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Title:	Photoswitchable Molecular Systems for Supramolecular Assembly and Reversible Modulation of Catalysis
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Abstract:	<p>Photoswitchable Molecular Systems for Supramolecular Assembly and Reversible Modulation of Catalysis Abstract Photoresponsive materials refer to those materials that can reversibly toggle between two isomeric forms and can undergo physical and chemical changes upon irradiation at appropriate wavelengths of light. Therefore, various properties such as planarity, geometrical structure, absorption spectra, dipole moment, dielectric constant, color, solubility, chemical reactivity, conjugation, covalent bonding, non-covalent interaction, coordination properties, etc. can be modulated with the help of light. Among the various classes of photoswitchable molecules, azobenzenes are one of the robust molecules with excellent photoisomerization properties between trans (thermodynamically stable) and cis-isomers and are readily accessible, which makes them attractive candidates for functionalization. The resulting photoresponsive molecular materials have widespread applications in numerous fields that include molecular recognition, molecular machines, photopharmacology, supramolecular assembly, liquid crystals, catalysis, sensors, logic operations, data storage, optical memory devices, molecular devices, etc. For various applications, understanding the factors influencing the photoswitching behavior and cis-isomer stability of azoarenes is crucial. In this regard, we have synthesized 18 photoresponsive molecular systems with variable connections and structural diversity in high yields through modular synthesis. We have also investigated the effect of structural modification on photoswitching characteristics and the thermal stability of the Z-isomers. Apart from that, the common amide functional group in all the derivatives has been explored for their aggregation and supramolecular behavior. The changes in the morphology of supramolecular assembly/microcrystals have been studied using polarized optical microscopy (POM), Scanning electron microscopy (SEM), and the effect of photoisomerization on their morphology has also been examined. Next, we have designed and synthesized two novel C₃-symmetric tripodal triazobenzene-based molecular systems with extended π-conjugation at internal and external positions. Here, we studied the effect of extended π-conjugation on photoswitching, thermal stability, and aggregation. We have investigated the impact of design on the supramolecular self-assembly, and also, demonstrated the morphological changes in the self-assembly behavior by atomic force microscopy (AFM), scanning electron microscope (SEM), transmission electron microscopy (TEM), and polarized optical microscopy (POM). X-ray diffraction studies (XRD) revealed that the external extended π-conjugation systems showed the columnar rectangular type of self-assembly and the internal one showed lamellar type assembly. In the last part of the thesis work, five tris-triazole-linked azo(hetero)arene-based molecular systems have been designed and synthesized that can act as photoswitchable catalysts. We envisioned that the catalytic activity can be light controlled by varying the anion-binding ability of the catalyst in its native and photoswitched states. Using these catalysts, temporal control of tritylation reaction rates of various nucleophiles has been achieved. Through HRMS data, NMR titrations, control experiments, and DFT computations, the mechanistic aspects, the mode of binding, and the importance of cooperative binding have been envisaged. Isothermal titration calorimetric (ITC) measurements revealed a two-fold difference in the dissociation constant between a chloride ion and the catalyst in its native (EEE) and photoswitched (ZZZ) states, which is very well corroborated with the differences in the isolated yields.</p>
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