Research Center for Molecular-Scale Nanoscience

VIII-C Synthetic Approach Toward Molecular Scale Electronics

Electric properties of organic and in-organic nano structures are challenging field in material science. Those of aggregates, crystals, or polymers which are made from a large number of molecules or atoms have been well studied and established. In contrast, nano scale electronics is the forefront of science, and has been revealed gradually to have diverse phenomena such as quantum conductance, the Kondo effect, the Coulomb blockade, resonance tunneling and so on. In order to establish this field, we are synthesizing new organic and in-organic nano strucutures by using usual synthetic methods together with non-conventional lithographic technique, and measure their electric properties mainly.

VIII-C-1 Linear Functionalized Terthiophene Phenanthroline Polymer for Nanodevices

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The development of molecular electronic devices requires the preparation of new funcional materials with suitable properties. Among them one have pursued the preparation of linear chain polymers constituted by porphyrins or ruthenium complexes that could be obtained in a controlled way. The redox and photophysical properties of those compounds are well known, such that one were atracted by the possibility of generating nanodevices by connecting a bunch or even a single strand of those polymers to a couple of nanogap electrodes. In this communication we report the synthesis and characterization of the monomer as well as the properties of the a new linear hexathiophene-phenanthroline based charge transfer polymer functionalized with [Ru(bipy)$_2$(phen)] complexes, obtained by electropolymerization. The 1,10-phenanthroline with thiophene (tphen) and tertiophene (ttphen) radicals at the 3,8-positions were obtained by conventional Ni catalyzed coupling reactions and the complexes by reaction with [Ru(bipy)$_2$(OH$_2$)] in DMF. Both complexes exhibited four reversible waves in the –1 to –2 V range assigned to the reduction of each of the bipy, phen and thiophene groups to the corresponding radical anion. In the anodic side a quite different behavior was observed. While the ttphen derivative exhibited a catalytic oxidation of ttphen ligand around 1.3 V responsible for the electropolymerization, a reversible Ru(III/II) wave was observed for the tphen derivative. One found out that the polymeric complex can be easily grown in between the nanogap electrodes. The conduction and photoconduction properties are being investigated.

VIII-C-2 Synthesis of Self-Standing Molecular Jacks Bearing Long Anchoring Arms

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A series of porphyrin derivatives bearing more than four lipoic acyl groups have been synthesized. The lipoic acyl group has disulfide moiety at the end of the acyl chain, and can be adsorbed to the gold surface. When rhodium metal is introduced in the center of the porphyrin, a variety of organic functional groups can be introduced as the axial group of the porphyrin plain. Thus, when the po rphyrin plain is anchored to the gold surface by the lipoic acyl groups, the axial organic functional groups will stand perpendicularly to the gold surface. We call the porphyirn part of the molecule as a “molecular jack,” because a variety of molecular wires can be connected to the electrode metal surface through the molecule.

One merit of the molecular jack is that the occuping area of the molecule on the electrode surface can be controlled by changing the length of the alkyl group connecting to the lipoic acyl group. We have synthesized a tetraarylporphyrin derivative whose aryl groups are subsitituted with (-O-(CH$_2$)$_{11}$-OCO-(CH$_2$)$_4$-C$_3$H$_5$(S–S)) at their 3,5-positions. The distance between one S–S group to that of the oposite side is about 6 nm. Consequently the molecule will occupy circular area of about 6 nm diameter on the adsorbed metal surface. Thus when the molecules are adsorbed to the metal electrodes with the size of 60 nm × 60 nm, only 100 molecules will be present on it at the most. By reducing the number of molecules present on the electrodes, it will become much easier to discuss about the electronic properties of the individual molecules.

VIII-C-3 Synthesis and Self-Assembly of Novel Porphyrin Molecular Wires

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Long π-conjugated molecular-wires have been focused much attentions because they can be used for organic conducting material, nonlinear optical material and molecular wire. The recently reported meso-meso-linked porphyrin wires were soluble in organic solvent in spite of their high molecular weight. The high solubility can be explained by the vertically crossed porphyrin π-plains to each other: because of the sterical requirement, intermolecular ππ-stacking was prevented. However at the same time because of the configuration, π-electronic conjugation was not effective, and the absorption band do not shift to the longer wavelength even for the long oligomers. Because tunnel resistance is generally less when the molecule has lower HOMO-LUMO gap, we need molecules of lower HOMO-LUMO gap for good molecular conductor.

We prepared sub-micrometer long oligo-diethynylporphyrins by usual copper catalyzed oxidative coupling of diethynylporphyrins. The products were purified by repeating gel permeation chromatography (GPC) and analyzed by analytical GPC, absorption spectroscopy, matrix assisted laser dissorption time of flight mass spectroscopy (MALDI-TOFMS), and atomic force microscopy (AFM). Although with the MALDI-TOFMS no molecular peaks greater than ca. 100,000 could be detected, GPC and AFM data clearly indicated the presence of sub-micrometer long molecules.

These sub-micrometer π-conjugated molecules self-assembled on HOPG to make some kinds of ordered super structures as observed by AFM. When the length of the molecule is less than 100 nm and the concentration of the solution is relatively high, a regular network structure was formed in which the distance between each molecules is *ca.* 16 nm and the hight is *ca.* 0.9 nm in average. In longer molecules with less concentrated solution, a rectangular sheet structure was observed with the distance of 4 nm and the hight of 0.3 nm. Judging from the size, we postulate that in the regular network sturucture two or three molecular wires are stranded to make thicker molecular rope.

VIII-C-4 Synthesis and Characterization of Dendrimer Protected Sub-Micrometer Long Conjugated Porphyrin Wires

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Direct measurements of electronic properties of single molecule are still a challenging target of materials science, and have been reported in several papers by using scanning probe microscopic methods (SPM), or break junction methods. However, no one has ever succeeded in the electronic measurement with observing the molecules between the electrodes. One reason is that the roughness of electrodes surface, which was fabricated by usual electron beam lithographic methods, is larger than the diameter of the molecular wires, and it is difficult to observe the molecules clearly by SPM. In order to overcome the problem, we synthesized long (> 100 nm) and thick (3–5 nm) porphyrin wires surrounded by dendrimer moiety. Surrounding the wire with the dendrimer has several merits: (1) The diameter become enough large to observe them with AFM on the gapped electrodes, (2) solubility is increased, and (3) the wire may become rigid because of the steric hindrance between the adjacent moiety. Synthesized porphyrin wires were analyzed with gel permeation chromatography (GPC) and atomic force microscopy (AFM). The GPC analyses showed that the molecules have molecular weight greater than one million, which correspond to *ca.* 500 mer. The AFM images showed that the wires have the hight of *ca.* 5 nm, and in some molecules the lengths were nearly 1 μm.