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# Bacteriorhodopsin Analogs, Bearing Modified Chromophore as a Basis for the Photochromic Materials

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Relationships of the chromophore structure and photochemical behaviour of bacteriorhodopsin analogs in solution and their possible technical applications were discussed.

*Keywords:* retinal; bacteriorhodopsin; chromophore modification; photochromic materials

## Introduction

Bacteriorhodopsin (BR) is a light-driven proton translocase from *Halobacterium salinarium,* discovered in 1971 by Oesterhelt and Stoeckenius. BR is localized in specialized areas of the cell membrane, so-called purple membranes (PM). It has a chromophore group - retinal (vitamine A aldehyde) protonated Schiff base ($SBH^+$) with an ε-aminogroup of $Lys^{216}$-residue [1-4]. After absorbing a quantum of light,

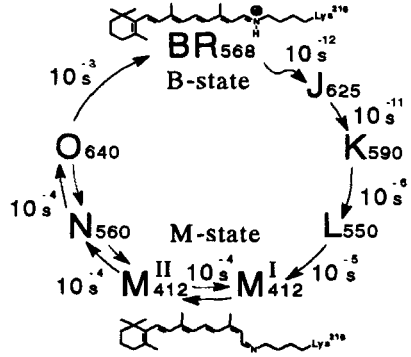
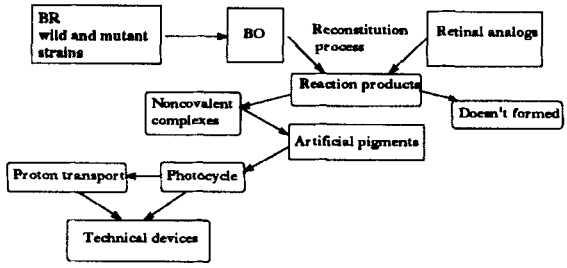



Fig. 1. A BR photochemical reactions' cycle [1,5].

BR undergoes a cycle of photochemical reactions (see Fig. 1), which are accompaning conformational changes in its chromophore and protein parts. The main key states are the B-state ( $\lambda_{max}$ 570 nm, $\varepsilon$ 63000 $M^{-1}$ $cm^{-1}$) and the M-state ($\lambda_{max}$ 412 nm, $\varepsilon$ 34000 $M^{-1}$ $cm^{-1}$, $\phi$ 0.64). This paper summarizes our results on modification chromophore structure affect on the spectral and on the photochemical characteristics of its analogs' interaction products with bacterioopsin (BO) [1,2].




Scheme 1. BR analogs' preparation procedure.

**Results and Discussion.**

Availability of a cycle of reversible photochemical reactions allowes to create a number of photochromic and holographic media on this protein

basis [3-5]. The changes in the molecule's photochromic properties during the photocycle can be utilized in information technology components with optical input- and optical output-signals. The proton release and intake around the M-state form the basis for components with optical input- and electrical output-signals. It was found that BR is a particularly promising photochromic material with a high reversibility quotient, surpassing many materials currently in use. Unfortunately, the practical application of such photochromic materials is limited by the fast M-form decay (~ 10 ms) in natural BR. Lately, several perspective directions were proposed in this area: 1) utilisation of natural BR incorporated into a polymer matrix, oriented Langmiur-Blodgett films or oriented layers' immobilisation on solid support; 2) using of mutants BR strains with slower photocycles [3]. Our approach includes the substitution of natural BR chromophore - retinal - for its analogs. During last years our group carried out a comprehensive investigation the influence of functional responsible element of the chromophore structure' (FRECS) nature on BR analogs' formation spatial restrictions and its photochemical behaviour.

Interaction of polyenals with BO starts from the formation of a noncovalent complex with $\lambda_{max}$ in the range 390 - 460 nm, which can, although not always be converted to the pigment (see Scheme 1). Such transformation is usually accompanied by bathochromic shift of absorption band, reflecting formation of protonated SB.

The comparative analysis of our database, including the information on spectral characteristics and proton transport efficiency of the interaction products more than 340 polyenic compounds with BO has shown, that,

