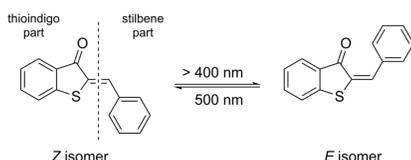


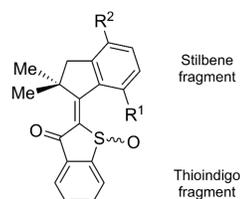
### The HTI-based molecular motor

The molecular motor is based on the photoswitch hemithioindigo (HTI)

- HTI undergoes efficient and reversible *Z/E* isomerisation at the central double bond upon irradiation with visible light (see [1] for a complete overview of the photochemistry)



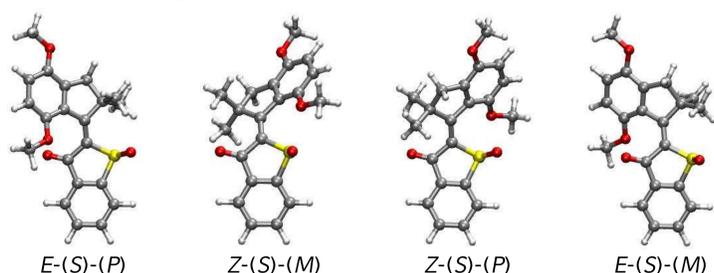
- Dube et al. implemented additional stereochemical elements into the HTI framework to achieve unidirectional rotation around the central doublebond [2]



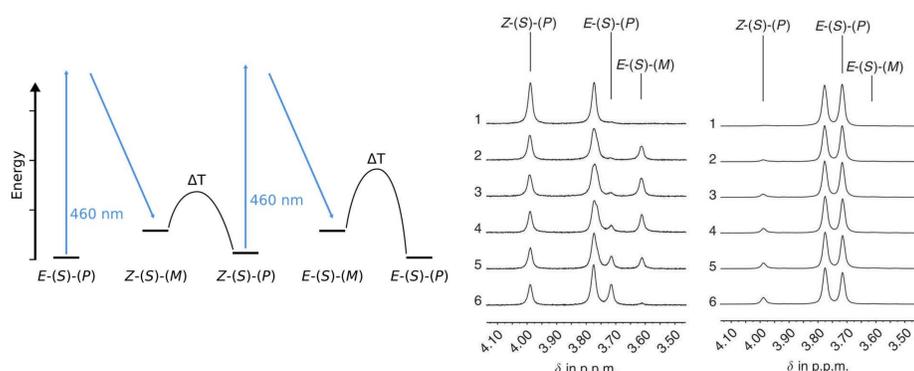
#### Stereochemical elements:

- oxidized sulfur atom introduces stereocenter (*R*- or *S*-configuration)
- sterical crowding at the ring-fused stilbene fragment results in a helical twisting (*P*- or *M*-helicity)

Combined with the *Z/E* isomerisation the motor can adopt four different diastereomeric structures per *R/S*-configuration of the sulfoxid



- Low temperature <sup>1</sup>H-NMR spectroscopy uncovered a four step process for the rotation, consisting of two thermal and two photoinduced steps [2]



### Quantumchemical studies

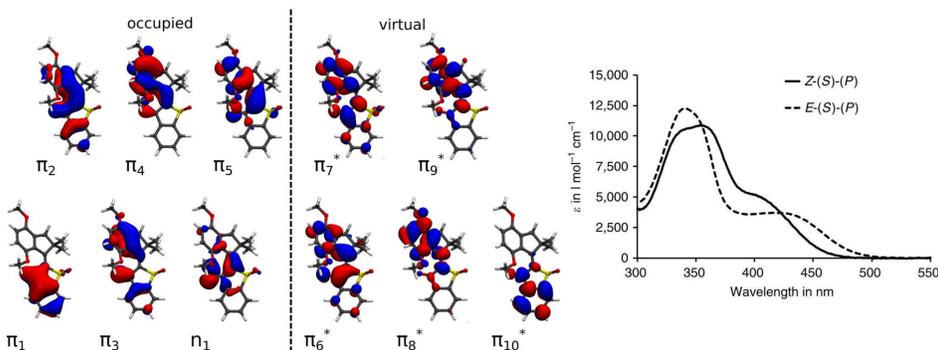
#### What do we want?

Elucidate the pathways for both photoinduced steps and identify the important points necessary for the rotation

#### What do we use?

All calculation were done at CASSCF level of theory utilizing a (12/11) active space and using the 6-31G\* basis set. (powered by MOLPRO 2015)

