

CHEMICAL MODIFICATION OF BACTERIORHODOPSIN: REMARKABLE RED SHIFTS
OF PYRROLE POLYENAL PROTONATED SCHIFF BASES AND RECONSTRUCTION OF
A BACTERIORHODOPSIN ANALOG BY THE USE OF A PYRROLE POLYENAL

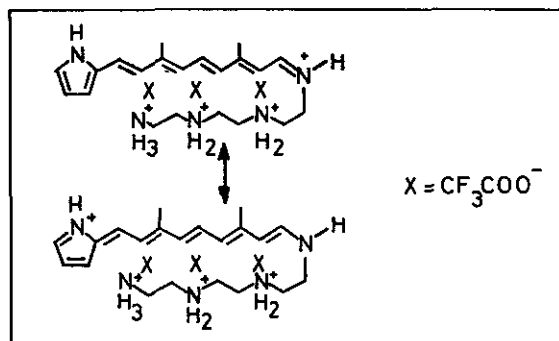
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3,7-Dimethyl-9-(pyrrol-2-yl)nona-2,4,6,8-tetraenal 1 was prepared as a retinal analog. 1 was reacted with $\text{H}_2\text{N}-(\text{CH}_2-\text{CH}_2-\text{NH})_n-\text{CH}_2-\text{CH}_2-\text{NH}_2$ 2 ($n = 0, 1, 2$ and 3) to form the corresponding Schiff bases. When protonated with CF_3COOH , large red shifts of the absorption maxima were observed on going $n = 0$ to $n = 2$. As the possible explanation of these shifts, effect of the presence of counter-anion CF_3COO^- , which are envisioned to be fixed by the polyamine chain as to be existed along the conjugated chain of the polyenal, was discussed.

Absorption Maxima of Protonated Salts of Aldehyde Schiff Base in EtOH/ CF_3COOH		
Amine	Aldehyde	λ_{max} (nm)
$n=0$	<u>1</u>	542
$n=1$	<u>2</u>	561
$n=2$	<u>3</u>	567
$n=3$	<u>4</u>	562
$t\text{-BuNH}_2$	<u>5</u>	530
$n\text{-BuNH}_2$	all trans-retinal	445



When 1 was incorporated into bacteriorhodopsin, it exhibited a purple color showing two absorption maxima at 537 and 550 nm ($\text{pH} = 7.0$). On acidification it turned blue showing an absorption maximum at 610 nm ($\text{pH} = 1.5$). The reconstructed bR analog behaved similarly to the native bacteriorhodopsin with respects to the photo-bleaching (M_{412} formation) and its thermal back-isomerization to the initial state ($M_{412} \rightarrow B_{550}$). The reconstruction process was studied by Lineweaver-Burk plots. The thermal back-isomerization process was studied by using low-temperature UV-Vis spectroscopy. The rates and thermodynamic parameters collected from the binding process and from the back-isomerizations were compared with those obtained from the native and bR analog formed from 3,7-dimethyl-9-(2-furyl)-nona-2,4,6,8-tetraenal. Finally, effects of puttig nitrogen atoms on termini of the conjugated polyene chain were discussed in the light of the pyrrole polyenal incorporated bacteriorhodopsin.