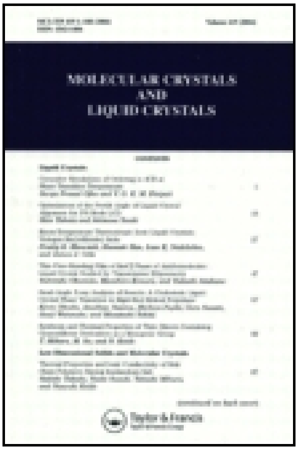

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Transient and Steady Photoelectric Responses of LB Films Containing Amphipathic Porphyrin and Redox Chromophores

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Version of record first published: 24 Sep 2006.

To cite this article: Toshihiko Nagamura , Shigenobu Kamata , Kenji Toyozawa & Teiichiro Ogawa (1993): Transient and Steady Photoelectric Responses of LB Films Containing Amphipathic Porphyrin and Redox Chromophores, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 227:1, 171-182

To link to this article: http://dx.doi.org/10.1080/10587259308030970

Mol. Cryst. Liq. Cryst. 1993, Vol. 227, pp. 171–182
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Printed in the United States of America

TRANSIENT AND STEADY PHOTOELECTRIC RESPONSES OF LB FILMS CONTAINING AMPHIPATHIC PORPHYRIN AND REDOX CHROMOPHORES

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Abstract Sandwich type cells of LB films containing amphipathic porphyrin monolayers (**P**) and carbazole or alloxazine derivatives in monolayers adjacent to **P** were constructed between ITO and Al electrodes. The action spectra of steady and transient photocurrents corresponded well with the absorption spectrum of porphyrin in LB films. Transient photocurrents upon excitation of porphyrins with a dye laser were observed in LB films, which showed a fast rise and a slow exponential decay. The decay behavior and the values of steady photocurrents depended on the nature of redox chromophores and the extent of their aggregation together with the bias voltage. From these results, redox chromophores were concluded to retard the decay of photocarriers in monolayers adjacent to LB films containing porphyrin which generated them.

INTRODUCTION

We have been studying photophysical and photochemical properties of LB films in order to construct molecular electronic and photonic devices in the near future.[1-16] Photoinduced electron transfer reactions in

LB films are among the most important to be controlled at the molecular level to achieve such purposes. We have already reported reversible colour changes[3,6,9,15] and photochemical control of second order optical nonlinearity[11,13] in LB films based on photoinduced electron transfer reactions. Several reports have recently been made on time-dependent photoelectric responses in LB films.[1,5,14,17-22] These experiments will give direct information on relaxation times of photocarriers or the mechanism of photoconduction in LB films. We have first reported transient photocurrents in LB films consisted of monolayers of photoreaction center porphyrin and monolayers of long-chain fatty acids.[1] We have also reported transient photocurrents in LB films containing porphyrin and redox chromophores.[5,14] It was found from these results that most photocarriers generated from excited porphyrins decayed in monolayers of fatty acids and that the decay was controlled by incorporating redox chromophores.[1,5,14] In the present paper transient and steady photoelectric responses of

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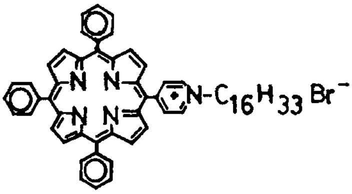

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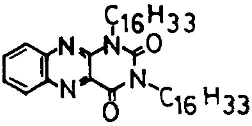

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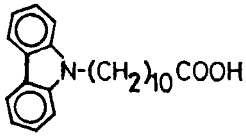

4 $C_{19}H_{39}COOH$

5 $C_{15}H_{31}COOH$

FIGURE 1 Structure and abbreviations of the compounds employed.

composite LB films consisted of amphipathic porphyrin 1 and redox compounds such as 1,3-dihexadecylalloxazine 2 or 11-(9-carbazolyl)-undecanoic acid 3 will be discussed in details.

