

Photochemical and Electrochemical Switching of Diarylethenes

Aleksandar Staykov and Kazunari Yoshizawa

IMCE, Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan

A combined theoretical and experimental study was performed on diarylethenes¹ and diarylethene-capped sexithiophenes² aiming the better understanding of the electrochemical and photochemical ring-opening and ring-closing mechanisms. Theoretical calculations, based on the DFT and TDDFT, suggested that the spatial distribution and the occupancy of the frontier orbitals determines and controls the diarylethenes' ring-opening and ring-closing upon photoirradiation, oxidation, and reduction.³ Optimized geometries, potential energy surfaces (PES), and activation energies between the open-ring and closed-ring forms were calculated for diarylethenes in ground state, excited states, mono- and dications. Analysis of the frontier orbitals was employed to understand the cyclisation and cycloreversion of diarylethenes and to predict and explain the switching properties of diarylethene-capped sexithiophene wires. The TDDFT data were verified with experimentally measured UV/Vis spectra. The DFT calculations estimated open-shell ground states of diarylethene-capped sexithiophene dications which were verified with EPR spectroscopy and the broadening of the peaks in the EPR spectra were explained with the calculated singlet-triplet splitting. The good agreement of experiments and theory allowed the understanding of switching behavior of diarylethenes in solutions, in metal break junctions, in monolayers on metal surfaces, and as a part of complex organic wires.

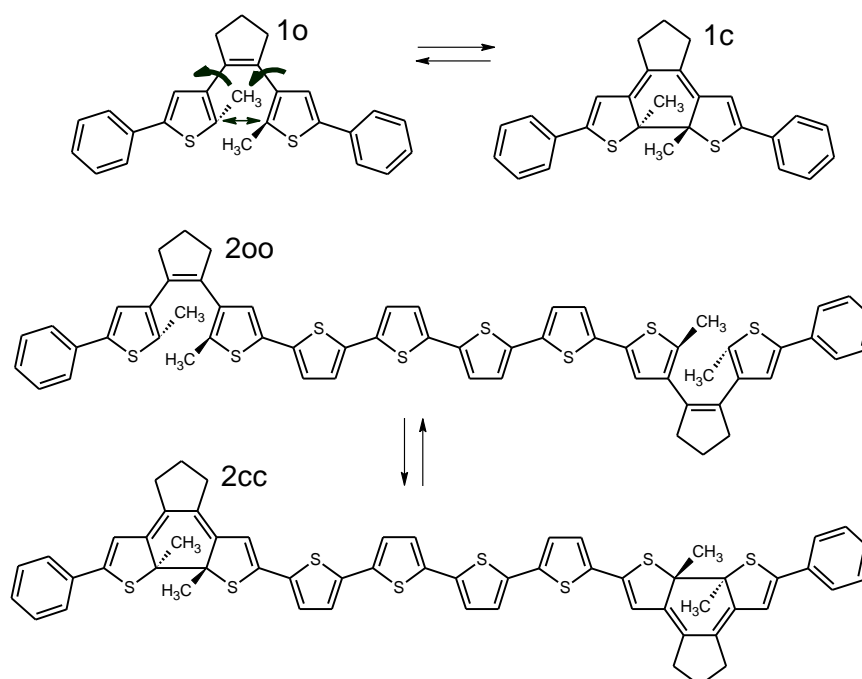


Figure 1. Investigated diarylethenes and diarylethene-capped thiophene wires.

An overview of the various different experimental data was made and a unified theory backed up by experimental evidences, which allows us to predict easily the switching properties of diarylethenes from the spatial distribution of their frontier orbitals was suggested. Both, the photochemical and electrochemical ring closings, are results of bonding interaction along the reaction coordinate within the LUMO and HOMO-1, respectively. The photochemical and electrochemical ring openings result from thermal distortions along torsion angles, which are favored by the anti-bonding interactions within the LUMO and HOMO-1, respectively. Thus, the right occupation of these orbitals can lead to the desired ring cyclization and cycloreversion. On the other hand the attachment of the diarylethenes to metal surfaces or complex organic molecules alters either the spatial distribution of the frontier orbitals or the probabilities for electron excitations to the desired excited states and in this way modifies significantly the switching properties. The suggested orbital control rule for control of switching properties can be applied to complex systems such as diarylethenes in mechanically controllable break junction and diarylethenes as a part of organic oligomeric wires. We performed calculations of PES of ground, cationic, and excited states with DFT and TDDFT. The theoretical studies are calibrated and compared with experimental UV/Vis and EPR spectra. We believe that our orbital rule will provide the experimentalists with additional tool for more effective molecular design of nanometric scale devices.

References:

1. Irie, M. *Chem. Rev.* **2000**, *100*, 1685.
2. Areephong, J.; Hurenkamp, J. H.; Milder, M. T. W.; Meetsma, A.; Herek, J. L.; Browne, W. R.; Feringa, B. L. *Org. Lett.* **2009**, *11*, 721.
3. Staykov, A.; Yoshizawa, K. *J. Phys. Chem. C*, **2009**, *113*, 3826.