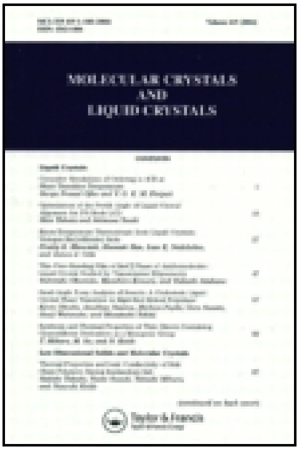

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Photodiodes Constructed by LB Films of Polyimides Possessing Triphenylamine Units

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Photodiodes Constructed by LB Films of Polyimides Possessing Triphenylamine Units

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Diaminotriphenylamines 4 possessing four different substituents were newly synthesized, and introduced to polyamic acids 6 by the reaction with aliphatic tetracarboxylic dianhydride 5. The LB films of polyimides 8 having triphenylamine units were fabricated on a glassy carbon electrode via the LB films of long chain alkylamine salts of 6 to measure cyclic voltammograms. The methoxy substituted triphenylamine afforded the lowest redox potential, that suggested the highest electron density on the nitrogen atom of the triphenylamine. The photoconductive devices (photodiodes) were constructed by the deposition of polyimides which possessed different chemical structure, i.e., triphenylamines as an electron donor (D), tetraphenylporphyrin as a sensitizer (S), and aromatic polyimide as an electron acceptor (A), giving polyimide LB multilayer films. Two types of photodiodes having E/D/S/A and E/A/S/D were prepared on the semitransparent gold electrodes (E). When the methoxy substituted triphenylamine was used as D layer, the highest photocurrent of 3 $\mu A/cm^2$ was obtained. The order of magnitude of photocurrent was in good agreement with the results of cyclic voltammometry. The dependence of numbers of D, S, and A layers on the photocurrent was examined by changing the number of each layer. It was found that the triphenylamine units had excellent electron donating ability and hole mobility, whereas the S and A layers did not transfer electron effectively.

INTRODUCTION

In biosystems, the molecules organize themselves into complex functional entities with cooperating compounds of molecular dimensions. For the design of artificial photosynthetic molecular devices, it is of great interest to mimic the elaborate molecular machinery.[1-3]

Electron transfer systems, which are the most important part of the biosynthesis, have been widely studied in Langmuir-Blodgett (LB) films from such view points.[4] In typical cases, the systems are constructed by LB films possessing electron acceptor (A), electron donor (D), and photosensitizer (S).[5-7] Part of the authors fabricated electrochemical photoconductive devices (photodiodes) by depositing mixed unimolecular layers which consisted of linear A-S-D triads and fatty acids.[8] The photoinduced vectorical flow of electrons could be achieved according to the energy diagrams depicted in Figure 1. The sytem works as follows: 1) S is excited by the irradiation of light, 2) the excited electrons are transferred to A, and 3) the lacking electrons in S are supplied from D.

In the previous paper, we reported a successful preparation of the triad photodiode system using polyimide LB films, where ferrocene, tetraphenylporphyrin (TPP), and aromatic polyimide units were used as D, S, and A, respectively.[9,10] This system afforded fairly high level of photocurrents, which was probably caused by lack of the long alkyl chain between the layers of the LB films.[11-13] However, it was troublesome that ferrocene unit was easily oxidized by the action of a small amount of oxygen. In the present paper, as a new improvement, triphenylamine unit, which has been known to be a functional group of large hole mobility, was applied to D layer, and the same chemical units of the previous system were used as S and A layers. The effect of substituents on triphenylamine unit and the dependence of the number of each layer on photocurrent were discussed in detail.

EXPERIMENTAL

Measurement

H-NMR spectra and IR spectra were recorded on a JEOL-FX-90Q FT-NMR spectrometer and a JASCO FT/IR-5000 spectrophotometer, respectively. Measurement of surface pressure-area (π-A) isotherms were performed by using a San-Esu FSD-20 Langmuir-Blodgett apparatus.

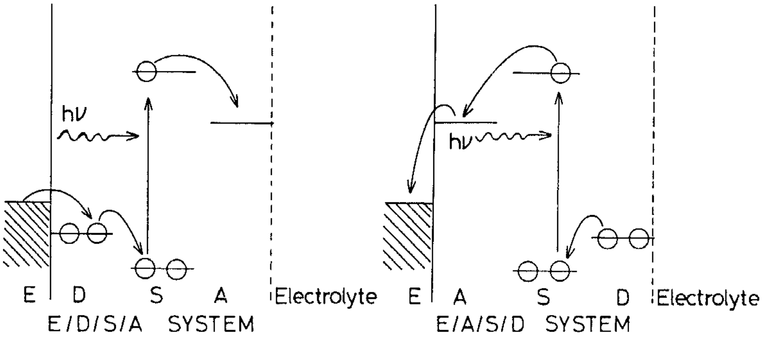
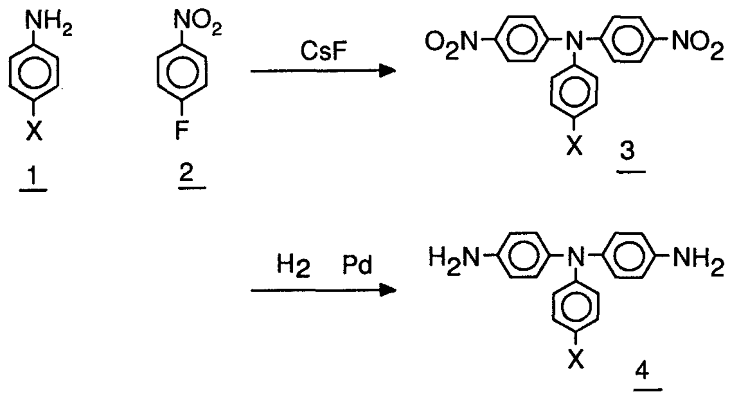


