Molecular Photodiodes consisting of Polyimide Langmuir–Blodgett Films possessing Electron Acceptor, Photo-sensitizer, and Electron Donor Units

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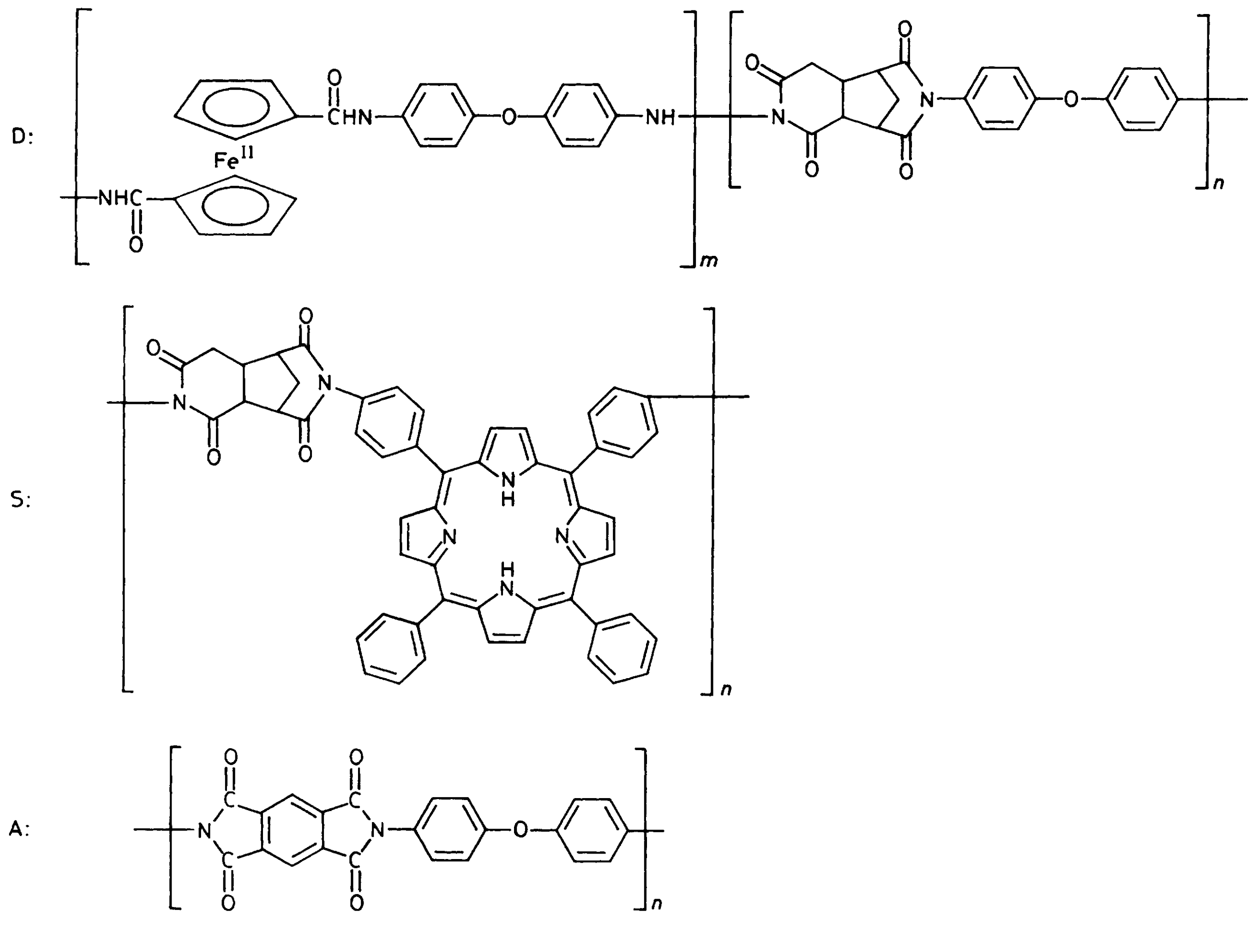
Molecular photodiodes possessing high efficiency for light–electricity conversion are constructed from polyimide Langmuir–Blodgett films consisting of electron acceptor, photo-sensitizer, and electron donor units.

It is well known that photosynthesis in plants is carried out by highly ordered electron transfer systems (redox systems). Artificial systems which mimic photosynthesis are of great importance from the viewpoint of biology[1] and energy transformation.[2] Simplified photosynthesis systems include the electron transfer model consisting of electron acceptor (A), photosensitizer (S), and electron donor (D),[3—7] where the system is driven as follows; the excited electron in S resulting from irradiaton transfers to A, and the electron missing from S is refilled from D. Thus, the electron transfer is observed as a unidirectional photocurrent only when the system is irradiated (photodiode). The important point of A–S–D photodiode systems is that the A, S, and D units should be well ordered with an asymmetric spatial arrangement to achieve the charge separation of electron donors and acceptors. The Langmuir–Blodgett (LB) technique is a suitable method for this purpose, because the films have an ordered layer structure at the molecular level.

We have reported the preparation and properties of polyimide LB films.[8—10] Since polyimide LB films have no long alkyl spacer chain between the layers (monolayer thickness 0.4—0.6 nm), electrons should be more readily transferred in A–S–D systems compared with conventional LB films. This paper deals with a new successful attempt to construct a photodiode consisting of three different types of polyimide LB films, *i.e.*, A, S, and D LB films.

