ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 138 (2001) 235–244

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

# Spectral properties of stilbazolium merocyanines oriented in stretched polymer films and Langmuir–Blodgett monolayers

Jędrzej Łukasiewicz [a,b], Masayuki Hara [a], Chikashi Nakamura [a], Jun Miyake [a], Danuta Wróbel [b], Danuta Frąckowiak [b,*]

[a] *National Institute for Advanced Interdisciplinary Research, Agency of Industrial Science and Technology, 1-1-4 Higashi, Tsukuba 305-8562, Japan*

[b] *Poznan University of Technology, Institute of Physics, Piotrowo 3, 60-965 Poznań, Poland*

Received 2 October 2000; accepted 5 October 2000

**Abstract**

Three stilbazolium merocyanines: 1-(6′-hydroxyhexyl)-4-[(4-oxocyclohexa-2,5-dienylidene)ethylidene]-1,4-dihydropyridine; 1-(11′-hydroxyhexyl)-4-[(4-oxocyclohexa-2,5-dienylidene)ethylidene]-1,4-dihydropyridine; 1-(10′-carboxydecyl)-4-[4-oxocyclohexa-2,5-dienylidene)ethylidene]-1,4-dihydropyridine salt HCl located in Langmuir–Blodgett monolayers and deposited on quartz plate as well as embedded in isotropic or stretched polyvinyl alcohol films were investigated. Dyes occur in protonated and free-base forms. The concentration ratio of these forms depends on pH of subphase (for monolayers) or resin addition (in polymer film).

The polarized absorption and fluorescence spectra were measured and coefficients of absorption and emission anisotropy were calculated. Dye molecules were in both matrices oriented, but degrees of orientation of various forms of dye were different. The anisotropies of absorption and emission are also different which strongly suggests the occurrence of dye forms with different yield of fluorescence and various orientations. The formation of mixed aggregates of protonated and free-base form is suggested. The orientation of stilbazolium merocyanines in anisotropic matrix is important in the application of these dyes as the sensors for measurements of the local electric field in biological membranes as well as for the formation polarizing absorption polymer film used in some types of two-colours liquid crystal displays. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Fluorescence; Langmuir–Blodgett films; Multilayers; Polymers; Sensors

## 1. Introduction

Merocyanine dyes in electrochemical cells are the source of photopotentials [1–3], and therefore can be used in a system converting light energy into electrical energy. Merocyanine dyes can also provide information about the microenviroment in natural and model membranes because they are easily oriented in anisotropic media [4,5] and exhibit electrochromic effects [6]. Therefore they can be used in several types of sensors for measuring the local electric fields in biological systems [6] or for the investigation of the orientation of biological tissue stained by dye elements, e.g. membranes [8]. Stilbazolium merocyanines are also promising dyes for application in photodynamic therapy [7,8].

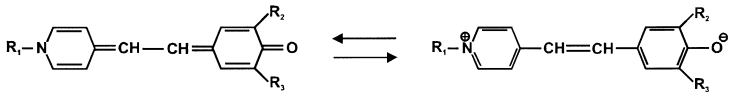
In most of these applications the orientations of dye molecules play important role, e.g. the tunnelling of electrons from excited dye to the semiconducting electrode depends on the arrangement of the dye molecules on electrode surface [9]. The anisotropic polymer films containing the ordered dye molecules can be used as polarizing absorption filter in some types of two-colours liquid crystal displays [10]. In this paper we compare the orientation and spectral properties of three stilbazolium merocyanine dyes in two different anisotropic matrices.

*Corresponding author.

*Abbreviations:* Mero-A: 1-(6′-hydroxyhexyl)-4-[(4-oxocyclohexa-2,5-dienylidene)ethylidene]-1,4-dihydropyridine; Mero-B: 1-(11′-hydroxyhexyl)-4-[(4-oxocyclohexa-2,5-dienylidene) ethylidene]-1,4-dihydropyridine; Mero-C: 1-(10′-carboxydecyl)-4-[4-oxocyclohexa-2,5-dienylidene) ethylidene]-1,4-dihydropyridine; ET: energy transfer; TM: transition moment; TMs: transition moments; LB: Langmuir–Blodgett monolayer; PVA: polyvinylalcohol

1010-6030/01/$ – see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S1010-6030(00)00390-7

**Mero A and mero B**



free base protonated

| notation | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| A | $(CH_2)_6$-OH | H | H |
| B | $(CH_2)_{11}$-OH | H | H |

**Mero C**

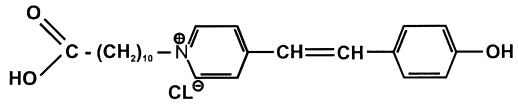


Fig. 1. Structure of merocyanine molecules.

## 2. Materials and methods

Following three stilbazolium merocyanines:

1. 1-(6′-hydroxyhexyl)-4-[(4-oxocyclohexa-2, 5-dienylidene)ethylidene]-1,4-dihydropyridine,
2. 1-(11′-hydroxyhexyl)-4-[(4-oxocyclohexa-2,5-dienylidene)ethylidene]-1,4-dihydropyridine
3. 1-(10′-carboxydecyl)-4-[4-oxocyclohexa-2,5-dienylidene)ethylidene]-1,4-dihydropyridine (Fig. 1) were gift from Dr. I. Gruda, University du Quebec, Canada. The method of synthesis of these dyes has been described by Gruda and Bolduc [11]. These dyes will be denoted as Mero-A, Mero-B and Mero-C, respectively. The investigated dyes can occur as a free-base form or as a protonated form (Fig. 1) [1–3,12]. The dipole moment of the protonated form is much smaller than that of the free-base form, especially when dye is dissolved in polar solvent.