FIGURE 1 Energy diagram of electron transfer.

Chemical Materials

Diaminotriphenylamines 4 were synthesized as shown in Equation 1.[14] Polyamic acids were prepared from the corresponding tetracarboxylic dianhydrides and diamines.

Typical synthetic procedures are as follows:



(1)

X : a = $-H$, b = $-CH_3$, c = $-OCH_3$, d = $-N(CH_3)_2$

4,4′-Diamino-4″-methoxytriphenylamine 4c

A solution of 3.08 g (25 mmol) of p-anisidine 1c, 7.00 g (50 mmol) of 2p-fluoronitrobenzene 2, and 7.60 g (50 mmol) of cesium fluoride in 60 ml of dimethyl sulfoxide (DMSO) was heated at 100°C with vigorous stirring for 5 h, and poured into 300 ml of water. The precipitate was filtered and dried at 70°C under reduced pressure. The brown colored mass including law materials was applied to silica gel column chromatography using chloroform as eluent, and 4,4′-dinitro-4″-methoxytriphenylamine was separated with the yield of 2.46 g (27%).

Mp: 208°C. IR (KBr, cm^{-1}): 2922, 1580, 1497, 1283, 1112, and 1020. ^1H-NMR ($CDCl_3$, δppm): 9.2–9.0 (m, a, 4H), 7.3–6.9 (m, a, 8H), and 3.9 (s, $-CH_3$, 3H). Elemental Analysis: Cald. C; 62.46, H; 4.14, N; 11.50, Found, C; 61.19, H; 4.09, N; 11.11.

In a flask, 3.65 g (10 mmol) of 3c and 1.00 g of 10% palladium on carbon, and 60 ml of tetrahydrofuran (THF) were placed, and the solution was stirred at room temperature for 24 h under hydrogen gas. The resulting mixture was filtered through Celite powder to remove the palladium on carbon. After the solvent was distilled off, 4,4′-diamino-4″-methoxytriphenylamine 4c was purified by distillation at 280°C/1 Torr. The yield was 1.61 g (53%).

Mp: 151°C. IR (KBr, cm^{-1}): 3342, 2836, 1628, 1506, 1267, 1236, and 828. ^1H-NMR ($CDCl_3$, δppm): 7.3–6.5 (a, 12H), 3.8 (s, $-CH_3$, 3H), and 3.3 (broad, $-NH_2$, 4H). Elemental Analysis: Cald, C; 74.72, H; 6.28, N; 13.76, Found, C; 75.03, H; 6.22, N; 13.74.

Polyamic Acid 6c

A 0.92 g (4.10 mmol) portion of 2,3,5-tricarboxycyclopentylacetic dianhydride 5 was added to a solution of 1.25 g (4.10 mmol) of 4c in 16.4 ml of N, N-dimethylacetamide (DMAc). The reaction mixture was stirred for 8 h at room temperature. A part of the solution was poured into methanol to obtain solid polyamic acid 6c. The inherent viscosity of 6c was 0.72 dl/g, measured at a concentration of 0.5 g/dl in DMAc at 30°C.

Preparation of LB Film of Polyimide 8c[11–13]

A solution of the polyamic acid 6c in a mixture of DMAc and benzene (1:1 by volume) with a concentration of 1 mmol/l, which was prepared by dilution of the preparative reaction mixture of 6c, was combined with a solution of N-eicosylpyrrolidine in the same mixed solvent with the same concentration to produce a solution of the polyamic acid amine salt 7c for spreading (See Equation 2). The measurement of π-A curve was carried out on a San-Esu FSD-20 trough (500 mm length and 150 mm width) with a compression speed of 0.32 mm/s at 20°C. The subphase used in this study was a distilled and deionized water.

The deposition of L film of 7c was carried out with vertical dipping method at the surface pressure of 20 mN/m onto a gold semitransparent electrode. The conversion of precursor LB film of 7c, thus obtained, to the LB film of polyimide 8c was carried out by a two-step treatment. First, the LB film of 7c was immersed in a mixture of acetic anhydride and benzene (1:5 by volume) and a few drops of pyridine at 20°C for 2 h. Next, it was dipped in a mixture of pyridine, acetic anhydride, and benzene (1:2:10 by volume) for 30 sec, and then dried at 60°C under reduced pressure.

