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Electrochemical cell with bacteriochlorophyll *c* and chlorophylls *a* and *b* in nematic liquid crystal

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Abstract

The photocurrent generation and current–voltage ($I(V)$) characteristics of the electrochemical cells consisting of a layer of chlorophyll *a*, chlorophyll *b* or bacteriochlorophyll *c* solution in a nematic liquid crystal sandwiched between two semiconducting (In_2O_3) electrodes covered by an orienting layer SiO_x were investigated. Bacteriochlorophyll *c* was introduced into the nematic liquid crystal in monomeric and in aggregated predominantly tetrameric forms. The photoelectrical properties of bacteriochlorophyll *c* in monomeric and aggregated forms are different. All investigated samples exhibit cathodic photocurrent related to the extraction of electrons from the conduction band of the illuminated semiconducting electrode. Amplitudes of generated photocurrents and the shapes of the current–voltage voltammogramic loops, at the same conditions of illumination, are for various chlorophylls different.

Keywords: Bacteriochlorophyll *c*; Chlorophyll *a*; Chlorophyll *b*; Nematic liquid crystal; Electrochemical cell; Photocurrent

1. Introduction

Chlorophylls play dual roles in photosynthesizing organisms: they work as antenna pigments responsible for the light absorption and the delivering of the excitation energy to the reaction centers and they form in the reaction centers special pairs in which the charge is separated [1]. Chlorophyll molecules and reaction centers are applied in artificial photosynthesis units [2] which are proposed as semi-artificial systems for the conversion of light energy to electrical energy. The photoelectric properties of the components of such systems have to be known in order to evaluate their possible role in energy conversion. In this study the photoelectrochemical properties of chlorophylls *a* (Chl *a*) and *b* (Chl *b*) and bacteriochlorophyll *c* (BChl *c*) in nematic liquid crystal (LC) solvents are compared. In such matrix pigment molecules can be uniaxially oriented as a result of the guest–host effect.

2. Material and methods

Chl *a* and Chl *b* were extracted from nettle leaves and column chromatographed on starch using the method described by Iriyama et al. [3]. The methods of green sulfur bacterium Prosthecochloris aestuarii cultivation, extraction and identification of 3^1R-8, 12 diethyl farnesyl BChl *c* (3^1R[E,E] BChl *c*) were described previously [4,5]. Pigments were dissolved in a nematic LC mixture: p-methoxybenzylidieno-p'-butylaniline (MBBA) and p-ethoxybenzylidieno-p'-butylaniline (EBBA) (3/2, w/w) or 4-(trans-4'-n-hexylcyclohexyl)-isothiocyanato-benzene (6CHBT). All LCs (Aldrich Chemical Co.) were used without further purification.

In order to introduce the monomeric form of the pigments into LC the solutions of pigments in chloroform were mixed with LC and then chloroform was slowly evaporated in vacuo [5]. In the case of the aggregated BChl *c* form, pigment was dissolved in a mixture of n-pentane and methylcyclohexane (1/1, v/v) and then mixed with LC and the organic solutions were evaporated in vacuo [6].

Pigmented LC solvents were located in a photoelectrochemical cell with the windows covered by a semiconducting In_2O_3 layer. The cells used for the BChl *c* investigations have additionaly deposited onto the semiconducting layer the orienting layer SiO_x. For such cells the contact between LC solution and semiconductor was weaker because of partial shielding by SiO_x. In such cell LC molecules were uniaxially oriented and BChl *c* molecules were also oriented as a result of the guest–host effect. As it was shown previously [5,6] in such cells the BChl *c* monomers and aggregates are in a high

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degree oriented but a degree of this orientation was strongly dependent on the pigment aggregation (the order parameter $S=(A_{\parallel}-A_{\perp})/(A_{\parallel}+2A_{\perp})$ of monomers was about $S=0.2$ whereas for aggregates it was about 0.7. The kinetics of photopotential and photocurrent generation and decay as well as the current–voltage dependence of the investigated cells were established using a home made arrangement with the computer being on line. The absorption spectra were recorded with Zeiss Specord M40.