The investigated Mero-A and Mero-B stilbazolium merocyanines were different from those previously introduced into polymer film [13] or nematic liquid crystal [3] and monolayers [2]. The Mero-C was previously [13] investigated in polyvinyl alcohol PVA film. It exhibits intensive fluorescence and is in high degree oriented in such anisotropic matrix. For Mero-A the generation of photopotential was shown [1]. Most of the previously investigated dyes contain $NO_2$ group reducing the solvatochromic effect or/and bulky di-*t*-butyl groups making the formation of stable dye complexes less probable (because of steric hindrance). Actually investigated dyes (especially Mero-A and Mero-B) can easily form complexes. These two dyes differ only in the length of $R_3$ group (Fig. 1). Last one (Mero-C) contains two ions ($N^+$ and $Cl^-$) similar to previously investigated merocyanine [13]. It is without steric groups, therefore we can predict some aggregation of these dye molecules. The investigated merocyanines are insoluble in water.

In order to obtain various concentration ratios of both forms the monolayers were deposited using Tris–HCl buffer as subphase with following pH: 2, 4, 6 and 8. The deposition of LB films was carried out in an LB-5000 trough (KSV Instruments, Finland). Merocyanines in chloroform/methanol mixture (1:19 v/v) were spread on the water Tris–HCl subphase containing $CaCl_2$. After spreading, the material was incubated for 15 min and the temperature was stabilized. Thereafter compression at 10 mm/min was carried out until a surface pressure of 8.5 mN $m^{-1}$ was reached. The monolayer was transferred under controlled surface pressure to a hydrophilic quartz slide glass. The vertical deposition method [2] was used for the deposition. All the measurements of LB samples were performed immediately after deposition.

The pH in polymer film was changed by the addition of resin (Bio-Rad Laboratories 1414 Harbour Way South, Richmond, CA 94804). As a result the following two pH (measured before film drying) were obtained: without resin pH = 6; with resin pH = 7. The method of film preparation and stretching has been described previously [14]. Absorption spectra were measured using Shimadzu UV-1601 UV–Visible Spectrophotometer, fluorescence spectra with Hitachi F4500. Both arrangements were equipped with polarizers and sample holders. The absorption components polarized parallel ($A_{||}$) and perpendicular ($A_{\perp}$) to the direction of film stretching were measured. All polarized fluorescence spectra were denoted by three letters in sequence referring to the electric vector of exciting light, the sample axis and the polarization of the fluorescence beam (H — horizontal, V — vertical, O — natural light or unstretched sample). The following four polarized components were measured: VVV, VVH, VHV and VHH. The following fluorescence anisotropy coefficients: $r_a = (VVV - VVH)/(VVV + 2VVH)$, $r_b = (VHV - VHH)/(VHV + 2VHH)$, $r_c = (VVV - VHV)/(VVV + 2VHV)$, $r_d = (VVH - VHH)/(VVH + 2VHH)$ were calculated [12].

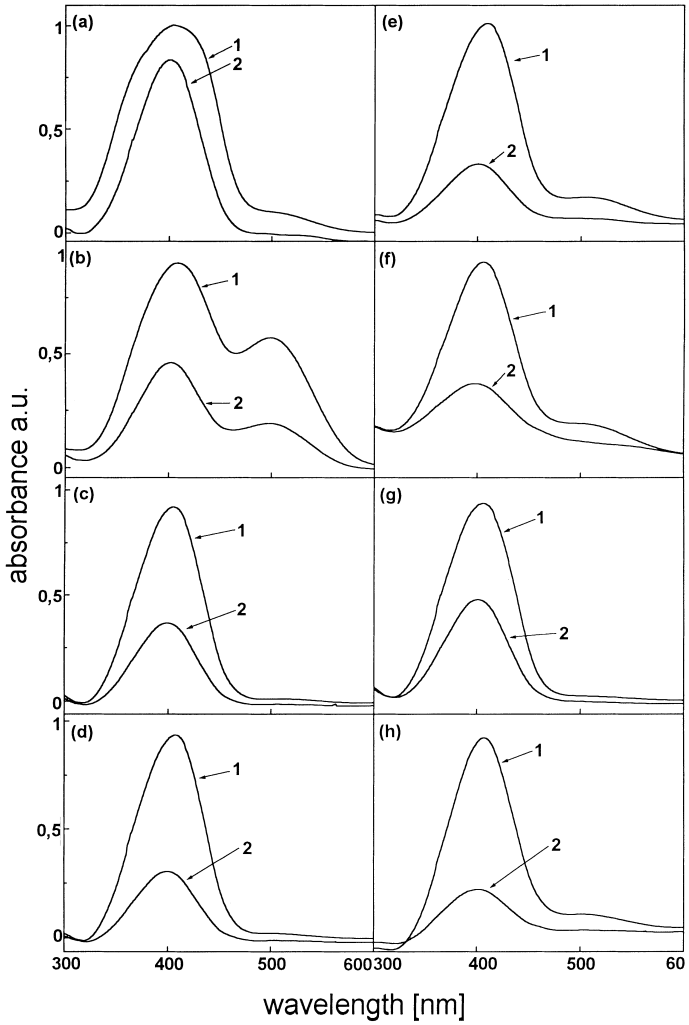



Fig. 2. Absorption of (a–d) Mero-A and (e–h) Mero-C in PVA films; (a, b, e, f) $C_1 = 10^{-3}$ M; (c, d, g, h) $C_1 = 0.2 \times 10^{-3}$ M; (a, c, e, g) without resin; (b, d, f, h) with resin. Curves 1 parallel (VV), perpendicular (VH) components.

