Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Effect of Chromophore Aggregation in the Langmuir Multilayer Photoconductors

Michio Sugi [a], Tsunekatsu Fukui [a], Sigeru Iizima [a] & Keiji Iriyama [b] [c]

[a] Electrochemical Laboratory, 1-1-4 Umezono, Sakura-mura, Niihari-gun, Ibaraki, Japan

[b] Research Institute for Polymers and Textiles, 1-1-4 Yatabe-Higashi, Tsukuba, Ibaraki, Japan

[c] Jikei University Medical School, Minato-ku, Tokyo, Japan

Version of record first published: 21 Mar 2007.

To cite this article: Michio Sugi , Tsunekatsu Fukui , Sigeru Iizima & Keiji Iriyama (1980): Effect of Chromophore Aggregation in the Langmuir Multilayer Photoconductors, Molecular Crystals and Liquid Crystals, 62:3-4, 165-172

To link to this article: http://dx.doi.org/10.1080/00268948008084019

Mol. Cryst. Liq. Cryst., 1980, Vol. 62, pp. 165–172
0026-8941/80/6204–0165$06.50/0

Printed in the U.S.A.

Effect of Chromophore Aggregation in the Langmuir Multilayer Photoconductors

MICHIO SUGI, TSUNEKATSU FUKUI, and SIGERU IIZIMA
Electrochemical Laboratory, 1-1-4 Umezono, Sakura-mura, Niihari-gun, Ibaraki, Japan.

and

KEIJI IRIYAMA†
Research Institute for Polymers and Textiles, 1-1-4 Yatabe-Higashi, Tsukuba, Ibaraki, Japan.

(*Received July 7, 1980*)

The effect of chromophore aggregation upon the photoconductivity in the dye-sensitized Langmuir films has been examined employing three derivatives of a surface-active merocyanine with a rhodanine nucleus. The values of the lateral component $\Delta\sigma t$ and the anisotropy ratio $\Delta\sigma_{\parallel}/\Delta\sigma_{\perp}$ for the case with a strongly developed aggregate are found to be more than a decade larger than those for no or incomplete aggregation.

Recently, a group of new surface-active dyes have been developed,[1–3] which are suitable to construct highly photoconductive Langmuir films. They are merocyanines with a rhodanine nucleus, whose chemical structures are shown in Figure 1 (a) as DX with X=O, S or Se.[4] Mixed monolayers of DX with arachidic acid (C_{20}) were found to be stable enough upon an aqueous subphase containing Cd^{++} ions to form multilayers.

In a previous paper,[2] we have reported the anisotropic photoconduction in a system $[DS]:[C_{20}] = 1:2$. The ratio between the lateral and the normal

---

† Present address: Jikei University Medical School, Minato-ku, Tokyo, Japan.