3. Results and discussion

Fig. 1 shows the absorption spectra for the investigated solutions. The spectra for Chl *a* and Chl *b* show that these pigments are predominantly in monomeric state [7,8]. Spectrum for the monomeric state of BChl *c* (Fig. 1) is similar to that reported previously [5,9]. The spectrum for the aggregated form shows that this sample contains predominantly two tetrameric forms (T1 and T2) which differ in their orientation in LC [6]. This sample also contains some admixture of dimeric and monomeric forms of BChl *c* [5,9]. Fig. 1 also shows the spectral distribution in used light. In a case of Chl *a* and Chl *b* the intensity of light in a region of both red and Soret are similar. For BChl *c* aggregates the red band illumination is much weaker than that in a region of the Soret band. Also the illumination in the red band region is more efficient for monomeric than for aggregated BChl *c* molecules.

Fig. 2 shows the photocurrent generation for Chl *a* solutions at two pigment concentrations. The amplitude of the photocurrent is increasing with the increase in pigment concentration, but the ratio of observed amplitudes is lower than the ratio of concentrations (Table 1). The amplitude for the

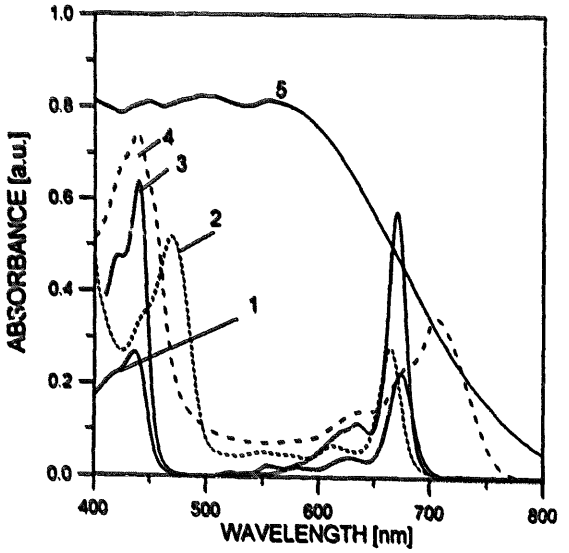

Fig. 1. Absorption spectra of investigated pigments in LC; Chl *a*: curve 1 ($c=10^{-3}$ M), Chl *b*: curve 2 (10^{-3} M), BChl *c* monomers: curve 3 ($c=5\times10^{-3}$ M) and BChl *c* aggregates: curve 4 ($c=10^{-2}$ M), curve 5, spectral distribution of actinic light in a.u.

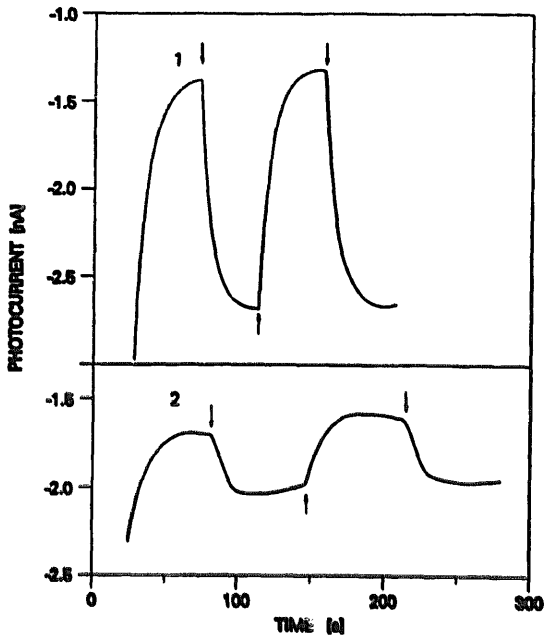

Fig. 2. Kinetics of generation and decay of density of photocurrent $I(t)$ (calculated on 1 cm^2) for Chl *a*: (1) $c=10^{-3}$ M; (2) $c=10^{-4}$ M; arrows: light on or off.

