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Approaches to Ultimate Functional Polymers: Quantum Functional and Molecular Engineering Materials

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SUMMARY: Both quantum functional material (Ψ-engineering material) and molecular engineering materials are of interest as ultimate functional materials. The former creates a novel property which is specific to the structure, and the latter gives he functional material of the smallest size. In this paper, some aspects to construct those materials with polymer having big varieties and flexible applications are described: 1. Conjugating polymer superlattice (conjugating polymer multilayers which is able to change wave length of emission light). 2. Porphyrin arrays connected with molecular wires (a proto-type photo-information housing-in and reading out polymeric material). 3. Oligonucleotide shackled with porphyrin (an artificial restrictive photoactive enzyme).

Conjugating polymer superlatttice

In the past few decades, ever since the proposal by Ezaki and Tsu in 1970[1)], inorganic semiconductor superlattice and multiple quantum wells have been developed. As almost all conjugated polymers are organic semiconductors, structural control, such as compositional control of a copolymer thin layer, corresponds to manipulation of the band structure of the thin layer. Functions due to carriers confined in the well structure i.e., quantum size effect, with mesoscopic 1-10nm scale shall be observable. In this study, such wave Ψ functional material[2),3)] with conjugating polymer by novel compositional modulation method realized. The electropolymerization is one of the most interesting methods to control the copolymer composition in molecular sequence or chain sequence. In the case that the property of the electropolymerized material is electroconductive and insoluble, a heterolayered structure and/or a sloped structure with conducting polymers are constructed on the electrode. The potential-programmed electrocopolymerization modulates the copolymer composition of conducting polymer thin layers to the depth direction. Thus, nm-order compositional controlled thin layers of conducting polymer, the alternate layered and graded structures, which approach ultimate functional materials such as the organic superlattice the sloped material, are constructed.[4)] A combination of conjugating homopolymers and/or copolymers leads to the fabrication of various superlattice structures. The electrochemical copolymerization results in the fabrication of copolymer multiheterolayers by simply changing the applied electrode potential.

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Fig. 1 shows an example of ultrathin conjugating pyrrol-methylthiophene copolymer heterolayers which was synthesized by a rectangular potential swept electrocopolymerization. The depth profile of the resulting conjugating polymer multilayers was also evaluated by EPMA line analysis on sulfur, SIMS, AES.[5)]

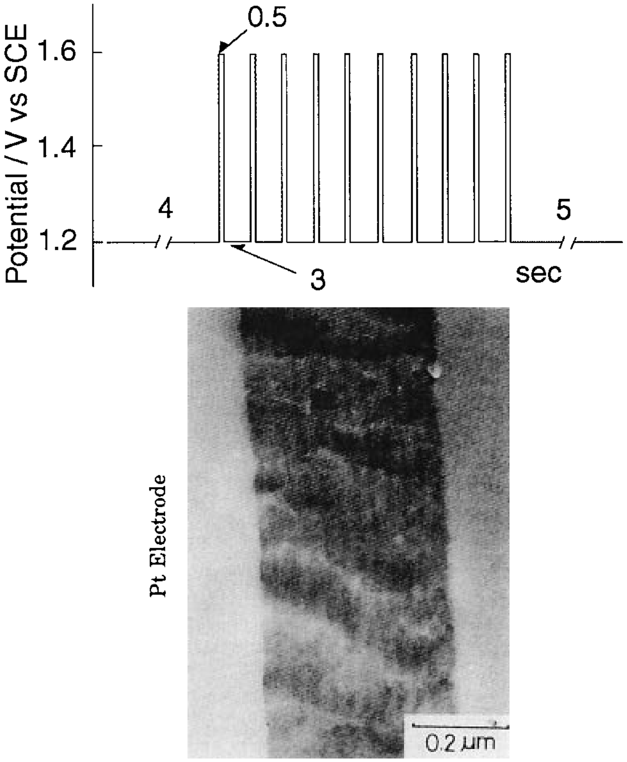

Figure 1. Ultrathinconducting polymer heterolayers by the potential sweep programmed electropolymerization of pyrrole and 3-methylthiophene: potential sweep programmes (upper) and TEM pictures of their cross-sections (lower).

