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Understanding the Molecular Origin of the Collective Movement in a Diarylethene-based Photo-Responsive Actuator

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Remotely controlling macroscopic movement is one of the key elements to realize intelligent materials for applications ranging from sensing to robotics. Over the last few years, a number of photomechanical materials based on diarylethene derivatives have been developed. However, a detailed picture of the structural evolution within these soft actuators is often missing. In this work, an atomistic investigation uncovers how the photo-induced molecular dynamics propagates to large-scale motion and results in macroscopic deformation of the crystal. By correlating the intramolecular rearrangement within the photo-responsive switching unit with the intermolecular packing, the molecular mechanism for the photomechanical phenomena is deciphered, which is fundamental for a rational development of photo-responsive actuators.

Motility is one of the fascinating phenomena of living organisms.[1] By propagating dynamics at the molecular level into collective behavior, the motion is amplified to macroscale movement. In this regard, stimuli-responsive structures, which change their dimensions, shape or morphology depending on external conditions, play a key role.[2] Inspired by nature, tremendous work has been done to develop artificial systems capable of transferring external stimuli such as light into motion.[3] This has result in a number of bio-inspired systems including artificial muscles, sensors, soft robots and microscopic pumps.[4] One promising approach is the self-assembly of responsive molecular switching units into hierarchical structures. The resulting functional materials enable to accumulate and transmit the well-defined motion from the nanoscale to macroscopic functionality e.g. contraction and expansion of the corresponding crystal.[5] To convert efficiently and with high precision, the external input into mechanical energy, a detailed understanding of the molecular mechanism is crucial. Elucidat-

ing the operation mechanism of such energy transducers is fundamental for the development of intelligent materials. In particular, a direct correlation of the structural evolution at the atomic scale with the resulting large-scale dynamics is important to achieve programmable and on-demand functionality. Light has attracted, as an external input to remotely control these systems, much interest by providing among other features high spatiotemporal control.[6]

Molecular switches, which perform up on light excitation well-defined structural changes, are, in this context, core units to realize photomechanical materials.[7] For the development of light-controlled actuators, one promising class of switching units are diarylethenes.[8] The open and closed-ring isomers of diarylethenes are photochemically interconvertible but thermally stable. In particular, thiophene substituents derivatives (Figure 1) show high quantum yield, fatigue resistance and rapid response.[9] As the photocyclization even takes place with high quantum yield in crystalline phase, a larger number of actuators based on this photo-responsive motif have been reported.[10] For example, in a pioneering work, Irie and co-workers presented pronounced, light-induced deformation of diarylethene based single-crystals.[11] Moreover, the experimental studies show a significant impact of the molecular structure on the shape change of these molecular crystals (e.g.
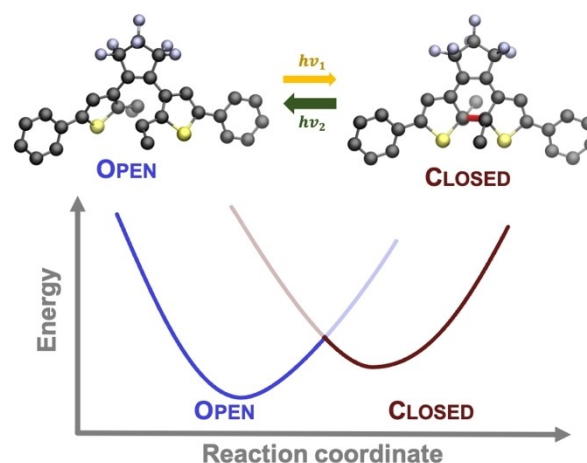
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Figure 1. Ball-and-stick model of the open and closed-ring isomer of 1,2-bis (2-ethyl-5-phenyl-3-thienyl)per-fluorocyclopentene (top, carbon: black, sulfur: yellow, fluorine: violet; hydrogen atoms are omitted for clarity, C–C bond formed up on photo-switching is highlighted in red) and schematic representation of the energy profile along the reaction coordinate connecting the two states of the photo-responsive unit, which was used as an ansatz to develop the force field (bottom).

elongation and bending) and thus highlight the potential to tailor the photomechanical properties of these actuators by well-defined modification of the diarylethene structure.

