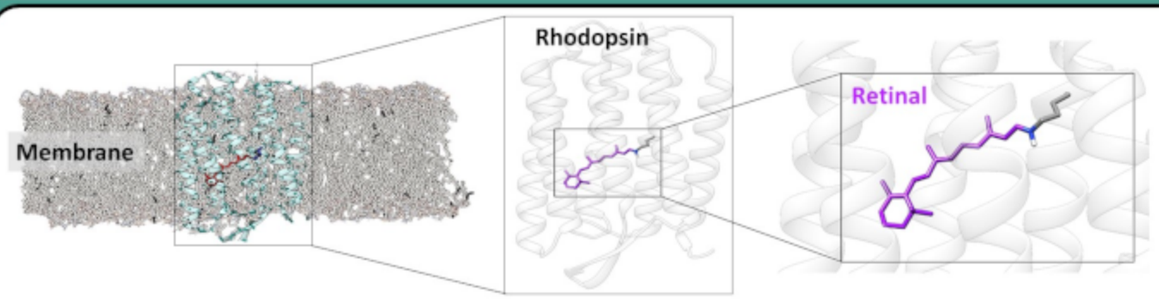
# Involvement of the Triplet State in Retinal Isomerization

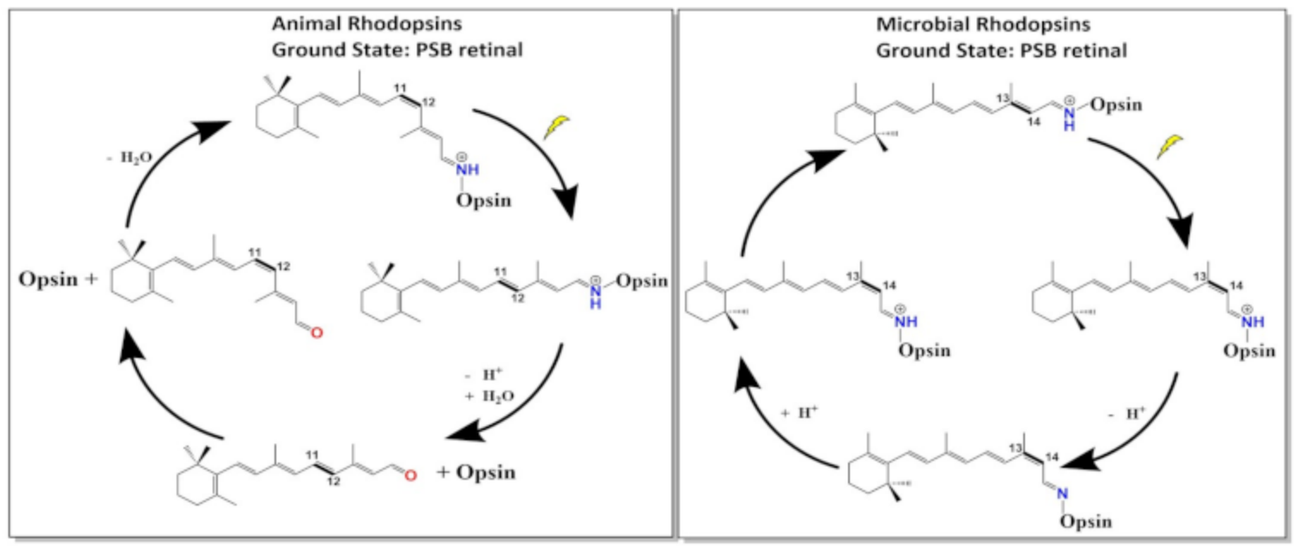
Ofer Filiba, Veniamin Borin and Igor Schapiro

Fritz Haber Center for Molecular Dynamics Research, Institute of Chemistry, The Hebrew University of Jerusalem, Israel