## 3. Results

### *3.1. Dyes in PVA films*

#### *3.1.1. Absorption spectra*

Fig. 2(a–d) shows the polarized absorption spectra of Mero-A in two types of films (without and with resin) at two dye concentrations ($C_1 = 10^{-3}$ M or $C_2 = 2 \times 10^{-4}$ M). The maximum belonging to the protonated form is located at about 400 nm. In some cases the parallel component of absorption is shifted with respect to perpendicular component towards longer wavelengths. The maximum of free-base form is deposited at about 500 nm. It is seen in a sample with resin at higher dye concentration. At low $C_2$ concentration, even in sample with resin, ratio of 500–400 nm absorption intensities is very low (Table 1). It shows that maximum at 500 nm is due, at least partially, to some aggregated form of dye. It was shown [5] that protonated and free-base merocyanines can form 1:1 complexes. Absorption of such complexes is usually [13] located at about 380 nm. Such complexes can be fluorescent. The short-wave absorption maximum of Mero-B in LB film is shifted towards shorter wavelengths with respect to the maximum in PVA film (Table 2). It can be due to the formation of the mixed aggregates of the protonated and free-base forms [5]. This effect is not observed in a case of Mero-C (Table 2). The difference between ratios of both main maxima in absorption and fluorescence spectra (Table 1) can be due to the formation of such mixed complexes. Mero-A and Mero-C exhibit more free-base form in PVA with resin than in sample without resin (Table 1) especially at higher dye concentration. Mero-B absorption spectra is much less sensitive on the change, the pH medium is from 6 to 7 (Table 1). It can be done by different aggregation properties of this dye.

The anisotropy of absorption (Table 2) for Mero-B is higher than that for Mero-A. It shows that longer molecules are in higher degree oriented in the same anisotropic matrix.

From Fig. 2(e–h), showing polarized absorption for Mero-C, follows that 500 nm maximum is in all samples low and degree of dye molecules orientation is high

Table 1
Ratios of fluorescence and absorption maxima belonging to free-base and protonated forms[a]

| Sample | Fluorescence | | | | | | Absorption | |
|---|---|---|---|---|---|---|---|---|
| | VVV | VVH | VHV | VHH | VOH | VOV | VV | VH |
| A (W) ($C_1$) | 1.54 | 1.27 | 1.07 | 1.30 | 0.91 | 0.94 | 0.10 | 0.00 |
| A (R) ($C_1$) | 6.47 | 5.47 | 4.23 | 8.49 | 2.99 | 2.56 | 0.12 | 0.04 |
| A (W) ($C_2$) | 0.70 | 0.62 | 0.63 | 0.61 | 0.52 | 0.58 | 0.15 | 0.13 |
| A (R) ($C_2$) | 0.84 | 0.71 | 0.76 | 0.74 | 0.49 | 0.55 | 0.63 | 0.42 |
| B (W) ($C_1$) | 1.60 | 1.41 | 1.19 | 1.45 | 1.18 | 1.19 | 0.63 | 0.55 |
| B (R) ($C_1$) | 1.30 | 1.43 | 1.27 | 1.49 | 0.78 | 0.79 | 0.25 | 0.37 |
| B (W) ($C_2$) | 0.82 | 0.69 | 0.72 | 0.71 | 0.59 | 0.65 | 0.01 | 0.03 |
| B (R) ($C_2$) | 0.89 | 0.82 | 0.87 | 0.84 | 0.89 | 0.95 | 0.01 | 0.04 |
| C (W) ($C_1$) | 1.19 | 1.11 | 0.98 | 1.31 | 0.48 | 0.55 | 0.08 | 0.10 |
| C (R) ($C_1$) | 1.35 | 1.22 | 1.14 | 1.15 | 0.68 | 0.69 | 0.02 | 0.02 |
| C (W) ($C_2$) | 0.80 | 0.72 | 0.67 | 0.60 | 0.53 | 0.60 | 0.02 | 0.07 |
| C (R) ($C_2$) | 1.05 | 0.95 | 0.86 | 0.94 | 0.60 | 0.61 | 0.04 | 0.08 |

[a] Concentrations: $C_1 = 10^{-3}$ M, $C_2 = 0.2 \times 10^{-3}$ M; (W) without resin, (R) with resin; A — Mero-A, B — Mero-B, C — Mero-C. Free-base form absorption and fluorescence is shifted towards longer wavelengths with respect to the protonated form.

(Table 2). A shift between two polarized components of the protonated form is similar to that observed for Mero-A (Fig. 2a–d) and Mero-B. The length of Mero-C molecule is comparable with that of Mero-B, anisotropy of absorption (Table 2) is also similar.

### 3.2. Fluorescence spectra

The sets of polarized fluorescence spectra for Mero-A and Mero-C in unstretched and stretched films are presented in Fig. 3. The maximum at about 490 nm is related to protonated form of dye, the maximum in a region 570–580 nm predominant to the free-base form of dye. The exact position of free-base form emission depends on the polarized component. Also the ratio of both components depends on polarization of exciting and fluorescence beams (Table 1). It shows that in this region is located emission of more than one form. All spectra were excited in a region of protonated form absorption. In this region is also located some absorption of mixed aggregates of protonated and free-base forms (maximum of absorption at 380 nm). At excitation in free-base form absorption the emission of the protonated form is very low (not shown), whereas excitation in a region of protonated form absorption, the fluorescence of the free-base form is in some cases high (Fig. 3). Evaluated yield of fluorescence of free-base form is higher than that of the protonated. The high intensity of free-base form fluorescence at excitation of the protonated form is due to excitation energy transfer (ET) and its high yield of fluorescence. In a case of only free-base emission in the 570–580 nm range, the ET from protonated to free-base form should be very efficient. This transfer has to be very efficient because the free-base form fluorescence is high even at rather low content of this form following from absorption spectra (Fig. 2). The absorption spectra can be changed as a result of the formation of the aggregate of both forms. The yield of excitation energy transfer depends strongly on the mutual orientation of the transition moment (TM) of absorption of short wavelength form and TM of emission of free-base form. Therefore it is different for various light polarization. For elongated merocyanine molecules the TM of absorption has to be almost parallel to the TM of fluorescence. Different situation can occur in a case of dye complexes. For Mero-A (Fig. 3b) in a sample with higher dye concentration in film with resin the long wavelength emission in a region of 570–580 nm predominates. The maxima of various polarized components are

