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Title: Synthesis and Photoswitching Studies of Water Soluble Azobenzene Based Molecules

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Abstract: Azobenzene is a photoswitchable molecular machine that can be switched between its two different isomers by the application of external stimuli, i.e. light. The trans to cis isomerization occurs following irradiation with UV light. The reverse isomerization (cis to trans) occurs either photochemically (under irradiation condition) or thermally (under the influence of temperature), due to the thermodynamic stability of the trans isomer. Since this isomerization process is reversible, azobenzenes can be used as photoswitches. The photochromic properties make them an integral part of many functional materials with multiple uses. The applications include molecular transporter- where it can be used for drug delivery, metal ion chelators- photoswitchable ligands for binding to metals, energy trap devices- mainly for storage of solar energy, and as an industrial dyes etc. Our current interest lies in creating photoswitchable reversible molecular transporters. In this regard, our goal is to connect multiple azobenzene moieties to a common linker moiety in such a way that a light controlled void or space can be created. This space can be used to encapsulate the guest and can be used as a small molecular transporter. A long-term goal would be to utilize such systems in drug delivery applications. Another research interest is to synthesize photoswitchable ligands that can be used as chelating agents for reversible metal ion binding. Besides, their photoswitching behavior can be exploited to study spin crossover through variation in ligand strength. In particular, the synthesis of macrocycles with photoswitchable groups to impart light-induced change in ligand strength can provide such application. Attempts have been made to synthesize and to study different azobenzene based molecular transporters, metal ion binding ligands and azomacrocycles. In this regard, the following targets as shown in scheme 1 have been chosen and synthetic attempts have been made: 1. Target 1: Epichlorohydrin was tried to couple with phloroglucinol under basic conditions. (Status: Reaction did not yield the desired product) 2. Target 2: Maleimide connected azobenzene was prepared; however, Heck coupling has been tried. (Status: Target has not been achieved) 3. Target 3: Acid amine coupling between 1,2,4,5-benzene tetracarboxylic acid and 4-aminoazobenzene. (Status: Product was not obtained) 4. Target 4: Pyromellitic diimide product. (Status: Product was insoluble in most of the solvents and so it was not characterized) 5. Target 5: Azamacrocycles for spin crossover was targeted by reacting 3-aminoazobenzene and 1,2-dibromoethane (Status: The target product was not obtained) 6. Target 6: Mannich reaction has been attempted (Status: Multiple products, which have not been able to be separated) 7. Target 7: Triamide synthesis (Status: The target product was obtained, however due to delay in purification, the photoswitching part was not able to be performed) 8. Target 8: The diacid product has been synthesized (Status: Photoswitching studies have been done)


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