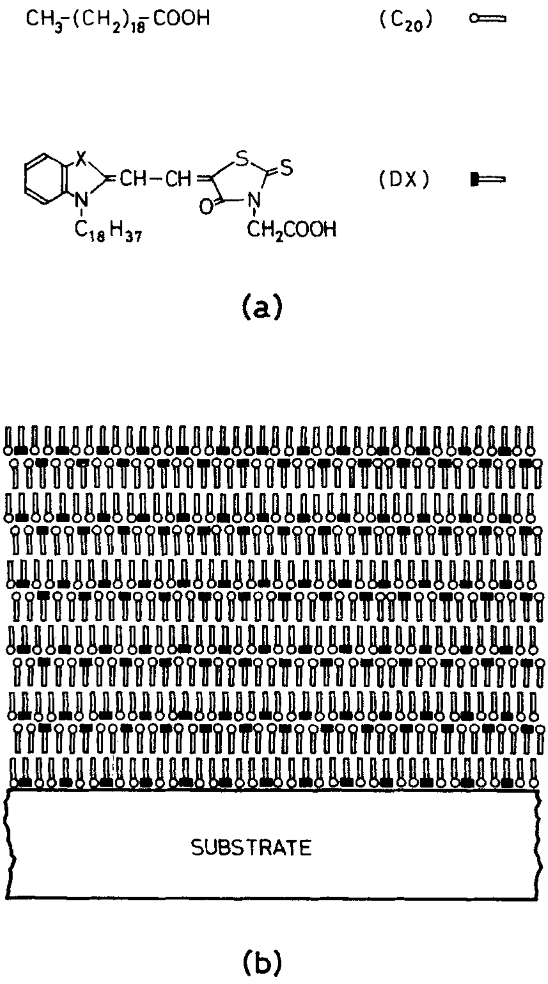

FIGURE 1 (a) Chemical structures of the monolayer-forming materials, arachidic acid (C_{20}) and the surface-active merocyanines (DX with X = O, S and Se). (b) Schematic representation of a Y-type Langmuir assembly of a mixed system DX–C_{20}, where the case of ideal mixing is shown.

photoconductivites was found in this system to be $\Delta\sigma_{\parallel}/\Delta\sigma_{\perp} = 10^3 \sim 10^4$. A remarkable difference in shape was observed between the photoconductivity action spectra for both directions and the absorption spectrum. The action spectra lacked structures corresponding to the red-shifted aggregate band seen in the absorption spectrum. This is rather striking, since it is widely accepted that a red-shifted band such as a J-band results in an enhanced photoelectric effect.[5] Indeed, Iriyama, Mizutani and Yoshiura[3] have reported the enhanced photocurrent of SnO_2 electrode with a cast-film of DS associated with the formation of J-like band when it is subjected to an alkaline electrolyte solution. Further, they successfully controlled, starting from their as-cast films without aggregate bands, the extent of aggregation of chromophores by changing the pH-value and the ionic strength of the electrolyte in their electrochemical measurements.

In the Langmuir multilayer samples, however, it is difficult to control the chromophore aggregation to that extent, since the required treatments often contradict to the conditions for retaining either the stable Y-type film structure or the good electrode contacts. To avoid this difficulty, we have employed the other two dyes, that is, DO and DSe in place of DS, mixed with C_{20}. The DO containing multilayer films exhibit no discernible aggregate band, while the DSe aggregate is typically formed to result in a prominent J-like band. In this paper, we report the effect of chromophore aggregation upon the photoconduction and its anisotropy by referring to the results from these two extremes represented by the DO and DSe systems in comparison to those for DS as the intermediate case.

The mixed solution of DX with C_{20} in $CHCl_3$ was applied onto an aqueous subphase containing about 4×10^{-4} M $CdCl_2$ to form a monolayer under a surface pressure of approximately 25 dynes/cm as before.[2] The molar ratio of the mixed solution was $[DX]:[C_{20}] = 1:2$ as in the previous work. The pH-value and the temperature of the subphase were pH $= 5.8 \sim 5.9$ and 22°C ~ 24°C for DO and DSe, while pH $= 6.4 \sim 6.5$ and 21°C ~ 23°C were adopted for DS in the previous experiment. The number of monolayers deposited was $M = 15$ or 31. After the deposition, three junctions were formed on each specimen by vacuum-evaporating aluminum through a mask as shown in either Figure 2(a) or Figure 2(b), each corresponding to the gap cells or the sandwich cells.

The admittance of junctions was obtained by analyzing Lissajous's figures,[6] as in the previous work,[2] The lateral and normal photoconductivities $\Delta\sigma_{\parallel}$ and $\Delta\sigma_{\perp}$ were evaluated from the conductance increments $\Delta G_{\parallel}$ and $\Delta G_{\perp}$ of the gap-cell and sandwich-cell junctions, respectively, under illumination in a dry nitrogen ambient (24°C ~ 26°C) by assuming the monolayer thickness $l = 2.8 \times 10^{-7}$ cm[7]. For the detailed description of the evaluation, the readers are referred to Ref. 2.