Table 2
Anisotropy of absorption coefficient[a]

| Dye | pH | Wavelength (nm) | $S$ |
|---|---|---|---|
| *PVA films* | | | |
| A (W) ($C_1$) | 6 | 415 | 0.10 |
| A (R) ($C_1$) | 7 | 408 | 0.25 |
| A (W) ($C_2$) | 6 | 405 | 0.34 |
| A (R) ($C_2$) | 7 | 408 | 0.42 |
| B (W) ($C_1$) | 6 | 415 | 0.18 |
| B (R) ($C_1$) | 7 | 414 | 0.55 |
| B (W) ($C_2$) | 6 | 405 | 0.39 |
| B (R) ($C_2$) | 7 | 409 | 0.5 |
| C (W) ($C_1$) | 6 | 409 | 0.43 |
| C (R) ($C_1$) | 7 | 405 | 0.30 |
| C (W) ($C_2$) | 6 | 405 | 0.22 |
| C (R) ($C_2$) | 7 | 407 | 0.60 |
| *Monolayers* | | | |
| B | 2 | 374 | 0.09 |
| | 4 | 389 | −0.013 |
| | 6 | 385 | 0.18 |
| | 8 | 392 | 0.01 |
| C | 2 | 400 | 0.03 |
| | 4 | 402 | −0.03 |
| | 6 | 402 | −0.02 |
| | 8 | 407 | 0.08 |

[a] (W) without resin, (R) with resin; concentrations: $C_1 = 10^{-3}$ M, $C_2 = 0.2 \times 10^{-3}$ M, $S = (A_{\parallel} - A_{\perp})/(A_{\parallel} + 2A_{\perp})$, accuracy $\Delta S = \pm 0.02$.

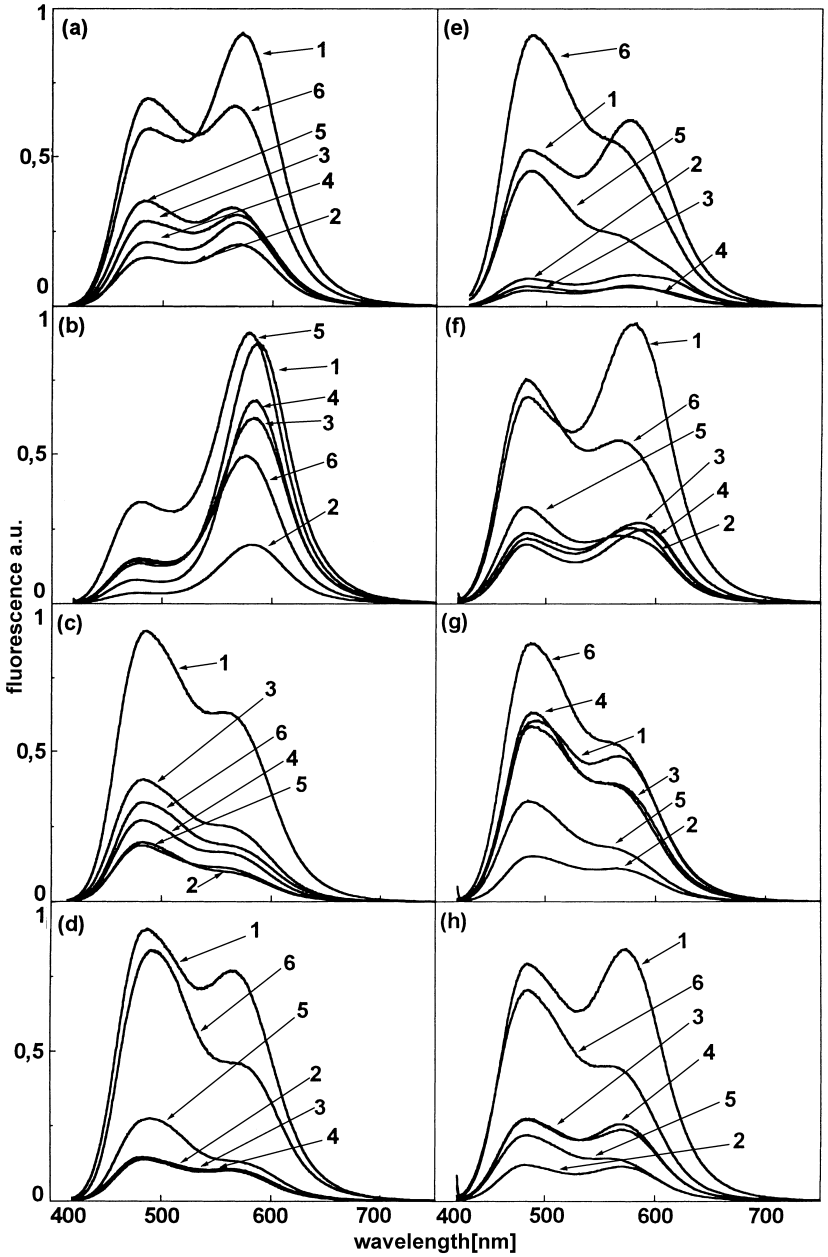



Fig. 3. Fluorescence of merocyanines (a–d) Mero-A and (e–h) Mero-C in PVA film. (a, b, e, f) $C_1$, (c, d, g, h) $C_2$; (a, c, e, g) without resin, (b, d, f, h) with resin. Notation of polarized components explained in text. 1 — VVV; 2 — VVH; 3 — VHV; 4 — VHH; 5 — VOH; 6 — VOV.