Fig. 2 shows the band structures of several homopolymers and pyrrole-bithienyl copolymers. A combination of conjugating homopolymers and/or copolymers leads to the fabrication of various superlattice structures. Especially, the electrochemical copolymerization results in the fabrication of copolymer multiheterolayers by simply changing the applied electrode potential. The copolymer multiheterolayer was constructed on a rotating HOPG disk electrode (working electrode, 1000 r.p.m), and showed a flat and sharp interface having a 10Å resolution. Fig. 3

shows an example of type II superlattice[6] by electrocopolymerization of pyrrol and bithiophene.

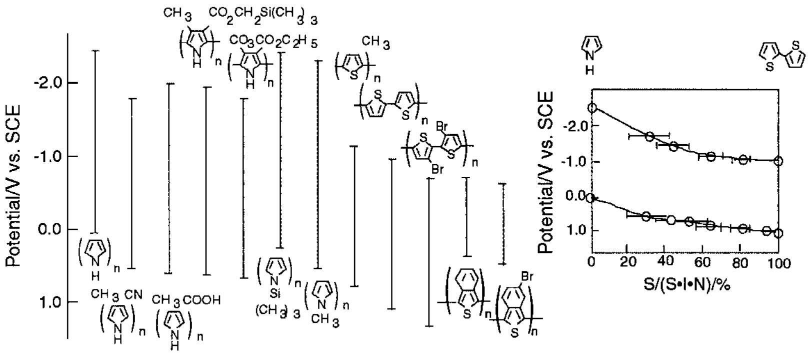

Figure 2. Band structures (E_c and E_v) of conjugating homopolymers (left) and copolymer (right).

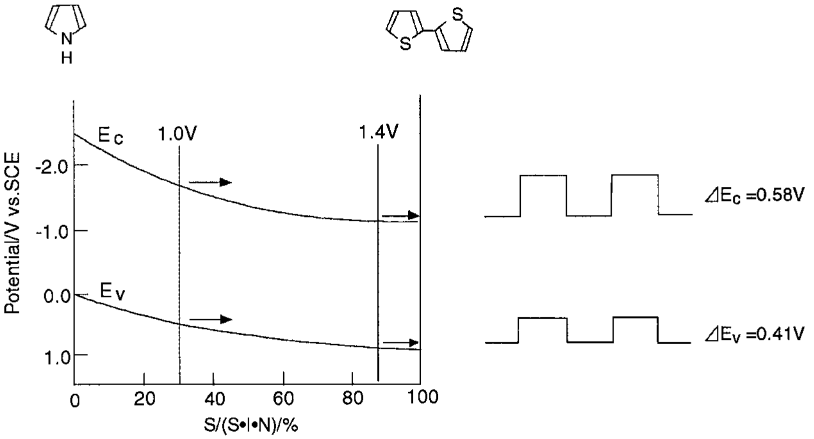

Figure 3. Fabrication of type II conducting polymer heterolayer superlattice by the electro-copolymerization of pyrrole (2.5×10^{-4} M) and bithiophene (2.5×10^{-2} M) CH_3CN solution. Sweep potentials, copolymer compositions and Ec, Ev of the resulting heterolayers. The lines correspond to band gaps.

The photoluminescence of the multilayers (10 layers) having 60Å of 87% thiophene layer and 100Å of 33% thiophene layer shifted to higher energy compared with that of the bulk (87% thiophene content) copolymer film. Quantitative analysis is presented in Fig. 4.[7),8)]

The photoluminescence of the above-mentioned multilayers shifted to higher energy as the thickness of the well layer (L_w) became smaller than 120Å, even when the barrier thickness (L_b) remained constant (100Å) and when the ratio L_w: L_b was constant (0.6). On the other hand, the bulk thin layer did not show a significant energy shift. Such a shift to higher energies is considered to be the result of the confinement of excited electrons in the quantum well layer. We have also found a good fit of experimental results to the Kronig-Penney model, which derives the energy-wave vector relationship in rectangular-type potential profile by assuming that m* electron mass (depicted as the solid line in Fig. 4) =0.6me.