EXPERIMENTAL

Arachidic acid 4 and palmitic acid 5 were also used to prepare good quality LB films of chromophores. The structure and abbreviations of the compounds employed in the present experiment are shown in FIGURE 1. Five monolayers of a mixture of 1 and 4 (1:5, denoted as **P**) were deposited from an aqueous subphase containing 0.25 mM $CdCl_2$ and 0.05 mM $NaHCO_3$ (pH 6.3) at 18 °C, 20 $mN{\cdot}m^{-1}$ as Y-type films on an ITO substrate. Two monolayers of 2 or 5 alone, mixtures of 5 and 3 (2 - 25 mol%) or 4 and 2 (17 mol%) were further deposited at 15 or 18° C and 20 $mN{\cdot}m^{-1}$. These LB films are abbreviated to PCUA0, PCUA2, PCUA5 and PCUA25, or PD0, PD17 and PD100 systems corresponding to the molar

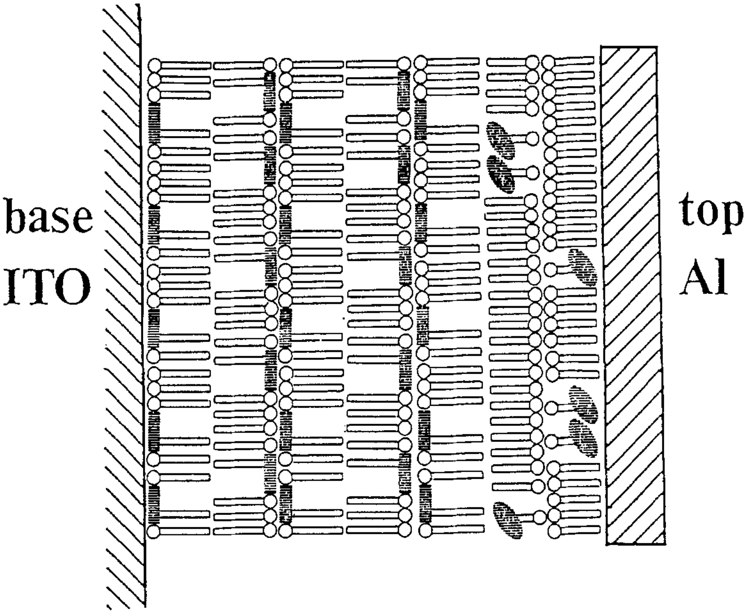

FIGURE 2 Schematic representation of composite LB films sandwiched between ITO and Al electrodes for a PCUA5 system as an example.

fraction(%) of 3 or 2, respectively. LB films of six monolayers of P deposited on one monolayer of 4 were also prepared, which is abbreviated to A1P6. Aluminum was vacuum evaporated onto LB films as a sandwich-type electrode. A schematic representation of a PCUA5 system between electrodes is shown in FIGURE 2.

These LB films set in a cryostat were irradiated by a 150 W Xe lamp through a 10 cm water filter, an L-35 or L-39 filter, and a monochromator. Steady photocurrents were observed by an electrometer. Transient photocurrents upon excitation of LB films with a dye laser (Molectron DL-14P pumped by UV24 nitrogen laser, about 30 μJ, 10 ns) were measured by the use of a high speed current amplifier (Ithaco 1211) at 10^5 - 10^6 V•A^{-1} gain and a digital memory (Iwatsu DM-2350, 10 bit, 2 channels). A block diagram of the measurement system of transient photocurrents is shown in FIGURE 3. The relative intensity of a dye laser was monitored by a photodiode and was recorded simultaneously with amplified photocurrents with a digital memory.

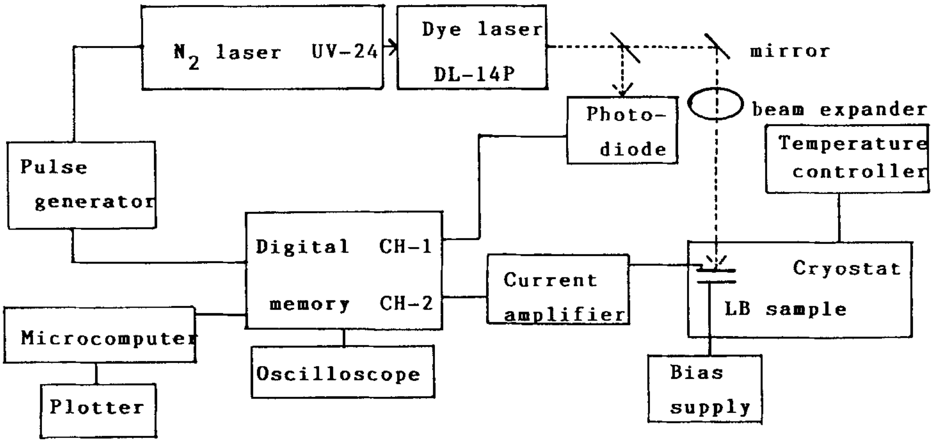

FIGURE 3 A block diagram of the measurement system of transient photocurrents in LB films excited with a dye laser.