Measurement of Cyclic Voltammograms

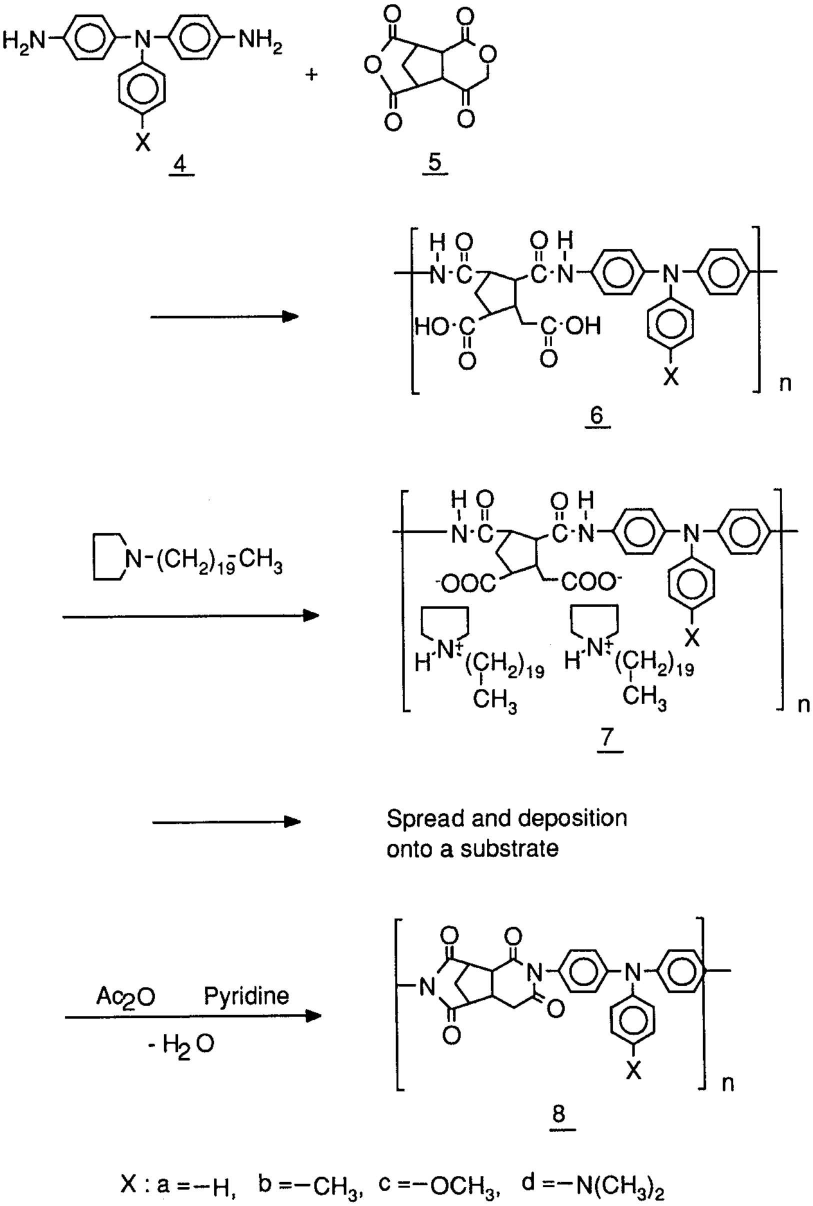
Ten layers of polyimide LB films possessing triphenylamine units were prepared on glassy carbon electrodes, whose geometrical surface area was 7.1 mm^2. The cyclic voltammograms were recorded in aqueous 0.1 M tetraethylammonium perchlorate (TEAP) solution under nitrogen using a saturated calomel electrode (SCE) and a gold wire as the reference and the counter electrodes, respectively.

Measurement of Photocurrent

The photoelectrochemical properties were investigated by the system as depicted in Figure 2, where the gold optically transparent electrode (OTE) with LB films, a gold line, and SCE were settled as working, counter, and reference electrodes, respectively.[9] The LB films on the electrode were kept in contact with an aqueous 100 mN KCl electrolyte solution. Monochromatic light (430 nm) was used to measure the photocurrent.

RESULTS AND DISCUSSION

In the present work, triphenylamine units were employed for electron donating layer. Triphenylamines are known as high electron donating ability and large hole



(2)

mobility. Furthermore, substituents which control the electron density of the nitrogen atom can be readily introduced into benzene ring. Four kinds of diaminotriphenylamines 4 were newly synthesized starting from p-fluoronitrobenzene and the corresponding anilines via dinitrotriphenylamines 3 as shown in Equation 1. Polyamic acids 6, which were prepared by the reaction of diamines 4 and aliphatic tetracarboxylic dianhydride 5, were applied to LB films after mixing with long chain alkylamine. The surface pressure-area (π-A) isotherms of the polyamic acid long chain alkyl amine salts 7 possessing different triphenylamine units are shown in

