

# Functionalized conjugating polymers: from molecule and ions transporting membranes to advanced electronic and photonic materials

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**Abstract:** Applications of conjugating polymers to advanced materials are demonstrated, especially focusing on artificial membrane, electronic and photonic advanced materials, such as (1) selective and transporting membrane, (2) functional molecular materials and devices including charge controllable membranes, (3) ultrahigh anisotropic conducting polymer material, (4) conjugating polymer superlattice and (5) one-dimensional (1-D) and two-dimensional (2-D) porphyrin arrays connected with conjugating and/or insulating molecular wires.

## INTRODUCTION

Active and selective transporting artificial membrane is much expected as an advanced material. To expand its substrate from molecule and ions to electron and photon is also considered to develop a new field of membrane science and technology and a new advanced material.

At present, molecular device and quantum functional material are appreciated as ultimate materials with its minimum size and its creation of novel nature, respectively. In this paper, some examples approaching to the ultimate material are described.

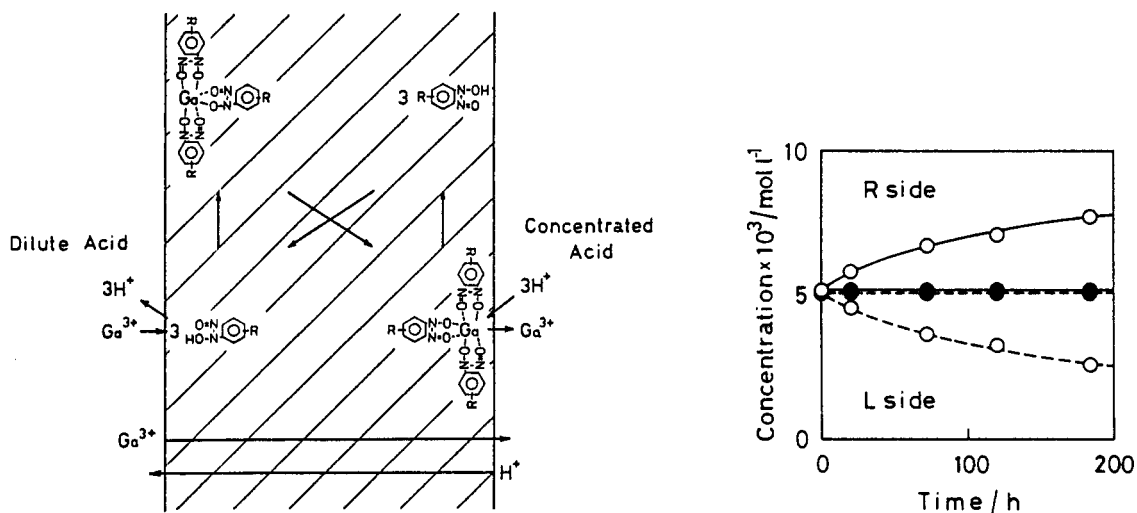
Conjugating polymer is considered to be one of the most suitable matrices for materialization of functional molecules, for its conductive property is able to reflect and convey electronic informations of these molecules whose functions are attributed to change and deviation of electronic structure and state of them. Several functional molecular materials and devices were demonstrated, firstly. One of the most useful application of conducting polymer can be found in this materialization of functional molecule with conducting/conjugating polymer. Secondly, structure depending functional materials with the conducting polymer such as the ultrahigh anisotropic conductive materials and with the conjugating polymer such as the organic superlattice, are presented. The former was fabricated by LB method and the latter was fabricated by the potential programmed electropolymerization method, a novel method we have developed. Thirdly, systematization of functional molecule is also important problem to synthesize advanced polymeric materials. Here, one- and two-dimensional porphyrin arrays connected with conjugating and/or insulating molecular wires were demonstrated.

