Towards understanding photomigration: insights from atomistic simulations of azopolymer films explicitly including light-induced isomerization dynamics

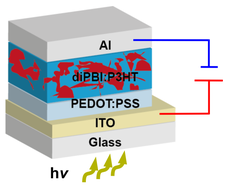
Marcus Böckmann and Nikos L. Doltsinis

Institut für Festkörpertheorie, Westf.-Wilhelms-Universität Münster, 48149 Münster, Germany
Center for Multiscale Theory and Computation, Corrensstr. 40, 48149 Münster, Germany

Westfälische Wilhelms-Universität Münster

1. Introduction

Photoinduced deformation in azopolymer thin films is one out of a wide variety of photoswitching effects of the parent azo chromophore [1]. This photomechanical surface patterning allows for the formation of regular structures using, e.g., crossed laser beams, and such patterned structures are employed to enhance the light trapping in bulk heterojunction (BHJ) organic solar cells [2,3].



BHJ solar cell

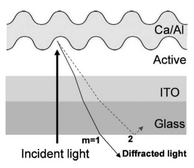


Fig. 4 of [3]

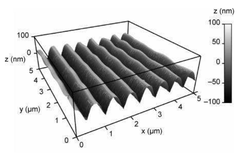
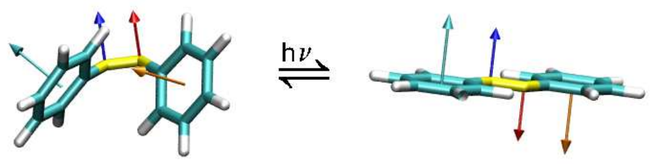


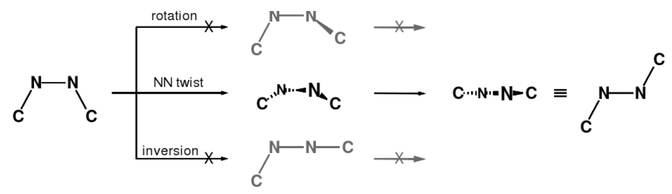
Fig. 1 of [2]

The macroscopic effects arise due to the considerable geometric changes of the photochromic azobenzene (AB) unit upon the light-induced E – Z isomerization of the -N=N- double bond:



Z–Azobenzene, $d \approx 6.6\,\AA$ E–Azobenzene, $d \approx 9.0\,\AA$

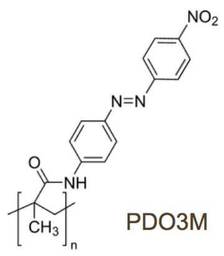
In contrast to earlier assumptions, the photoisomerisation mechanism is neither a rotation about the nitrogen double bond nor an in-plane inversion of the CNN bond angle, but rather a concerted twist motion of the two nitrogen atoms accounting for ultrafast photoisomerisation in, e.g., bridged azobenzene [4, 5].

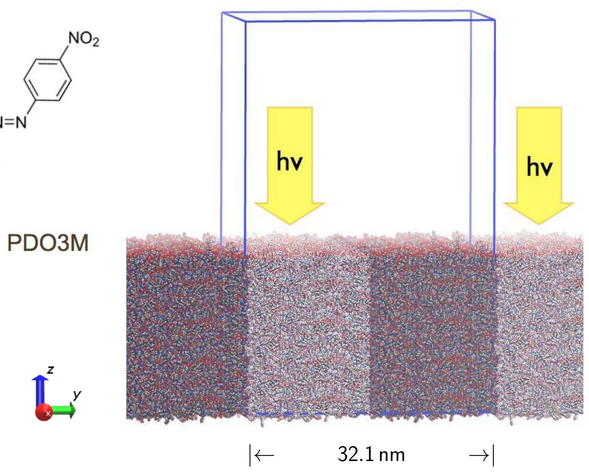


2. Azopolymer Film

- System modeled as NPT equilibrated ensemble of 1944 16-mer units of poly-Disperse-Orange-3-Metacrylate (PDO3M) in a periodic simulation box of $19.3\times32.1\times19.7\,\mathrm{nm}^3$ employing MM parameters based on the 45a3 GROMACS force field modified for AB [6, 7].