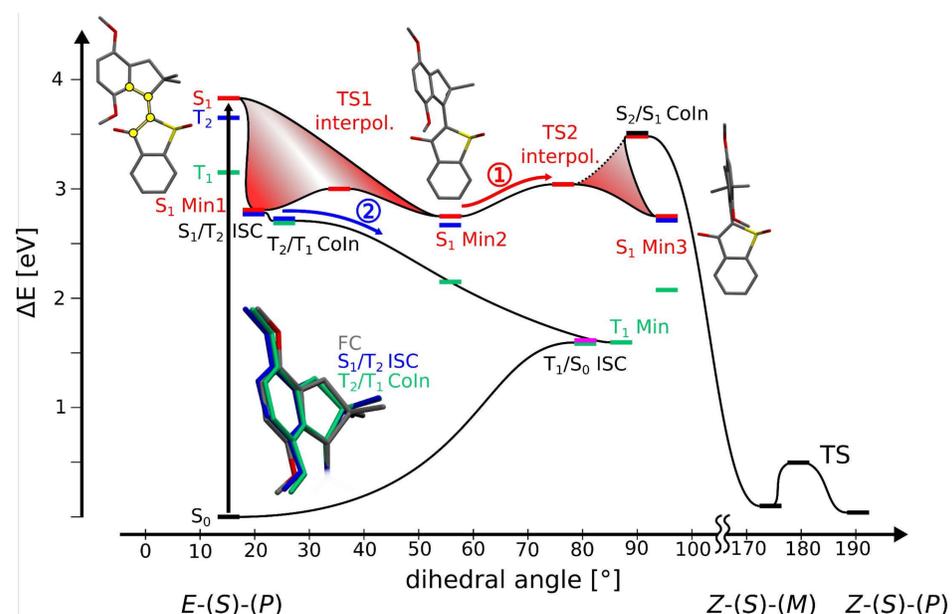
#### Active space and absorption spectra



#### Vertical excitations and oscillator strengths

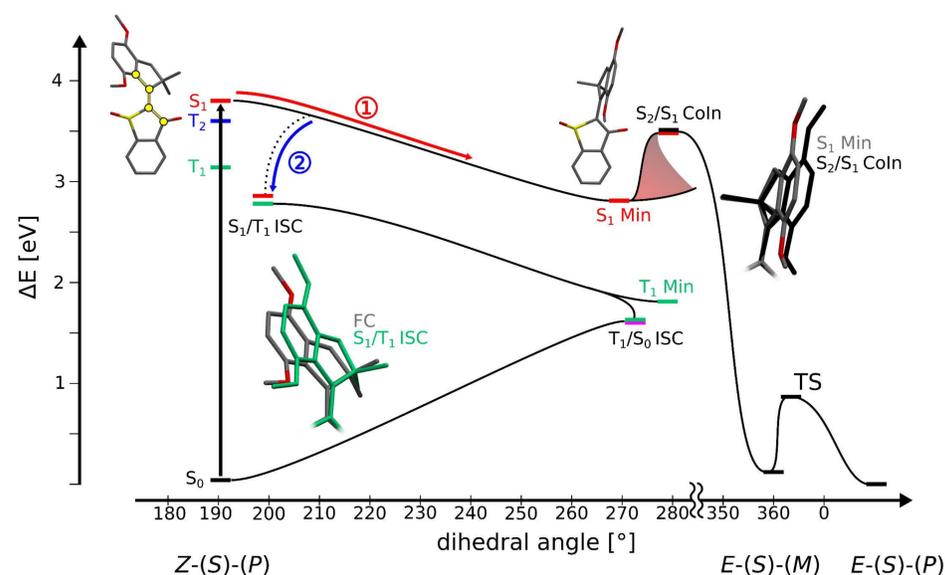
Char.	CAS [eV]	RS2C [eV]	CCSD [eV]	TDDFT [eV]	Exp. [eV]	CAS [a.u.]	CCSD [a.u.]	TDDFT [a.u.]
S1	$n\pi^*$	3.83	3.53	3.50	3.37	2.88	0.001	0.029
S2	$\pi\pi^*$	5.40	4.19	3.85	3.64	3.64	0.148	0.114
S3	$\pi\pi^*$	5.94	4.46	4.33	4.07		0.507	0.147
T1	$n\pi^*$	3.16	3.04		2.39			
T2	$\pi\pi^*$	3.66	3.40		3.05			

### Reaction path for the step from *E*-(*S*)-(P) to *Z*-(*S*)-(M)



- Excitation (460 nm) leads to population of the  $S_1$  state
- The system can relax to both  $S_1$  minima ( $S_1$  Min 1/2), connected via a small barrier
- Depending on the minimum two pathways are possible:
  - From the  $S_1$  Min2 a third  $S_1$  minimum is reachable; After passing the barrier (TS2 interpol.) the system can relax to the groundstate of *Z*-(*S*)-(M) via the  $S_2/S_1$  Con
  - At the  $S_1$  Min1 the system can cross over to the  $T_1$  via ISC; After relaxation to the  $T_1$  minimum, the *E*-(*S*)-(P) isomer is repopulated via a second ISC to the groundstate

### Reaction path for the step from *Z*-(*S*)-(P) to *E*-(*S*)-(M)



- Excitation (460 nm) leads to population of the  $S_1$  state
- The system relaxes to the  $S_1$  Min and is able to reach the groundstate of the *E*-(*S*)-(M) isomer via the  $S_2/S_1$  Con
- On the path to the  $S_1$  Min, crossing to the  $T_1$  state is possible via ISC; After relaxing to the  $T_1$  Min the *Z*-(*S*)-(P) isomer is repopulated via ISC to the groundstate

### Conclusion

- In both photoinduced steps the motor is able to complete the rotation in the  $S_1$  state via a conical intersection with the groundstate
- We found loss channels where the groundstate of the starting isomers is repopulated after reaching the  $T_1$  state
- Both pathways agree with femtosecond pump-probe experiments performed in the Riedle group → **Puplication in preparation**

### References

- [1] A. Nenov, T. Cordes, T. T. Herzog, W. Zinth, R. de Vivie-Riedle, *J. Phys. Chem. A* **114** (2010), 13016-13030  
 [2] M. Guentner, M. Schildhauer, S. Thumser, P. Mayer, D. Stephenson, P. J. Mayer, H. Dube, *Nat. Commun* **6** (2015), 8406