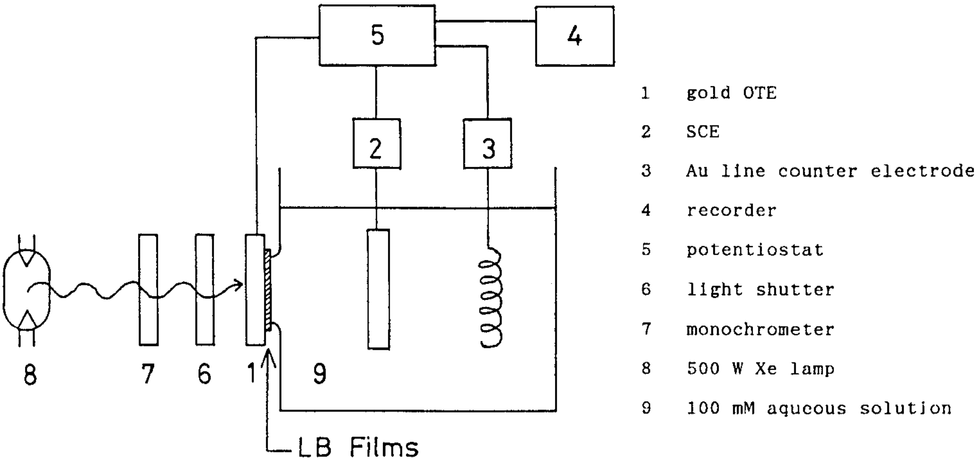


FIGURE 2 Photocurrent measurement system.

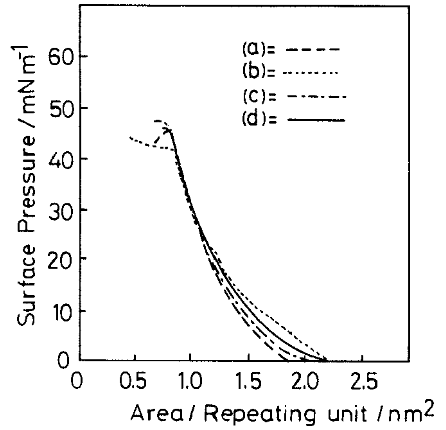


FIGURE 3 Surface pressure-area (π-A) isotherms of polyamic acid long alkyl amine salts 7a–d. (a): 7a, (b): 7b, (c): 7c, and (d): 7d.

Figure 3. These π-A curves show almost the same behavior with stable condensed monolayer films forming at around 1.25 nm²/repeating unit.

The redox potential of 8a–d was measured to investigate the influence of substituents to the electron donating ability of the triphenylamine units. Figure 4 shows the cyclic voltammograms of 10 layers of 8a–d on the glassy carbon disk electrode, where a couple of redox peaks were observed. The results of the redox behavior of the LB films are summarized in Table I. The negative shift of the redox peaks in LB films possessing the substituted triphenylamines can be ascribed to increasing the electron density on triphenylamine unit. The value of $E_{1/2}$ indicated that the order of electron donating ability of each substituent was $—OCH_2 > —N(CH_3)_2 > —CH_3 > —H$, although the order of electron donating ability of these substituents was usually $—N(CH_3)_2 > —OCH_3 > —CH_3 > —H$. The cyclic voltammogram of 8d which was measured by sweeping to the high voltage is shown in Figure

