Macromol. Symp. **131,** *147–153 (1998)*

ENHANCED CARRIER-TRANSFER IN MULTI-LAYERED ORGANIC THIN FILM: APPLICATION TO ELECTROCHROMISM AND ELECTROLUMINESCENCE

Naoki Toshima*

Department of Materials Science and Engineering, Science University of Tokyo in Yamaguchi, Onoda-shi, Yamaguchi 756, Japan

Tsuyoshi Tominaga

Department of Applied Chemistry, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113, Japan

ABSTRACT: Multi-layered organic thin films were prepared by stepwise vapor deposition of planar molecules with delocalized π-electrons on indium tin oxide (ITO) glass or KCl crystalline surface. The order of the deposition of π-planar molecules with different redox potential can control enhancement or inhibition of the hole or electron transfer according to the concept of "sequential potential field", or a potential cascade by the organization of redox components. This concept is here applied to electrochromic or electroluminescent devices composed of multi-layered organic thin films.

INTRODUCTION

Macromolecular metal complexes have been expected to be one of the most promising candidates for advanced materials due to their interesting properties, especially multifunctionalities (Ref. 1). Macromolecular metal complexes are often compared with natural enzyme, where the metal complex and the macromolecule in macromolecule complexes play a role of active cite and protein in natural enzyme, respectively (Ref. 2). Thus, macromolecules can control the exact position of a series of active cites, since the order and distance among the active cites are very important for the functions of natural enzyme. A typical example is the case of the photosynthetic reaction center of green plants. In this well-designed system, several molecules are precisely oriented in an ordered arrangement to play a role of charge separation, charge (electron and/or hole) transfer and redox reaction, respectively. Such a well-designed arrangement could be followed by the novel concept of "sequential potential field", i.e., a concept to produce a potential cascade by the designed alignment of redox components having different energy states, which allow effective and vectorial electron and/or hole transfer as a whole (Ref. 3). In order to realize this concept to develop a novel electronic device, the alignment of redox components

CCC 1022-1360/98/$ 10.00

must be considered carefully for the construction of a sequential potential field.

Here we choose planar molecules with delocalized π-electron as the redox components, and align these components by stepwise vapor deposition. Since a phthalocyanine (pc) ligand has the ability to coordinate to different kinds of metal, forming metallophthalocyanine ([M(pc)]), which has various redox potentials depending on the kind of central metal and is enough stable against heat treatment for vapor deposition (Ref. 4, 5), [M(pc)]s were used as the components for hole transfer. The double-layered metallophthalocyanine thin films prepared by stepwise vapor deposition were examined for electrochromism. The results have shown that the "sequential potential field" concept can be applied to the present electrochromism. The same double-layered thin films can be applied to the hole transfer layer of the electroluminescent device. The results are again consistent with the novel concept. In the case of double-layered thin films composed of perylene derivatives as an electron transfer layer, in contrast, the results in electrochromism show that not only the order of the deposition but also the substrates used for the deposition are important to control the electron transfer. In other words, not only the order of the redox components but also the alignment of each molecules must be controlled for the exact construction of the "sequential potential field".

RESULTS AND DISCUSSION

Electrochromism of Double-layered Metallophthalocyanine Thin Films

Metallophthalocyanine ([M(pc)] has attracted a great deal of attention in connection with its electrochemical and photochemical properties. As for electrochromism, rare-earth bis(phthalocyanine) has been widely studied from the viewpoint of applications to a new-type of displays (Refs. 6-8). However, few attempts have ever been made to examine the electrochromism of light transition-metal complexes of phthalocyanine in thin film (Refs.9-13), since their electrochromisms were reported to be irreversible.

In 1993, we first reported that a reversible electrochromism is available for a copper phthalocyanine ([Cu(pc)]) thin film, prepared by vapor deposition, if the film is enough thin and the scanning conditions are well controlled (Refs. 14, 15). In addition, the oxidation potentials of metallophthalocyanine thin films were found to be enough different from each other depending on the kind of central metal (Ref. 16). The oxidation potentials of four M(pc) thin films are illustrated in Fig. 1. This results suggest us that a combination of two kinds of M(pc)s with enough different oxidation potentials may be used to control the hole transfer according to the construction of a "sequential potential field".