Figure 3 shows the action spectra for the DO multilayer together with the absorption spectrum. The photoconductivities $\Delta\sigma_{\parallel}$ and $\Delta\sigma_{\perp}$ in the figure are either interpolated or extrapolated values for an illumination level of 10 mW/cm^2 as in the previous report for the DS containing system.[2] The absorption spectrum for the DO system shows no discernible aggregation and can be characterized as a single-peaked monomer band centered around 500 nm with a fair symmetry. The action spectra are correspondingly

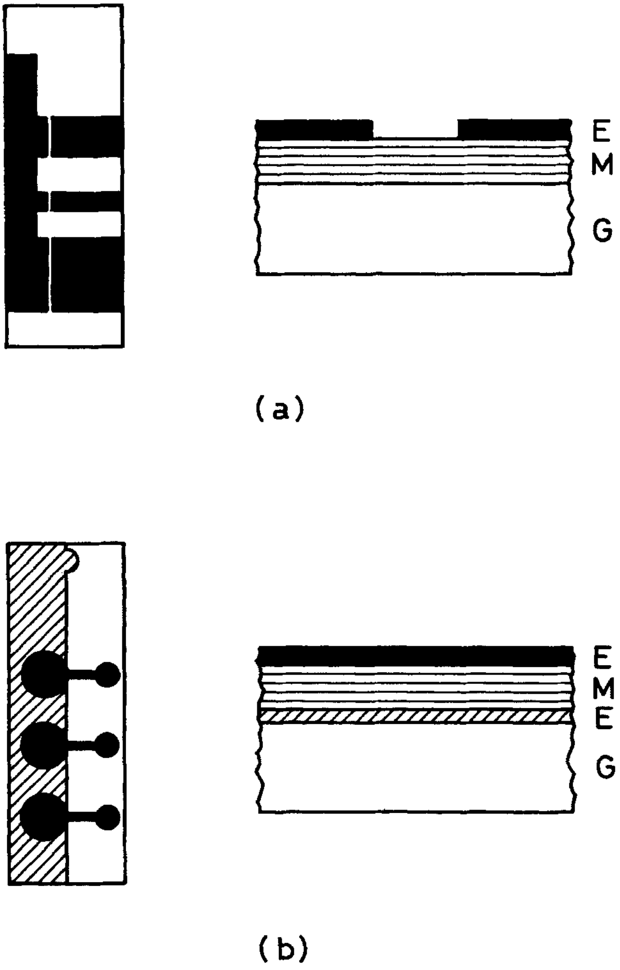

FIGURE 2 The specimen geometries of a gap cell (a) and a sandwich cell (b). G is the glass substrate ($\frac{1}{4}$ of an ordinary slide glass), M the Langmuir multilayer film, and E. the electrodes, where the hatched one denotes that it is semitransparent (about 50 %).

single-peaked with their maxima coinciding well with that of the absorption spectrum. These present a keen contrast to the case of DS reported before, in which the action spectra share a common feature but lack counterparts of the aggregate band clearly seen in the absorption spectrum.

The three spectra for the DSe multilayer are shown in Figure 4. The chromophore aggregation is the case with the DSe containing film, which exhibits a pronounced band around 600 nm as seen in the figure. The two action spectra are in this case largely different from each other. The lateral

