Electrochemical Characteristics of 5,10,15,20-Tetrakis-Octadecyloxymethylphenyl-Porphyrin-Zn(II) Langmuir-Blodgett (LB) Films

Ja-Ryong Koo, Don-Soo Choi, Young Kwan Kim and Jung-Soo Kim

Abstract - Since Metallo-Porphyrin (MP) is very interesting compound due to its unique electronic and redox properties and it is also chemically and thermally stable, MP has been studied for potential memory and switching devices. In this study, thin films of 5,10,15,20-Tetrakis-Octadecyloxymethylphenyl-Porphyrin-Zn(II) were prepared by the Langmuir-Blodgett (LB) method and characterized by using UV/vis absorption spectroscopy and cyclic voltammetry. It was found that the proper transfer surface pressure for film deposition was 25 mN/m and the limiting area per molecule was 135 Å^2/molecule. The current-voltage (I-V) characteristics of these films were investigated. Further details on the electrical properties of Porphyrin-Zn(II) derivative films will be discussed.

Keywords - Langmuir-Blodgett(LB) film, Cyclic-Voltammetry(C-V), Resonant tunneling

1. Introduction

Molecules that might be suitable for use in molecular electronic devices have recently been the subject of much attention.[1][2] Current approaches are based on the development of molecular-scale switches, which can be used in both logic and memory circuits. Because the basic paradigm for electronic information storage is the retention of charge in a capacitor, the most straightforward approach to molecular scale memory will store charge at the molecular level. One example of this type of approach employs quantum-dot cellular automata (QCA).[3] The QCA approach retains the basic paradigm of binary information storage. Another, more fundamental approach will utilize the oxidation states of individual molecules to store charge. This approach has an advantage that multiple oxidation states within one molecule can be addressed to access >1 bit.[4]

The study on organic ultrathin films has recently attracted greast interest due to the potential technological applications of these materials, in molecular photo-electronic devices, medical applications, and other appliances.[5][6][7][8][9] One of the main problems related with the fabrication of these organic films is controlling the orientation and aggregation of molecules. This problem is particularly important in the case of porphyrins due to the high tendency of these molecules to form different types of aggregates.

In this study, we have investigated the possibility of redox-active organic monolayers as molecular-scale information storage systems. The memory elements are porphyrin molecules; information is stored in the oxidation states of these molecules. While both porphyrin anions and cations can be formed electrochemically, we have selected to employ the cations due to their greater chemical stability. The basic fabrication process of porphyrin LB films was explained and the UV/vis absorption spectra, cyclic voltammetry, and current-voltage (I-V) characteristics of porphyrin LB films were obtained and discussed.

2. Experimental

2.1 Materials & π-A isotherm

In this study, 5,10,15,20-Tetrakis-Octadecyloxymethyl-phenyl-Porphyrin-Zn(II) (Zn-Porphyrin) ($C_{120}H_{184}O_4N_4Zn$, molecular weight = 1744.754) molecules, one of the porphyrin derivatives, were used as a material for a memory device. The molecular structure of a Zn-porphyrin derivative is shown in Fig. 1. The π-A isotherm of the Zn-porphyrin Langmuir film was measured using a Kuhn-type LB trough (NIMA 611), where purified water (18.3 MΩ · cm) was used as the subphase. Chloroform (CH_3Cl) was used as a solvent for Zn-porphyrin with concentration of 1×10^{-4} mol/ℓ.

2.2 Film deposition

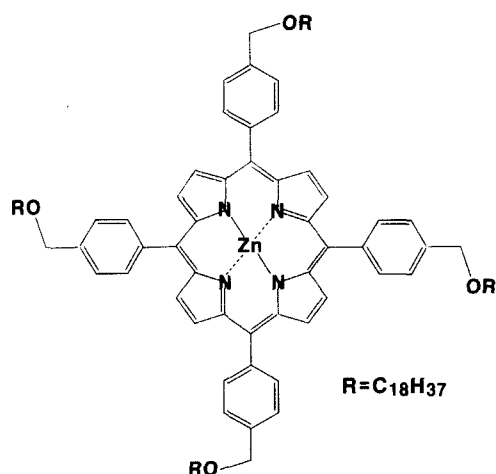In the Langmuir trough experiments, 400$\mu\ell$ of a

Fig. 1 Molecular structures of a Zn-porphyrin derivative.

solution was carefully spread onto the subphase by a gas-tight syringe. After the solvent was evaporated (ca. 10 min), the floating film was continuously compressed at a speed of 25 cm²/min. Surface pressure was simultaneously monitored by a Wilhelmy Balance while getting an isotherm of the sample. The film was then transferred onto the substrate by a usual vertical dipping method at the surface pressure of 25 mN/m and at a speed of 5 mm/min during the upstroke. Microscope-slide glass and quartz were used as substrates for I-V measurement and UV/vis absorption spectroscopic measurement, respectively. The Zn-porphyrin LB film was formed with a Y-type.