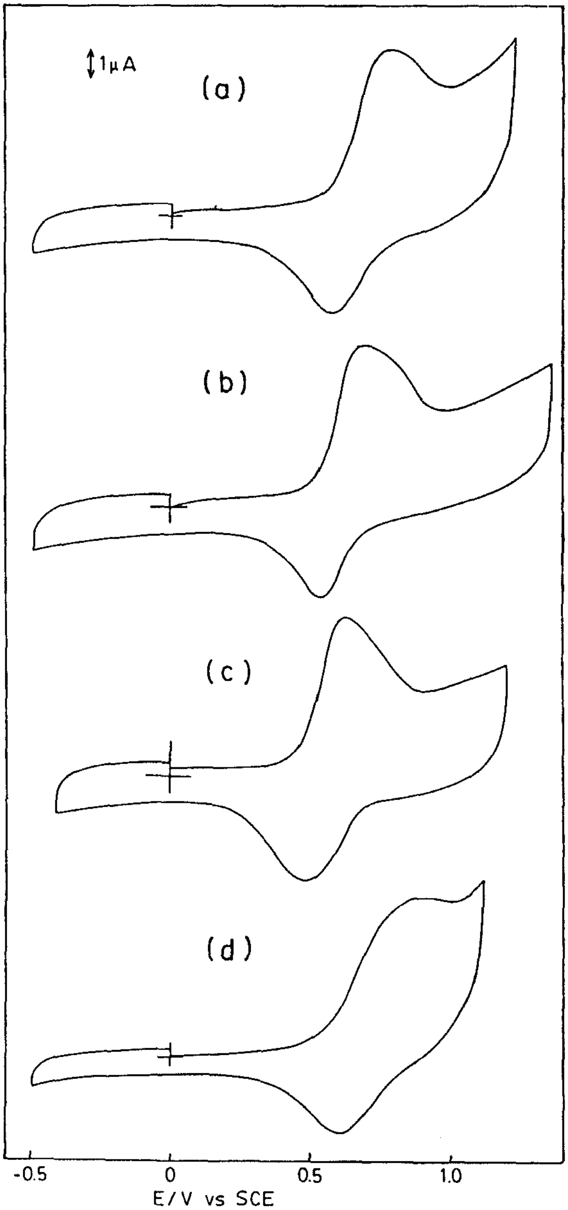


FIGURE 4 Cyclic voltammograms of LB films of 8a–d (10 layers) using a glassy carbon disk electrode in 0.1 M TEAP in acetonitrile. The potential sweep rate was 0.1 V/s. (a): 8a, (b): 8b, (c): 8c, and (d): 8d.

5. Two oxidation peaks were observed, where the first oxidation peak tended to shift to higher voltage by the overlapping effect of the second peak. This should be the reason that the observed electron donating order was different from the theoretical one.

TABLE I

Electrochemical properties of 1a–d

	E_{ox}	E_{red}	$E_{1/2}$
	(V vs. SCE)		
a) X= H	0.69	0.58	0.63
b) X= CH_3	0.69	0.53	0.61
c) X= OCH_3	0.63	0.51	0.57
d) X= $N(CH_3)_2$	0.67	0.50	0.58

a) Determined by cyclic voltammograms at a sweep rate of 0.1 V/s using 0.1 M TEAP in acetonitrile.

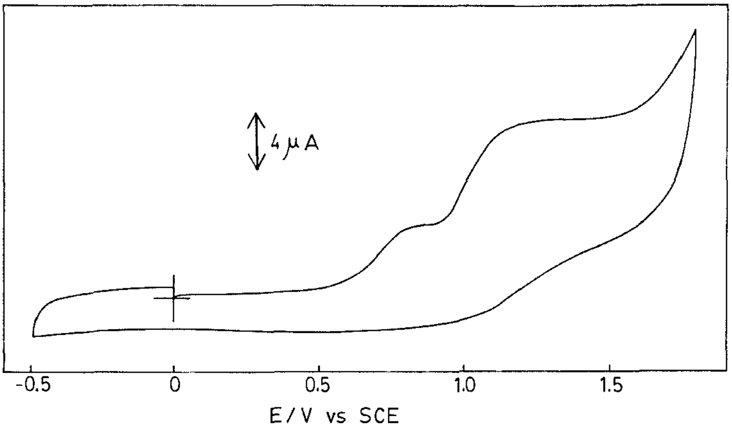
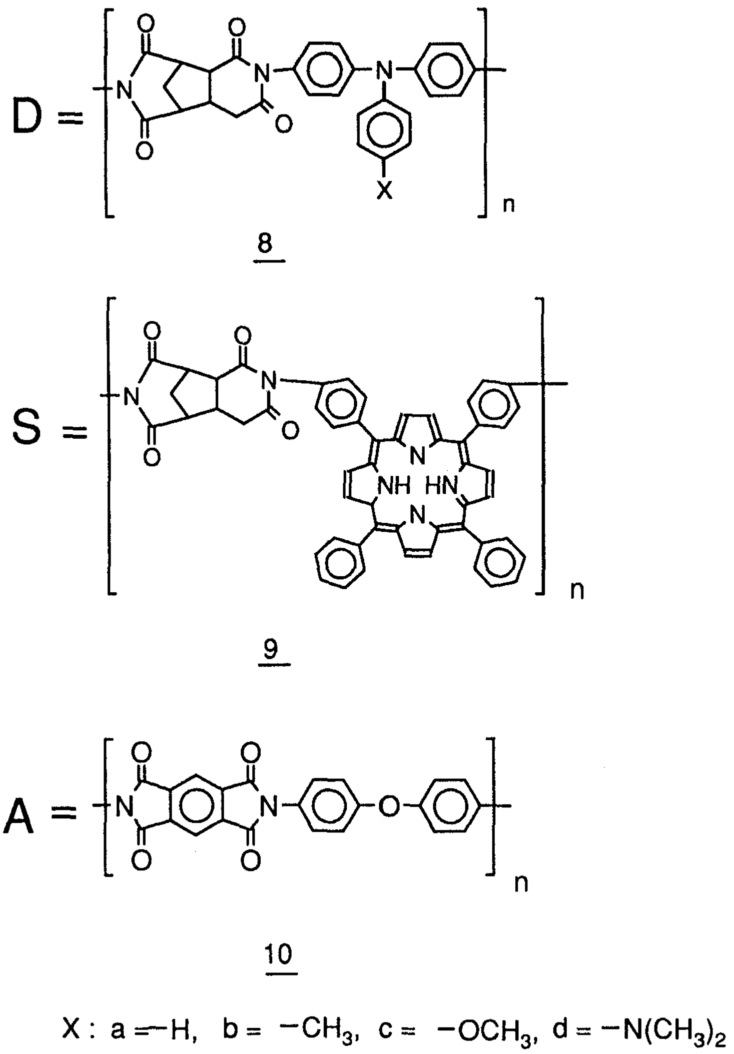


FIGURE 5 Cyclic voltammogram of LB film of 8d (10 layers) using a glassy carbon disk electrode in 0.1 M TEAP in acetonitrile. The potential sweep rate was 0.1 V/s.