Table 1
Properties of the investigated cells

Pigment in nematic liquid crystal	Concentration (M)	Intensity of illumination (mW cm^{-2})	Amplitude of photocurrent (nA)
Chl *a* in EBBA/MBBA	10^{-3}	60	1.40
	10^{-4}	60	0.40
Chl *b* in EBBA/MBBA	10^{-3}	60	0.63
	10^{-4}	60	0.46
Bchl *c* in 6CHBT	10^{-2}	60	0.27
		100	0.32
(aggregates)	2×10^{-3}	60	0.16
		100	0.25

photopotential generation (not shown) is, in the case of these samples, from 10–45 mV depending on the sample concentration and the illuminating light intensity.

Fig. 3 shows the kinetics of generation and decay for BChl *c* aggregates in LC for two light intensities. In a case of aggregated BChl *c* samples the dark current was not stable during the first minutes of the cell investigation, but it reached saturation after 3–4 min. The increase in light intensity (Fig. 3) at the lower pigment concentration causes the increase in the photocurrent amplitude in approximation such as one can expect from the increase in the light intensity (Table 1). At the higher pigment concentration the ratio of photocurrent amplitudes is lower than the ratio of used light intensities (Table 1). The shape of kinetic curves for all investigated samples was similar and the changes with pigment concentration and light intensity exhibit similar characteristics. The amplitudes of photocurrent and photovoltage for various pig-

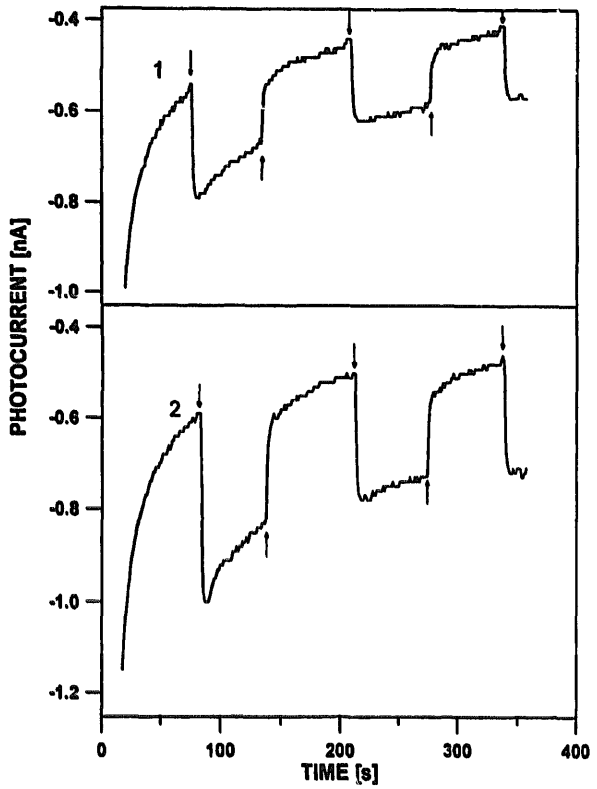

Fig. 3. Kinetics of photocurrent density $I(t)$ for two intensities of illumination for aggregates of BChl c ($c = 2 \times 10^{-3}$ M): (1) 60 mW cm^{-2}; (2) 100 mW cm^{-2}; arrows: light on or off.