mutually shifted showing that more than one form of dye is present and that various forms are differently oriented. The intensities and anisotropies of fluorescence are not closely related to the intensities and anisotropies of absorption (Tables 1–3 and Figs. 2 and 3). It shows the occurrence of several forms of dyes characterized by different yields of fluorescence and various mutual orientations in PVA matrix. The anisotropy of fluorescence $r_a$ coefficients of both forms are in first approximation similar (Table 3) which shows that both main dye forms TMs are mutually almost parallel. It explains efficient excitation ET between these forms. Various values of $r_c$ suggest different degree of orientation of transition moments of various forms. In such a case similar $r_a$ coefficients are due to effect of photoselection by polarized light of similarly ordered molecules. Fluorescence anisotropy coefficients are different for various forms of dye concentrations and are usually changed by the resin addition (Table 3). The influence of the resin addition on anisotropy of emission is different for various dye concentrations (Table 3). It suggests once more the occurrence of some aggregated form differently oriented in a presence of the resin in PVA films. The coefficient $r_a$ gives information about the polarization of emission due to molecules oriented under low angle with respect to film

Table 3
Anisotropy of fluorescence coefficients[a]

| Dye | Excitation (nm) | Observation (nm) | pH | $r_a$ | $r_b$ | $r_c$ | $r_d$ |
|---|---|---|---|---|---|---|---|
| *PVA films* | | | | | | | |
| A (W) ($C_1$) | 415 | 486 | 6 | 0.46 | 0.09 | 0.26 | −0.08 |
| | | 572 | | 0.53 | 0.02 | 0.41 | −0.09 |
| A (R) ($C_1$) | 408 | 479 | 7 | 0.47 | 0.21 | −0.02 | −0.22 |
| | | 588 | | 0.53 | −0.02 | 0.12 | −0.31 |
| A (W) ($C_2$) | 405 | 486 | 6 | 0.56 | 0.14 | 0.29 | −0.11 |
| | | 553 | | 0.61 | 0.15 | 0.33 | −0.11 |
| A (R) ($C_2$) | 408 | 488 | 7 | 0.63 | 0.01 | 0.64 | 0.02 |
| | | 564 | | 0.68 | 0.01 | 0.67 | 0.01 |
| B (W) ($C_1$) | 415 | 490 | 6 | 0.53 | 0.04 | 0.37 | −0.11 |
| | | 578 | | 0.57 | −0.02 | 0.47 | −0.11 |
| B (R) ($C_1$) | 412 | 483 | 7 | 0.45 | −0.03 | 0.48 | −0.01 |
| | | 580 | | 0.42 | −0.01 | 0.49 | 0.06 |
| B (W) ($C_2$) | 412 | 489 | 6 | 0.65 | 0.05 | 0.37 | −0.19 |
| | | 565 | | 0.69 | 0.05 | 0.41 | −0.21 |
| B (R) ($C_2$) | 412 | 488 | 7 | 0.68 | 0.01 | 0.29 | −0.29 |
| | | 513 | | 0.71 | 0.03 | 0.29 | −0.3 |
| C (W) ($C_1$) | 412 | 486 | 6 | 0.59 | 0.07 | 0.69 | 0.19 |
| | | 576 | | 0.62 | −0.02 | 0.74 | 0.13 |
| C (R) ($C_1$) | 412 | 483 | 7 | 0.45 | 0.02 | 0.38 | −0.03 |
| | | 581 | | 0.48 | 0.02 | 0.45 | −0.01 |
| C (W) ($C_2$) | 412 | 492 | 6 | 0.49 | −0.02 | 0.01 | −0.33 |
| | | 568 | | 0.53 | 0.01 | 0.07 | −0.31 |
| C (R) ($C_2$) | 412 | 484 | 7 | 0.65 | 0.01 | 0.38 | −0.22 |
| | | 574 | | 0.68 | −0.02 | 0.46 | −0.22 |
| *Monolayers* | | | | | | | |
| B | 374 | 480 | 2 | 0.02 | 0.14 | 0.01 | 0.11 |
| | 389 | 482 | 4 | 0.01 | 0.14 | 0.01 | 0.12 |
| | 385 | 480 | 6 | 0.01 | 0.05 | 0.07 | 0.12 |
| | 392 | 481 | 8 | −0.07 | 0.02 | 0.04 | 0.11 |
| C | 400 | 481 | 2 | −0.07 | −0.02 | 0.08 | 0.14 |
| | 402 | 480 | 4 | −0.03 | −0.02 | 0.02 | 0.03 |
| | 402 | 482 | 6 | 0.01 | 0.01 | 0.23 | 0.25 |
| | 407 | 481 | 8 | −0.05 | −0.01 | 0.08 | 0.13 |

[a] Coefficients of emission anisotropy: $r_a = (VVV-VVH)/(VVV+2VVH)$, $r_b = (VHV-VHH)/(VHV+2VHH)$, $r_c = (VVV-VHV)/(VVV+2VHV)$, $r_d = (VVH - VHH)/(VVH + 2VHH)$; concentrations: $C_1 = 10^{-3}$ M, $C_2 = 0.2 \times 10^{-3}$ M; (W) without resin, (R) with resin; accuracy of coefficients $\Delta r = \pm 0.02$.

axis. It is high in a case of the presence of the large pool of "well oriented" molecules and at low amount of randomly oriented molecules. From Table 3 it follows that $r_a$ is high in all cases. This effect can be caused by efficient uniaxial orientation, but can be also, at least partially, due to photoselection by polarized light on the pool of molecules not transferring excitation energy to the differently directed TMs. From rather high values of $r_c$ one can conclude that strong anisotropy of the distribution of TMs around film axis occurs. In a case when values of $r_a$ and $r_c$ are comparable rather the uniaxial orientation than photoselection is responsible for observed polarization of fluorescence. Coefficient $r_b$ describes the fluorescence anisotropy of molecules forming a large angle with the film axis or having large angular distribution around this axis. As follows from Table 3 in most cases this coefficient has low value showing that "badly oriented" molecules are scarce. The exception is Mero-A at higher concentration in PVA with resin. The $r_d$ shows anisotropy of emission of the molecules emitting fluorescence polarized under large angle with respect to the film axis. It is high and positive in a case of absorption by the "well ordered" molecules transferring the excitation to some worse ordered dyes having projection of emission TMs on horizontal direction. Table 3 shows that the content of such molecules in various samples is different. For Mero-C $r_d$ is negative at low dye concentration showing that in this case VHH > VVH. It means that it is a pool of molecules with the absorption TMs located under large angle with respect