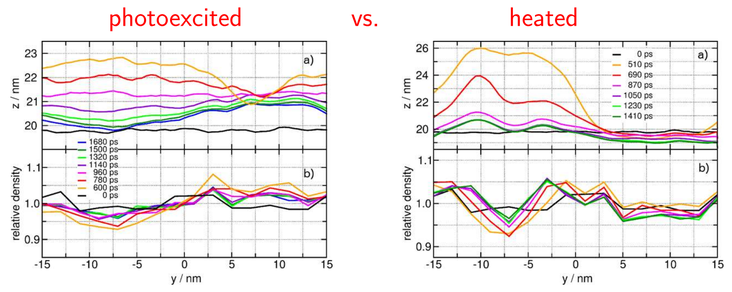
  A surface slab is realised by adding ca. 30 nm of vacuum in the z-direction and fixing the backbone atoms at the bottom; one half of the top surface then serves as the active region [8].





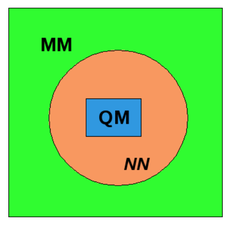
- Benchmark calculation reveals fundamental differences between photoexcitation and thermal activation after cooling [8].

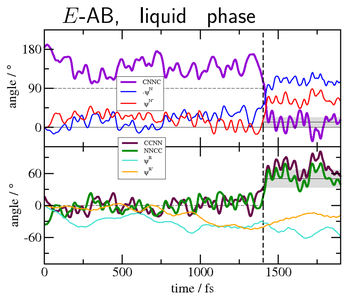
photoexcited vs. heated



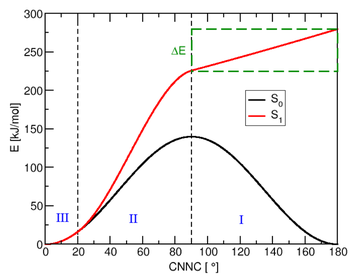
3. MM-Switch for AB Photoisomerisation

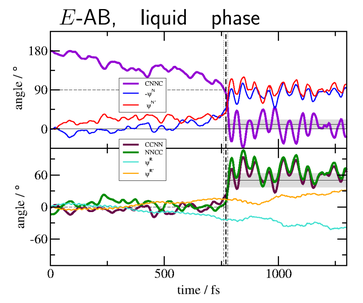
- na-QM/MM approach [7]:

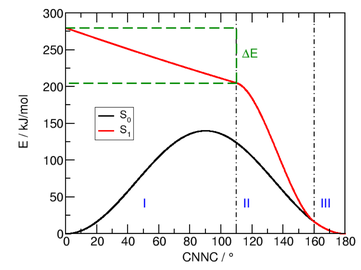


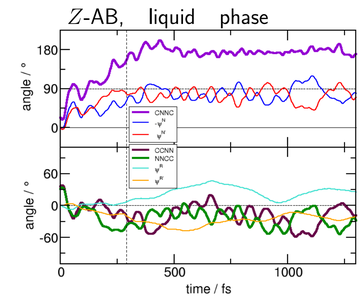


- all-MM approach: Molecular Mechanics switch







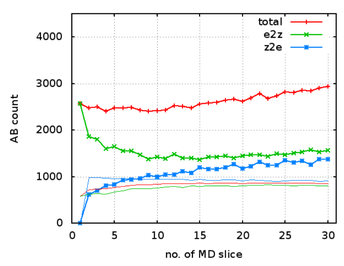


The molecular mechanics (MM) switch for AB photoisomerisation is designed to mimick the observed ab initio pathway [8,9]. The method is implemented in an in-house version of the CPMD package [10].

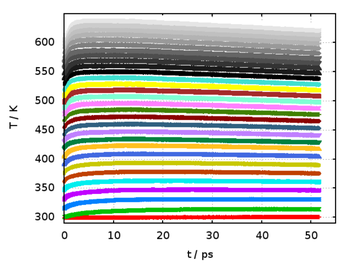
4. Probing the Effect of Light Polarisation

- AB chromophores selected in time intervals of 50 ps for photoactivation w.r.t. electric transition dipole moment to account for polarisation direction of incoming laser beam.

AB activation statistics

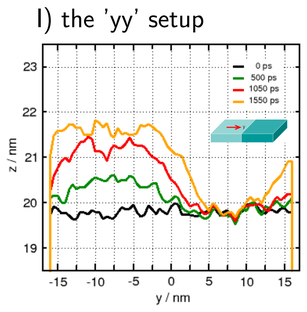


temperature per MD slice

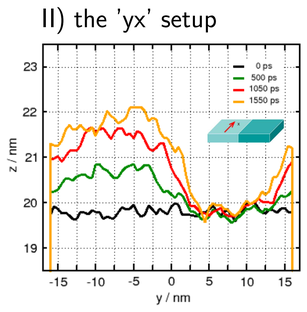


- height profiles perpendicular to slab surface:

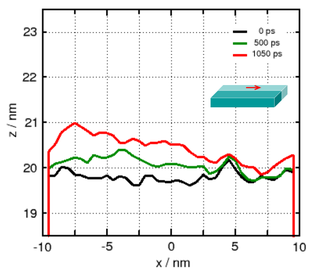
I) the 'yy' setup



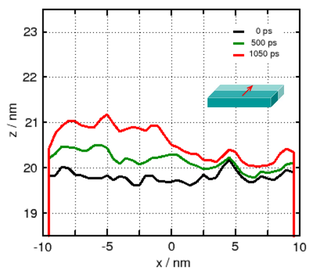
II) the 'yx' setup



III) the 'xy' setup



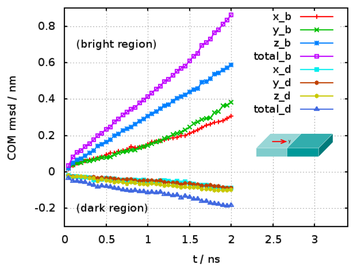
IV) the 'xx' setup



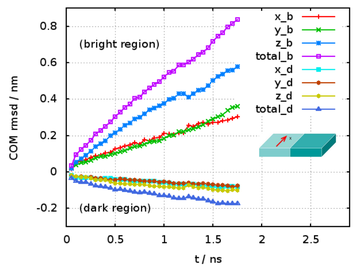
5. Analysis of Molecular Motion

- centre of mass (COM) motion split into bright/dark as well as cartesian components x, y, z.

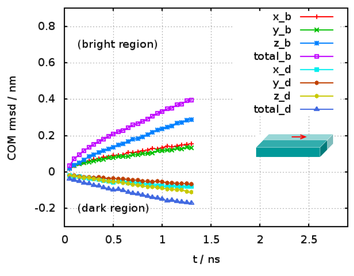
I) the 'yy' setup



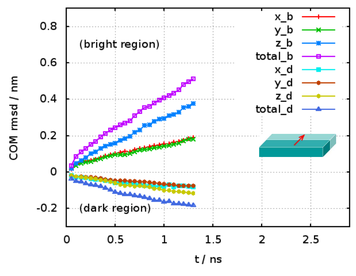
II) the 'yx' setup



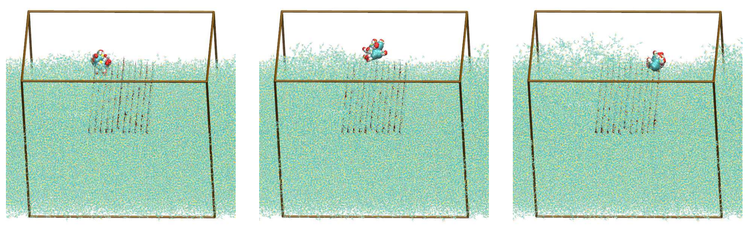
III) the 'xy' setup



IV) the 'xx' setup



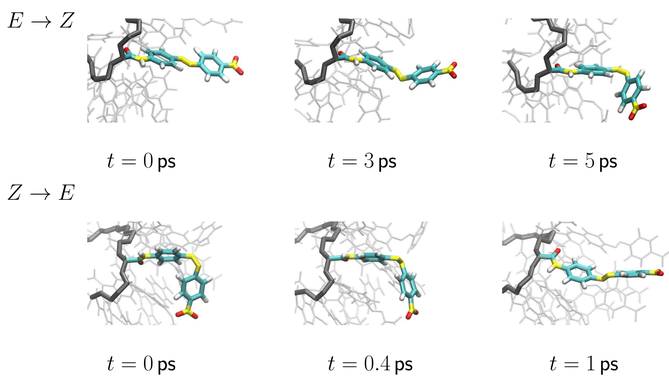
- example of large scale molecule movement from benchmark MD [8].


$t = 150\,\mathrm{ps}$ $t = 300\,\mathrm{ps}$ $t = 450\,\mathrm{ps}$

6. Conclusion & Outlook

- Multiple photoswitching cycles indicate mass transport out of the illuminated region and subsequent height growth in the 'dark' region upon cooling; this is in stark contrast to pure thermal activation [8].

- Propeller-like motion of loose end of AB chromophore.



$t = 0\,\mathrm{ps}$ $t = 3\,\mathrm{ps}$ $t = 5\,\mathrm{ps}$

$t = 0\,\mathrm{ps}$ $t = 0.4\,\mathrm{ps}$ $t = 1\,\mathrm{ps}$

- Investigate implication of spacer unit linking AB to backbone.

Acknowledgement

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References

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