Polyimides possessing ferrocene and tetraphenylporphyrin (TPP) units, and an unusual aromatic polyimide were chosen as D, S, and A, respectively. Since aromatic polyimides themselves act as electron acceptors,[11] aliphatic-based polyimides were used for D and S layers. The structures of each component are shown in Scheme 1. The polyimide LB films were prepared on a gold semitransparent electrode by the reported method.[8,9] Two kinds of electrodes were prepared. One possessed six layers of A, two layers of S, and six layers of D in this order from the gold electrode surface to the electrolyte (electrode I), and the other had the same structure without the layers of D (electrode II). Thus, these electrodes were A–S–D and A–S systems, respectively. The photoelectrochemical properties of the electrodes were investigated under nitrogen in electrochemical cells, in which the electrode I or II, a gold plate, and a saturated calomel electrode (SCE) were the working, counter, and reference electrodes, respectively. The LB films on the electrode were kept in contact with



Scheme 1

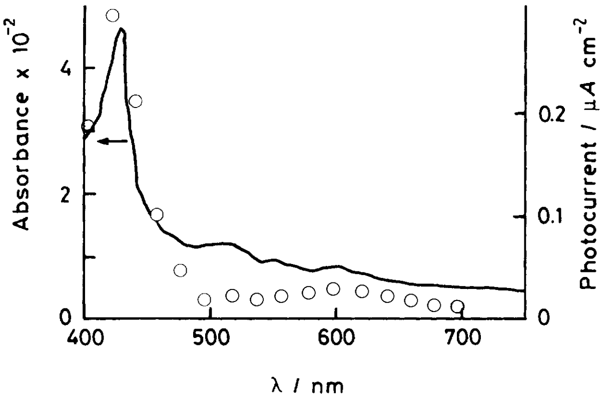


Figure 1. Photocurrent and visible absorption spectra of electrode I. Open circles: photocurrent spectrum; solid line: absorption spectrum.

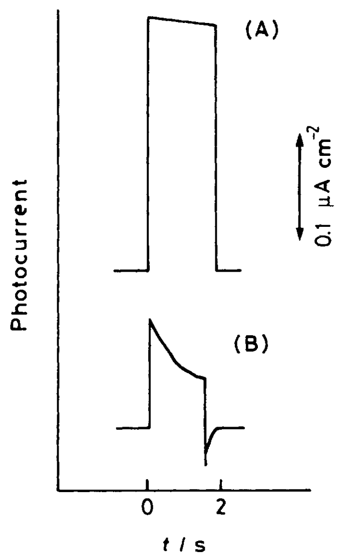


Figure 2. Photocurrent–time curve. (A): electrode I; (B): electrode II.

an aqueous electrolyte solution containing 100 mM KCl. Monochromatic light (430 nm) was used to measure the photocurrent.

Figure 1 shows the absorption and photocurrent spectra of electrode I in the visible region >400 nm. The absorption spectrum was almost the same as that of the LB film of S itself, because D and A had very weak absorptions in this region. The fact that the two spectra in Figure 1 are very similar to each other suggests that the photocurrent was generated only by the absorption of the light through the TPP unit. The photocurrent–time curves under stepped illumination at 0 V *vs.* SCE are shown in Figure 2. The photocurrent was observed only on irradiation; for electrode I the photocurrent was 0.28 μA/cm^2 with a long lifetime, and the quantum efficiency was as high as 1.1 × 10^{-2}. These magnitudes are about 5—10 times larger than those for photodiode systems reported by us previously.[5—7] In contrast, the photocurrent of electrode II decreased within a second with a lower current. These results indicate that electrons were smoothly transferred from D to S to refill the electron deficit in S.

In conclusion, an A–S–D type molecular photodiode with a high photocurrent could be successfully constructed using polyimide LB films. The high efficiency of the light–electricity conversion results from the absence of a long alkyl chain between each layer.

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References

1 *E.g.*, A. L. Lehninger, 'Biochemistry,' 2nd edn., Worth, New York, 1975.

2 *E.g.*, H. Kuhn, *Thin Solid Films*, 1983, **99**, 1.

3 N. Mataga, A. Karen, T. Okada, S. Nishitani, N. Kurata, Y. Sakata, and S. Misumi, *J. Phys. Chem.*, 1984, **88**, 5138.

4 T. A. Moore, D. Gust, P. Mathis, J-C. Mialocq, C. Chachaty, R. V. Bensasson, E. J. Lando, D. Doizi, P. A. Liddell, W. R. Lehman, G. A. Nemeth, and A. L. Moore, *Nature*, 1985, **307**, 630.

5 M. Fujihira, K. Nishiyama, and H. Yamada, *Thin Solid Films*, 1985, **132**, 77.

6 M. Fujihira and H. Yamada, *Thin Solid Films*, 1988, **160**, 125.

7 M. Fujihira, K. Nishiyama, and H. Yoneyama, *Nippon Kagaku Kaishi*, 1987, 2119.

8 M. Suzuki, M. Kakimoto, T. Konishi, Y. Imai, M. Iwamoto, and T. Hino, *Chem. Lett.*, 1986, 395.

9 M. Kakimoto, M. Suzuki, T. Konishi, Y. Imai, M. Iwamoto, and T. Hino, *Chem. Lett.*, 1986, 823.

10 Y. Nishikata, M. Kakimoto, A. Morikawa, I. Kobayashi, Y. Imai, Y. Hirata, K. Nishiyama, and M. Fujihira, *Chem. Lett.*, 1989, 861.

11 S. Mazur, P. S. Lugg, and C. Yarnitzky, *J. Electrochem. Soc.*, 1987, **134**, 346.