

Photoswitchable Imines Drive Dynamic Covalent Systems to Nonequilibrium Steady States

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- **Who are the corresponding authors and what are their research areas?**

Dr. Jake Greenfield

Group Leader: 2023 to date.

Institute of Organic Chemistry, University of Würzburg, Germany

Ph.D. with **Jonathan R. Nitschke**, Department of Chemistry, Uni of Cambridge

*This group uses simple building blocks (**generally aldehydes and amines**) that might come together around templates, often metal ions to create complex structures with targeted functions. – Recently published work on **Light-driven molecular active transport between organic compartments**.*

Postdoctoral Fellow with **Matthew J. Fuchter**, Imperial College London

*This group investigates the development of photoswitches usually **arylazopyrazoles** due to their quantitative photoswitching and high thermal stability of the Z-isomers (**$t_{1/2}$ of up to 46 years**).*

Postdoctoral Fellow with **Frank Würthner**, Julius-Maximilians-Universität Würzburg

Molecular Exploration: Adding to the variety of switchable molecules already reported, they are keen on designing novel stimuli-responsive motifs that grant new properties and functionality. Other areas include **Controlled Assembly** and **Achieving Function**.

- **What is the main claim of the article?**

Uses imine-based photoswitches to energetically enhance the rate of transamination reactions in an autonomous, dissipative system to achieve a nonequilibrium steady state (NESS).

NESS- is a condition in which an OOE system remains constant over time. Despite ongoing processes (like energy flow or chemical reactions), certain properties of the system, such as temperature, concentration, or pressure, do not change over time.

- **How is it demonstrated?**

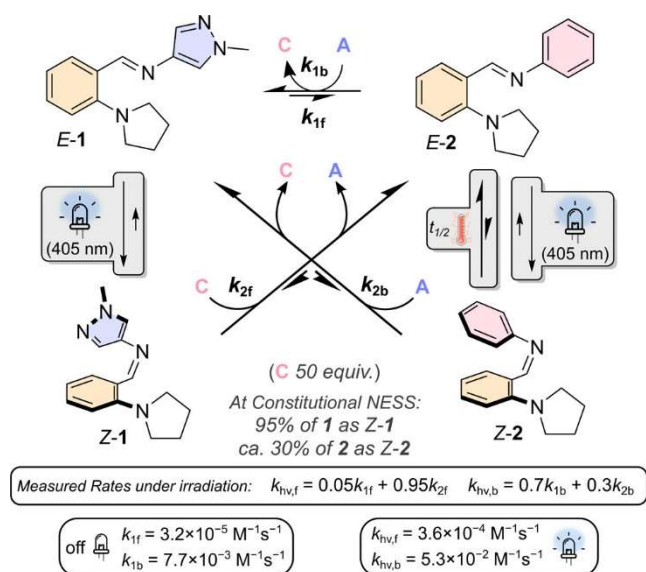


Figure 2. The simplified reaction network of that shown in Figure 1b, highlighting the key transformations probed in 1 H NMR measurements. The thermal pathway for the conversion of the E-isomers to the Z-isomers is depicted here, but not observed practically, and thus considered negligible. The reactions shown in the shaded boxes represent unimolecular reactions, while the others are bimolecular.