RESULTS AND DISCUSSION

Surface pressure - molecular area (π - A) isotherms for (a) 4, (b) 4 + 2 (17%), and (c) 2 on an aqueous subphase containing 0.25 mM $CdCl_2$ and 0.05 mM $NaHCO_3$ (pH 6.3) at 18°C showed stable solid condensed phase. The limiting area was (a) 0.20, (b) 0.30, and (c) 0.78 nm^2, respectively, which showed a homogeneous mixing of 4 and 2 in (b). The π - A isotherms for mixtures of 5 and 3 have been reported previously.[12]

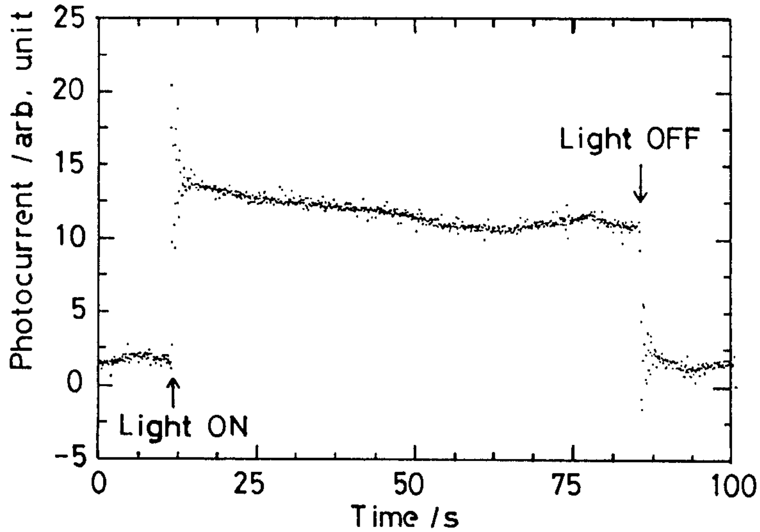

FIGURE 4 Steady photocurrents observed for an AlP6 system excited at 525 nm with a Xe lamp.

Steady photocurrents were observed for these LB systems as shown in FIGURE 4 for an AlP6 system excited at 525 nm and zero bias voltage. The action spectra of steady photocurrents corresponded well with the absorption spectrum of 1 in LB films for all systems studied except those containing 2 which gave additional photocurrents below about 425 nm due to alloxazine chromophore.[2] The action spectrum of short circuit photocurrents for an AlP6 system is shown in FIGURE 5 as an example together with the intrinsic current quantum efficiency ϕ, which was independent of the wavelength. LB films of 3 did not absorb above about 380 nm. Positive steady photocurrents were observed with bias voltages higher than about -0.4 V to Al, below which the polarity reversed. Steady photocurrents increased with bias voltages in all LB films containing redox chromophores and/or long-chain fatty acids