## 1. SELECTIVE AND ACTIVE TRANSPORT MEMBRANES [1-5]

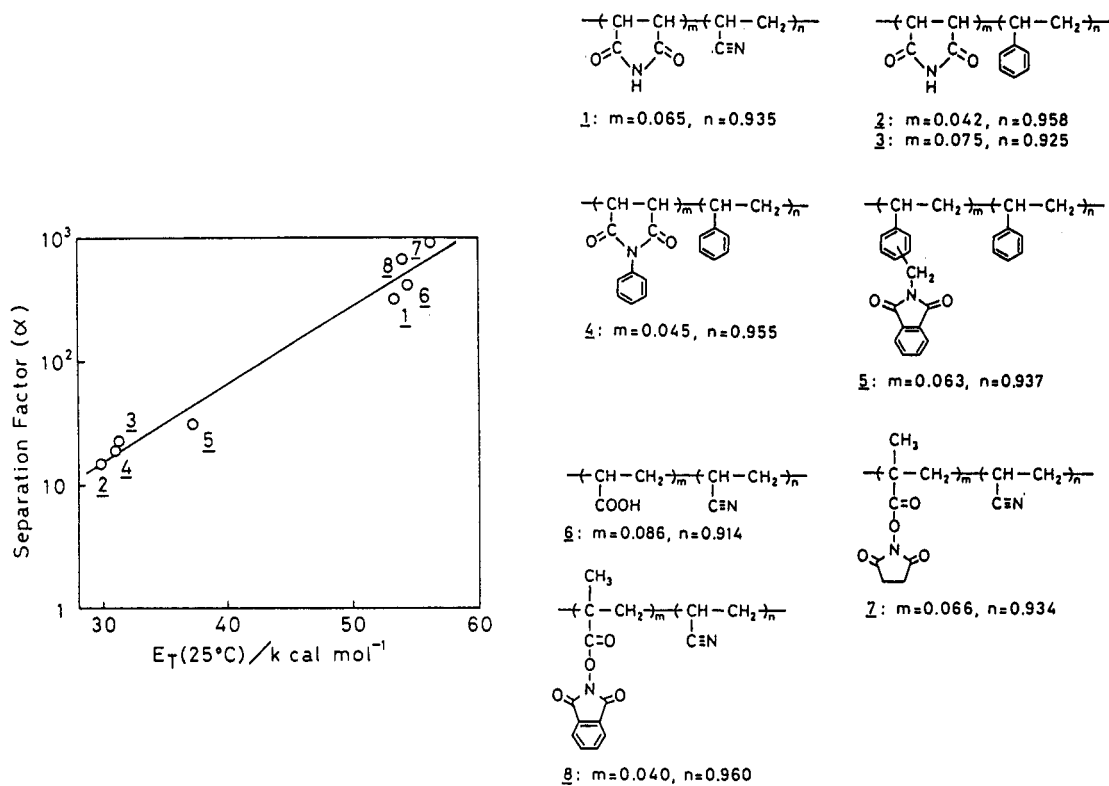
A selective and active transport by membrane system is important research subject. Here, two examples such as a gallium ions concentrating membrane and an ethanol-water separating membrane are chosen. They are represented in Figures 1 and 2.

## 2. FUNCTIONAL MEMBRANES BY INCORPORATION OF FUNCTIONAL MOLECULE IN CONDUCTING POLYMER [6-20]

Conducting polymers are unique conducting materials which can incorporate molecules and ions and convey their electronic informations being directly connected to their functions. Functional molecule and ions incorporating conducting polymers are expected as functional molecule materials which show specific functions attributed to the incorporated functional molecules.



**Figure 1.** The mechanism of  $\text{Ga}^{3+}$  transport through the membrane impregnated with alkylated cupferron. (Left) and the time-transport curve of a  $\text{Ga}^{3+}$ - $\text{Al}^{3+}$  binary solution.