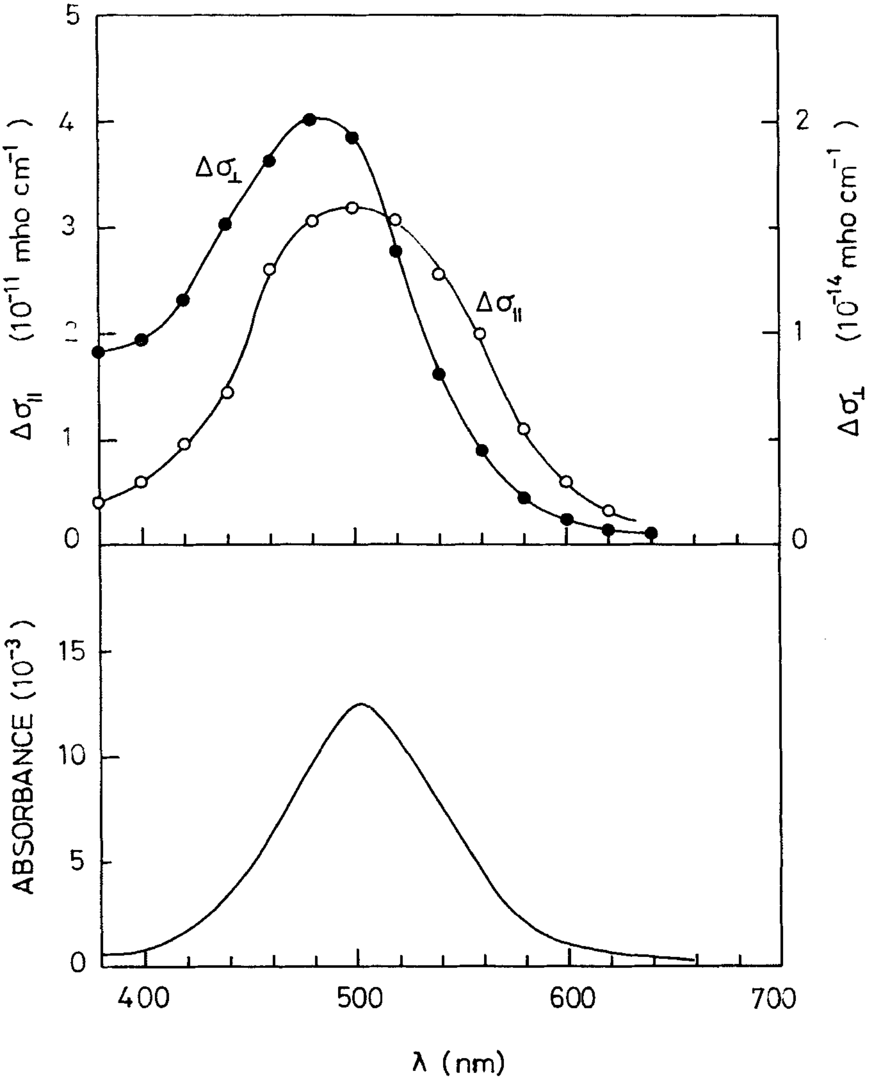

FIGURE 3 Examples for DO system. The lateral and normal photoconductivities $\Delta\sigma_{\parallel}$ (○) $\Delta\sigma_{\perp}$ (●) at 10-mW/cm^2 illumination level, and the absorbance per monolayer of a fifteen-layer film.

