Resolving Temperature-Independent Electron Transport across 6 nm Protein Monolayer: Effect of Conjugated Cofactor

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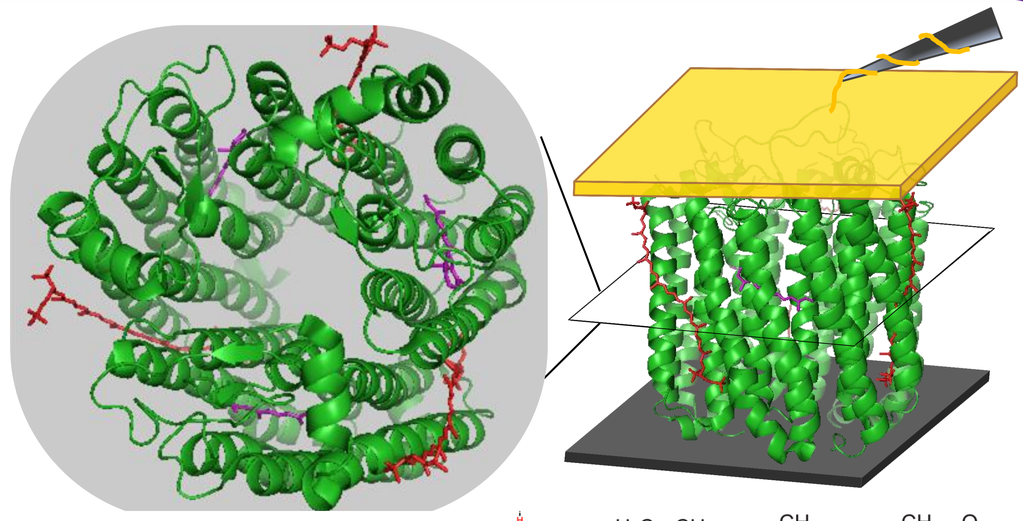
Halorhodopsin (phR)

- Seven-transmembrane protein of the retinal protein family related to light-gated ion channel, specific for chloride ions.
- Found in phylogenetically ancient archaea, known as Halobacteria Salinarum.
- phR contains photoactive retinal (as bacteriorhodopsin) and an additional cofactor, bacterioruberin, a carotenoid like chromophore, located along the long axis of the protein.



① Aim –

- To reveal the contribution from ~ 4 nm long, π-conjugated, carotenoid like protein-cofactor (bacterioruberin) in solid state electron transport (ETp).
- Realization of ETp(T) mechanism across the protein-chromophore complexes (peptide matrix with retinal and bacterioruberin cofactors)

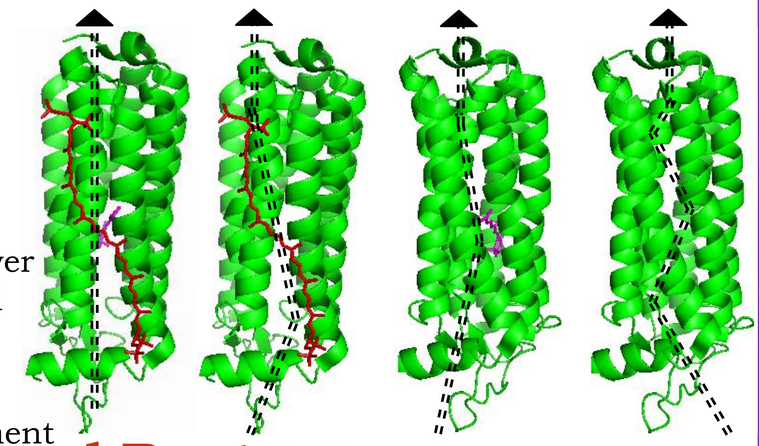
② Our Approach –

1. Temperature dependent ETp studies across phR monolayers in sandwiched configuration between two electronically conducting, ionically blocking electrodes.

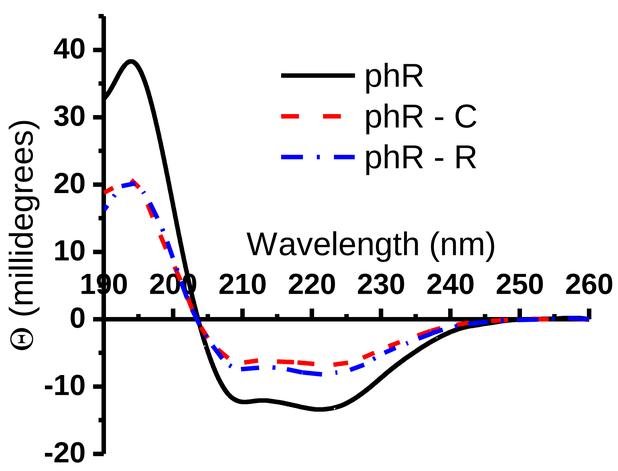
2. Depict the role of bacterioruberin and retinal in ETp efficiencies across monolayer of phR and its' different derivatives as a function of temperature-