Despite these advances, a molecular mechanism is often missing due to the lack of atomic insight into the structural evolution. To reveal how the absorbed photon energy is converted into macroscopic movement, a detailed picture of the influence of the light-triggered atomic motion on the intermolecular interaction is crucial. Based on this, the resulting large-scale motion could be rationalized, providing a strong foundation to engineer photo-responsive actuator.

To study the structural evolution of the phase transition at the atomistic level an efficient representation of the diarylethene based molecular crystal is needed. Considering the reported ultra-fast decay process from the electronic excited state (ps-regime),[12] in this work, a model is developed to cover the long-scale relaxation and rearrangement at the molecular level (ms-regime), which predominantly take place in the electronic ground state. Within the framework of a molecular mechanics (MM) approach, an effective representation of the structural rearrangement is accomplished by switching between two potentials accurately describing each isomer (Figure 1). As will be discussed in detail below, this rather simple model is able to reproduce the experimentally reported contraction and expansion of a molecular crystal based on a thiophene substituted diarylethene: 1,2-bis(2-ethyl-5-phenyl-3 -thienyl)perfluorocyclopentene (Figure 1).[11] Moreover, a so-far not accessible detailed structural analysis is reported, which enables to reveal the molecular mechanism.

Following the previously reported protocol,[13] a genetic algorithm is used together with quantum mechanical (QM) references data to parametrized force fields representing each isomer (Figure 1). The developed force fields accurately describe both the structural and dynamic properties of each diarylethene isomers (see SI, Figure S1). In a next step, the validated potential was applied to investigate the structural change of the periodic system, starting from the experimentally reported single-crystal data of the open-ring structure.[11] By applying the developed force fields, the structural evolution is analyzed as a function of the switching state. The latter is defined by the percentage of molecules in the closed-ring isomer state. Using a simulation box containing 108 molecules and applying periodic boundary conditions, 50 independent initial configurations were randomly generated for each switching state. Subsequently, both the geometry and cell parameters were fully optimized at different switching states (Figure 2).

The structural analysis of these fully optimized periodic systems revealed a detailed picture of the phase transition. On the one hand the molecular crystal distinctly expands along the b-axis (ca. 6.3%) and on the other hand the systems contracts along the c-axis (ca. 8.5%) (Figure 3). This structural change is in perfect agreement with the reported experimental observation of the light-induced macroscopic crystal deformation,[11] which validates the applied theoretical approach. The atomistic simulations show further a continuous structural evolution as a function of the switching state. Experimentally not accessible, these data point out a direct correlation between the photo-
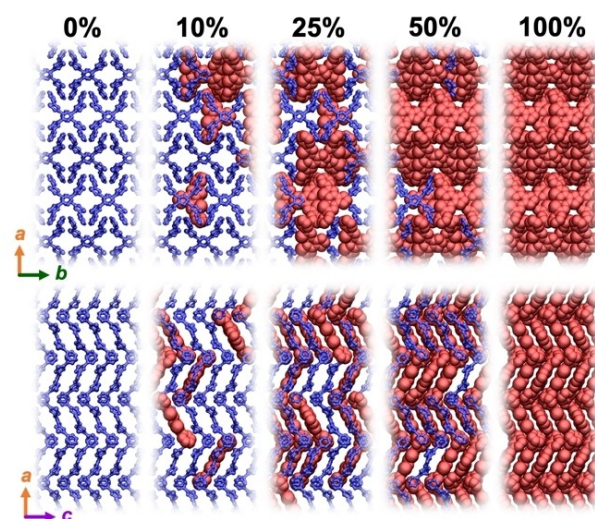