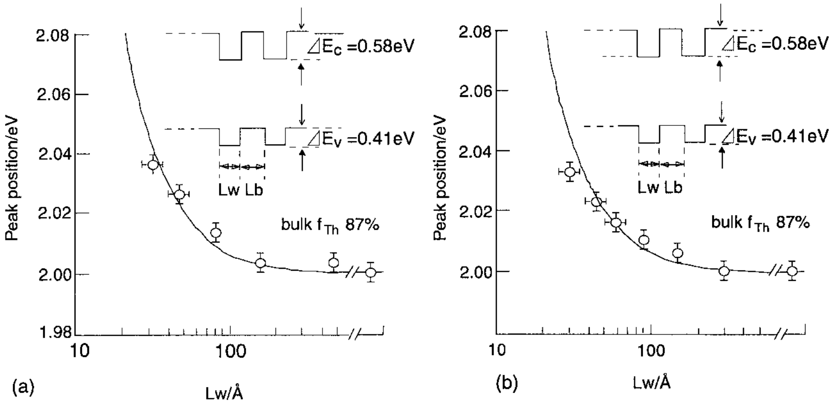

Figure 4. Structure of type II heterolayer superlattice and emission peak shift as a function of layer thickness. Solid line is estimated from Kronig-Penney model. (a) L_w/L_b=0.6; (b) Lb=100Å Const.

These results suggest that the conjugating polymer hetero-layer fabricated by the present potential-programmed electrocopolymerization method shows a quantum size effect. This result also leads to the expectation that many other novel functional materials and devices whose properties reflect their designed structure may be fabricated by this method.

Porphyrin arrays connected with molecular wires

The nanofabrication of molecular semiconductors for the construction of molecular photoelectronic devices is an important area. The incorporation of a photosensitizer and a suitable electron donor and/or acceptor into a polymeric chain has been proposed as a molecular system based on photoinduced electron transfer. However, the synthesis of such polymers containing a number of large aromatic moieties or metal complexed is difficult because of the intractable solubility and flexibility. In order to overcome these difficulties, electrochemical polymerization is useful, since the polymr is deposited directly on the terminal electrode. We have synthesized a series of one- or two-dimensional porphyrin arryas connected with conjugating and insulating, by esterification for the latter. In addition, lateral polymerization can be combined with axial polymerization to afford three-dimensional molecular systems.[2,3,9-13] They are illustrated in Fig. 5.

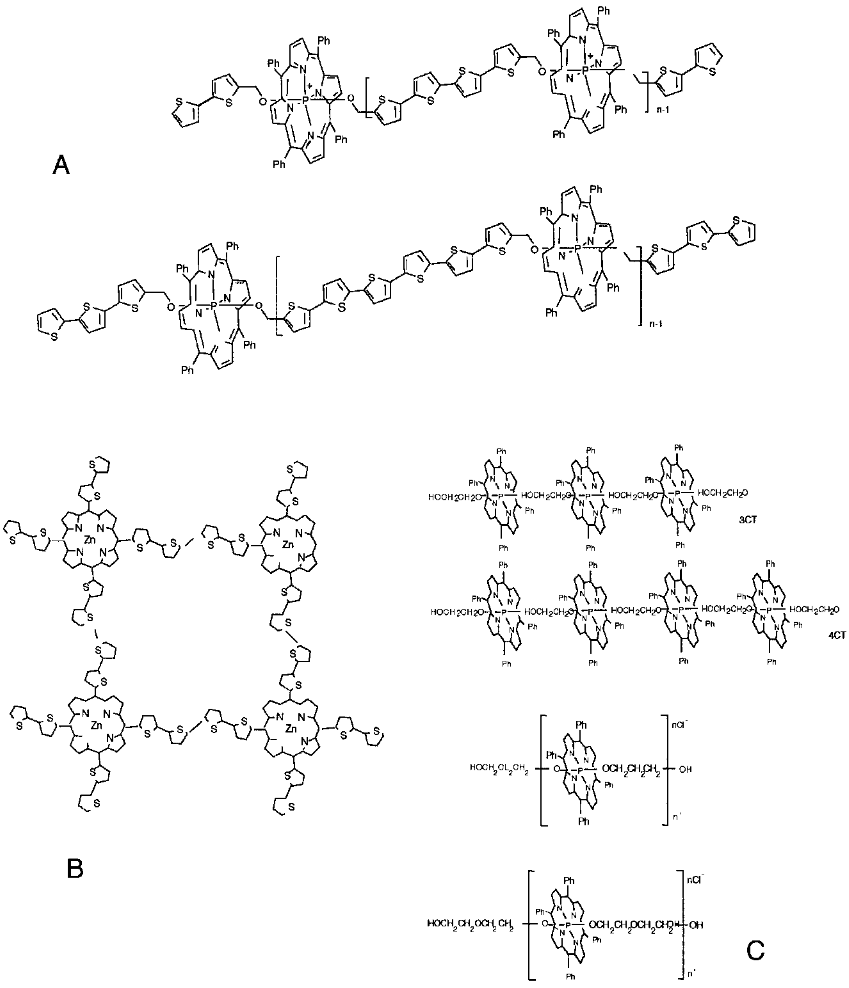

Figure 5. 1D and 2D porphyrin arryas linked with conjugating and/or insulating wires.