The photodiodes were constructed by deposition of polyimides which possessed different chemical structure, i.e., triphenylamines as D, tetraphenylporphyrin as S, and aromatic polyimide as A as shown in Scheme 1. Aliphatic polyimide structure was incorporated into D and S layers, because aromatic polyimides readily accept electron. Two types of photodiodes having the structure of E/D/S/A and E/A/S/D were prepared on the semitransparent gold electrodes (E). E/D/S/A indicates that LB films are fabricated from the electrode to the electrolyte in the order of D, S, and A. The photocurrent-time curves were measured in two different systems, E/D/S/A = E/2/2/6 (a) and E/A/S/D = E/6/2/6 (b) as shown in Figure 6. E/A/S/D = E/6/2/6 means that the device is constructed by six layers of A, two layers of S,



X : a = $-$H, b = $-CH_3$, c = $-OCH_3$, d = $-N(CH_3)_2$

SCHEME 1

and six layers of D in this order from the electrode. The system of E/D/S/A gave cathodic photocurrent which included an initial large photocurrent (i_o) for a short period, followed by decaying process and the final residual photocurrent (i_r). This i_r, which was observed continuously until stopping the illumination of light, could be explained by the existence of a small amount of oxygen dissolved in the electrolyte solution which act as an electron acceptor (Figure 6 (a)). The magnitude of the i_r increased with increasing oxygen content controlled by stopping the babbling of nitrogen in the measurement system. On the other hand, the system of E/A/S/D gave anodic photocurrent, where the i_o was slightly smaller than that of the E/D/S/A system (Figure 6 (b)). The fact that the residual photocurrent (i_r) after the strong i_o was not observed in the E/A/S/D system supported existence of oxygen in the electrolyte.

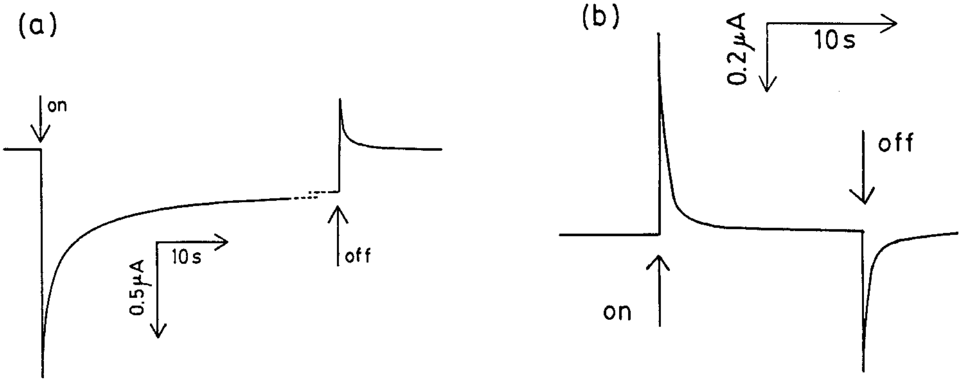


FIGURE 6 Photocurrent-time curves of (a): E/D/S/A = E/2/2/6, (b): E/A/S/D = E/6/2/6 systems under stepped illumination of monochromatic light of wavelength of 430 nm at an electrode potential of 0 V vs. SCE.

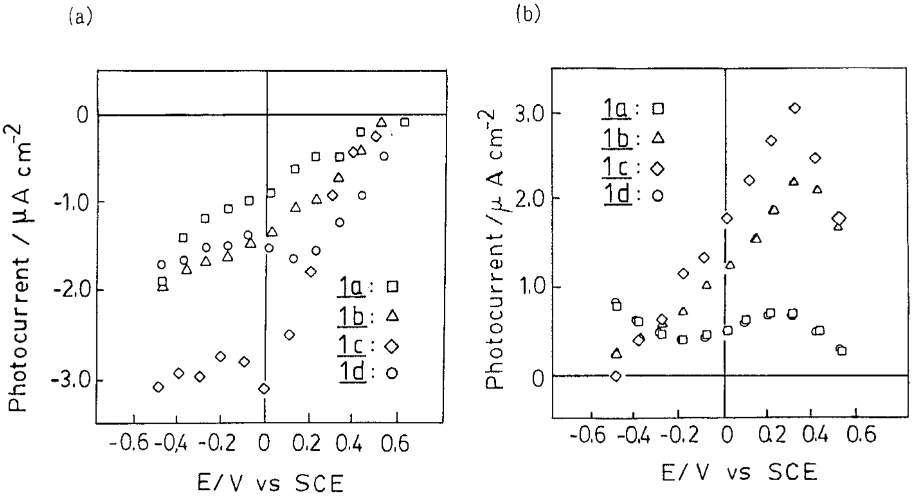


FIGURE 7 Potential dependence of peak photocurrents in the system of (a): E/D/S/A and (b): E/A/S/D.