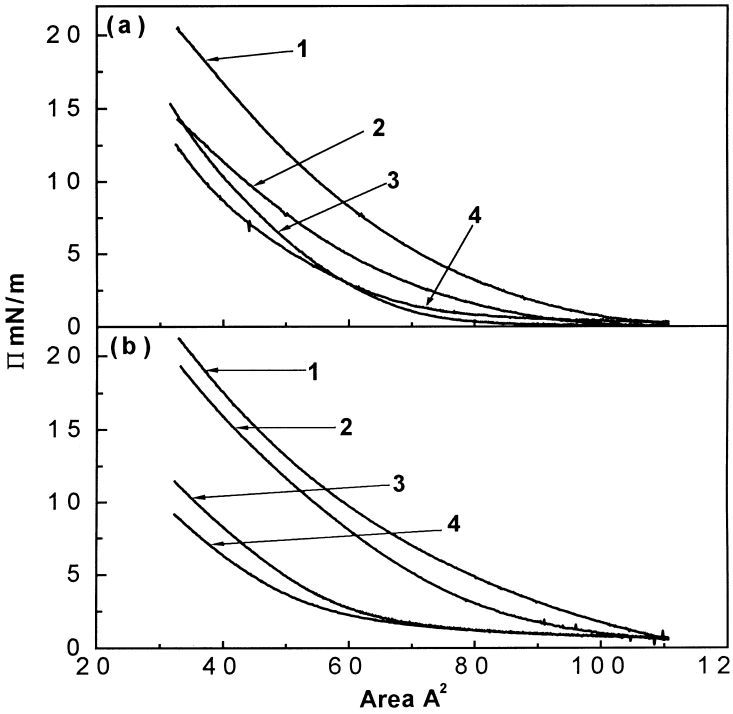



Fig. 4. Pressure–area isotherms of merocyanine monolayers: (a) Mero-B, (b) Mero-C. 1 — pH8; 2 — pH6; 3 — pH4; 4 — pH2; pH in measured subphase.

to the film axis; having TMs of absorption and emission parallel.

### 3.3. Merocyanines in Langmuir–Blodgett monolayers

The Mero-A, having shortest chain, is not forming LB monolayers in the applied experimental conditions. Mero-B and Mero-C form monolayers. Pressure–area isotherms of these dyes are shown in Fig. 4. This figure suggests that investigated dyes occur in various forms at different pH. The limiting areas per molecule, obtained by extrapolation from the rising part of isotherm to $\pi = 0$ were, for Mero-B at pH = 2, pH = 4, pH = 6 and pH = 8 equal 75, 72, 60, 57 Å, respectively, whereas 75, 70, 58, 55 Å for Mero-C. The limiting areas are decreasing with the increase of pH. It is logical because at higher pH Coulomb repulsion is lower. The area obtained for both dyes are similar and lower than that reported previously for other merocyanines [12].

Fig. 5 shows the absorption spectra of 20 monolayers of Mero-B and Mero-C on the support. The not normalized absorption values (not shown) are increasing with the value of pH which is reasonable because the molecules are more tightly packed in monolayers. The anisotropy of absorption (Table 2) is changed in irregular way with the pH. For Mero-B it is highest at pH = 6. It is an unexpected result. From Fig. 5 showing polarized absorption, taken with the LB film plane located perpendicular to the light beam, it follows that TM of investigated days are not uniformly distributed in the LB film plane; they exhibit some uniaxial orientation because in most cases anisotropy of absorption is observed (Table 2). In order to prove whether molecules are located parallel to the film plane or they are directed under some angle with respect to this plane the polarized absorption, using 30° angle between light beam and a normal to the surface of plate, was measured. At such geometry anisotropy of absorption is lower than that at perpendicular arrangement (not shown). For example, for Mero-C (pH8) in perpendicular film position $S = 0.08$ (Table 2) whereas at 30° position was found to be equal 0.02. Previously [2] the TMs of investigated merocyanines were uniformly distributed in LB film plane which gives opportunity to evaluate the tilt angle of TMs. In this case the anisotropy of absorption due to 30° geometry was negative for protonated form. It was calculated that protonated form TMs were tilted at about 60°, whereas the free-base form were located almost in a plane [2]. In the present experiment most of dye molecules are in the protonated form. The decrease in anisotropy of absorption suggests that, as observed previously, this form is located under some angle with respect to the LB film. Fig. 6 presents the fluorescence spectra of Mero-B and Mero-C in monolayers. Main maxima of emission of protonated form are located around 480 nm. At all pH values the small maximum at 550–570 nm due to the free-base form is seen. The fluorescence spectra of LB film (Fig. 6) are strongly perturbed by light scattering.

There are much more reports about absorption spectra of LB monolayers than about their fluorescence [14]. The optics of multilayers is rather complex [15]. Investigated dyes exhibit enough high fluorescence enabling measurement of even the polarized fluorescence spectra (Fig. 6) but the emission spectra are more strongly perturbed by secondary effects (such as scattering, reflections, etc.) than