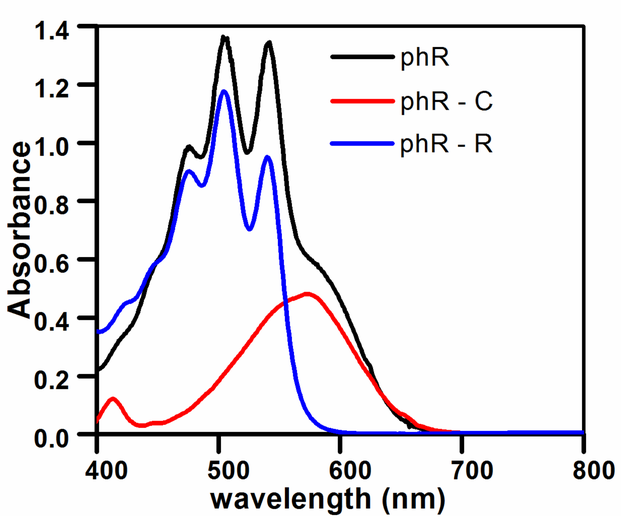
phR Derivatives

- **Apo(ruberin)-phR (phR-C)**
  Oxidization of bacterioruberin with $K_2S_2O_8$
- **Apo-retinal phR (phR-R)**
  Hydroxylamine treatment to sever the retinal-protein covalent bond
- **Apo retinal-bacterioruberin phR (phR – R|C)**
  Successive Hydroxylamine treatment and oxidization of bacterioruberin

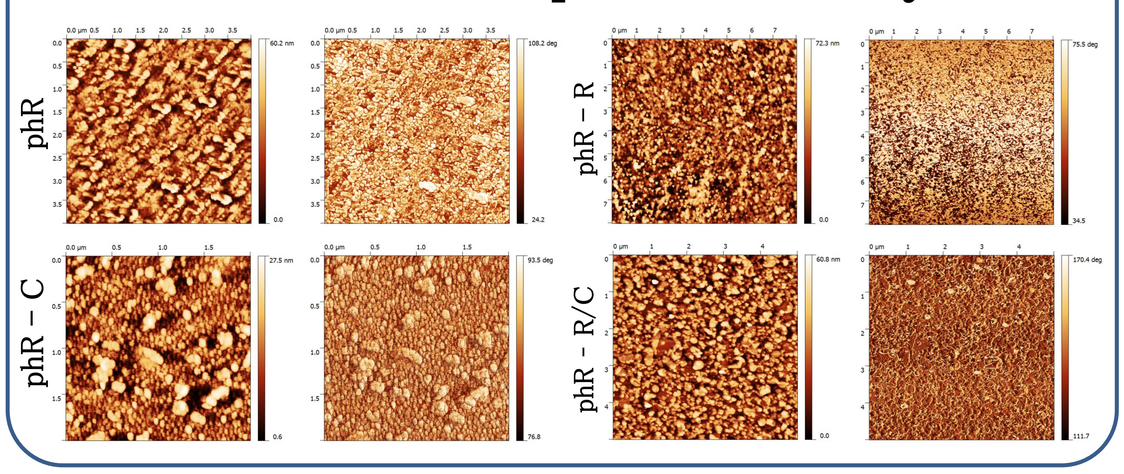


Preservation of protein structures & optical properties



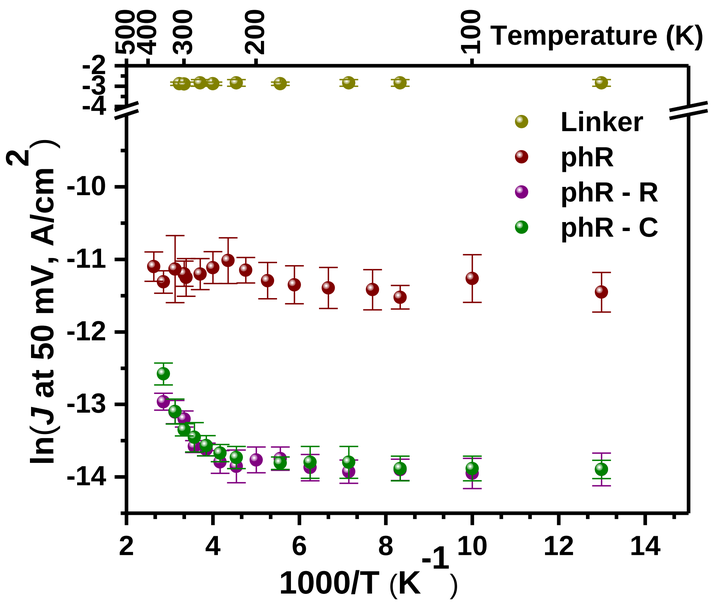


Topographical characterization of phR and its derivative protein-monolayers



Temperature Dependent ETp

- **6 nm** thick phR monolayer – **Temperature independent** ETp like Linker (APTMS) and holo-Azurin protein monolayer
- Temperature dependent ETp (> 180K) via both phR-C and phR–R monolayer (~ 6 nm)
- Modification of both cofactors significantly lower ETp efficiencies in both tunneling and hopping regimes



ETp efficiencies of phR and its' derivative protein monolayer at 300K (measured in terms of Current-Voltage)

Comparison of ETp efficiencies between (Current density @ 50 mV) phR protein families with other different proteins

③ Conclusions –

- ✓ Conjugated cofactor, bacterioruberin enables room temperature tunneling-like electronic transport across ~ 6 nm long halorhodopsin – possibly superexchange-mediated transport following efficient coupling with both electrodes.
- ✓ Bacterioruberin by itself is not sufficient to provide activation-less transport in phR as obtained with phR-R protein.
- ✓ ETp via phR is cooperatively supported by both retinal and bacterioruberin cofactors.
- ✓ Activation-less and thermally activated multiple transport pathways are co-exist across different proteins structure.

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