2.3 Measurement

The UV/vis absorption spectra of Zn-porphyrin LB films were measured with an HP 8452 Diode Array Spectrophotometer. The current-voltage (I-V) characteristics of the film along the direction vertical to the substrate were measured using a Keithley 238 Electrometer. Voltage was applied from -2 to 2 V in an interval of 100 mV/s. Aluminum top and bottom electrodes for electrical measurement was vacuum-deposited at a pressure of 10^{-5} Torr. The thickness of top and bottom electrodes was 1,000Å and 1,500Å, respectively.
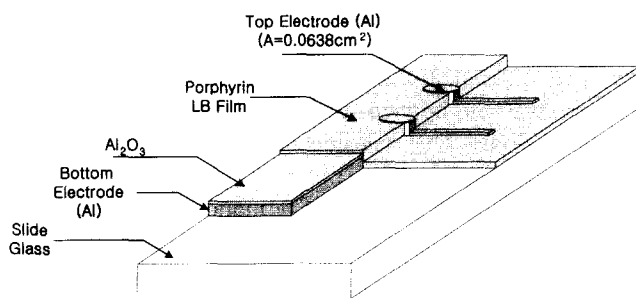

Fig. 2 Top view of the device structure prepared in this study.

The device structure is shown in Fig. 2. For the electrochemical measurement of the Zn-porphyrin derivative, EI Electroanalysis (PIMACS Co.) equipment was used, where Bu_4NClO_4 and acetonitrile were used as an electrolyte and a solvent, respectively. Counter, reference, and working electrodes were each used with Pt wire, Ag/Ag^+(0.1 M $AgNO_3$), and ITO/Al.

3. Results and Discussion

3.1 π-A isotherm, film deposition and device characteristics

Fig. 3 shows typical π-A isotherm characteristics of 5,10,15,20-Tetrakis-Octadecyloxymethylphenyl-Porphyrin-Zn(II) derivative. The limiting area per molecule was about 135 $Å^2$ and relatively low collapse pressure of 45 mN/m was shown. Because the limiting area for the face-on and edge-on orientation of porphyrin rings arranged in a monolayer is known to be about 160 $Å^2$ and 70 $Å^2$, respectively[10], this value implies that porphyrin rings are tilted away from the air-water interface. Proper surface pressure for film deposition was from 15 to 35 mN/m. In this study, the surface pressure of 25 mN/m was chosen for film deposition. The film deposition ratio for pulling out the substrate through the floating film onto water was always in the range from 1.00± to 0.1.
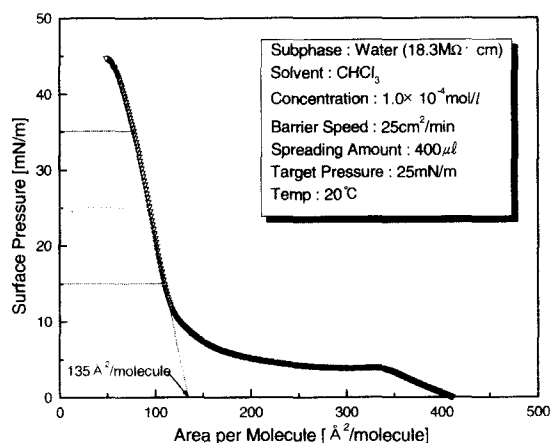

Fig. 3 π-A isotherm characteristics of the Langmuir film of the Zn-porphyrin derivative.