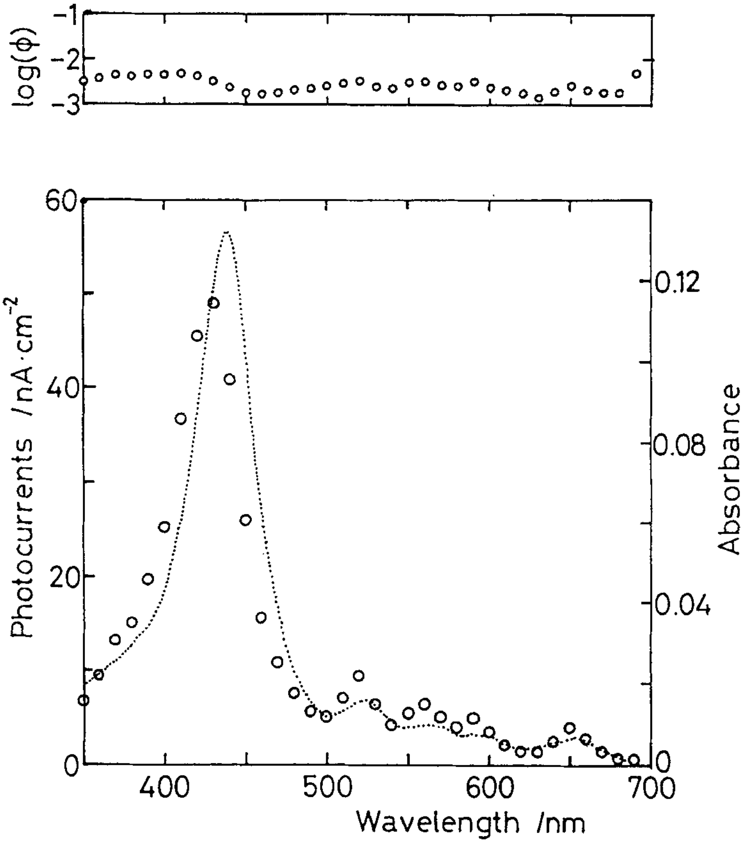

FIGURE 5 The action spectrum of steady photocurrents for an AlP6 system and the intrinsic current quantum efficiency ϕ.

in addition to **P** as shown in FIGURE 6 for LB films containing 3 as an example. Steady photocurrents in LB films containing redox chromophores further depended on the molar fraction of chromophores. They decreased in the order of PCUA5 > PCUA25 > PCUA2 > PCUA0 in LB films containing carbazole derivatives as shown in FIGURE 6. Meanwhile, they increased with increasing the molar fraction of 2 in the case of LB films of alloxazine derivatives.[5] These results indicated that the incorporation of carbazole or alloxazine derivatives into LB films of long-chain fatty acid contributed to increase steady photocurrents.

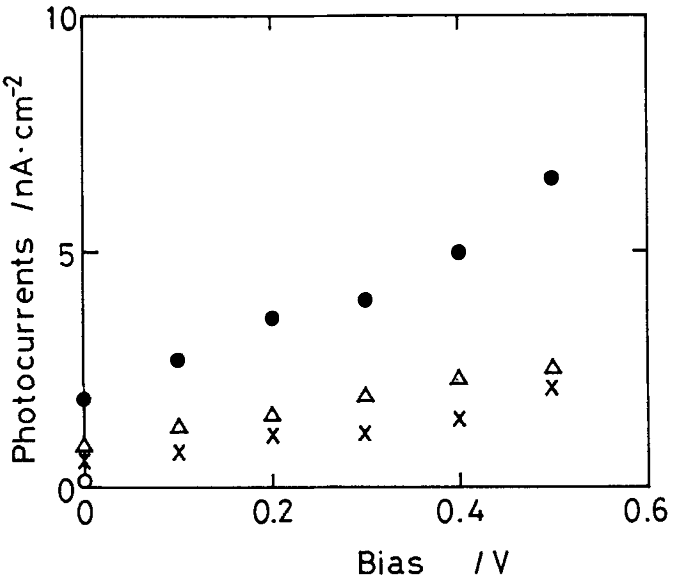

FIGURE 6 Steady photocurrents with various bias voltages for (●) PCUA5, (△) PCUA25, (X) PCUA2, and (○) PCUA0 LB systems excited at 525 nm .

Transient photocurrents upon excitation of porphyrin 1 in LB films with a pulsed dye laser showed a fast rise and a slow decay in all LB films containing porphyrin 1.[1,5,14] No transient photocurrents were observed for LB films of fatty acid 4 or 5 alone. The dependences of transient photocurrents on the wavelength of a dye laser corresponded well with the absorption spectrum (Q-band) of 1. These results clearly indicated that observed transient photocurrents were due to the movement of photocarriers generated by the excitation of porphyrin in LB films. The rise was controlled by the time resolution of a current amplifier (4 - 6 μs). The decay was found to depend on the bias voltage, the nature and fraction of chromophores in mixed monolayers with fatty acids adjacent to porphyrin LB films. The logarithmic plots of transient photocurrents are shown in FIGURE 7 for an AlP6 system at various bias voltages to Al at 525 nm. Transient photocurrents were hardly detected at bias voltage of -0.4 V, below which the polarity of transient photocurrents reversed. The effects of bias voltages on the polarity and values of transient photocurrents cor