**Figure 2.** Relationship between separation factor,  $\alpha$ , and Dimroth's solvent polarity value,  $E_T(25^\circ\text{C})$ . Downstream pressure, 333-430 Pa (2.5-3.2 Torr); operating temp.,  $15^\circ\text{C}$ ; weight fraction of water in feed,  $\sim 0.5$ .

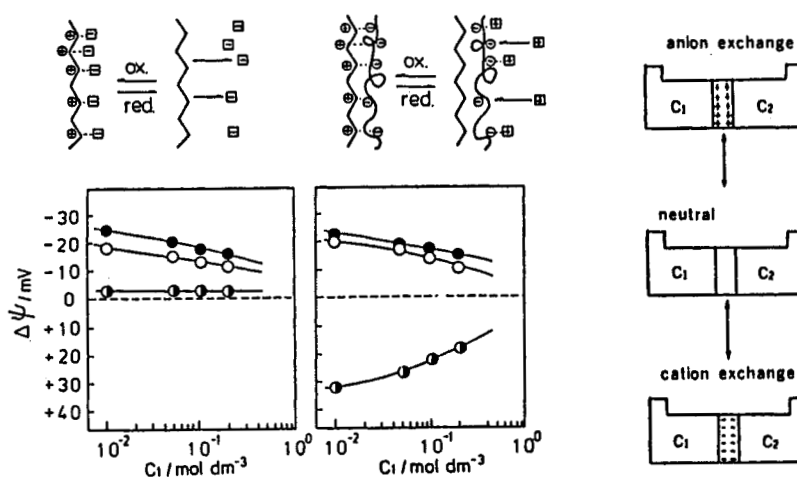
**TABLE 1.** Functions of Functional Molecule Incorporating Conductive Polymers.

Functional dopant	Function	Procedure
Anthraquinone 2-sulphonate	Electrochromism	1, 3
Lu(PTS) <sub>2</sub>	Electrochromism	1, 3
Fe(BPS) <sub>n</sub> (BP) <sub>3-n</sub>	Electrochromism	1, 3
Ru(BPS) <sub>n</sub> (BP) <sub>3-n</sub>	Electrochemiluminescence	1, 3
MTPPS <sub>4</sub> (M=Zn, Pd, etc.)	Photosensitized electrode	1, 3
MTMPyP	Photosensitized electrode	2
Indigo carmine	Photosensitized electrode	1, 3
Anionic polyelectrolyte	Charge-controllable membrane	1, 3
Nafion <sup>®</sup>	Charge-controllable membrane	1, 4
Nucleotide, Polynucleotide	Nucleic acid sensor	1, 3
Urease	Sensor	1, 3
Porous filter	Filtration	4
Phosphotungstate	Electrochromism	1
PtCl <sub>2</sub> <sup>-</sup> , AuCl <sub>4</sub> <sup>-</sup>	Highly dispersed metal	1, 3

1, electrochemical anodic doping; 2, electrochemical pseudo-cathodic doping;  
3, vapor-liquid interface chemical polymerization; 4, bulk chemical polymerization.

A systematic materialization of functional molecules by their incorporation in the conducting polymer matrix was demonstrated by polymerizations 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 conducting 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, a chemical polymerization and a matrix supporting methods are useful to prepare functional molecule incorporating conducting polymer material.

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. Figure 3 shows a charge-controllable membrane synthesized by the present method.

