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Title: Azoheteroarene Based Visible Light Photoswitches

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Abstract: Azobenzenes are one of the important classes of molecular photoswitches and are widely used in molecular motors, memory, manipulators, solar thermal storage etc. E-to Z-isomerization of azobenzene happens under UV irradiation. This limits the use of azobenzene as a photoswitch in photobiology as UV light is less penetrating in tissues. To circumvent this issue, attempts have been made to develop visible light photoswitches by introducing Lewis acids, tetra-ortho-substitution, ring strain or push pull effects into the photoswitching molecule. Nevertheless, the reported visible light photoswitches suffer from low Z-isomer half-life. Since tuning of half-life is equally important as visible light photoswitching, our aim was to combine these two properties and come up with a new genre of photoswitches. Here, we present a series of visible-light azoheteroarene photoswitches with varying Z-isomer lifetimes and good photochemical conversions by using ortho-amination. In this regard, we have utilized isoxazoles and N-methylpyrazoles as heterocycles. The advantages of these systems are very long Z-isomer half-life apart from visible light photoswitching. Toward this end, 18 ortho-substituted azoheteroarenes have been synthesized. Their photoswitching behaviour, solvatochromism, forward and reverse photoisomerization conversion at their respective photostationary states (PSS), and kinetics were investigated and estimated using UV-Vis and NMR spectroscopic techniques.


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