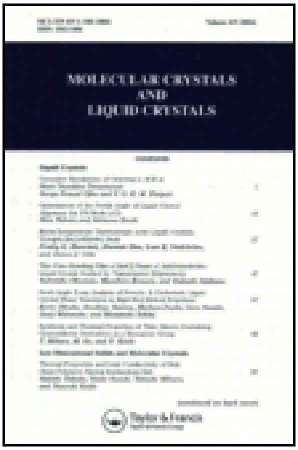

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FUNCTIONALIZATIONS OF CONDUCTING POLYMERS TOWARD MOLECULAR DEVICES

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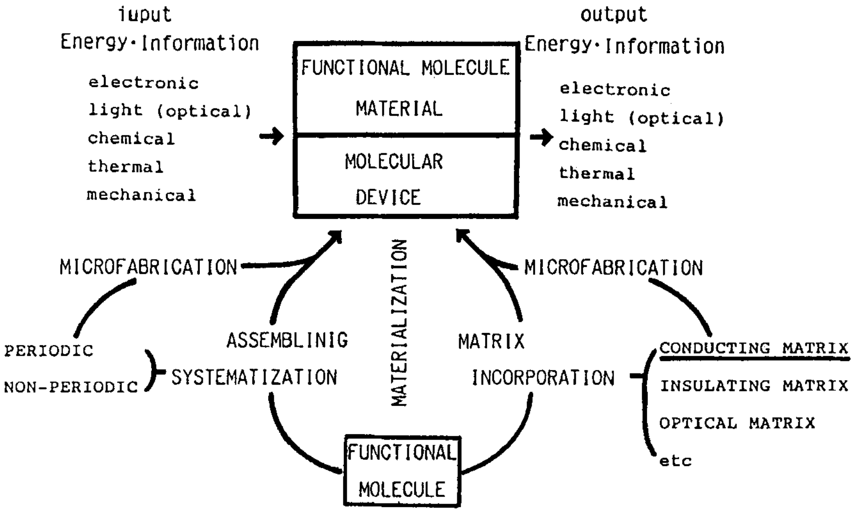
Introduction

There are many molecules and they have their own specific functions. For their exploitation through materialization, conducting polymers are considered as a suitable matrix, for its electron conductive property is to be used to prove the electronic structure and state which relate directly functions of these molecules. To construct molecular device, materialization of those functional molecules and the ultra-fine fabrication of the conducting polymer are essential problems. The concept of the functional molecular material in which molecular device is to be included is illustrated in the following scheme.



The present paper proposes with mainly three practical approaches toward molecular device construction: (1) Materialization of functional molecules with conducting polymer by their incorporations. (2) Ultra-thin and molecular level fabrication of conducting polymers. (3) Multi-functionalization of functional molecules to be incorporated in the functional molecular material and molecular device.

Materialization of functional molecules by their incorporations in conducting polymers

Conducting polymers are unique conducting materials which can incorporate molecules and ions and convey their electronic informations being directly connected to their functions. A systematic materialization of functional molecules by their incorporation in the conducting polymer matrix was demonstrated by electrolytic polymerization of pyrrole, thiophene, aniline etc., in the presence of negatively charged functional molecules. This method is one of the most smart procedure to incorporate the functional molecule. The incorporation of the functional molecules is driven electrostatically by the positive charges of the partially oxidized conductive polymer matrices through a doping process. When anionic polyelectrolyte is used as a dopant, the resulting conducting polymer in electrochemically reduced state catches a cationic species, a cationic functional molecule, to keep electroneutrality, as to be said a pseud-cathodic doping. On the other hand, both vapou-liquid interface chemical polymerization method and matrix supporting one are useful to prepare functional molecule incorporating conducting polymer material. By these methods, any kinds of functional molecule can be incorporated in the conducting polymer.

The resulting functional molecule incorporating conducting polymers display the specific functions which are attributed to the incorporated functional molecules. Examples are shown in Table 1.

Table 1

Functions of Functional Molecule Incorporating Conductive Polymers

Functional dopant/matrix [a]	Charge	Function	Procedure [b]
Anthraquinone 2-sulphonate	Sulphonate	Electrochromism	1, 3
$Lu(PTS)_2$	Sulphonate	Electrochromism	1, 3
$Fe(BPS)_n(BP)_{3-n}$	Sulphonate	Electrochromism	1, 3
$Ru(BPS)_n(BP)_{3-n}$	Sulphonate	Electrochemiluminescence	1, 3
$MTPPS_4$ (M = Zn, Pd, etc.)	Sulphonate	Photosensitized electrode	1, 3
MTMPyP	Pyridinum	Photosensitized electrode	2
Rose bengal	Carboxylate	Photosensitized electrode	1, 3
Indigo carmine	Sulphonate	Photosensitized electrode	1, 3
Poly(vinyl sulphate)	Sulphate	Charge-controllable membrane	1, 3
Poly(styrene sulphonate)	Sulphonate	Charge-controllable membrane	1, 3
Nafion®	Sulphonate	Charge-controllable membrane	1, 4
Polynucleotide	Phosphate	Nucleic acid sensor	1, 3
Nucleotide	Phosphate	Nucleic acid sensor	1, 3
Porous filter	–	Filtration	4
Phosphotungstate	Heteropoly acid	Electrochromism	1
$PtCl_4^{2-}$	$PtCl_4^{2-}$	Highly dispersed metal	1, 3
$AuCl_4^-$	$AuCl_4^-$	Highly dispersed metal	1, 3

[a] PTS = phthalocyanine tetrasulphonate; BP = bathophenanthroline; BPS = BP disulphonate; $TPPS_4$ = tetra(4-sulphophenyl)porphyrin; TMPyP = tetra(4-methylpyridyl)porphyrin.