3.2 UV/vis absorption spectrum

The absorption spectrum of the Zn-porphyrin derivative in monolayer LB films deposited on quartz glass is shown in Fig. 4. The absorption peaks of the LB films occurred at 444 nm (Soret band), and 502, 555 nm (Q bands).
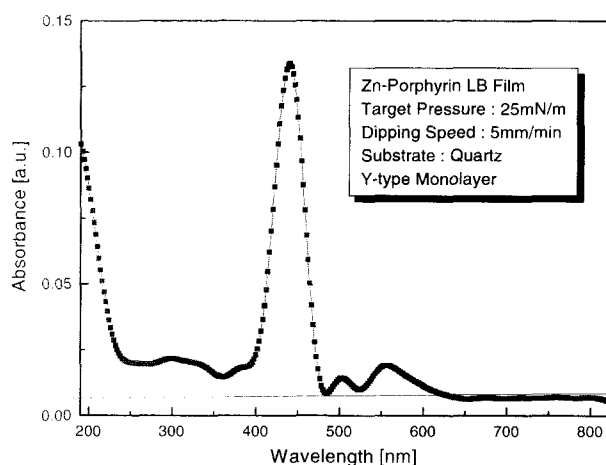
Fig. 4 UV/vis absorption spectrum of the LB films of the Zn-porphyrin derivative.
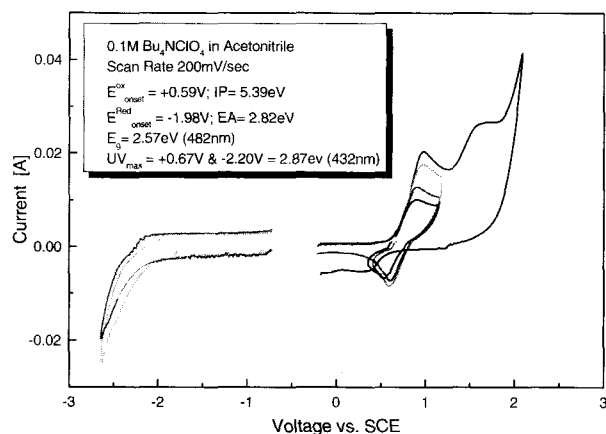
3.3 Cyclic voltammetric measurement

Fig. 5 Cyclic voltammogram of the Zn-porphyrin derivative.

The cyclic voltammogram of the Zn-porphyrin derivative is shown in Fig. 5. The electrochemical analysis of Zn-porphyrin was done by using the three-step analytic method. First, the film of the Zn-porphyrin derivative was formed on the working electrode (ITO, Al electrode) by spin-coating. Second, this working electrode was put in the electrochemical cell, and the oxidation/reduction potential of the Ag/Ag$^+$ reference electrode was measured and analyzed with cyclic voltammetry. Third, the potential conversion of the reference electrode was carried out by criterion materials, and the ionization potential (IP), electron affinity (EA), and band gap of the Zn-porphyrin sample were finally confirmed. In this potential conversion, ferrocene and AlQ3 were used as criterion materials. The potential conversion constant of SCE reference electrode vs. the Ag/Ag$^+$ reference electrode was + 0.31 V, and the potential conversion constant of the SCE reference electrode vs. the ionization potential, the electron affinity of the electro-

chemical potential, was 4.8. The scan rate of cyclic voltammetry was 100 mV/sec. Fig. 5 shows that the onset point of the oxidation/reduction potential appeared at +0.59 V and -1.98 V, respectively. It was also found that IP and EA were 5.39 eV and 2.82 eV. The electrochemical band gap of the oxidation/reduction potential was 2.57 eV and 482 nm. Because oxidation reaction by electron donating and removing was symmetric, Zn-porphyrin has a reversible characteristic, which means that this material is very stable.

3.4 Current-voltage (I-V) characteristics[11][12]

The current-voltage characteristics of the devices made from Zn-porphyrin monolayers are shown in Fig. 6. These devices, initially probed at forward bias (positive) voltages, show a remarkably nonlinear current increase with the applied voltage (Fig. 6, "1st scan"). Subsequent scans yield slightly lower current levels from 0.1 V to 0.8 V. A reverse bias scan (Fig. 6, inset) is characterized by a reduced current level. Here, we have the basis for a singly confi - gurable molecular switch which is initially "closed" (positive bias) and then, after negative biasing, "open." The configurability of this junction was recently exploited to make logic gates from the parallel array of molecular-based devices[1].