One-dimensional porphyrin arrays connected with conjugating oligothoenyl molecular wire were synthesized by the electrochemical polymerization of axial oligothienyl derivatives of P(V) porphyrin. 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 was strongly enhanced by the photo-irradiation. It is understandable that the photoinduced carrier formation occurs efficiently in the 1D polymers. A simple layered sandwich cell of 1D polymer and polybithiophene showed the electric rectifying properly and the photo-current under the photoirradiation.9)10) An importatnt point is that the P(V)TPP is able to act as a good photoinduced hole generator in the donor-acceptor molecules with oligothienyl moieties and is therefore expected to play a similar role in donor-acceptor polymers.11)

Two-dimensional porphyrin arrays connected with oligothienyl molecular wire was also synthesized by the electrochemical coupling of *meso*-oligothienyl derivatives. The resulting polymer showed similar functions as the one-dimensional porphyrin arrays connected with oligothienyl molecular wire.

One-dimentional porphyrin arrays connected with insulating molecular wire were synthesized by polycondensation of corresponding monomers, axial hydroxyalkyl derivatives of P(V)TPP.

This porphyrin arrays connected with an insulating molecular wire showed that both photoexcited singlet and triplet states are localized in a short molecular wire but not localized in a long one.11) This suggests photoinformation storing capability at a certain porphyrin ring which in turn suggests a photoinformation housing-in molecular system. Fig. 6 shows a schematic picture of photoinformation housing-in by localized and delocalized excitations.

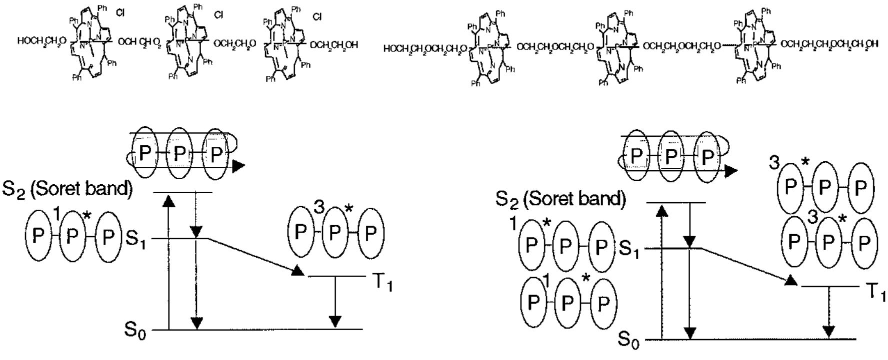

Figure 6. Singlet and triplet photoexcited states of 1D porphyrin arrays connected with insulating molecular wires of short and long chains.

Oligonucleotide shackled with porphyrin

The synthetic photonuclease which cleaves DNA at the specific site by photoreaction may bring us many applications. We have proposed that one of the most interesting candidate of the synthetic photonuclease is oligoucleotide shackled with tetraphenylporphyrin at internucletidic phosphodiester linkage. The idea to design the photonuclease is composed of antisense and photoactive moiety in DNA chain, which hybridizes tightly with complementary DNA and has capability of a direct electron transfer from the target site of DNA. Thus the sharply-targeted photocleavage of DNA can be achieved.[14-16] The circular dichroism and UV absorption behavior suggests that the photoactive P(V)TPP moiety locates in close proximity to the target site of DNA. The synthesis of the oligonucleotide deriatives proceeded readily by use of DNA synthesizer (Fig. 7).

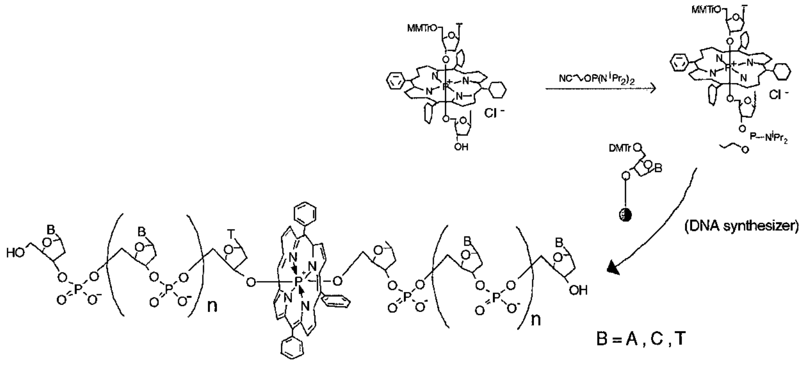

Figure 7. Synthesis of oligonucleotides shackled with tetraphenylporphyrin.