## Introduction



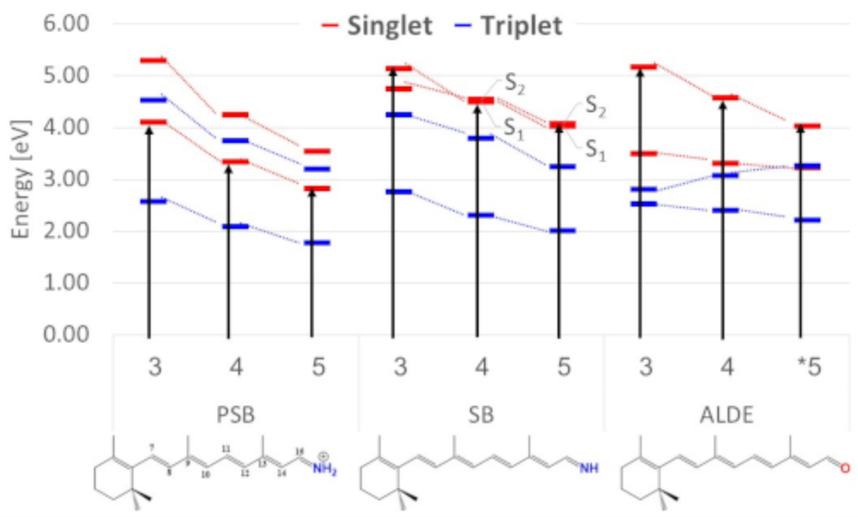

- The activation of microbial and animal rhodopsin is initiated by the photoexcitation of the **PSB Retinal** that is followed by an ultrafast isomerization
- The following sequence of events is distinct for each type of rhodopsin, but nevertheless share a common principle which states that the isomerization is initiated in the $S_1$ excited state
- A study of the **PSB Retinal** by González-Luque *et.al* [4] suggests that populating the lowest triplet state lowers the quantum yield of the *cis*-to-*trans* isomerization through an intersystem crossing (ISC)
- To date, the involvement of the triplet state in the initial step of the **PSB Retinal** isomerization is unclear. In this work we have studied three retinal analogues




## Computational Methodology

All calculations were performed at the extended multi-state complete active space second order perturbation (**XMS-CASPT2**) level of theory and the cc-pVDZ basis set[1,2]. The active space includes all π-orbitals for PSB Retinal models. Due to the presence of the lone pairs on oxygen (aldehydes) and nitrogen (SB) atoms, the n-orbitals are also included in the active space. Consequently, the active space of SB and aldehyde retinal models consist of $2N+2$ electrons $(2N\pi+2n)$ and $2N+1$ orbitals ($2N$ $\pi$-type orbitals and one n-orbital), where $N$ is the number of double bonds.