Figure 7 shows the electric potential dependence of peak photocurrent (i_o) in E/D/S/A (a) and E/A/S/D systems (b) measured with varying the potential from −0.5 V to 0.5 V by 0.1 V step. The values of i_o depended on the electron donation of the functional groups attached to the triphenylamine unit, where the order was —OCH_3 > —$N(CH_3)_2$ > —CH_3 > —H. In the system using 8c as D layer, the best results of the maximum photocurrent (I_o) of 3 μA/cm^2 which was 5–10 times as large as that of the previous study[9] in both E/D/S/A and E/A/S/D systems were obtained. The order of I_o of each system was in agreement with the results of $E_{1/2}$ in the cyclic voltammograms.

Figures 8 and 9 show the dependence of photocurrent on the number of layers. For example, "E/D/S/A = E/X/2/6" indicates that the LB films were fabricated in the order of X layers of D, two layers of S, and six layers of A from the semi-

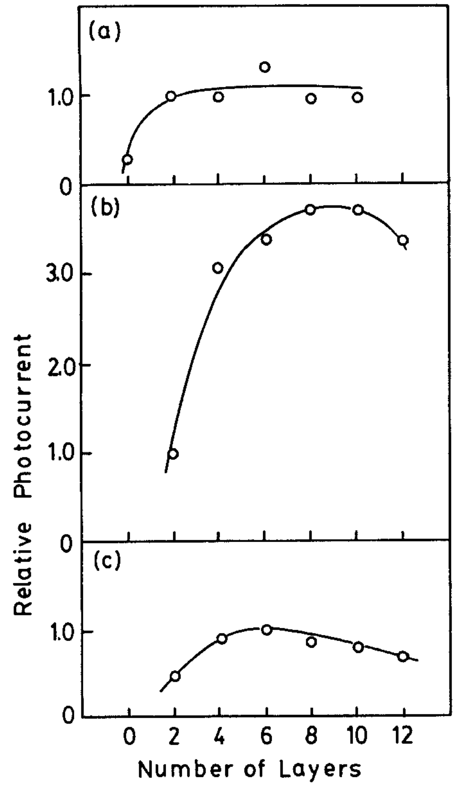


FIGURE 8 Dependence of the number of layers on relative photocurrent in the system of E/D/S/A. (a): E/X/2/6, (b): E/2/X/6, (c): E/2/2/X. The curves are normalized to the value of E/D/S/A = E/2/2/6.

transparent electrode surface to the electrolyte, where X means the number of variable layers and was changed from 0 to 10 or from 2 to 12. Polyimide 8c was used as D layer because of the excellent performance among the polyimide LB films possessing triphenylamines. The vertical axis of the figures is the relative value of the photocurrent and the curves are normalized to the value of E/D/S/A = E/2/2/6 or E/A/S/D = E/6/2/6. Such normalizing treatment was necessary because they were sensitive to the systematic adjustment, and the values of photocurrents observed in this study varied widely in each sample. For example, the formal efficiency of E/D/S/A = E/2/2/6 in Figure 8(a), 8(b), and 8(c) were 3.43×10^{-4}, 8.94×10^{-4}, and 4.60×10^{-4}, respectively.

As shown in Figure 8(a), only a small magnitude of photocurrent was observed in the case of D = 0, while the value of photocurrent increased with the existence of D layer, and kept almost the same value in the range from D = 2 to D = 12. Similarly, the photocurrent increased with increasing the number of D layer in the other photodiode system as shown in Figure 9(a). It was interesting that this system afforded the cathodic photocurrent (opposite direction photocurrent of D = 2–12) in the case of D = 0. This unusual observation should be caused by a small amount of oxygen dissolved in the electrolyte.

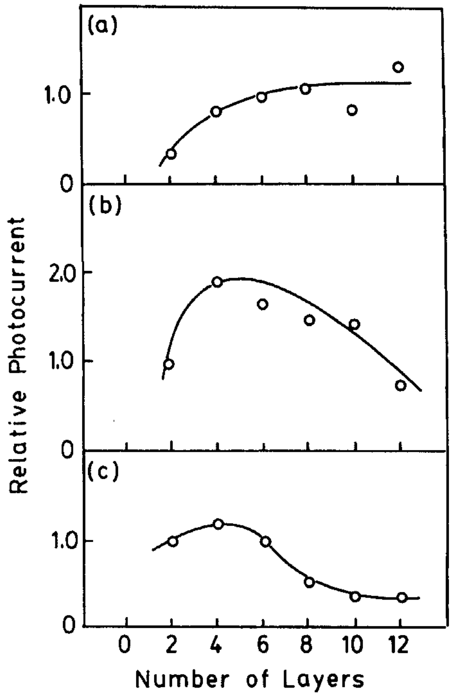


FIGURE 9 Dependence of the number of layers on relative photocurrent in the system of E/A/S/D. (a): E/6/2/X, (b): E/6/X/6, (c): E/X/2/6/X. The curves are normalized to the value of E/A/S/D = 6/2/6.

