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New insights into thermal switching kinetics of molecular photoswitches revealed by protonation and metal coordination

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Azobenzene photoswitches are an indispensable tool in light-responsive materials design. When irradiated by light, azobenzenes undergo a reversible *trans-cis* photoisomerization about the azo bond (N=N), a robust process used to photocontrol the properties of various materials, including metal organic frameworks, chemical sensors, biomimetic coatings, and liquid crystals. The isomerization process however is also thermally reversible. Depending on photoswitch design and environmental conditions, thermal lifetimes can vary from nanoseconds to years, yet the precise engineering of azobenzene-based materials depends strongly on exquisite control of this lifetime. Protonation and metal coordination are emerging as tools to control the mechanism and lifetime of thermal isomerization, however a complete understanding of their diverse effects is still lacking.

In this study, azobenzene was modified with a bidentate ligand to create the photoswitch HPAS, which possesses both pH responsivity and metal coordination abilities. Using density functional theory, complete active space self-consistent field, and spin-flip quantum mechanical methods, we explored the effect of protonation and Cu^{2+} coordination on the thermal isomerization kinetics of HPAS. Protonation studies revealed an equilibrium exclusively for the *cis* isomer involving proton transfer to the azo group and significant weakening of the double bond. We show, for the first time, that rapid rotation about the ruptured azo bond involves two torsional degrees of freedom and an ammonia-like inversion process. Due to the unpaired electron of Cu^{2+}, novel consequences on intersystem crossing along the rotation pathway are discussed.

Keyword-1

Photoswitches

Keyword-2

Protonation and metals

Keyword-3

Density functional theory

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