

Unraveling Excited-State Mechanisms: Computational Insights into Photoswitching

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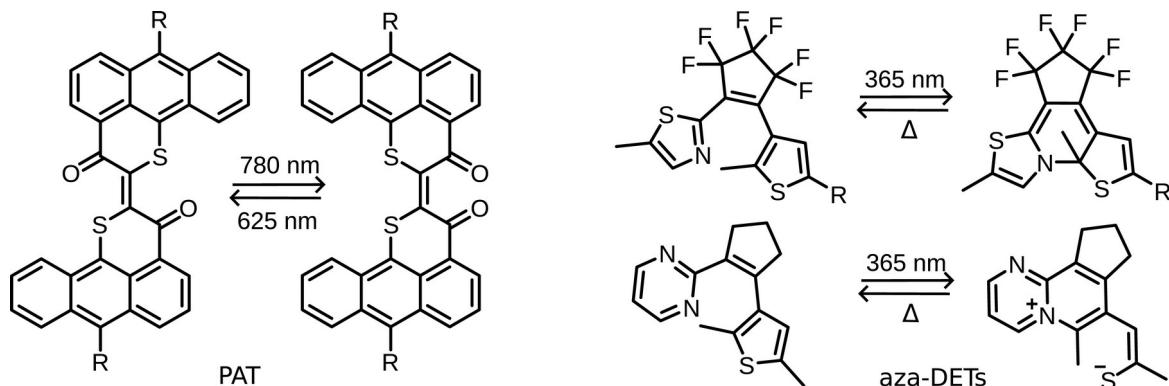
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Light-driven molecular motion is at the heart of photochemistry, enabling the conversion of photon energy into electronic and structural changes. In particular, photoswitches and photomotors have emerged as key players in applications spanning nanotechnology, catalysis, and drug delivery. However, understanding their photoreaction mechanisms remains a formidable challenge due to the ultrafast nature of light-induced processes, which complicates a targeted reaction optimization. While spectroscopic experiments provide crucial insights, they often lack the structural details needed to comprehend excited-state dynamics. Consequently, computational methods have become essential tools in unraveling excited-state reactivity. In this context, we present different approaches to elucidate the fundamental principles governing photochemical reactivity.

In a first case study, we explore π -extended thioindigoid photoswitches, particularly peri-anthracene-thioindigo (PAT),^[1] which represents a breakthrough in shifting absorption into the red and near-infrared region, along with its small brother peri-naphthalenethioindigo (PNT). Combining (TD-)DFT and ADC(2) calculations with steady-state and femtosecond time-resolved spectroscopy, we reveal an *E/Z*-isomerization mechanism driven by efficient population of the triplet manifold.

Secondly, we investigate aza-diarylethenes (aza-DETs),^[2,3] a novel class of photoswitches exhibiting distinct photochemical pathways. Using state-of-the-art quantum chemical methods such as QD-NEVPT2 and MRSF-TDDFT, we dissect the mechanistic differences between aza-DETs forming closed-ring and zwitterionic photoproducts.

These insights enhance our understanding of photochemical transformations and pave the way for the rational design of next-generation photoswitches.



[1] L. Köttner et al., *Angew. Chem. Int. Ed.* **2023**, 62, DOI: 10.1002/anie.202312955

[2] M. Sacherer et al., *J. Am. Chem. Soc.* **2024**, 146, DOI: 10.1021/jacs.3c11803

[3] S. Hamatani et al., *J. Phys. Chem. Lett.* **2023** 14, DOI: 10.1021/acs.jpclett.3c02207