ (**2**) (dmbpyZ4,40-dimethyl-2,20-bipyridine). The X-ray diffraction studies of **2** reveal that six Fe–N bond distances are in the range 1.959(3)–1.971(3) Å suggesting the formation of the low-spin Fe(II) complex.

### IX-A-9 Morphology and Electric Properties of Nonathiophene/Au Nano-Composite Thin Films Formed between 1 μm Gapped Electrodes

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[*Mol. Cryst. Liq. Cryst.* **455**, 299–303 (2006)]

A nano-composite conductive film is formed between gold electrodes by immersion of the electrode pair in a chloroform solution of nonathiophenedithiol and gold nanoparticles. The homogeneous thin film is formed over an area of 3 mm × 3 mm surrounding the 1μm-gapped electrodes. The thickness of the film (20 nm) corresponds to 2–3 layers of the dithiol-bridged Au nanoparticles. Temperature-dependent *I-V* curves reveal that a thermionic mechanism dominates in the high-temperature region (>80 K), while molecular tunneling is the main transport process at lower temperatures.

### IX-A-10 Synthesis of End-Functionalized π-Conjugated Porphyrin Oligomers

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[*Tetrahedron* **62**, 4749–4755 (2006)]

4-(S-acetylthiomethyl)phenyl- and pyrenyl-functionalized π-conjugated porphyrin oligomers were synthesized. The distribution of the length of the oligomers could be controlled by changing the ratio of the starting porphyrin to the capping molecules. Oligomers from dimers to heptamers were isolated using size exclusion chromatography. The spectroscopic properties of these oligomers were measured to determine the influences of the number of porphyrin units and capping molecules on the absorption and emission spectra.

### IX-A-11 Fabrication of Nanoscale Gaps Using a Combination of Self-Assembled Monolecular and Electron Beam Lithographic Techniques

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[*Appl. Phys. Lett.* **88**, 223111 (2006)]

We describe a new method of fabricating nanogaps using a combination of the self-assembled molecular lithographic and the electron beam lithographic techniques. The method enables us to control the size of a gap with an accuracy of ~2 nm, and design the positions, where the nanogap should be formed, in the high-resolution patterning by employing an electron beam lithography. The utility of the fabricated nanogap is demonstrated by measurement of a single electron tunneling phenomenon through the dodecanethiol-coated Au nanoparticles placed in the fabricated nanogap.

### IX-A-12 Synthesis and Photochemical Behavior of Metalloporphyrin Complexes Containing a Photochromic Axial Ligand

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[*Thin Solid Films* **499**, 219–223 (2006)]

Metalloporphyrin complexes with a photochromic axial ligand were synthesized and photoisomerization behavior of those complexes wasinvestigated. In this study, 3,3V-azopyridine (AZP) was used as the axial ligand. We found that the structure of the axial-coordinated complexes depended on the center metal of porphyrin. When magnesium was employed as the center metal, a 1:1 coordinated complex was obtained. On the other hand, zinc or rhodium porphyrins formed the sandwich-bonded complexes. The photoisomerization behavior also depended on the center metal of the porphyrins, and the *cis*-to-*trans* “one-way” photoisomerization of the AZP axial ligand took place in the complexes of zinc and rhodium porphyrins. The one-way isomerization may be interpreted as the results of the photoinduced electron transfer from porphyrin to AZP.