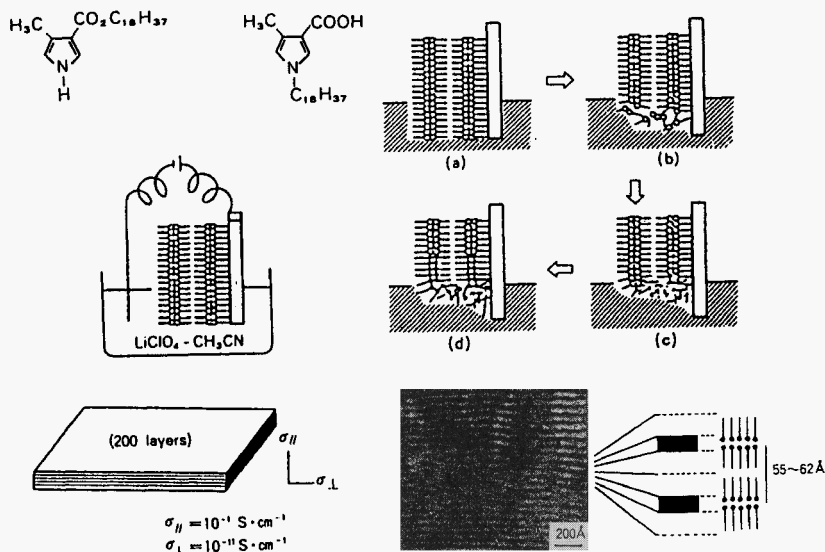


**Figure 3.** Polarity change of fixed charges in the pentanesulfonate-PPy membrane (left) and PVS-PPy membrane (right) for the oxidized and the reduced states, which were suggested by the membrane potential ( $\Delta\psi$ ) measurement in KCl concentration cell. (o) original membrane, (o) reduced membrane at -1.0V, (o) oxidized membrane at +2.0V.

### 3. ULTRAHIGH ANISOTROPIC CONDUCTING MATERIALS BY CONSTRUCTION OF CONDUCTING POLYMER LB MULTILAYERS [7, 18, 21-23]

A mixed monolayer of an amphiphilic pyrrole, CPy or EPy and octadecane was very stable over a neutral aqueous subphase. The oxidative electropolymerization of 200 layers of the mixed EPy-octadecane (2:1) on ITO-dposited substrate, in acetonitrile containing LiClO<sub>4</sub>, resulted conducting polymer LB multilayers. Both X-ray diffraction analysis and the TEM image of the cross-section showed a fine multilayered structure. The TEM bilayer spacing is  $d=55\text{-}62\text{\AA}$ , which almost the same as obtained from the X-ray diffraction method.

This electropolymerized LB multilayer had a remarkably high anisotropic dc-conductivity by ca. 10 orders of magnitude ( $\sigma = 10^{-1}\text{ S/cm}$ ,  $\sigma = 10^{-11}\text{ S/cm}$ ), as was suggested from its layered structure. (Figure 4)



**Figure 4.** Polymerization of pyrrole derivative LB multilayers, TEM picture of the resulting polymer multilayers, and its anisotropic conductivity.

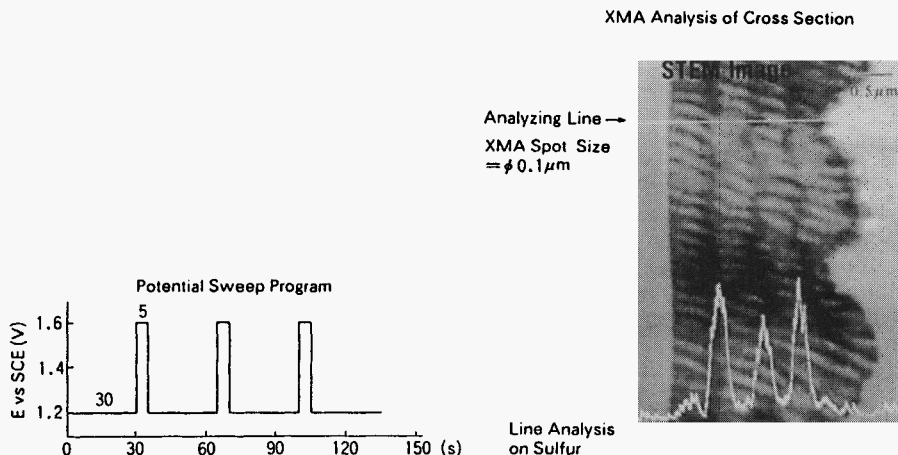
### 4. ARTIFICIAL SUPERLATTICE WITH CONJUGATING POLYMER [7,18,24-28]

Electropolymerization method is one of the most interesting method to control the copolymer composition in molecular sequence or chain sequence, drastically. Accordingly, in the case that the property of the electropolymerized material is electro-conductive and insoluble, a heterolayered structure and/or a sloped structure with conducting polymers are constructed on the electrode.