ments at the same conditions of illumination and concentration were different (Table 1). At the same pigment type and concentration is always observed a change in the amplitude of the current generation after the exchange of the illuminated and dark electrode. This effect is predominantly due to the formation of the charged layers during first illumination. But also the properties of the electrodes are not identical as it follows from the comparison of the similar cells having an identical history of previous illumination. Therefore the data shown in Figs. 2 and 3 can be treated only as characteristic examples of the observed effects. In all cases the illumination causes a quick decreases in the absolute value of the negative dark current. It means that in darkness some negative charges are accumulated on the electrode and that these charges are partially neutralized by illumination. At the dark electrode, the negative potential is not changed. The amplitude of the photocurrent depends on the type of pigment and previous illumination of the cell but the current has always a cathodic character. The decays of photogenerated currents and potentials are faster than their increase in the beginning of the illumination. For an explanation of the observed direction of the photocurrent we can use the mechanism proposed by Haraguchi et al. [10] for the sensitization of SnO_2 electrode by the dye aggregates. For cathodic photocurrents they proposed the extraction of the conduction-band electrons from the semiconducting electrode by light created molecular excitons. These electrons could be supplied to some oxidizing agents in the sample. Similar positive values of photopotentials and photocurrents were previously observed in photoelectrochemical cells filled out with biological pigment–protein complexes [11] and for artificial complexes of pigments with polymers [12]. Similar sign of photogenerated currents and potentials was observed previously for the LC cell with merocyanine dyes [13]. The shape of the voltammograms means that the current–voltage dependences taken at so-called linear sweep, i.e. when the applied voltage V increases linearly with time ($dV/dt = \text{const}$) provides the information about the electrical properties of the pigmented cells [12,13]. Using simplified equivalent electrical circuits it is possible to evaluate the capacity and resistance of the measured cell [12].

Fig. 4 shows the current–voltage ($I(V)$) dependences measured for Chl a and Chl b at various voltage scan rates. The shapes of the $I(V)$ dependence exhibit not ohmic characteristics but also they are not similar to the dependance previously observed for merocyanines in the LC-semiconductor junction [13]. The hysteresis loop is much wider than observed before [12,13]. The shape of the $I(V)$ dependence

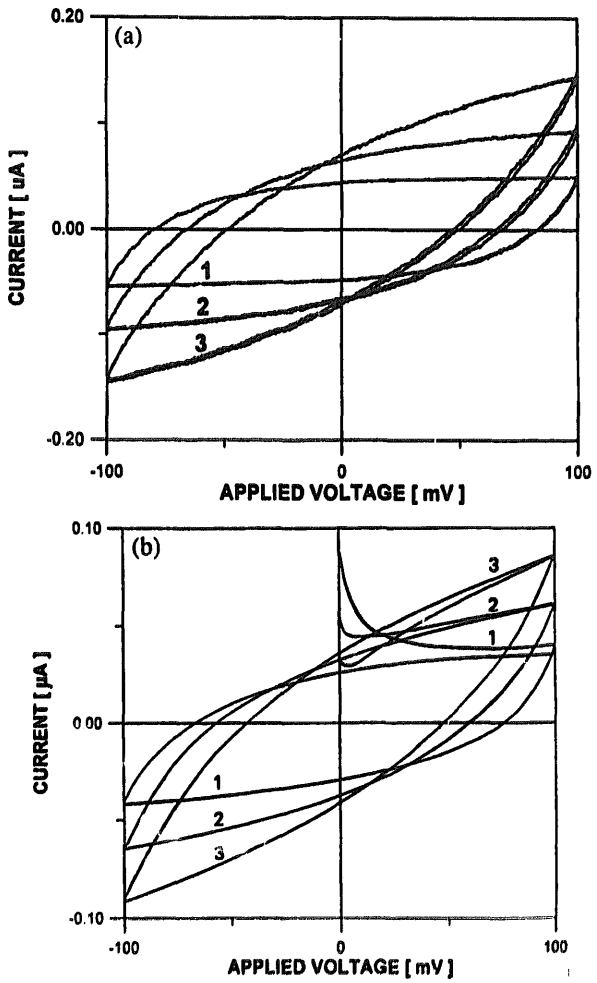

Fig. 4. Current–voltage dependences at various voltage scan rate: (a) Chl a; (b) Chl b ($c = 10^{-3}$ M); (1) 5 mV s^{-1}; (2) 10 mV s^{-1}; (3) 20 mV s^{-1}.