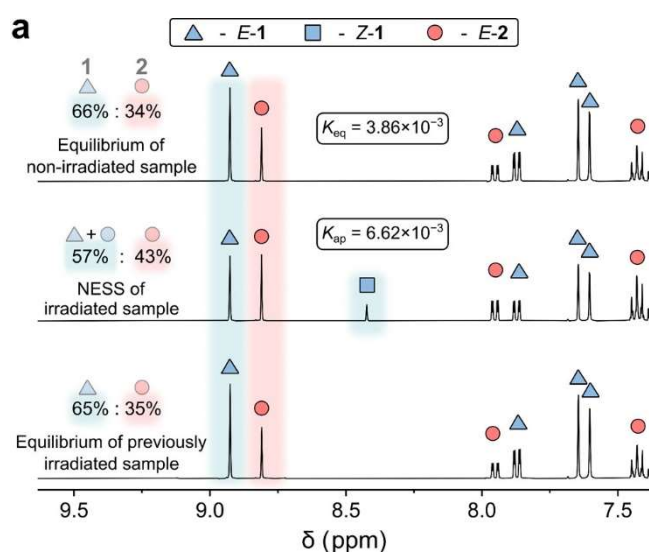


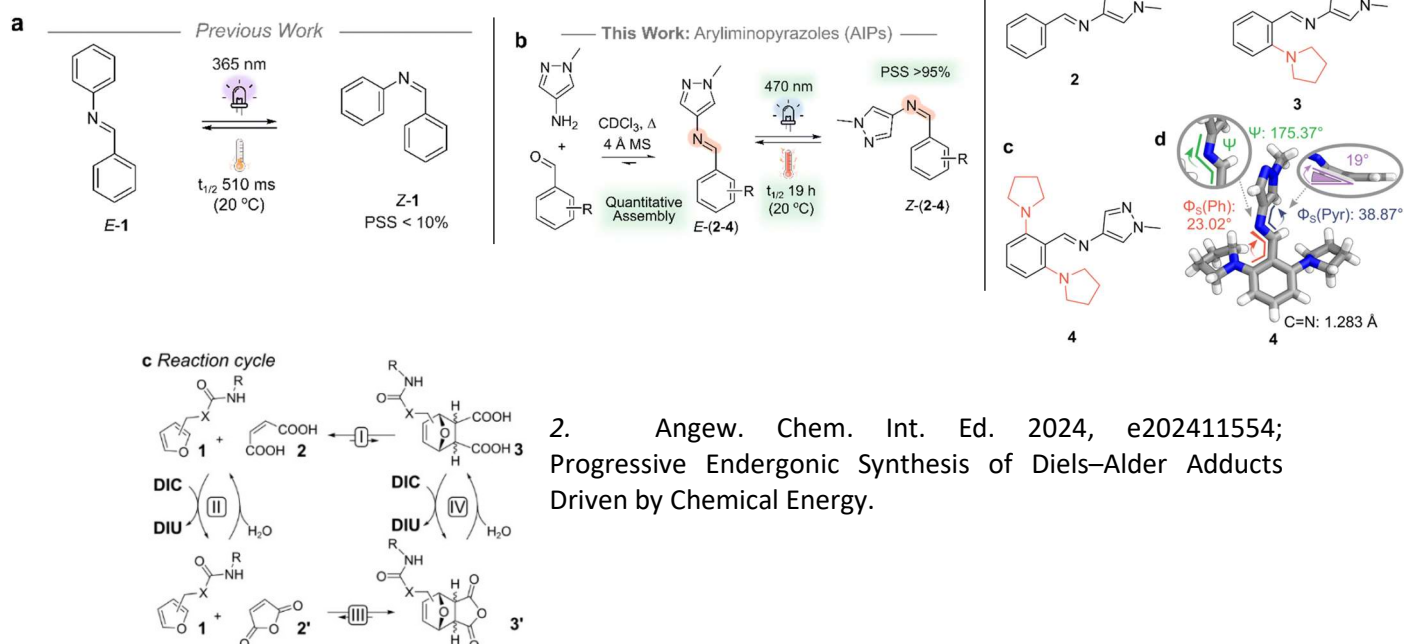
Figure 3. (a) 1 H NMR spectra (400 MHz, CD₃CN, 298 K) of a sample consisting of E-1 and C (50 equiv): (top) at equilibrium in the dark; (middle) at the NESS achieved with 405 nm irradiation; (bottom) the equilibrium of a previously irradiated sample left in the dark for 18 h. The distribution of the imines, shown as percentages, was determined from the signals shaded in blue and red. Note that the photoisomerism-induced NESS is not directly observed here due to the relaxation of the Z-isomers back to the thermodynamically stable E-state.

- **What are the typical experimental conditions?**

- 6 mM of Imine-1, 50 equivalence of C, CD₃CN, Irr at 405 nm

- **Which are the key related papers?**

1. *Chem. Sci.*, 2024, **15**, 3872-3878; Photoswitchable imines: aryliminopyrazoles quantitatively convert to long-lived Z-isomers with visible light.



2. *Angew. Chem. Int. Ed.* 2024, e202411554; Progressive Endergonic Synthesis of Diels–Alder Adducts Driven by Chemical Energy.