Disequilibrating azobenzenes by visible-light sensitization under confinement

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Azobenzenes are best known for their reversible photoisomerization from the stable *E* isomer to the metastable *Z* state. However, direct *E*-to-*Z* isomerization typically requires UV excitation and has remained elusive after indirect excitation, unlike the opposite *Z*-to-*E* process.¹ Recently, we presented disequilibration by sensitization under confinement (DESC),² a supramolecular approach for the *E*-to-*Z* isomerization with visible light of a desired color. DESC relies on the combination of a macrocyclic host and a photosensitizer, which selectively bind and sensitize *E*-azobenzenes for isomerization in aqueous solution. The macrocyclic host dramatically increases intersystem crossing yield of the photosensitizer and protects the formed triplet state under ambient conditions. We show that the DESC mechanism operates via triplet energy transfer by using time-resolved spectroscopy and illustrate how even poor triplet sensitizers, such as BODIPY, can act as efficient photosensitizers for DESC.

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References

- [1] A. Goulet-Hanssens, et al. Hole Catalysis as a General Mechanism for Efficient and Wavelength-Independent $Z \rightarrow E$ Azobenzene Isomerization. *Chem*, 2018, 4(7), pp. 1740–1755.
- [2] J. Gemen, et al. Disequilibrating azobenzenes by visible-light sensitization under confinement. *Science*, 2023, **381**(6664), pp.1357–1363.