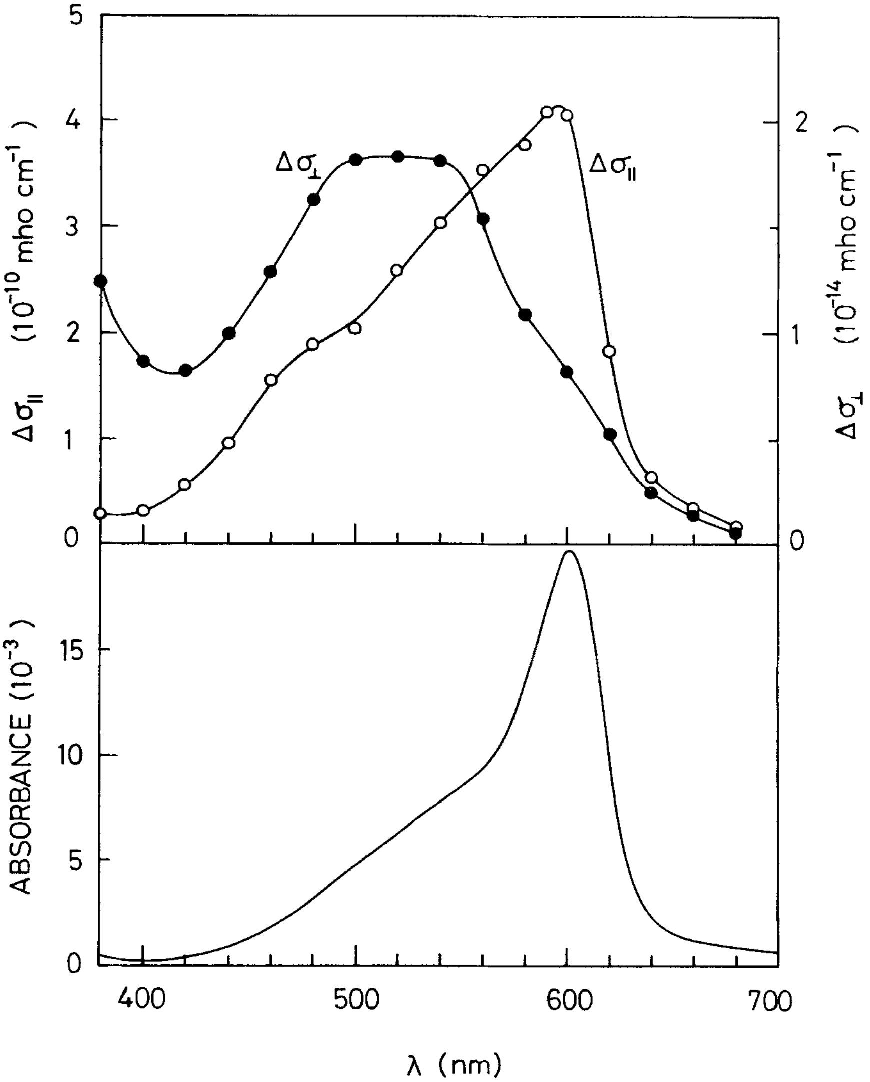

FIGURE 4 Examples for DSe system. The lateral and normal photoconductivities $\Delta\sigma_{\parallel}$ (○) and $\Delta\sigma_{\perp}$ (●) at 10-mW/cm^2 illumination level, and the absorbance per monolayer of a fifteen-layer film.

TABLE I

Characterization of the anisotropic photoconduction in the DX systems

Dye	Aggregate band	Absorption maximum λ_a (nm)	Lateral photoconduction: Maximum $\lambda_{\|}$ (nm)	Lateral photoconduction: $\Delta\sigma_{\|}^{b}$ (mho cm^{-1})	Anisotropy ratio at $\lambda_{\|}$ $\Delta\sigma_{\|}/\Delta\sigma_{\perp}^{b}$
DO	absent	500	500	$10^{-10.65\pm0.18}$	$10^{3.1\pm0.2}$
DS[a]	present	590	530	$10^{-11.04\pm0.25}$	$10^{3.4\pm0.4}$
DSe	present and major	600	600	$10^{-9.47\pm0.18}$	$10^{4.7\pm0.2}$

[a] The data for DS were taken at 20°C ~ 23°C and partly released in Ref. 2.

[b] The values are geometrical averages of the data for 10^{-3} Hz at 10 mW/cm^2 illumination.

photoconductivity $\Delta\sigma_{\|}$ exhibits a sharp peak near 600 nm in accordance with the optical behaviour, while $\Delta\sigma_{\perp}$ has there only a slightly projected shoulder.

The main aspects of photoconduction in the DO, DS and DSe systems are summarized in Table I for comparison to each others. The aggregate band, which is absent in the DO system, is strongly developed in the DSe system to such an extent that other bands, such as monomer and dimer bands, are hardly observable. In the DS system, however, clear structures were still seen besides the aggregate band; around 500 nm and 530 nm, each identifiable as the dimer and the monomer bands,[3] The $\Delta\sigma_{\|}$ maximum is, therefore, located around the monomer band for both DO and DS, but around the aggregate band for the DSe system, in which the magnitude of $\Delta\sigma_{\|}$ is more than a decade larger than other two.