Figure 2. Representative example of the optimized structure at different switching states along the c- (top) and b-axis (bottom). For clarity, the open-ring isomer is represented in blue (ball-and-stick model) and the closed-ring state is shown in red (van-der-Waals representation).
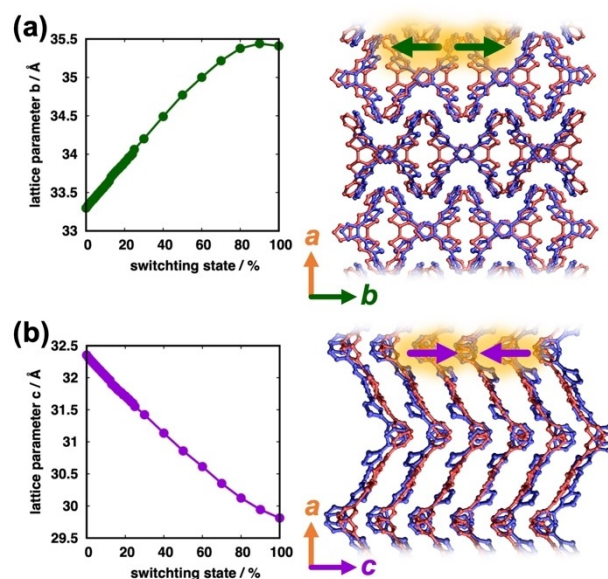

Figure 3. Change of the lattice parameters as a function of switching state along (a) the b-axis and (b) the c-axis together with the structural comparison of the molecular crystal consisting of only the open-ring (blue) and close-ring isomers (red).

induced isomerization state at the molecular level and the macroscale motion.

Going beyond the reported single-crystal data, the atomistic investigation enables to decipher the impact of the local structural rearrangement on the molecular packing and thus the molecular origin of the macroscopic movement. Based on the optimized geometries, a structural rearrangement of the ethylene groups up on interconversion from the open- to the closed-ring form is observed. (Figure 4a) This is a result of the
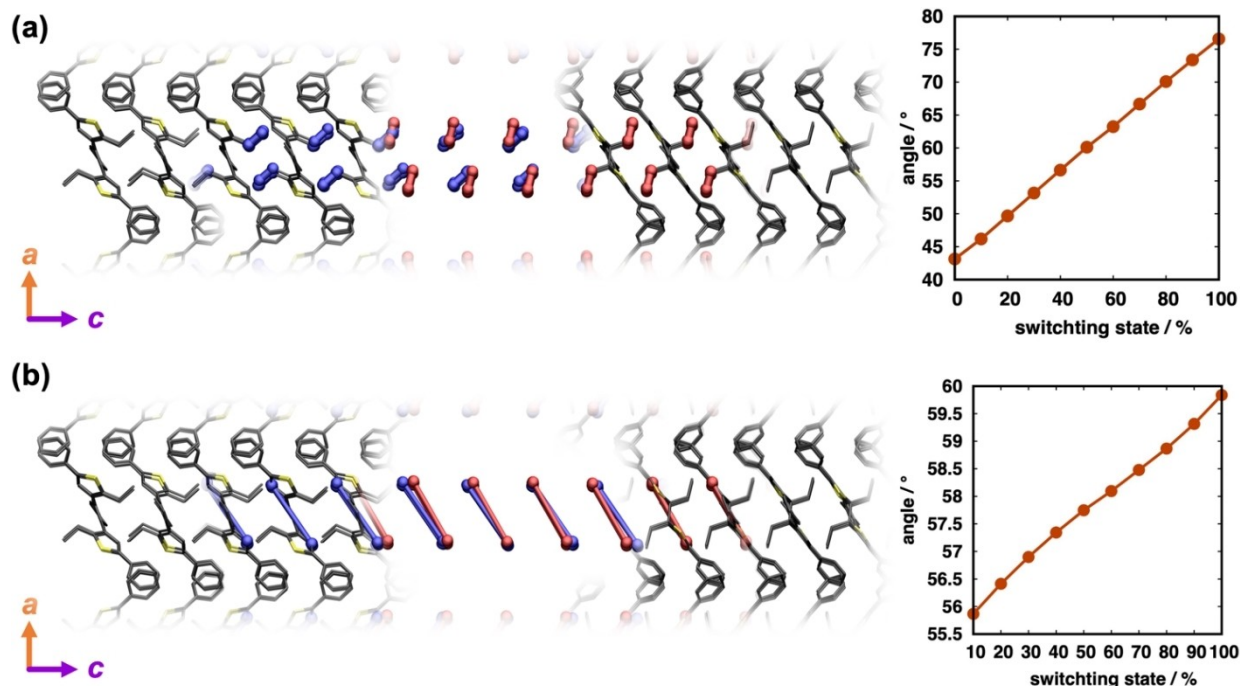
Figure 4. Structural analysis of the intra- and intermolecular properties by evaluating the orientation of (a) the ethylene groups of the core unit of the photo-responsive molecules and (b) the alignment of the molecules with respect to the c-axis. The structural transition from the open- to the closed-ring isomer is visualized (from left to right), by highlighting in (a) the carbon atoms of the ethylene group and the carbon involved in the cyclization reaction and in (b) the overall molecular axis (blue: open-ring state; red: closed-ring state). In addition, the averaged angles of the ethylene bond and of the molecular axis with respect to the c-axis is plotted as a function of the switching state.