We develop the potential-programmed electropolymerization method for modulating the composition of conducting polymer composite thin films to the depth direction. In this study, nm-order compositional control of composite thin films of conducting polymer, the alternate layered and graded structures, which is approached to organic superlattice are demonstrated.

The monomers for conducting polymers, such as pyrrole, thiophene, and their derivatives, are electropolymerized, so that the corresponding conducting polymer thin films were obtained on the surface of a working electrode. The current-potential curve (*i*-*E* curve) on electropolymerization depends on the monomer and its concentration and additionally on the solvent and the supporting electrolyte. The growth rate of the film thickness is proportional to current *i*. A layered structure is fabricated by a rectangular function and a graded structure is done by a sloped function.

Figure 5 (TEM cross section and EPMA line analysis on sulfur reflecting thiophene content) is conducting copolymer hetero-multilayers of pyrrole and 3-methylthiophene by the present PPEP method. The depth profiling of the resulting conducting polymer multilayers were carried out by

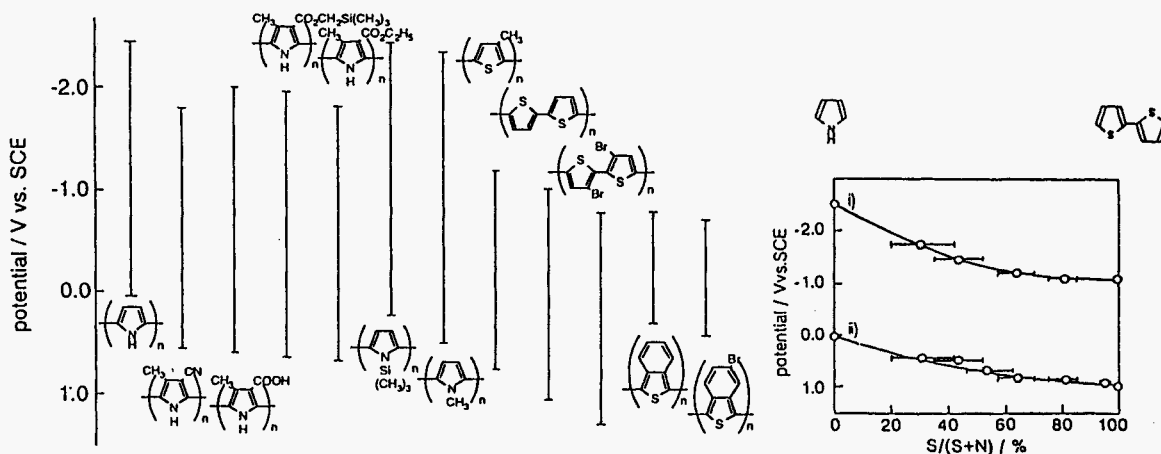


**Figure 5.** Ultrathin conducting polymer heterolayers by potential sweep programmed electrocopolymerization of pyrrole and 3-methylthiophene: Potential sweep programs and TEM pictures of their cross sections.

SIMS, AES, TEM and EPMA. These results proved the structure of the multilayers which was depended on the potential sweep function. The dimension of every layer could be lowered to 20 Å level. An alternate layered structure was fabricated by a rectangular potential sweep function, a stairlike layered structure was done by a step sweep function, and a triangular sloped structure was done by a triangular sweep function.

Figure 6 shows band structures of several homopolymers and pyrrole-bithiophene copolymers, as examples. With a combination of these homopolymers and copolymers, various superlattice structures can be fabricated.