It should be noted that the smallest $\Delta\sigma_{\|}$ was obtained for DS in spite of the presence of the aggregate band. Therefore, to examine the effect of aggregation, it is better to refer to the anisotropic ratio $\Delta\sigma_{\|}/\Delta\sigma_{\perp}$, since the influences of different X upon $\Delta\sigma_{\|}$ is more or less cancelled by those involved in $\Delta\sigma_{\perp}$. The ratio seems to increase superlinearly with the extent of aggregation, and the value for DSe is again more than a decade larger than the others. The DO case can be plausibly interpreted within the hopping scheme in the multilayer system[8] as the case of DS in the previous paper.[2] The larger value of $\Delta\sigma_{\|}/\Delta\sigma_{\perp}$ for DSe with the marked difference in shape between both action spectra is, however, difficult to explain by the same scheme. The apparent similarity of $\Delta\sigma_{\|}$ to the absorption spectrum for the DSe case suggests that the chromophore aggregation affords a different type of conduction beyond the hopping mechanism; such a type that is low-dimensional in accordance with the occurrence of aggregation, favoring the carrier transport in the lateral direction.

The ineffectiveness of aggregation for DS or the superlinear dependence will be interpreted by reference to the transport studies of systems with semimacroscopic inhomogeneity. According to Last and Thouless[9] and Kirkpatrick,[10] the overall conductivity $\langle\sigma\rangle$ of a two-dimensional sheet composed of patches [1] and [2] with different conductivities σ_1 and σ_2 ($\sigma_1 > \sigma_2$) shows an anomalous dependence upon the path concentration p_1 or p_2. The model experiment[9] or the computer simulation[10] indicated that $\langle\sigma\rangle$ increases superlinearly with p_1, and that a critical concentration p_{1c} can be defined if $\sigma_1 \gg \sigma_2$; $p_{1c} \simeq 0.6$[9] or 0.5[10] below which the conductivity $\langle\sigma\rangle$ is identified with σ_2. These are quite consistent with the ineffectiveness of incomplete aggregation seen in the present experiment.

We have reported the enhancement of lateral photoconduction observed in the Langmuir multilayer system with the strongly aggregated chromophores. So far, nothing decisive can be said about the mechanism of the enhanced lateral transport, although it is speculated to be a band type conduction rather than the hopping. Further investigation shall be made to characterize the mechanism. This will be important in practical applications, since it suggests that the efficiency of organic photoelectric devices, such as solar cells, can be substantially enhanced by choosing the optimum molecular arrangement.

Acknowledgements

The authors are indebted to Dr S. Yasui, of Japanese Research Institute for Photosensitizing Dyes, Co., Okayama, Japan, for supplying us with the surface-active merocyanines used in the experiments. Discussions with Drs F. Mizutani and M. Yoshiura are gratefully acknowledged.

Reference

1. K. Iriyama, M. Yoshiura, and F. Mizutani, *Thin Solid Films*, **68**, 47 (1980).
2. M. Sugi and S. Iizima, *Thin Solid Films*, **68**, 199 (1980).
3. K. Iriyama, F. Mizutani, and M. Yoshiura, *Chem. Lett.*, **1980**, 1399 (1980).
4. The fundamental chromophore structure is identifiable with those well-known photoconductors, see, for example, the following. H. Meier, W. Albrecht, and U. Tschirwitz, *Angew. Chem.*, **84**, 1077 (1972). D. L. Morel, *Mol. Cryst. Liq. Cryst.*, **50**, 127 (1979). K. Iriyama, M. Shiraki, K. Tsuda, A. Okada, M. Sugi, S. Iizima, K. Kudo, S. Shiokawa, T. Moriizumi, and T. Yasuda, *Jpn. J. Appl. Phys. Suppl.*, **19-2**, 173 (1980).
5. For a systematic investigation, see, for example, H. Schreiber, thesis (Marburg 1968).
6. M. Sugi, T. Fuki, and S. Iizima, *Phys. Rev.*, **B18**, 725 (1978).
7. T. Fukui, unpublished data.
8. M. Sugi, T. Fukui, and S. Iizima, *Mol. Cryst. Liq. Cryst.*, **50**, 183 (1979).
9. B. J. Last and D. J. Thouless, *Phys. Rev. Lett.*, **27**, 1719 (1971).
10. S. Kirkpatrick, *Phys. Rev. Lett.*, **27**, 1722 (1971).