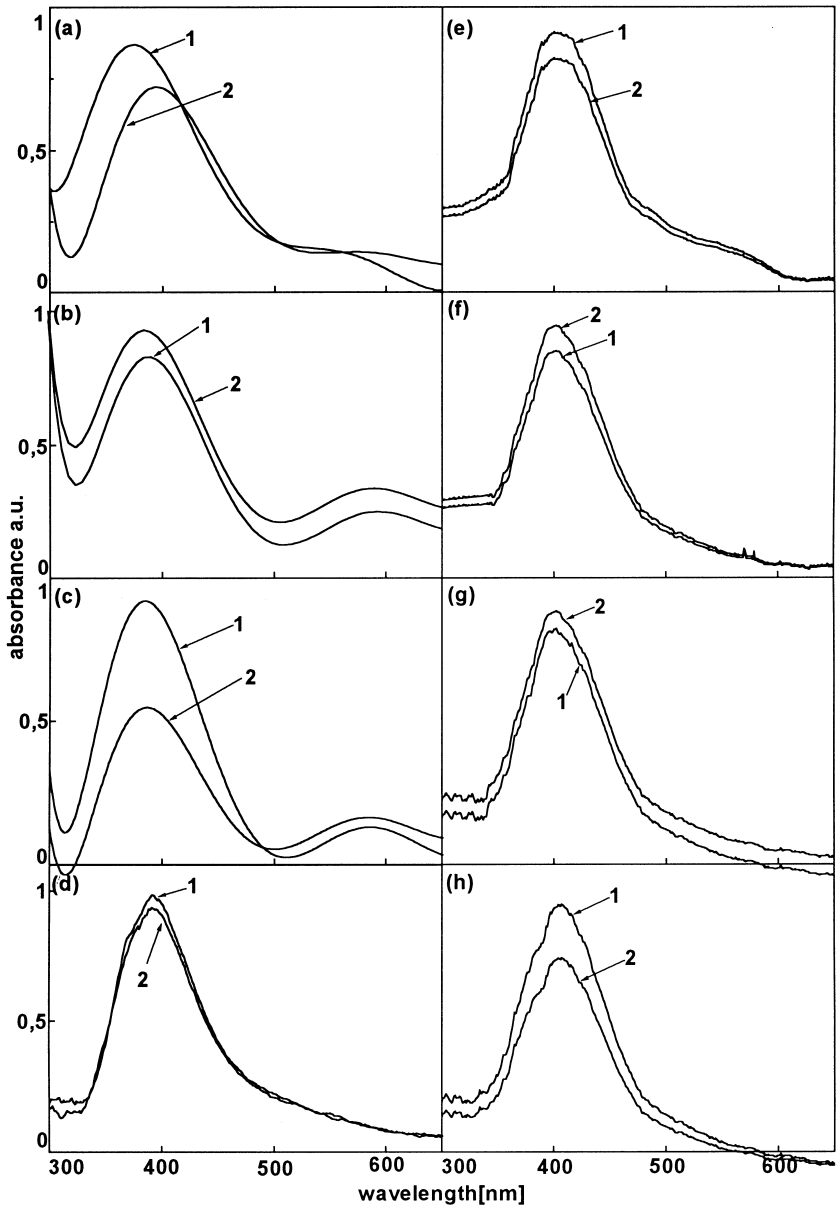



Fig. 5. Absorption spectra of 20LB monolayers of merocyanines: (a–d) Mero-B; (e, f, g, h) Mero-C. (a, e) pH2; (b, f) pH4; (c, g) pH6; (d, h) pH8.

absorption spectra (Fig. 5) which are diminished practically to zero outside of absorption region. From fluorescence spectra only components VVH and VHH, both having mutually perpendicular directions of the electric vectors of the exciting and fluorescence beams, exhibit reasonable shapes, similar to the emission of the protonated form of the same dyes in PVA films (Fig. 3). The free-base emission (in 600 nm region) is in these two VVH and VHH components, practically not observed. It is even for the films with Mero-B at pH = 4 and pH = 5 having contribution from free-base form in absorption (Fig. 5). It seems that in LB multilayers this form fluorescence is not effective. We decided not to analyze all secondary effects perturbing the VVV and VHV components. As far as we know up to now the polarized emission spectra of such systems have not been measured. We plan to establish this effect by additional experiments in the next paper. Now, we calculated all coefficients of anisotropy of emission (Table 3). Anisotropy of fluorescence coefficient $r_a$ is similar for all pH (Table 1). Only unperturbated $r_d$ dependent on VVH and VHH, can be compared with the same coefficient obtained for PVA films (Table 3). From this comparison it follows that TMs of dye are in LB films orientation. There are more molecules with their absorption TMs directed parallel (under low angle) to orientation axis than the molecules oriented perpendicularly (VVH > VHH). The observed in both components is the projection of emission TMs on horizontal direction.

Mero-C (Fig. 5, Table 1) exhibits comparable anisotropy of absorption at various pH. Both polarized components of

