

IV-L Organic Synthesis for Molecular Electronic Devices

The mechanism of electronic conduction through a single molecule is quite different from that of the bulk organic conductive materials. In the latter the charges are carried by soliton, however in the former theories predict that the conduction generally involves tunneling or a resonant tunneling mechanism. A few experiments support the prediction, however there is neither systematic experimental studies nor established theory for single molecular conduction. We use (1) scanning probe microscopic (SPM) technique in ultra high vacuum, and (2) planner nano-gap electrodes for the measurements. Design of the target organic molecules and the measurement system is important for reliable results. We have been preparing (1) self standing organic molecules for measurement by SPM, (2) photo-responsible molecular wires, (3) long molecular wires with low E_g which can be observed optically on nano-gap electrodes. Conduction of gold nano-particles / organic dithiols composite system is also studied.

IV-L-1 "N-Fused Porphyrin": A New Tetrapyrrolic Porphyrinoid with A Fused Tri-Pentacyclic Ring

FURUTA, Hiroyuki^{1,3}; ISHIZUKA, Tomoya¹; OSUKA, Atsuhiko¹; OGAWA, Takuji^{2,3,4}
(¹Kyoto Univ.; ²Ehime Univ.; ³JST; ⁴IMS)

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The syntheses and X-ray structures of novel porphyrinoids, "N-fused porphyrins (NFPs)," and their reactivity were described. NFP was spontaneously produced from the bromo-substituted N-confused tetraarylporphyrin in a pyridine solution at room temperature. X-ray diffraction analyses revealed that the porphyrinoid core containing a fused tri-pentacyclic ring is almost planar. The deviation from the mean plane of 4e ϕ , for example, was within 0.30 Å. The peripheral aryl substituents were tilted 50.4, 53.5, 64.4, and 12.4° relative to the porphyrin mean plane, respectively. The occurrence of a three-centered hydrogen bonding in the NFP core was inferred by the downfield shift of the inner NH signal (e.g., 8.48 ppm for 4e ϕ) in 1 H NMR and the short distances (within 2.4–2.9 Å) among the inner core nitrogens, N2, N3, and N4. The optical absorption spectra of NFPs exhibit Soret-like transitions around 360, 500, and 550 nm and weak Q-like bands around 650, 700, 850, and 940 nm in CH₂Cl₂. The electrode process of 4e ϕ showed the first oxidation at 0.08 V and reduction at -1.37 V (vs. Fc/Fc+), which suggested the small energy gap attributed to the unusual long-wavelength absorption was mainly due to the rising of the HOMO energy level. The first-order rate constants (kf) for the transformation from NCPs to NFPs were largely affected by the substituents at the meso position, showing a good correlation with Hammett ρ + parameters. Moreover, the reverse reaction from NFPs to NCPs was observed in the CH₂Cl₂ solution by treating with a base. Dynamic ring inversion in the tetrapyrrolic porphyrin core is discussed.

IV-L-2 Chemical Approach Toward Molecular Electronic Device

OGAWA, Takuji^{1,2,3}; KOBAYASHI, Keiji²; MASUDA, Go²; TAKASE, Takuya²; SHIMIZU, Yuusuke²; MAEDA, Seisuke²
(¹JST; ²Ehime Univ.; ³IMS)

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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.

IV-L-3 Prospects and Problems of Single Molecule Information Devices

WADA, Yasuo¹; TSUKADA, Masaru²; FUJIHIRA, Masamichi³; MATSUSHIGE, Kazumi⁴; OGAWA, Takuji^{5,7}; HAGA, Masa-aki⁶; TANAKA, Shoji⁷
(¹Hitachi Co.; ²Univ. Tokyo; ³Tokyo Inst. Tech.; ⁴Kyoto Univ.; ⁵Ehime Univ.; ⁶Chuo Univ.; ⁷IMS)