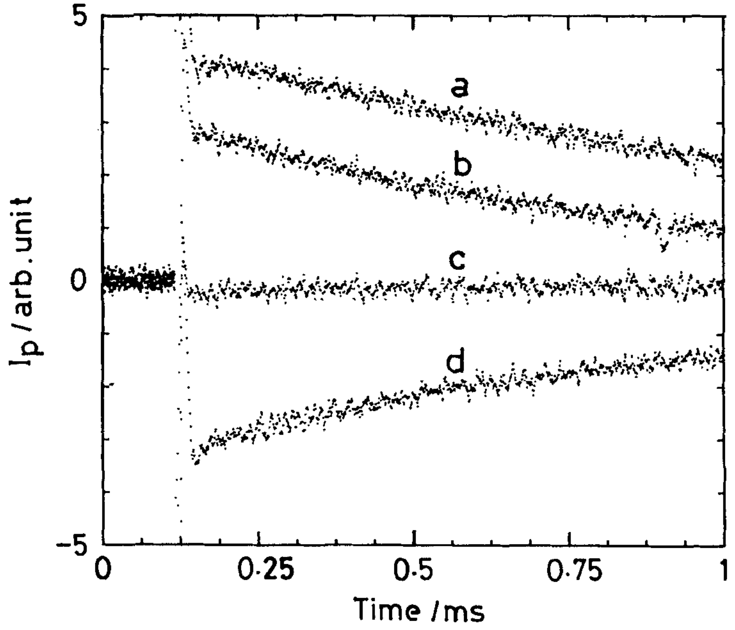

FIGURE 7 Logarithmic plots of transient photocurrents for an AlP6 system at bias voltage to Al: (a) +0.80, (b) +0.20, (c) -0.40, and (d) -1.20 V.

responded well with those of steady photocurrents mentioned above. It was due to the difference of work functions of Al (4.26 eV) and ITO.[23] Similar logarithmic plots are shown in FIGURE 8 for short circuit photocurrents in (a) PD100, (b) PD17, and (c) PD0 systems, all of which showed the exponential decay. The decay became slower by incorporating alloxazine derivatives 2 in cadmium arachidate matrix. In a PD100 system which contained two monolayers of pure 2, the decay was markedly retarded. With increasing bias voltages, the decay became slower and the extent of changes depended on the molar fraction of 2.[5] Transient photocurrents decayed exponentially in all LB systems studied. The lifetime defined as the slope of logarithmic plots of transient photocurrents vs. time depended on the molar fraction of 3 and bias voltage. The lifetime gradually increased with increasing bias voltages in all systems.[1,5,14] The lifetime at the same bias

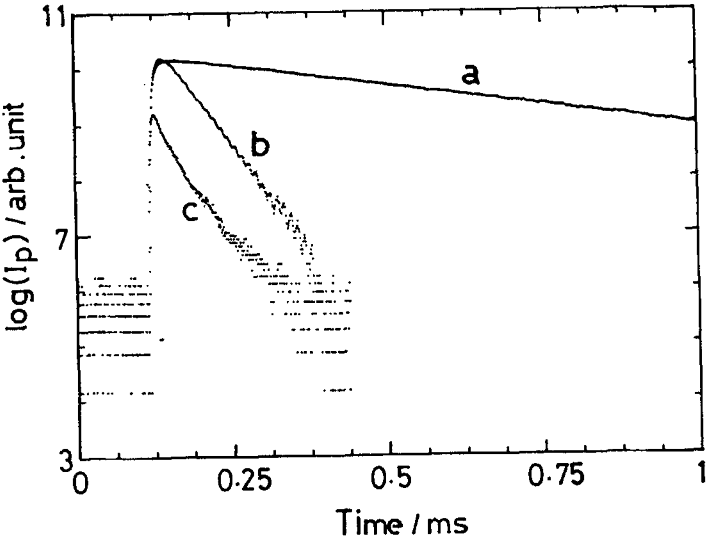

FIGURE 8 Logarithmic plots of short circuit transient photocurrents for (a) PD100, (b) PD17, and (c) PD0 systems excited at 525 nm.

voltage for LB films containing 3 decreased in the order of PCUA5 > PCUA25 > PCUA2~PCUA0.