The [Ni(pc)]/[Zn(pc)] double-layered thin film was prepared by stepwise vapor deposition of [Ni(pc)] and [Zn(pc)] on an indium tin oxide (ITO) glass substrate. The film thickness was maintained to be about 20 nm for each [M(pc)] film. In order to measure the electrochromism, the ITO glass covered with [Ni(pc)] and [Zn(pc)] (ITO/[Ni(pc)]/[Zn(pc)]) was connected as a working electrode, and a

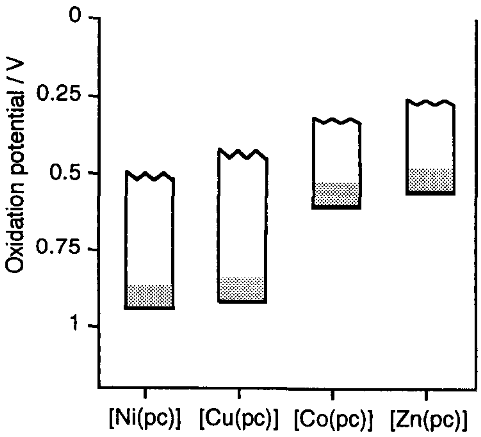

Fig. 1. Oxidation potentials in deposited thin films

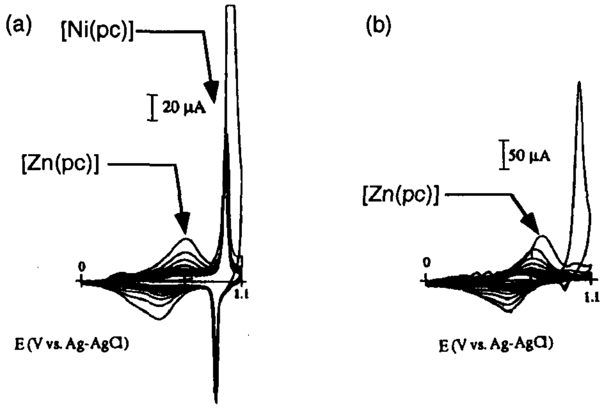

Fig. 2. Cyclic voltammograms (1st-10th) during the second oxidation cycle of a [Ni(pc)]/[Zn(pc)] (a) and a [Zn(pc)]/[Ni(pc)] (b) double-layered thin films in a 0.1 mol dm^{-3} $NaNO_3$ aqueous solution at the scanning rate of 20 mVs^{-1}

platinum wire and an Ag/AgCl saturated KCl electrode were used as a counter and a reference electrode, respectively. The resulting cyclic voltammograms in a 0.1 mol dm^{-3} $NaNO_3$ aqueous solution at room temperature are shown in Fig. 2 (a), which clearly indicates that both [Ni(pc)] and [Zn(pc)] are oxidized under the present conditions and that both oxidations can be reversibly repeated. On the other hand, the double-layered film, composed of the same metallophthalocyanines but deposited in the reverse order,

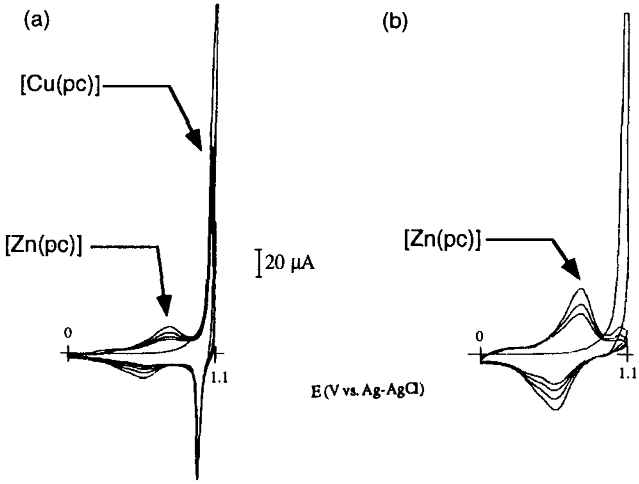

Fig. 3. Cyclic voltammograms of [Cu(pc)]-[Zn(pc)] sequentially deposited double-layered thin films: (a) ITO/[Cu(pc)]/[Zn(pc)] ; (b) ITO/[Zn(pc)]/[Cu(pc)] thin films in 0.1 mol dm^{-3} $NaNO_3$ solutions at the scanning rate of 20 mVs^{-1}

(ITO/[Zn(pc)]/[Ni(pc)]) shows a quite different cyclic voltammograms (Fig. 2 (b)). Thus, only the [Zn(pc)] film can be oxidized under the same conditions. In other words, hole can not pass to the [Ni(pc)] film through the [Zn(pc)] film and the [Ni(pc)] film cannot be oxidized. Since the oxidation potential of [Ni(pc)] film (0.94 V) is more positive than that of [Zn(pc)] film (0.55 V), the above results, shown in Fig. 2 (a) and 2 (b), are quite reasonable and consistent with the "sequential potential field" concept.