[b] Incorporation procedure: 1, electrochemical anodic doping; 2, electrochemical pseudo-cathodic doping; 3, vapour-liquid interface chemical polymerization; 4, bulk chemical polymerization.

Molecular level and ultrathin fabrication of conducting polymers

The molecular level and ultrathin fabrications of conductin polymer provide not only an integrated molecular material but also a possibility to construct a quantum material, as to be said an organic superlattice.

Ultrahigh anisotropic conductive polymer LB multilayers

Some amphiphile pyrrole derivatives give stable Langmuir monolayer and more than 600 layers can be transferred onto a hydrofobic substrate such as silated ITO-deposited glass or polyester film as Y-type multilayers. The oxidative electropolymerization is to be carried out, and a well ordered conducting polymer LB multilayers are obtained. The multilayers have a remarkably high anisotropic dc-conductivity by ca. 10 orders. This method allows molecular regulation of conductiong polymer material fabrication on a wide range up to nm level, as is seen in Figure 1.

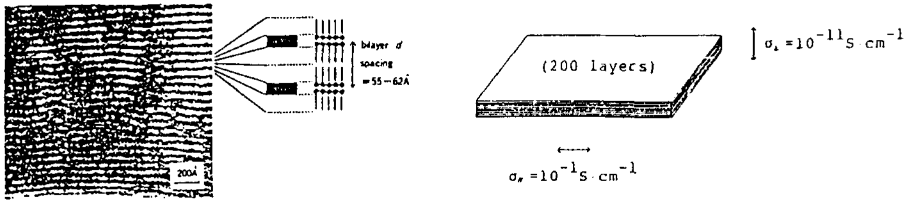


Figure 1. TEM picture of a cross-section and anisotropic conductivity of a conductive polymer LB multilayers

Conducting polymer hetero-multilayers

Conductivity and so-called band structure of organic conductive polymer are controlled not only by monomer component in homopolymer but also by monomer composition in copolymer.

Utilyzing electrocopolymerization technique, various and desired hetero-multilayers of conducting polymers can be fabricated. The copolymer composition and the thickness of the polymerized copolymeric material deposited on the electrode are easily controlled by the potential sweep program of the electrocopolymerization. Figure 2 shows examples of finely heterolayered structures of pyrrole ans 3-methylthiophene in nm level, as a priodical and a non-periodical ones. These fine heterolayered structures are proved by TEM picture of the cross section as the Figure, by Auger electron spectroscopy and by SIMS. The resulting hetero-multilayers correspond exactly with the potential sweep program in the electrocopolymerization and a clear interface is observed. These results suggest that the present electrocopolymerization provides an useful method to fabricate finely structure controlled multi-heterolayers. And such mesoscopic-level heterolayered conducting material should take an important place in both electronic ond optical devices, to be compared with an ultrathin or a super layer (superlattice) of semiconductor, of which Esaki and Tsu had proposed and defined as types I, II and III heterolayers, and it will provide a novel organic conducting materials having various quantum well and function, with periodic and/or non-periodic structure.

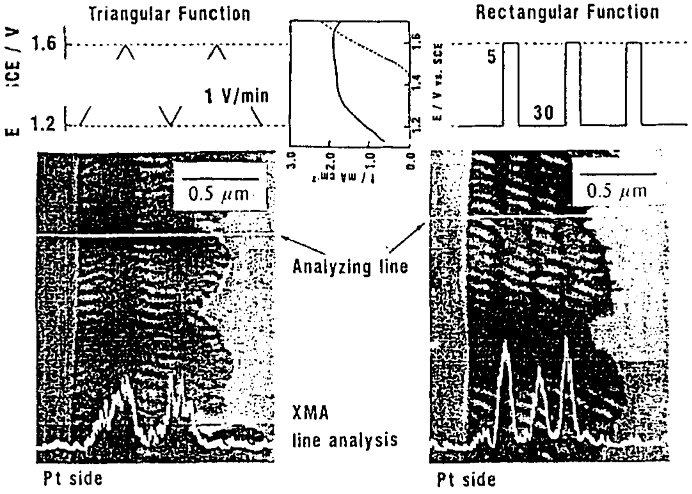


Figure 2. A non-periodica (left) and a periodical (right) hetero-multilayers of conducting copolymer of pyrrole and 3-methylthiophene

Patterning of conducting polymer network

The photopolymerization is considered as one of distinctive properties of organic molecules. A photosensitized polymerization of pyrrole and a photopolymerization of isothianaphthene were investigated. A two dimensional conducting polymer networkfabrication was demonstrated by the former method and a three dimensional network of the conducting polymer is suggested. On the other hand, an ultrafine heterolayers fabrication of the lowest band material is suggested with polyisothianaphthene by the latter method.

Multi-mode chemical signal transducer molecule

It is an important problem to donate highly integrated transformation modes to one molecule, in order to construct an advanced functional molecular device. A few model melcules of a new class of chemical transducer is demonstrated. They have a plurality of transformation modes via independent stimulations, as a result of which response by one stimulation can be regulated by another stimulation. Consequently, a molecule with n responsive regions would have 2^n states corresponding to n transformation processes by every independent stimulation.

Based the above concept, we have investigated the conjugated transformation of multi-mode chemical signal transducers, such as 2-(4'-methoxyphenylazo)anthraquinone, which has a photoresponse and chemical redox response, etc. Such multi-mode signal transducer molecules hold the prospect of promoting the functionality of molecular devices.