Here, if the rate of photocurrent decay ($T(t)$) is expressed as follows:

$$T(t) = i(t)/i_o \qquad (3)$$

where $i(t)$ is the value of the photocurrent at t second after illumination starts, and i_o is the value of initial photocurrent. In Figure 10, the values of $T(5)$ are plotted against the number of D layers, where $T(5)$ value increased with increasing the number of D layers. When the illumination of the light was stopped, anodic currents (i_b) due to the back electron transfer to oxidized D layer was observed in the E/D/S/A system. Figure 11 shows relationship between i_b and the number of D layer. The value of i_b decreased with increasing the number of D layer. These results of $T(t)$ and i_b suggested that the D layer had large hole mobility and led the systems effectively to charge separation.

Total charge, which was obtained in E/A/S/D systems by a sufficiently long period of illumination until the photocurrent completely decayed, was plotted against the number of D layers (Figure 12). Proportional increase of the charge was observed with increasing the number of D layers. The ratio of charges detected as photocurrent to the number of triphenylamine unit was estimated to be about 0.01.

Figure 9(b) and 9(c) indicate that the value of photocurrent decreased in the case more than 4 layers of A or S. Thus, both A and S layer had lower electron

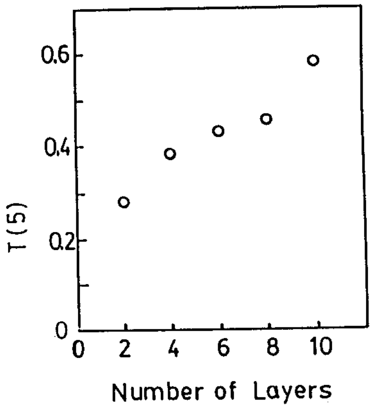


FIGURE 10 Dependence of the number of D layers on $T(5)$ in the system of E/D/S/A = E/X/2/6.

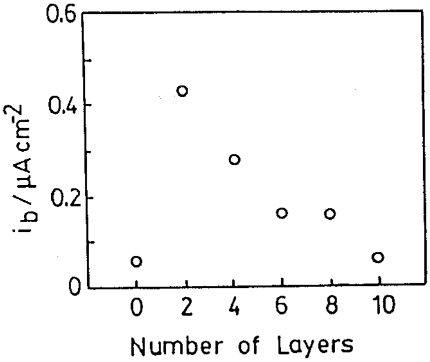


FIGURE 11 Dependence of the number of D layers on i_b in the system of E/D/S/A = E/X/2/6.

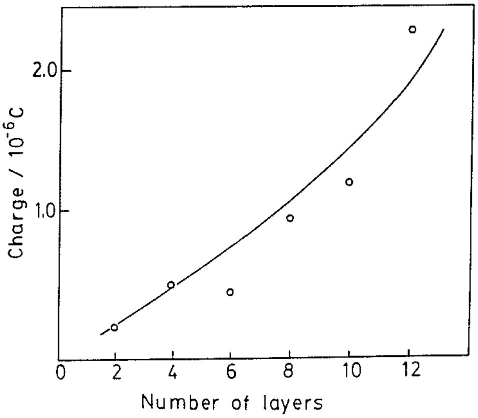


FIGURE 12 Dependence of the charge detected as photocurrent on the number of D layers in the system of E/A/S/D = E/6/2/X.

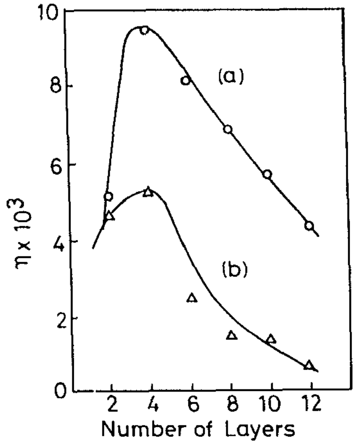


FIGURE 13 Dependence of the number of S layers on the quantum efficiency (η) in the system of a): E/D/S/A = E/2/X/6, and b): E/A/S/D = E/6/X/6.

mobility compared to D layer. The efficiency of transformation of the energy from light to electricity is expressed by the quantum efficiency (η) given in Equation (4)

$$\eta = i_e/i_2 \tag{4}$$

where i_e is the number of flowing photoelectrons and i_2 is the number of photons absorbed by S layers. The value of η is plotted against the number of S layers in Figure 13. The maximum of η was observed in the case of S = 4 in both systems of E/D/S/A (a) and E/A/S/D (b), and it decreased steeply if S had more than 4 layers. These phenomena suggested that the excited electron and the generated hole seemed to be difficult to move into S-A and D-S interfaces in the case of thicker S layers (S = 6–12). Thus, the charge separation should occur around the A-S and S-D interfaces.

In conclusion, novel photoconductive devices which showed extremely high photocurrents could be fabricated by using triphenylamine units as electron donating layer. The hole mobility in D layer seemed to be high, whereas the electron mobility in S and A layers was relatively low. The sensitizing unit only near D-S and S-A interfaces seemed to be excited and causes the electrical flow.

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