## Excitation Energies (XMS-CASPT2)

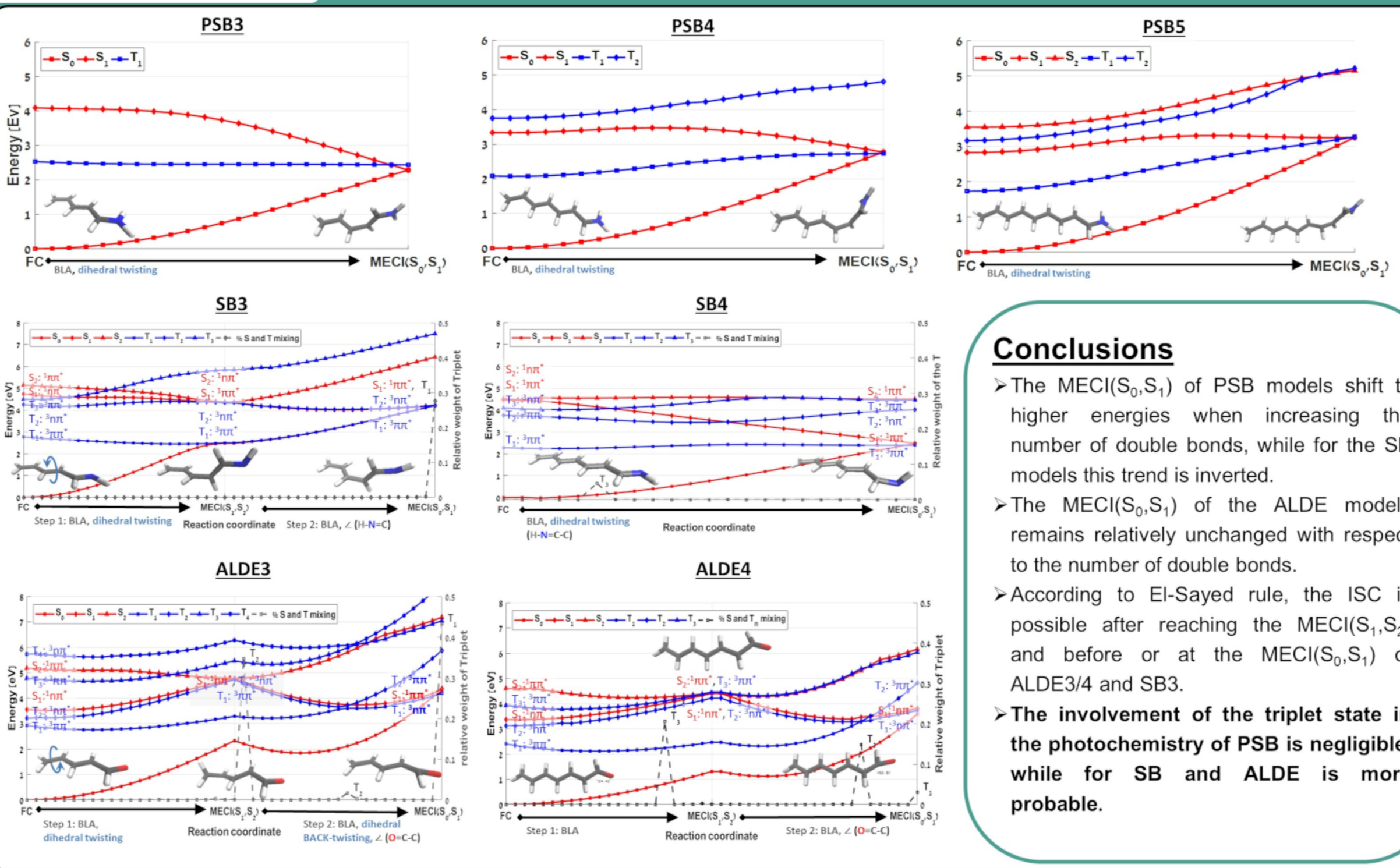



**PSB:**
- $S_1$ is always the bright state and one triplet state is found below.

**SB:**
- $S_2$ is the bright state in SB3 but for longer chains it changes to $S_1$
- Two triplet states are found below the bright singlet excited state. The second triplet state has nπ* character

**Aldehydes:**
- $S_2$ is the bright state for all models
- Two triplet states are found below the bright singlet excited state

## Potential energy scan




## Conclusions

- The MECI($S_0$,$S_1$) of PSB models shift to higher energies when increasing the number of double bonds, while for the SB models this trend is inverted.
- The MECI($S_0$,$S_1$) of the ALDE models remains relatively unchanged with respect to the number of double bonds.
- According to El-Sayed rule, the ISC is possible after reaching the MECI($S_1$,$S_2$) and before or at the MECI($S_0$,$S_1$) of ALDE3/4 and SB3.
- **The involvement of the triplet state in the photochemistry of PSB is negligible, while for SB and ALDE is more probable.**

## References

1. BAGEL, Brilliantly Advanced General Electronic-structure Library. http://www.nubakery.org under the GNU General Public License.
2. Shiozaki, T. WIRES Comp. Mol. Sci. 2018, 8, 1331. DOI: 10.1002/wcms.1331
3. Levine, B. G.; Coe, J. D.; Martínez, T. J., J. Phys. Chem., 2008,112B, 405. DOI: 10.1021/jp0761618
4. González-Luque, R.; Olaso-González, G.; Merchán, M.; Coto, P.B.; Serrano-Andrés, L.; Garavelli, M., Int. J. Quantum Chem., 2011, 111, 3431, DOI: 10.1002/qua.23079

## Acknowledgement

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