formation of the C−C bond and the change of the hybridization of the central carbon atom due to the ring closing known for diarylethene molecules. The structural analysis shows a continuous alinement of the ethylene group along the c-axis (Figure 4a). At the same time, this intramolecular rearrangement influences the molecular environment leading to a change of the molecular packing. This is characterized by an "up-standing" of the molecules with respect to the c-axis (Figure 4b) enabling a closer arrangement of the molecules and thus contraction along the c-axis (Figure 3b).

Due to the interdigitated packing of the molecules, this alteration of the molecular packing also influences the structure along the b-axis (Figure 5). The contraction of the molecules along the c-axis forces the system to expand along the other dimension. Based on the atomistic study, the macroscopic deformation can be rationalized by a delicate interplay of intra- and intermolecular properties.

In summary, the molecular origin of the light-triggered structural change of an actuator is disclosed by using atomistic simulations. By parametrizing and employing an effective representation of the diarylethene based molecular crystal, a unique insight into the structural evolution is reported. Based on this, the molecular mechanism of the photo-responsive actuator was reveal. Intramolecular rearrangement of ethylene groups due to the photocyclization, which is so-far not resolved experimentally, leads to a reduced volume demand along one cell dimension and thus molecular packing. The latter includes an up-standing of the molecules which propagates to large-
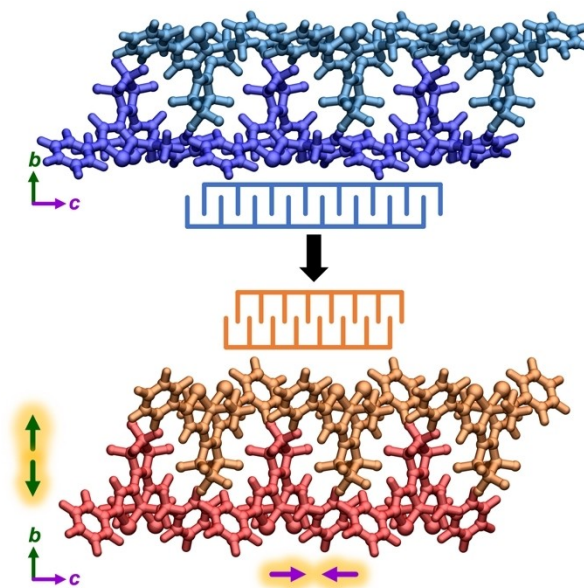

Figure 5. Ball-and-stick and schematic representation of the interdigitated molecular packing of the open- (blue) and closed-ring isomers (red). (For clarity the molecules in different layers along the b-axis are shown in light-blue/dark-blue and light-red and dark-red, respectively.)

scale contraction of the periodic matrix. The reported study provides a strong foundation to correlate dynamic phenomena at the molecular level with the macroscopic features. This is in

particular crucial for the tuning of corresponding photo-mechanical functional materials by molecular design.

The strategy, reported here, to apply a potential, which, despite its limitations to explicitly describing the excited-state energy landscape of an individual species, enables to accurately mimic the light-induced dynamics of the ensemble. By capturing how the externally addressable dynamics at the molecular level is transferred to macroscopic deformation, the presented theoretical approach opens the path for screening of systematically modified diarylethene based molecular crystal and also to study corresponding co-crystalized systems. In addition, such atomistic investigations together with the previously reported mathematic models, which allow to describe the mechanical properties of the system,[14] provide a comprehensive theoretical framework to optimize photo-responsive actuators. Finally, it should be pointed out that due to the consistent development of the force field using only QM reference data without any experimental results, a systematic extension of the model to describe non-ideal systems including structural fatigue effects is possible, which will further facilitate the rational development of these responsive materials.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

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