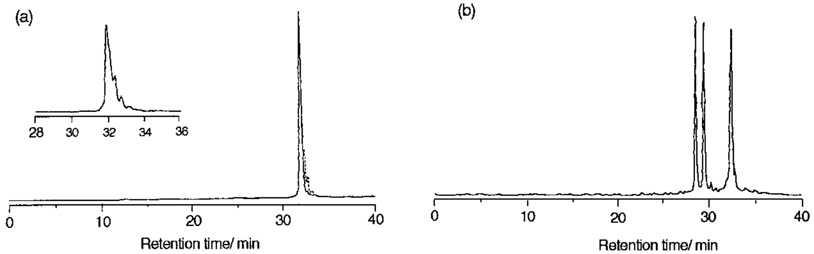

Figure 8. HPLC profiles of the products formed by photoirradiation of duplex 2 detected at (a) 285 nm and (b) 265nm.
(a) before irradiation (———) and after irradiation (-----).
(b) products obtained by irradiation followed by piperidine treatment.

The oligonucleotides shackled with tetraphenylporphyrin cleaved its complementary oligonucleotide in high efficiency, in both aerobic and anaerobic conditions. The photoreaction and the subsequent piperidine treatment gave the targeted photocleavage of DNA. Fig. 8 shows the HPLC profile of photoirradiated product of the duplex, 5'-TTATAAATTT**p**TTTAAATATT-3' and 3'-AATATTTAAGAAATTTA,TAA-5', as an example. Decrease of the complememtary oligomer and formation of photoproducts were observed. After piperidine treatment, only two DNA fragments were obtained. This indicates that the complementary oligomer is cleaved at only one site. These results suggest that the oligonucleotide shackled with porphyrin cleaves DNA at the targeting site via a direct electron transfer, and many applications are expected.

References

1. L. Ezaki, Tsu, IBM J. Rev. Dev., 14, 61 (1970).
2. T. Shimidzu, Pure & Appl. Chem., 67, 2039 (1996).
3. T. Shimidzu, in Molecular Electronics, IUPAC, A Chemistyr for the 21st Century, J. Jortner and M. Ratner (Eds). Blackwell Science, p.381 (1998)..
4. T. Iyoda, H. Toyada, M. Fujitsuka, R. Nakahara, H. Tsuchiya, K. Honda, T. Shimidzu, J.Phys.Chem., 95, 5214 (1991).
5. T. Iyoda, H. Toyada, M. Fujitsuka, R. Nakahara, K. Honda, T. Shimidzu, S. Tomita, Y. Hatano, F. Soeda, A. Ishitani, Thin Solid Films, 205, 258 (1991).
6. R. Aviram, M. Ratner, Chem.Physics Lett. 29, 281 (1974).
7. M. Fujitsuka, R. Nakahara, T. Iyoda, T. Shimidzu, T. Tsuchiya, J. Appl. Phus., 74, 1283 (1993).
8. T. Shimidzu, T. Iyoda, H. Toyoda, M. Fujitsuka, M. Nakahara, Synth.Metals, 55, 1335 (1993).
9. H. Segawa, N. Nakayama and T. Shimidzu, J. Chem. Soc. Chem. Commun., 784 (1992).
10. H. Segawa, N. Nakayama, F. Wu and T. Shimidzu, Synth. Metal, 55, 966 (1993).
11. H. Segawa, K. Kunimoto, K. Susumu, M. Taniguchi and T. Shimidzu, J. Am. Chem. Soc., 116, 11193 (1994).
12. T. Shimidzu, H. Segawa, F. Wu and N. Nakayama, J. Photochem. Photobiol. A: Chem., 92, 121 (1995).
13. K. Susumu, K. Kunimoto, H. Segawa and T. Shimidzu, J Phys Chem, 99: 29, (1995).
14. A. Nomura, M. Morimoto, K. Fukui, H. Segawa and T. Shimidzu, Nucleic Acids Res. Symp., 34, 185 (1995).
15. T. Shimidzu, A. Nomura, K. Fukui, H. Segawa and A. Morimoto, ibid, 35, 101 (1996).
16. T. Shimidzu, Phosphorus, Sulfur and Silicon, 109, 269 (1996).