The similar results are observed for the electrochromism of double-layered thin films composed of [Cu(pc)] and [Zn(pc)]. The cyclic voltammograms of ITO/[Cu(pc)]/[Zn(pc)] films have two oxidation peaks corresponding to [Cu(pc)] and [Zn(pc)], while those of the film with the reverse order (ITO/[Zn(pc)/[Cu(pc)]) have only one peak corresponding to [Zn(pc)] (Fig. 3). These results are again consistent with the concept of a "sequential potential field".

Electroluminescence of Multi-layered Devices Containing Metallophthalocyanine Thin Films

Recently electroluminescent (EL) devices using organic materials have widely been studied from a viewpoint of applications to a new type of displays (Refs. 17, 18). These EL devices consist of a multi-layered thin film of oranic materials (Refs. 19, 20). The multi-layers often involve a light-emitting layer and carrier transport layers. Since the [M(pc)] thin film works as a hole transfer layer in the experiments of electrochromism in the previous section, we have examined the hole transfer property of double-layered [M(pc)] films as a hole transfer layer of EL devices.

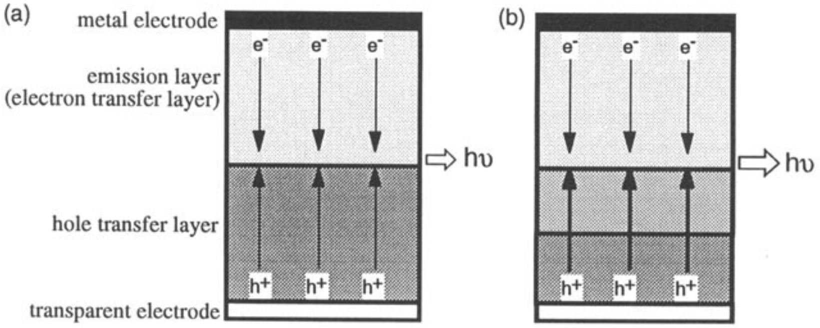

Fig. 4. Electroluminescent device using Alq_3 and [M(pc)]

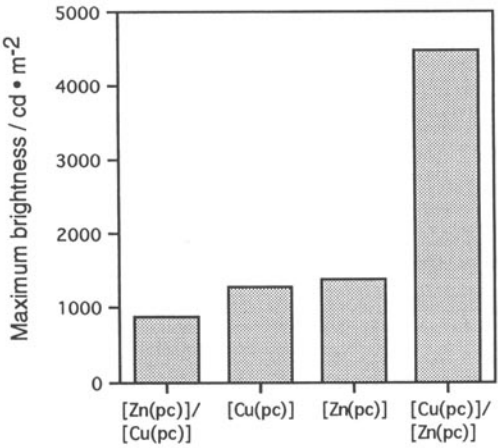

Fig. 5. The maximum brightness of the EL device using various hole transfer layers

EL devices were prepared by vapor deposition of [M(pc)] as a hole transfer layer on ITO transparent glass electrode, followed by deposition of tris(8-hydroxyquinoline)aluminium (Alq3) as an emittion layer and then co-deposition of magnesium and silver as a metal electrode (Fig. 4(a)). When the double-layered film was used as the hole transfer layer, the total thickness was kept to be the same as the mono-layered one as shown in Fig. 4(b).

The results of the EL brightness are quite interesting. Figure 5 shows the maximum brightness of the EL devices using various [M(pc)] hole transfer layer (Ref. 21). In the case of the ITO/[Zn(pc)]/[Cu(pc)]/Alq3/MgAg device, the maximum brightness is lowest among the devices

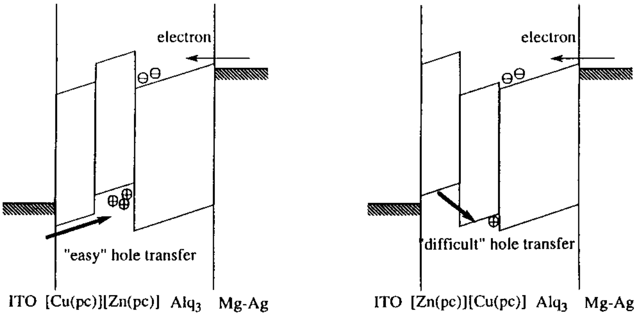

Fig. 6. Schematic band diagrams of the EL device with [tM(pc)] double hole transfer layers; (a) [Cu(pc)]/[Zn(pc)] and (b) [Zn(pc)]/[Cu(pc)]

examined here. In contrast, the ITO/[Cu(pc)]/[Zn(pc)]/Alq3/Mg-Ag device has about 5 times higher brightness than the former. This is probably due to the easy hole transfer in the hole transfer layer of the latter because the oxidation potential of the [Cu(pc)] film is more positive than [Zn(pc)] one (Fig. 6(a)). The reverse ordering of [M(pc)] films in the hole transfer layer makes the hole transfer difficult (Fig. 6(b)). These results are consistent with the concept of "sequential potential field". The similar results were observed in the combination of [Ni(pc)] and [Zn(pc)], supporting the same concept in the case of [Cu(pc)] and [Zn(pc)].

