Switching Sides: Driving Reactions Uphill and Defining Design Rules for Photoswitchable Imines

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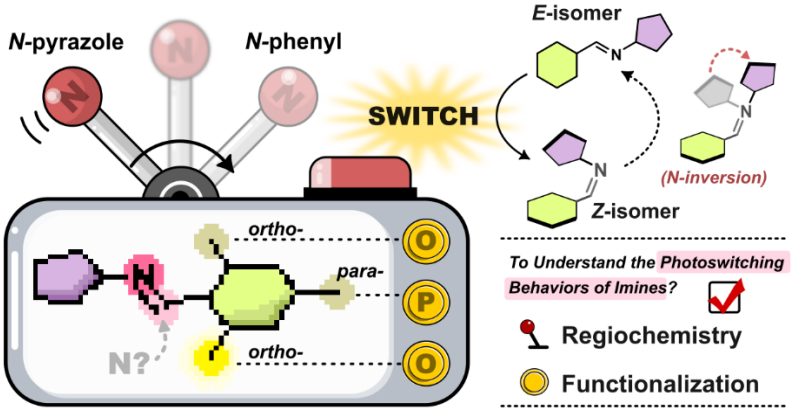
Molecules and materials comprised of dynamic-covalent imine bonds display many desirable properties, including stimuli-responsiveness, recyclability, and effortless preparation, among others. However, the *E*/*Z* photochromism of imines has often been overlooked due to historically poor performance compared to other photoswitches, typically showing less than 50% conversion to the metastable state and thermal half-lives of under one minute.[1] Recently, we developed a strategy that significantly improves these photoswitching properties, achieving quantitative *E*-to-*Z* conversion with visible light and extending the thermal half-lives of the metastable *Z*-state to over one day.[2,3]

With these improved properties, we explored the light-dependent dynamic-covalent chemistry of these photoswitches. To our surprise, we found that they can drive transimination reactions energetically uphill when irradiated with light,[4] operating via a mechanism akin to a light-driven information ratchet.[5] Beyond pushing thermodynamic equilibria into non-equilibrium steady states, we found that the regiochemistry of the C=N bond plays a significant role in the switching behavior.[3,6] Through a systematic investigation, a set of design rules for this novel class of imine photoswitch has now been reported, along with the first crystal structure of an arylimine in its metastable *Z*-conformation.[6] This talk will provide an overview of our recent progress in this area.



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