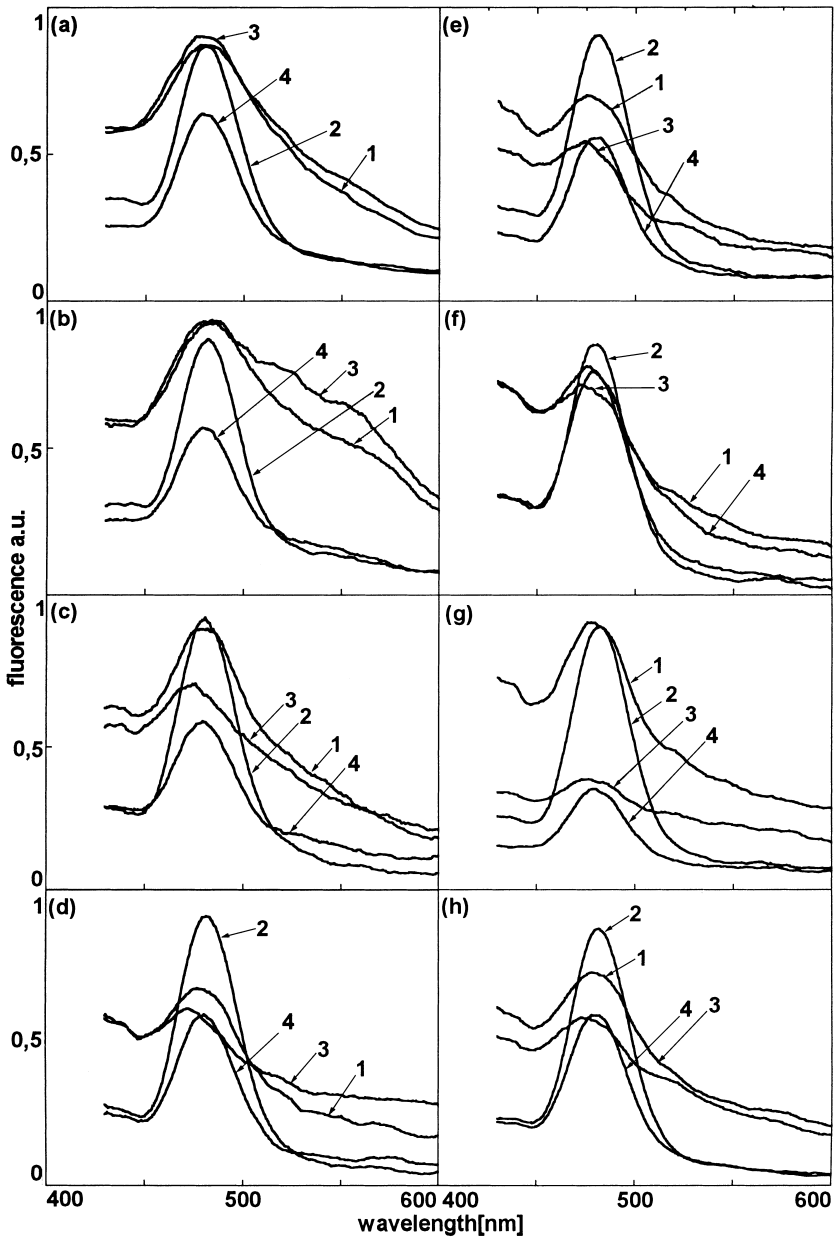



Fig. 6. Fluorescence spectra of 20 monolayers of merocyanines: (a–d) Mero-B; (e–h) Mero-C. (a, e) pH2; (b, f) pH4; (c, g) pH6; (d, h) pH8. Notation of polarized components explained in text. 1 — VVV; 2 — VVH; 3 — VHV; 4 — VHH.

absorption are located at the same wavelengths. Absorption at 550 nm is seen only as a small shoulder. The absorption of both dyes in monolayers are more similar to the absorption in PVA without resin (Fig. 5) than to samples in PVA with resin (Fig. 5). It suggests that protonated forms are predominant in LB films.

## 4. Conclusions

In both matrices stretched PVA film and LB multilayers stilbazolium merocyanines are oriented. In LB films the molecules are tilted with respect to the film plane.

Dyes occur in several forms: protonated, free-base and complexes of these forms exhibiting different orientations and yields of fluorescence. The excitation energy transfer between protonated and free-base forms seems to be very efficient. It is not excluded that to the emission in 570–580 nm region can contribute some mixed complexes or exciplexes of protonated and free-base forms. In LB monolayers the protonated form predominates.

The polymer film with uniaxially oriented dichroic dyes can be used as a part of two-colours liquid crystal displays [10]. The colours of display depend on the absorption of dye dissolved in liquid crystal and absorption of polymer film. The change, due to the electric field application in orientation

of the dye in liquid crystal, causes the change in display colours. In some cases polymer films with two dyes: one oriented and second randomly distributed were used [10].

In the applications of dyes as a sensor of local electric field [16] or as a sensitizer in photodynamic therapy [8] very important is the orientation of molecules, introduced into tissue, with respect to the membranes or proteins.

## Acknowledgements

JŁ is obliged to NAIR for the fellowship for the stay in Tsukuba. DF thanks KBN (6 PO4A 010 17) for financial support. DW thanks PUT for Grant PB 62-161/99.

## References

[1] A. Ptak, A. Der, R. Toth Boconadi, N.S. Naser, D. Frąckowiak, J. Photochem. Photobiol. 104 (1997) 133.
[2] T. Martynski, T. Tateishi, J. Miyake, A. Ptak, D. Frąckowiak, Thin Solid films 306 (1997) 154.
[3] J. Goc, D. Frąckowiak, J. Photochem. Photobiol. A 59 (1991) 233.
[4] I. Gruda, S. Hotchandani, D. Frąckowiak, Photobiochem. Photobiophys. 12 (1986) 267.
[5] I. Gruda, S. Laliberte, M. Niedbalska, D. Frąckowiak, J. Luminescence 39 (1987) 1.
[6] D. Frąckowiak, M. Niedbalska, M. Romanowski, I. Gruda, Stud. Biophys. 123 (1988) 135.
[7] I. Gruda, M. Page, F. Bolduc, S. Laliberte, C. Noel, Anticancer Res. 7 (1987) 1125.
[8] D. Frąckowiak, K. Wiktorowicz, J. Cofta, M. Niedbalska, Acta Biochem. Polon. 42 (1995) 61.
[9] R. Eiberger, F. Willing, Chem. Phys. 141 (1990) 159.
[10] D. Frąckowiak, Z. Salamon, D. Bauman, K. Fiksiński, T. Martyński, Polish Patents No. 174 400 (24 February 1984); No. 177 262 (16 September 1985).
[11] I. Gruda, F. Bolduc, J. Org. Chem. 49 (1984) 3300.
[12] S.J. Davidson, W.P. Jencks, J. Am. Chem. Soc. 91 (1969) 225.
[13] D. Frąckowiak, I. Gruda, M. Niedbalska, M. Romanowski, A. Dudkowiak, J. Photochem. Photobiol. A 54 (1990) 37.
[14] K. Fiksiński, D. Frąckowiak, Spectrosc. Lett. 13 (1980) 873.
[15] G. Mungen, R.M. Leblanc, B. Zelent, A.G. Volkov, M.I. Gugeshashvili, J. Gallant, H.A. Tajmir-Riahi, J. Aghion, Thin Solid Films 210/211 (1992) 739.
[16] H. Ti, Tien Bilayer Lipid Membranes (BLM): Theory and Practice, Marcel Dekker, New York, 1974, pp. 75–115 and 281–296.