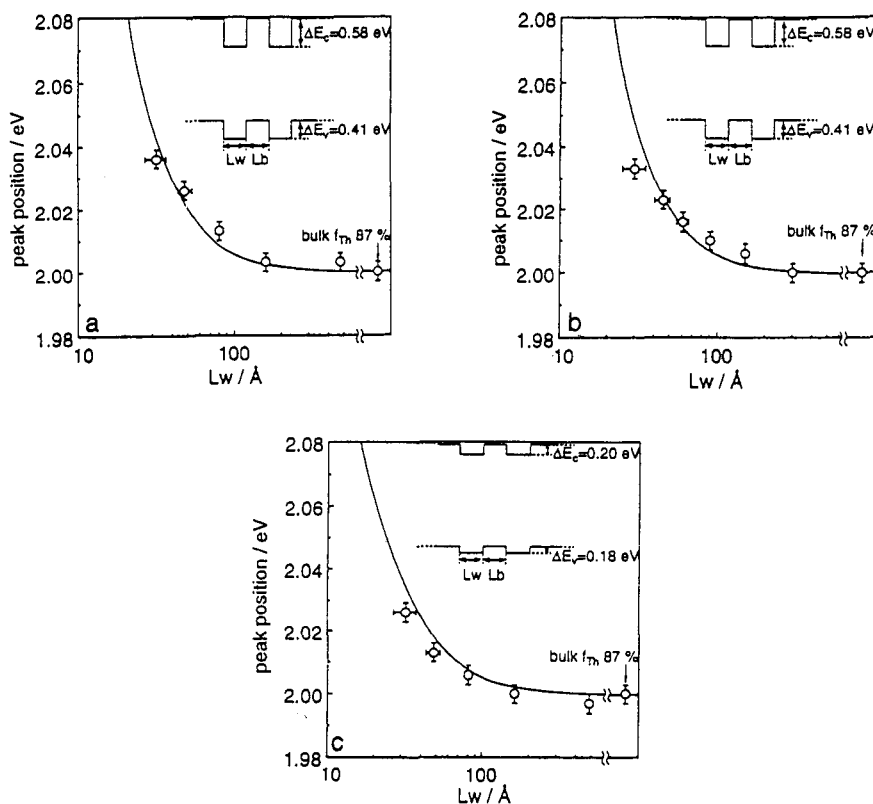
The multilayers fabrication was carried out on a rotating HOPG disk electrode (working electrode; 1000 r.p.m.) which is effective to realize the copolymer layered structure with 10Å order resolution. The electro(co)polymerization of the mixture of pyrrole ( $2.5 \times 10^{-4}$  M) and bithiophene ( $2.5 \times 10^{-2}$  M) by a rectangular potential sweep on 1.0V and 1.4V gave a superlattice multilayers (the barrier layer composed of 33% bithiophene and 67% pyrrole; the well layer composed of 87% bithiophene and 13% pyrrole), which was expected to be a Type II superlattice. Of this superlattice,  $\Delta E_C$  is 0.58V and  $\Delta E_V$  is 0.41V, as illustrated in Figure 7. The layers with 87% thiophene content would work as a well for electron and the layers with 33% thiophene content as a barrier.



**Figure 6.** Band structures ( $E_C$  and  $E_V$ ) of conducting homopolymers (left) and copolymer (right).

Photoluminescence spectra of copolymer of pyrrole and bithiophene films whose thiophene content is higher than 50% consist of three peaks around 2.0, 1.8, 1.7 eV corresponding to phonon side bands, at 10K. These peaks have been considered to be radiative relaxation from self-trapped exciton levels. The peak at the highest energy reflects band gap.