Fig. 7 shows the current density-voltage (J-V) characteristics of the Al/Al$_2$O$_3$/LB film/Al reverse rectifying junctions. The same data as Fig. 6 are plotted as log (J) versus V$^{1/4}$. Some molecular rearrangements occur in the monolayer (Al$_2$O$_3$ has no role to play in the rectification behavior). In the inset of Fig. 6, the I-V curves show small hysteresis. According to the Aviram-Ratner model, the rectification mechanism depends on a match (resonant tunneling) between the Fermi levels of metal electrodes and the HOMO and LUMO levels of the molecule sandwiched between the metal layers, followed or preceded by inelastic tunneling within the molecule.[13] Generally speaking, the use of metal electrodes with different work functions may also hinder the observation of molecular rectification, or at least complicate the metal/LB film/metal junctions. It is well known that higher currents are always observed in metal-insulator-metal junctions when a positive bias is applied on the electrode with lower work functions. This consideration leads us to use Al for both electrodes. The Ln(J) $\propto$ V$^{1/n}$ with n~4 has been previously observed in LB mono- and multilayers sandwiched between metal electrodes,[12] but our data were not equal. Even though the physical meaning of our data is not clear, such a behavior has been attributed to the conduction dominated by the memory characteristics of Zn-porphyrin in the LB films. LB

transfer is responsible for a more disordered molecular architecture in the negatively rectifying junctions than in the positively rectifying junctions. Molecular rearrangments in the monolayer may arise after LB deposition, during storage periods, during metal deposition, or even during electrical measurements, because of possible interaction between dipole moments and the applied electric field, if molecular density of the monolayer is low enough to allow molecules to have enough free volume to bend and "flip-flop."
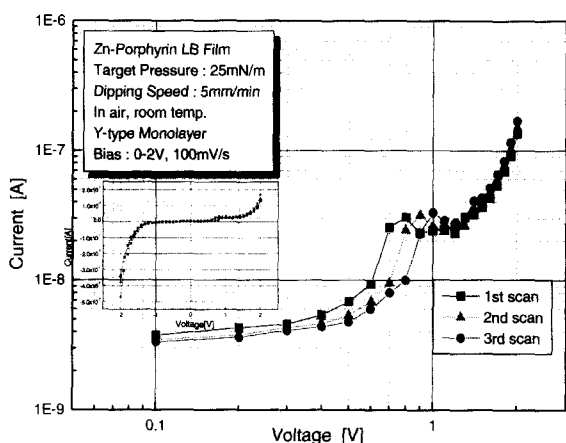

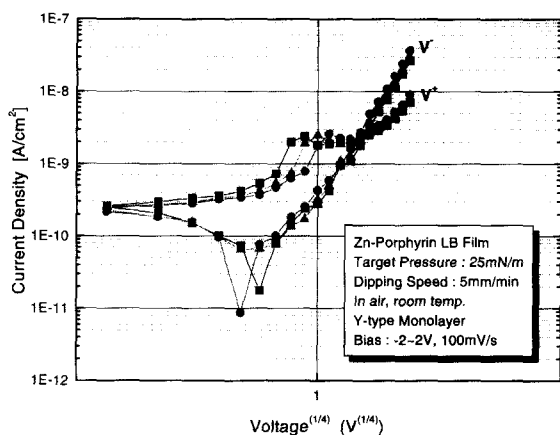**Fig. 6** I-V characteristics of the Zn-porphyrin derivative (at positive bias).

Fig. 7 J-V characteristics of the Zn-porphyrin derivative (reverse rectifying junctions).