Electron Transfer in Double-layered n-Type Organic Semiconductors

The [M(pc)] films work as a p-type organic semiconductor. In contrast, porphyrin and perylene derivatives can work as an n-type organic semiconductor. Thus, we examined some systems containing these organic thin films. The results are the similar to the case of [M(pc)] films for hole transfer. The largest difference were observed in the alignment of the planar molecules. In the case of [M(pc)] films the double-layer thin films prepared by vapor deposition on ITO glass, in which the molecular plane of [M(pc)]s is perpendicular to the substrate, can work to enhance or inhibit the hole transfer. In contrast, in the case of n-type organic semiconductor films, the film prepared by vapor deposition on ITO glass, in which the molecular plane is perpendicular to the substrate, does not work to construct a "sequential potential field", but the film prepared on KCl crystalline substrate, in which the molecular plane is parallel to the substrate, does work to construct the "sequential potential field". These results suggest that the molecular alignment is very important to construct the "sequential potential field".

REFERENCES

(1) cf. A series of books, *"Macromolecular Complexes Functions and Applications"*, Scientific Societies Press, Tokyo, 1982-1991

(2) N. Toshima, M. Kaneko, Y. Seki, *"Macromolecular Complexes"*, Kyoritsu, Tokyo, 1990

(3) M. Toshima, *"Macromolecular Complexes: Dynamic Interactions and Electronic Processes"*, E. Tsuchida, Ed., VCH, New York 1991, p.331

(4) F. H. Moser, A. L. Thomas, *"The Phthalocyanines"*, CRC Press, Boca Raton 1983

(5) M. Tanaka, S. Koma, *"Phthalocyanine"*, Bunshin Pub., Tokyo 1991

(6) C. W. Tang, *Appl. Phys. Lett.*, 48, 183 (1986)

(7) D. Wöhrle, D. Meissner, *Adv. Mater.*, 30, 129 (1991)

(8) Y. Machida, Y. Saitoh, a. Taomoto, K. Warasagi, S. Asakawa, *Jpn. J. Appl. Phys.*, 28, 297 (1989)

(9) J. M. Green, L. R. Faulkner, *J. Am. Chem. Soc.*, 105, 2950 (1983)

(10) J. L. Kahl, L. R. Faulkner, K. Dwarakanath, H. Tachikawa, *J. Am. Chem. Soc.*, 108, 5434 (1986)

(11) J. Silver, P. Lukes, P. K. Hey, M. Ahmet, *J. Mater. Chem.*, 1, 29 (1981)

(12) J. Silver, P. Lukes, P. K. Hey, M. Ahmet, *J. Mater. Chem.*, 2, 841 (1992)

(13) M. shimura, K. Sato, T. Okumura, Y. Shimura, K. Ozawa, *Denki Kagaku*, 61, 922 (1992)

(14) N. Toshima, S. Kawamura, T. Tominaga, *Chem. Lett.*, 1993, 1299

(15) N. Toshima, T. Tominaga, S. Kawamura, *Bull. Chem. Soc, Jpn.*, 69, 245 (1996)

(16) N. Toshima, T. Tominaga, *Bull. Chem. Soc. Jpn.*, 69, 2111 (1996)

(17) C. W. Tang, S. A. Van Slyke, *Appl. Phys. Lett.*, 51, 913 (1987)

(18) C. Adachi, S. Tokito, T. Tsutsui, S. Saito, *Jpn. J. Appl. Phys. 1*, 27, L713 (1988)

(19) Y. Shirota, Y. Kuwabara, H. Inada, T. Wakimoto, H. Nakada, Y. Yonemoto, S. Kawami, K. Imai, *Appl. Phys. Lett.*, 65, 807 (1994)

(20) J. Kido, M. Kimura, K. Nagai, *Science*, 267, 1332 (1995)

(21) T. Tominaga, K. Hayashi, N. Toshima, *Appl. Phys. Lett.*, 70, 762 (1997)