The photoluminescence of the above-mentioned multilayers shifted to higher energy as the thickness of the well layer ( $L_w$ ) became smaller than 120 Å, in both cases that  $L_w / L_b$  (barrier thickness) is a constant (0.6) and  $L_b$  is a constant (100 Å) (Figure 7). On the other hand, the bulk thin layer did not show such a higher energy shift. Such the higher energy shift is considered to be resulted from confinement of the excited electron in the quantum well structure. Also, a good fit of experimental result with the Kronig-Penney equation which derives energy-wave number vector relationship in rectangular type potential profile, by assuming  $m^* = 0.6 m_e$  ( $m_e$ ; electron mass) (solid line in Figure 7).



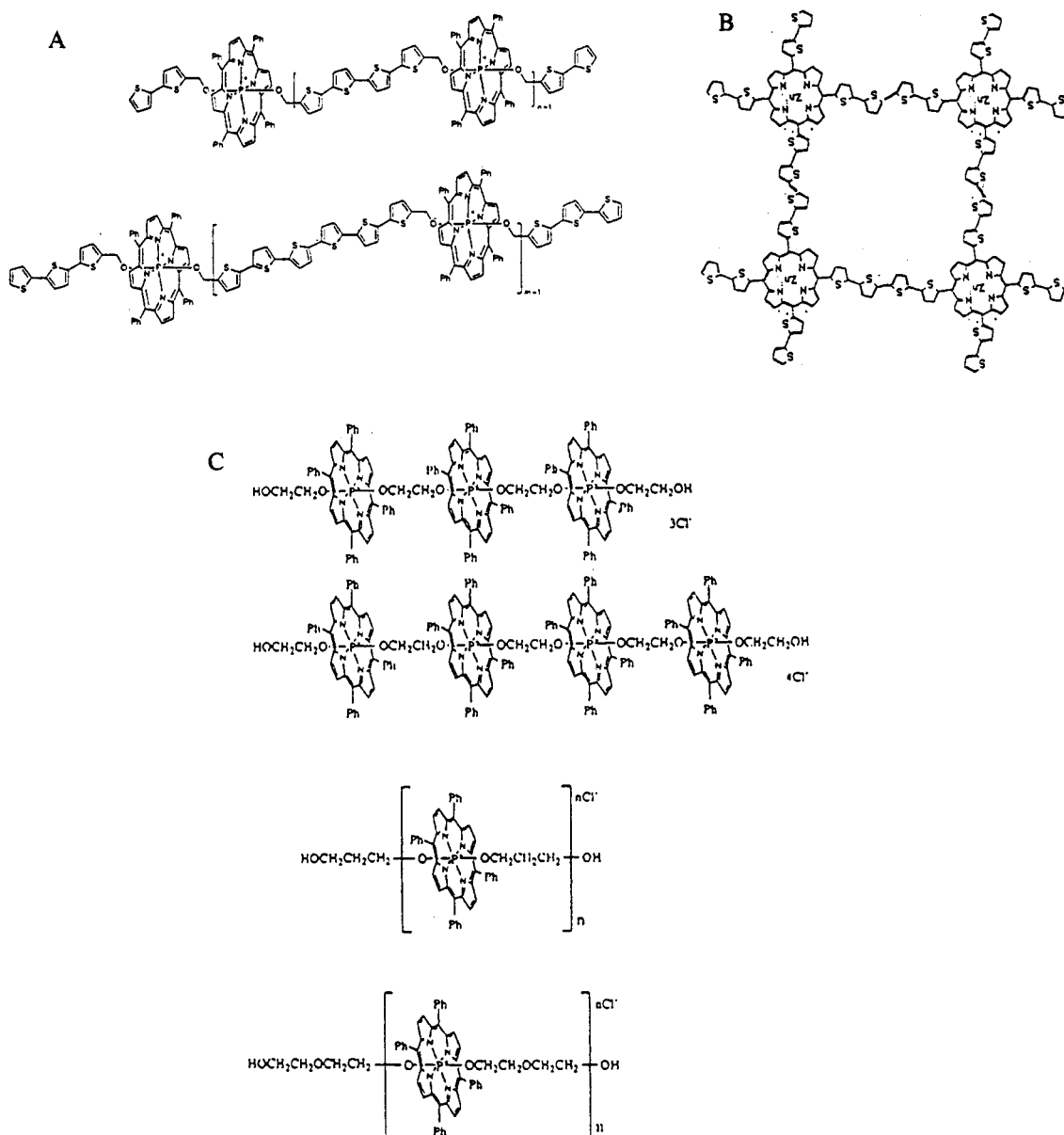
**Figure 7.** Structure of Type II heterolayer superlattice and emission peak shift as a function of layer thickness. (solid line is estimated from Kronig-Penney model. (a)  $L_w / L_b = 0.6$ . (b) (c)  $L_b = 100 \text{ \AA}$  const.).

