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Title: Azoheteroarene Photoswitches: Structure Property relationship towards photoswitching using visible light, in the water medium, and solid state

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Keywords: Photoswitches  
Visible light  
Water

Issue: Jun-2023  
Date:

Publisher: IISER Mohali

**Abstract:** Abstract Azobenzenes are one of the prominent classes of molecular photoswitches that exhibit widespread applications, from smart materials (photo-controlled actuators, adhesives, energy storage materials, non-linear optics, etc.) to biology (bioimaging, drug delivery, photopharmacology, etc.). They are known for photoisomerization between a thermodynamically stable E-isomer and a metastable Z-isomer. The forward (E-Z) isomerization is mainly driven by UV light, whereas reverse (Z-E) isomerization can be induced by visible light or heat. However, UV light is harmful and potentially causes damage to the surface of the material. The utility of azobenzenes in real-life applications demands excellent bidirectional performance, long Z-isomer stability, photoswitching with visible light, photoswitching in aqueous media, and photoswitching in the bulk state, some of which are challenging. Recent explorations on replacing one of the six-membered azobenzene rings with a five-membered heterocyclic ring led to outstanding photoswitching behavior and exceptional thermal stability of Z-isomer. Motivated by the recent progress in this direction, we considered designing bidirectional visible light photoswitchable azo compounds with a long stable Z-isomer, photoswitching in water, and the bulk state as the major objectives of the thesis. Towards designing bidirectional visible light-driven azo photoswitches, we introduced cyclic aliphatic amine at the ortho position of azoheteroarenes. Furthermore, we synthesized 22 derivatives with different azoheteroarenes (azopyrazole, azoisoxazole, and azopyrrole), varying the size of the cyclic aliphatic amines using a simple synthetic strategy with excellent yields. To understand the effect of substitution on the photoswitching properties and Z-isomer stability, we performed UV-Vis and <sup>1</sup>H-NMR spectroscopic studies. Substitution at 3,5- position of azoheteroarenes (azopyrazole and azoisoxazole) with phenyl shows further red- shifted absorption compared to methyl substitution. To stabilize the Z-isomer, fluorine substitution is introduced at the ortho position of azoheteroarenes and cyclic amines. All the molecules exhibit bidirectional photoswitching under visible light with tuneable half-lives between minutes to hours/days. More importantly, moderate to good conversions were observed with forward (E-Z) isomerization with violet to green light and reverse (Z-E) isomerization with blue to red light. Through this, a structure-activity relationship has been established. The next aim was to construct azo compounds capable of bidirectional photoswitching in water with tuneable or high Z-isomer stability. In the first approach, we quaternized the pyridine nitrogen of pyridylazoheteroarenes to make the ionic photoswitches. We synthesized eight derivatives of heteroaryl azopyridinium ionic photoswitches (HAPIPs) with varying azoheteroarenes (azopyrazole and azoisoxazole), substitution at azoheteroarene ring (Me vs Ph), counter anions. All the molecules showed moderate to good bidirectional photoswitching in water. Apart from that, the derivatives exhibit thermal stability of Z-isomer from seconds to days. Further, to achieve quantitative photoswitching with the exceptional thermal stability of Z-isomer, we have designed 36 arylazopyrazolium ionic photoswitches (AAPIPs) derivatives by quaternization of substituted arylazopyrazoles. All the derivatives showed quantitative forward photoisomerization, while reverse photoisomerization was moderate to excellent in water and organic solvents such as DMSO, CH<sub>3</sub> CN, MeOH, chloroform, and toluene. The parent derivative shows 157 days half-life in the water and 55 days in DMSO at room temperature. In the last part of the work, to achieve photoswitching in the bulk state in multiple azo(hetero)arenes synthesized in a tripodal C<sub>3</sub>-symmetric mode. The azopyrazole-based C<sub>3</sub> derivatives show excellent photoswitching in solution, solid state with photochromic behavior confirmed by UV-Vis, <sup>1</sup>H-NMR, and PXRD techniques. The solid-state photoswitching was exploited towards fully light-driven image writing and erasing applications. Upon bringing flexible connection, the phenomena can be observed as photochromism in the forward and thermochromism in the reverse direction.

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