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Current information technologies use semiconductor devices and magnetic/optical discs, however, it is foreseen that they will all face fundamental limitation within a decade. This paper reviews the prospects and problems of single molecule devices, including switching devices, wires, nanotubes, optical devices, storage devices and sensing devices for future information technologies and other advanced application in the next paradigm. The operation principles of these devices are based on the phenomena occurring within a single molecule, such as single electron transfer, direct electron-hole recombination, magnetic/charge storage and legand-receptor reaction. Four possible milestones for realizing the Peta(10¹⁵)-floating operations per second (P-FLOPS) personal molecular supercomputer are described, and the necessary technologies are listed. These include, (1) two terminal conductance measurements on single molecule, (2) demonstration of two terminal molecular device characteristics, (3) verification of three terminal molecular device characteristics and (4) integration of the functions of "molecular super chip." Thus, 1000 times higher performance information technologies would be realized with molecular device.

IV-L-4 Synthesis and Characterization of N-Confused Porphyrinatoantimony(V): Toward Low Energy Gap Molecular Wire

OGAWA, Takuji^{1,2,3}; FURUTA, Hiroyuki⁴; MORINO, Ayako²; TAKAHASHI, Minako²; UNO, Hidemitsu²

(¹JST; ²Ehime Univ.; ³IMS; ⁴Kyoto Univ.)

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N-Confused tetraarylporphyrinatoantimony(V) dimethoxides were synthesized, and their X-ray crystallographic structure, absorption spectra and voltammetric spectra were studied. X-ray crystallographic structure revealed neutral molecules with no counter anion. From the absorption spectra and voltammetric studies we estimated their energy gaps to be about 0.2 eV less than the corresponding porphyrinatoantimony(V). The axial ligands could easily be exchanged in solvent alcohol by acid promotion. These characteristics of N-confused porphyrinatoantimony(V) indicate that they are good candidates for the molecular wire component.

IV-L-5 N-Confused Double-Decker Porphyrins

FURUTA, Hiroyuki^{1,3}; KUBO, Naoko¹; MAEDA, Hiromitsu¹; ISHIZUKA, Tomoya¹; OSUKA, Atsuhiko¹; NANAMI, Hideki²; OGAWA, Takuji^{2,3,4}

(¹Kyoto Univ.; ²Ehime Univ.; ³JST; ⁴IMS)

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IV-L-6 Electronic Conductive Characteristics of Devices Fabricated With 1,10-Decanedithiol And Gold Nano Particles Between 1000 nm Electrode Gaps

OGAWA, Takuji^{1,2,3}; KOBAYASHI, Keijiro²; MASUDA, Go²; TAKASE, Takuya²; MAEDA, Seisuke²

(¹JST; ²Ehime Univ.; ³IMS)

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Electronic conductive characteristics of composite made from 1,10-decanedithiol and gold nano particles were studied with the pressed pellet and with the devices made from organic dithiols, gold nano particles and *ca.* 1 μm gap gold electrode. The I-V curve of the former pellet was ohmic and the temperature dependence ($\log(\sigma)$ -1/T) of the conductance was not linear. In contrast with it, the micro-gap device exhibited sigmoidal I-V curve. The activation energy for the latter was 6×10^{-3} eV that was one order smaller than the former pellet of 4×10^{-2} eV.

IV-L-7 Synthesis and Characterization of Photo-responsive Molecular Wires Based on Ruthenium Complex Moiety and Thiol Groups

OGAWA, Takuji^{1,2,3}; KOBAYASHI, Keijiro²;

MASUDA, Go²; SHIMIZU, Yuusuke²

(¹JST; ²Ehime Univ.; ³IMS)

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Molecular wires with a ruthenium complex moiety and thiol group precursors for connecting to gold electrodes were synthesized, and their optical and electrochemical properties were investigated. An electronic device was fabricated with one of the ruthenium complexes bearing two thiol groups using 2 nm gold nano-particles as connecting bond on 1- μm -gapped gold electrodes to show that the device had a sharp photo-response.