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Switching of electrical conductance through diarylethenes and reversibility of the photochemical and electrochemical reactions on electrode surfaces and in solutions

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Quantum mechanical methods were applied in the investigation of diarylethenes' cyclisation and cycloreversion. A theoretical concept based on the orbital control of ring closing and ring opening along the reaction coordinate was suggested. We have calculated the potential energy surfaces (PES) for the ground state, excited states, monocation and dication of the investigated diarylethenes. The profile of the PESs and the activation barriers for the ring cyclisation and cycloreversion can be explained and predicted by the spatial distribution of the frontier orbitals and their occupancy. The theoretical results obtained in this study were used to explain the irreversible and reversible photoswitching of diarylethenes as well as their electrochemical switching. In this work we suggest an explanation for the experimental study on the cyclisation and cycloreversion of diarylethene capped sexithiophene wires. The experimentally obtained data, which are in agreement with the theoretical predictions, provided useful information for the dication multiplicity, and enriched the orbital control concept.

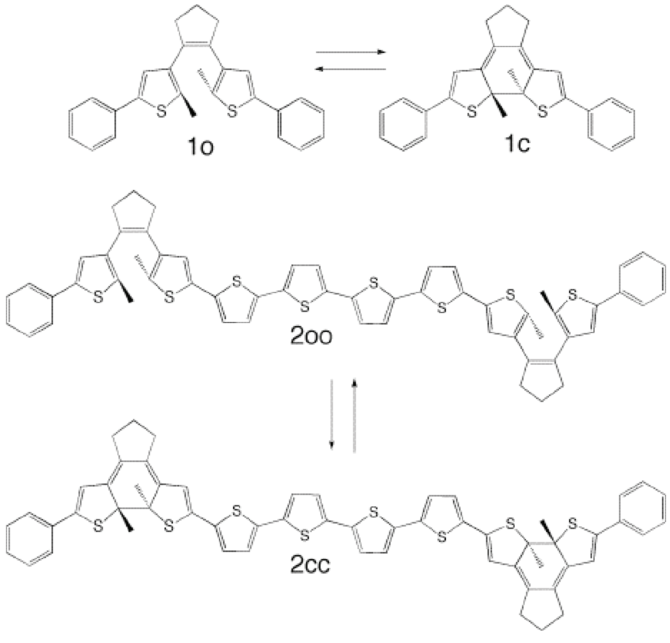

Figure 1:
Investigated diarylethenes. 1: 1,2-bis[5'-phenyl-2'-methylthien-3'-yl]cyclopentene; 2: Diarylethene capped sexithiophne wire. With index **o** are denoted the open-ring forms and with index **c** are denoted the closed-ring forms.

We have made an overview of the various different experimental data and suggested 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.

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 dihedral angles, which are favored by the antibonding interactions within the LUMO and HOMO-1, respectively. Thus, the right occupation of these orbitals can lead to the desired ring cyclisation 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. Our 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.

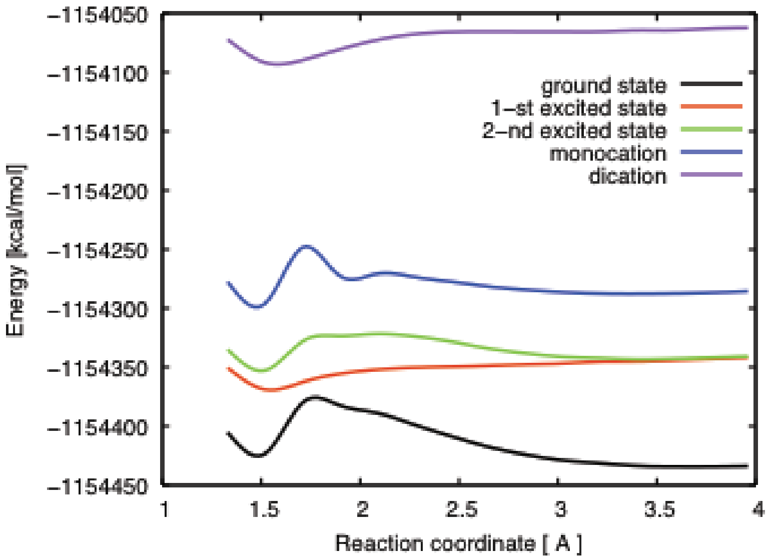

Figure 2:
PESs for the ground state, first excited state, second excited state, monocation, and dication, of 1,2-bis[5’-phenyl-2’-methylthien-3’-yl]cyclopentene.