it is possible directly to change a $\lambda_{max}$ in BR analogs' spectra in the rather wide interval (from 412 to 830 nm) by diversified the FRECS nature, though not all of these pigments are capable to cyclic photochemical reactions [1,2]. However, the problem of a quantitative estimation of influencing FRECS on chromophore - protein interaction character in BR is quite complicated. For this purpose the next parameters were proposed: - "opsin shift" (Os) [6] and - "red shift" ($\Sigma$RS) = (Os) + ($\Delta$SB) + ($\Delta$SBH$^+$), responsible for spectral shift of analog relatively model - nonprotonated all-E-retinal SB with n-butylamine [7]. These parameters reflect the following contributions: a) interaction with microenvironment of BR chromophoric centre cavity - (Os) = $1/\lambda_{max}$ SBH$^+$ - $1/\lambda_{max}$ ($P^{L-A}$); b) shift of $\lambda_{max}$ position due to replacement of natural retinal in nonprotonated SB by its analog - ($\Delta$SB) = $1/\lambda_{max}$ SB - $1/\lambda_{max}$ SB(all-E-retinal); c) shift accompanying protonation of retinal analog - ($\Delta$SBH$^+$) = $1/\lambda_{max}$SB - $1/\lambda_{max}$ SBH$^+$. We conducted the calculations of these parameters for BR analogs' selection serie (shown in Table 1 and Fig. 2), which are by our opinion, the most promising for technological applications (photochromic materials, holographic media, optic memory elements, etc., see [4,5]).

The BR (1,2) analogs' photocycle kinetics is very similar, but others BR analogs have a slow component of M-state decay and slow relaxation of B-state back reaction part of the its photocycle. This slow component is only slightly appeared in BR (7,8), arised in BR (6) and rather significant in BR (4) (slow in several times). The most drastically retardation takes place in 4-ketoBR, where back-reaction velocity was slowed-down on ~3 orders.

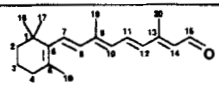
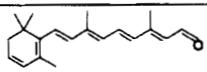
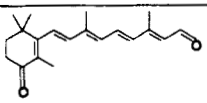
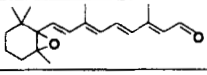
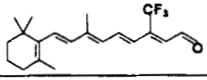
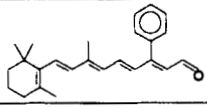
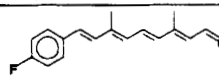
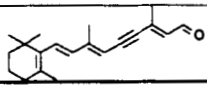
aromatic BR analogs:
y(SB) = 21.542 + 0.884x; (R 0.98);
y(SBH$^+$) = 160.7 + 1.57x; (R 0.99);
y(P(LA)) = -3.015 + 1.283x; (R 0.90).

BR analogs with C-13-substituted chromophore:
y(SB) = 138.40 + 0.578x; (R 0.51);
y(SBH$^+$) = -173.0 + 1.614x; (R 0.82);
y(P(LA)) = -756.8 + 3.433x; (R 0.75).

11,12-didehydro BR analogs:
y(SB) = 70.997+ 0.776x; (R 0.82);
y(SBH$^+$) = 74.632 + 0.969x; (R 0.88);
y(P(LA)) = -15.13 + 1.306x; (R 0.90).

BR analogs with substituted trimethylcyclohexene ring:
y(SB) = -40.27 + 1.609x; (R 0.91);
y(SBH$^+$) = 36.305 + 1.059x; (R 0.86);
y(P(LA)) = 99.43 + 1.53x; (R 0.69).

TABLE 1. Structure and photochemical properties of BR analogs.

| N | Bacteriorhodopsin chromophore analog structure | $\lambda_{max}$ $P^{LA}$form (B-state) nm | $\lambda_{max}$ M-state nm | M-state decay type | (OS) $cm^{-1}$ | Σ(RS) $cm^{-1}$ |
|---|---|---|---|---|---|---|
| 1 |  6-s-cis- **1a** 6-s-trans- **1b** | 568 | 412 | fast | 5120 3900 | 10480 9870 |
| 2 |  | 603 | 425 | fast | 5010 | 8440 |
| 3 |  | 506 | 410 | slow | 3770 | 6970 |
| 4 |  | 452 | ≤375 | slow | 1680 | 8370 |
| 5 |  | 624 | 430 | fast | 5390 | 11000 |
| 6 |  | 572 | 415 | slow | 4500 | 9100 |
| 7 |  | 514 | 395 | slow | 3040 | 7640 |
| 8 |  | 539 | ~410 | slow | 5370 | 12280 |

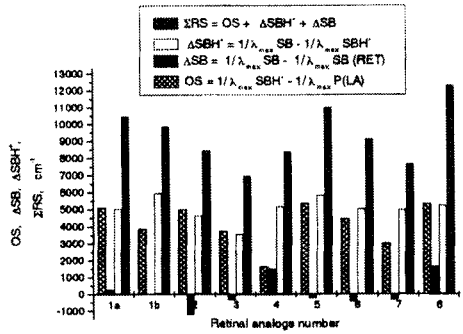



Fig.2 Individual components' contribution in ΣRS of BR analogs spectra.

Also, our data show that in the frames of defined type modification relationship between $\lambda_{max}$ position in dependence of FRECS nature adequately described by linear regression equations in axes (Y) - $\lambda_{max}$SB or ($SBH^+$, $P^{LA}$) / (X) - $\lambda_{max}$(CHO).

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