is different for various types of solvent [11,12] and even for various dyes added to the LC matrix [13]. The cyclic voltammograms are usually broader in the presence of dye than for LC alone [13], because the density of the surface charge on the electrode and in the vicinity of the electrodes increases. This increase is much stronger for chlorophylls (Fig. 4) than for merocyanines located in the same LC matrix [13]. Because the I/V ratio at the same voltage increases with the increase of dV/dt the charge reorganisation seems to be a rather slow process. The area inside the loop is practically independent of the rate of the voltage change but it depends on the pigment concentration (not shown) and on the type of pigment (Figs. 4 and 5).

Evaluated cell capacity values decrease with the increase in scan rate (Fig. 6). This shows that a quick change in V perturbed the charge distribution which gives at stable voltage condition a strong increase in the capacity of the cell in comparison with those calculated from the geometry of the cell and LC dielectric constants. For unpigmented cells the calculated capacity is about 1×10^{-9} F, whereas the cells with pigments exhibit a capacity evaluated from $I(V)$ curves in the of order 10^{-6} F (Fig. 6). This difference is related to the spacial charge distribution in a cell [12]. This distribution is strongly perturbed by light as it follows from current generation. The capacity of the cells with Chl *b* is lower than that caused by the Chl *a* addition (Fig. 6). A much lower increase in the capacity values for all monomeric dyes samples is due to BChl *c* aggregates addition. As seen in Fig. 5 showing the cyclic voltammograms for BChl *c* monomers and aggregates, the dye aggregation has strong influeneces on the electrical properties of LC cells. In a case of several redox reactions [14] the character of the cyclic voltammograms should be more complicated, therefore it seems that in every one pigment only one type of redox reaction is occurring in every type of investigated cells.

From Fig. 6, giving the values of the cells capacities calculated from the $I(V)$ dependences at various voltage scan

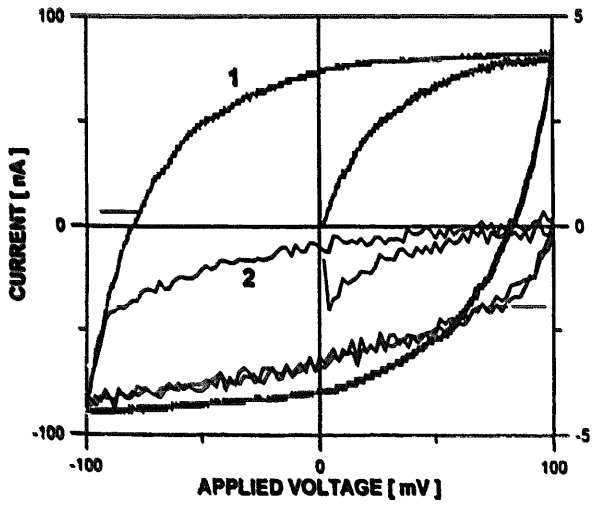

Fig. 5. Current–voltage dependences for monomeric BChl *c* (1) and for BChl *c* aggregates (2). Voltage scan rate: 10 mV s^{-1}.