## 3.5 Resonant tunneling through molecular states

The I-V characteristics of the solid state device can be understood in terms of the molecular properties observed in the solution. Current flow in both the solid-state devices and the solution is reversible at positive andirreversible at negative potentials. This correspon- dence between the solution and solid-state results suggests that the fundamental molecular electronic properties are
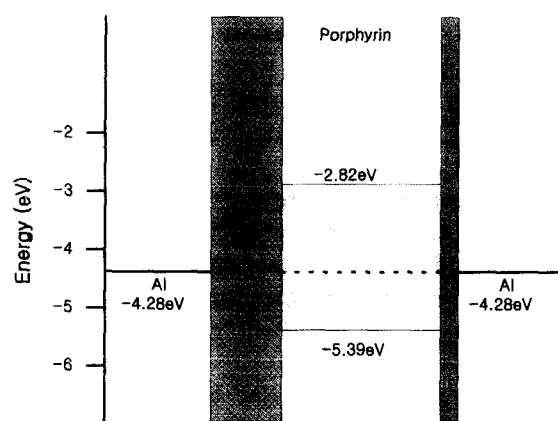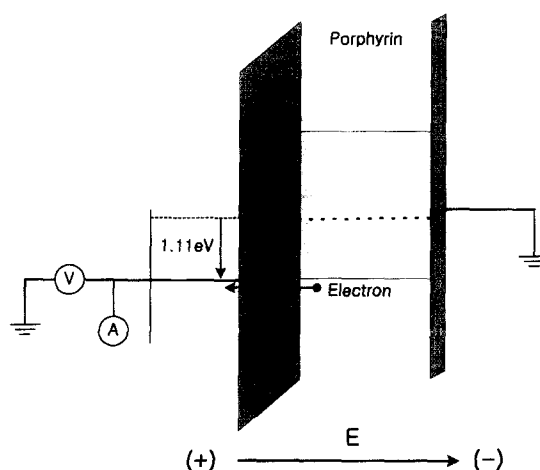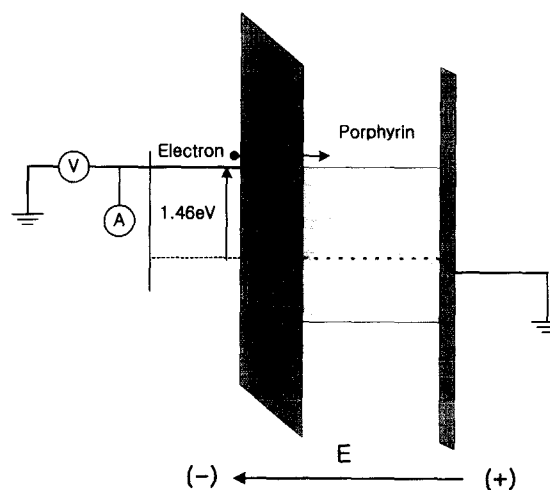
Fig. 8 Band diagram of the Zn-porphyrin device (a) equilibrium (V=0), (b) positive bias (V>0), (c) negative bias (V<0).

retained in the solid-state devices. If this is the case, then the forward bias current flow should be determined by HOMO states (Fig. 8b), whereas the reverse bias current should be determined by LUMO states (Fig. 8c).

4. Conclusion

The following conclusions have been obtained from the experiments with the Zn-porphyrin LB films:

1. The proper surface pressure for film deposition was found to be about 25 mN/m from the π-A isotherm of the Zn-porphyrin Langmuir film.
2. In the cyclic voltammetry experiment, the IP, and EA of the Zn-porphyrin derivative were 5.39 and 2.82 eV, respectively.
3. From cyclic voltammogram, the band diagram of the Zn-porphyrin derivative was obtained. In this result, the resonant tunneling phenomena of electrons were explained.

Acknowledgment

References

[1] C. P. Collier, E. W. Wong, M. Belohradsky, F. M. Raymo, J. F. Stoddart, P. J. Kuekes, R. S. Williams, and J. R. Heath, *Science* 285, 391 (1999).
[2] J. Chen, M. A. Reed, A. M. Rawlett, and J. M. Tour, *Science* 286, 1550 (1999).
[3] C. S. Lent, *Science* 288, 1597 (2000).
[4] K. M. Roth, N. Dontha, R. B. Dabke, D. T. Gryko, C. Clausen, J. S. Lindsey, D. F. Bocian, and W. G. Kuhr, *J. Vac. Sci. Technol.* B 18(5), 2359 (2000).
[5] S. Miyama and H. S. Nalwa, Eds. *In Organic Electroluminescent Materials and Devices*; Gordon and Breach: Amsterdam, (1997).
[6] C. W. Tang and S. A. van Slyke, Appl. Phys. Lett. 51, 913 (1987).
[7] Y. Yang, *MRS Bull*, 22, 31 (1997).
[8] I. H. Stapff, V. Stümpflen, J. H. Wendorff, D. B. Spohn, and D. Möbius, *Liq. Cryst*, 23, 613 (1997).
[9] S. C. M. Gandini, I. E. Borissevitch, J. R. Perusi, H. Imasato, and M. Tabak, *J. Lumin*, 78, 53 (1998).
[10] X. Qian, A. Tai, X. Sun, S. Xiao, H. Wu, Z. Lu, and Y. Wei, *Thin Solid Films*, 285, 433 (1996).
[11] E. W. Wong, C. P. Collier, M. Behloradsky, F. M. Raymo, J. F. Stoddart, and J. M. Heath, *J. Am. Chem. Soc.*, 122, 5837 (2000).
[12] D. Vuillaume, B. Chen, and R. M. Metzger, *Langmuir*, 15, 4016 (1999).
[13] A. Aviram and M.A. Ratner, *Chem. Phys. Lett.*, 29, 277 (1974).

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