The apparent lifetime of the transient photocurrents increased with bias voltages in all systems studied. The extent of the increase was much smaller in a PD100 system as compared with other systems. As pointed out previously[1], these results cannot be explained by a simple tunneling mechanism in which no decay of carriers are assumed before reaching electrodes, but strongly suggest that most photocarriers are disappeared or are trapped on the way of transfer processes. As long as the relaxation time required for tunneling conduction which was estimated to be 1 - 10 ms for arachidate monolayers or their equivalent[24,25] is longer than the "lifetime" of the photocarriers, determined by various decay processes, the apparent lifetime observed will increase as the probability of capture of photocarriers decreases. The increase of lifetime with bias voltages can be explained qualitatively by assuming that the increased velocity of photocarriers at high bias voltage decreased the probability of capture of the photocarriers by recombination sites or "traps".[1] It has been shown that such decay of photocarriers observed by transient photocurrents also controls the steady photocurrents, which are namely shown to be directly proportional to the lifetime of transient photocurrents if they decay exponentially.[1]

The incorporation of 2 or 3 having redox chromophores such as alloxazine or carbazolyl groups into LB films composed of arachidic acid 4 or palmitic acid 5 increased the lifetime of photocarriers as shown in FIGURE 8 for 2. These results contributed to increase steady photocurrents in LB films containing 2 or 3 as mentioned above. The thickness of 2 or 3 in LB films was presumed to be almost equal to that of 4 or 5, respectively, from X-ray diffractions[12] or the CPK molecular packing model. Therefore, it can be concluded that redox chromophores are effective to retard the decay of photocarriers in LB films composed of saturated hydrocarbons during their transfer processes presumably by superexchange interactions, which are considered to be effective in long distance electron (hole) transfer in rigid matrix or in biological systems.[26-29] This idea was based on wave function propagation via nearest-neighbor exchange interactions and was applied to the through bond electron transfer. Aromatic chromophores having -electrons have been reported to facilitate the electron transfer reaction by a superexchange mechanism between donors and acceptors linked by them as a bridge.[30] Redox chromophores in LB films are expected to make the transfer of photocarriers easier by through-bond electronic exchange interactions and to form much less "deep" traps as would be expected in long-chain fatty acid monolayers.

In the case of LB films containing carbazolyl chromophores, both steady photocurrents and the lifetime of transient photocurrents decreased in a PCUA25 system as compared with a PCUA5 system. It can be explained as follows.[14] From the energy transfer experiments it was found that the extent of aggregation of carbazolyl chromophores in mixed LB films of 3 with long-chain fatty acids markedly depended on the molar fraction of 3.[8] Chromophores of 3 were almost homogeneously dispersed in LB films if their fraction was less than about 5%. Above that value molecules 3 became segregated in a matrix of fatty acids, the extent of which rapidly increased with the molar fraction of 3. The excimer emission was observed in LB films with higher molar fraction of 3.[8] The excimer sites in poly(N-vinylcarbazole) are known to work as traps of singlet excitons and photocarriers. The probability of photocarriers to be trapped at such excimer sites will be much higher in LB films with higher molar fraction of 3 since the extent of aggregation of carbazolyl chromophores became considerably larger.[8] No excimer was observed in LB films of alloxazine derivative 2, the chromophores of which were arranged in LB films as parts of hydrophilic groups.[2] These results most probably contributed the longest lifetime and much smaller change of the lifetime with bias voltage in the PD100 system containing 100% alloxazine derivatives.

CONCLUSION

From transient and steady photoelectric responses of LB films composed of porphyrin monolayers and adjacent monolayers of carbazole or alloxazine derivatives, it was indicated that redox chromophores effectively increased photocurrents in LB films by decreasing the decay processes of photocarriers generated from the excited porphyrin.

Acknowledgment

This work was partly supported by the Grant-in-Aid for the Priority Area Research Project (No. 03205055, 04205059) from the Ministry of Education, Science and Culture, Japan, and the CIBA-GEIGY Foundation (Japan) for Promotion of Science.

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