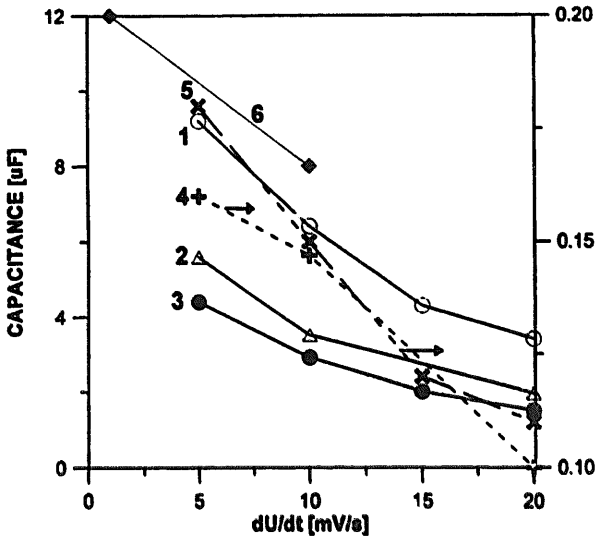

Fig. 6. The dependence of evaluated cell capacities on the voltage scan rate: (1) Chl *a*, $c = 10^{-3}$ M; (2) Chl *b*, $c = 10^{-3}$ M; (3) Chl *b*, $c = 10^{-4}$ M; (4) BChl *c*, $c = 10^{-2}$ M; (5) BChl *c*, $c = 2 \times 10^{-3}$ M (curves 4 and 5: aggregates); (6) BChl *c*; $c = 5 \times 10^{-3}$ M (monomeric form).

rates it follows that the same pigment (BChl *c*) at various states of aggregation is responsible for very different space charge generated near to the electrodes. The dye aggregation in the LC sample is depending on the state of aggregation of the dye introduced into the LC, because the LC solvent prevents the change in pigment aggregation [6]. Tetrameric and monomeric forms of BChl *c* differ in their order of uniaxial orientation in LC as well as in the angle formed by Q_y transition moments with the direction of preferential LC orientation axis. As a result the amount of light absorbed by these two forms at the same illumination incident perpendicular to the cell window should be different. Also the interaction of monomers and tertramers with LC can be different. The much lower capacity values of the cells filled out with BChl *c* aggregates compared with these observed for all pigments monomers (Fig. 6) shows the space charge generated in darkness for cell with aggregates is much lower than that for pigment monomers. It suggested the weaker interaction between electrode and aggregated pigment than in a case of pigment monomers. The strong dependence on the speed of the voltage change suggests the slow processes of charges displacements.

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References

[1] J. Amesz, *The Photosynthesis*, Elsevier, Amsterdam, New York, Oxford, 1987.

[2] J. Goc, M. Hara, T. Tetsuya and J. Miyake, *J. Photochem. Photobiol. A: Chem.*, *93* (1996) 137.
[3] K. Iryama, N. Ogura and A. Takamiya, *J. Biochem.*, *76* (1974) 901.
[4] A. Dudkowiak, C. Francke and J. Amesz, *Photosynth. Res.*, *46* (1995) 427.
[5] A. Dudkowiak, C. Francke, J. Amesz, A. Planner, I. Hanyz and D. Frackowiak, *Spectrochim. Acta, A: Biomolecular Spectroscopy, 52* (1996) 251.
[6] A. Dudkowiak, C. Francke, J. Amesz, A. Planner and D. Frackowiak, *Spectrochim. Acta, A: Biomolecular Spectroscopy*, in press.
[7] D. Frackowiak, D. Bauman and M.J. Stillman, *Biochim. Biophys. Acta, 681* (1982) 273.
[8] D. Frackowiak, S. Hotchandani and R.M. Leblanc, *Photobiochem. Photobiophys.*, *6* (1983) 339.
[9] J.M. Olson and R.P. Cox, *Photosynth. Res.*, *30* (1991) 35.
[10] A. Haraguchi, Y. Yonezawa and R. Hanawa, *Photochem. Photobiol.*, *52* (1990) 307.
[11] D. Frackowiak, L.E. Erokhina, Cz. Jadzyn, L.M. Shubin and A.Ya. Shkuropatov, *Photosynthetica, 15* (1981) 36.
[12] D. Frackowiak, M. Romanowski, S. Hotchandani, L. LeBlanc, R.M. Leblanc and I. Gruda, *Bioelectrochem. and Bioenerget., 19* (1988) 371.
[13] J. Goc and D. Frackowiak, *J. Photochem. Photobiol. A: Chem., 51* (1991) 233.
[14] J. Redepennig and N. Tao, *Photochem. Photobiol., 58* (1993) 532.