The other multilayers also showed similar phenomena. Those spectral behaviors lead to a conclusion that a conducting polymer heterolayer having a quantum size effect has been fabricated by the present PPEP method.

## 5. PHOTOACTIVE PHOSPHORUS(V)PORPHYRIN ARRAYS LINKED WITH MOLECULAR WIRES [29-31]

Molecular systems containing multiple porphyrin units have been important for the elucidation and the application of the energy and electron transfer functions of the photosynthetic reaction center. In principle, porphyrin arrays connect with conducting and/or insulating molecular wire are considered to be converted into the elements of molecular photo-electronic devices. Especially, their systematization with appropriate electron mediators into large polymeric systems is one of the feasible approaches to the molecular systems based on the electron transfer. For the construction of the molecular systems, we used the electrochemical polymerization of thienyl porphyrin derivatives, in which the thiophenes were attached to their axial (A) or lateral (B) positions. By their polymerization, one-dimensional (1D) or two-dimensional (2D) porphyrin polymers with ordered oligothieryl molecular wire can be obtained.

Herein, the electron transfer function of the 1D or 2D porphyrin polymers and the composites with some conjugating polymers are presented. On the other hand, the utilization of the axial bond on the central atom of P(V)porphyrin could reduce the difficulty of the systematic construction of the porphyrin oligomers. We also synthesized the various types of P(V)porphyrin array (C). (Figure 8)



**Figure 8.** 1-D and 2-D Porphyrin arrays linked with conjugating and/or insulating molecular wires.

### One-dimensional (1D) Porphyrin Array Linked with Conjugating Molecular Wire

By the electrochemical polymerization of A, their polymers having an alternating quasi-1D structure of the P(V)porphyrin and oligothiophene moieties were deposited on the electrode. The conductivity of the 1D polymers were strongly enhanced by the photoirradiation. It is understandable that the photoinduced carrier formation occurs efficiently in the 1D polymers. The photo-switching devices were made by the hybridization of the 1D polymers and polybithiophene. Simple layered sandwich cell of 1D polymer and polybithiophene showed the photocurrent under the photoirradiation. A microscopic photodiode device was constructed by successive electrochemical polymerization in the nucleopore membrane.

**Two-dimensional (2D) Porphyrin Array Linked with Conjugating Molecular Wire**

Metal complexes of B were polymerized by the electrochemical coupling of *meso*-oligothienyl groups. The layered sandwich cell showed the electric rectifying property. The rectifying property is considered to arise from the molecular interface between the polymers.

**One-dimensional Porphyrin Array Linked with Insulating Molecular Wire.**

The "wheel-and-axle-type" P(V)porphyrin oligomers were synthesized by the condensation of the dichloro P(V)porphyrin and corresponding diol. The absorption properties of the porphyrin arrays are elucidated from the exciton coupling between the porphyrin rings. The lifetime of the singlet excited state of the "wheel-and-axle-type" P(V)porphyrin derivatives was dependent on the numbers of porphyrin rings and the solvent polarity. Upon the photoexcitation, singlet states of the present porphyrin arrays connected with dioxyethane and dioxyethoxyethane are not delocalized, but of the former, the triplet excited state is localized in inner porphyrin moiety. These results suggest that their excited state properties are tunable systematically.

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