



# Library Indian Institute of Science Education and Research Mohali



DSpace@IISERMohali / Thesis & Dissertation / Integrated PhD / MP-15

Please use this identifier to cite or link to this item: <http://hdl.handle.net/123456789/5293>

Title:	Azobenzene-based Supramolecular Systems for Light Controlled and Reversible Fluorescence Modulation of Guest, Hydrogelation, and Multianalyte Probes
Authors:	<a href="#">Srivastava, Anjali</a>
Keywords:	Supramolecular Fluorescence Hydrogelation Multianalyte Probes
Issue Date:	Feb-2023
Publisher:	IISER Mohali
Abstract:	<p>Abstract Photoswitches are those molecules that can undergo reversible transformation between two isomeric forms on irradiation with a suitable wavelength of light. Changes in physical and chemical properties such as dielectric constant, oxidation/reduction potential, refractive index, and molecular geometry accompany this reverse photoisomerization. Among different classes, azobenzenes are one of the important photoswitches because of their robustness, bidirectional photoswitching between E- and Z-isomers, fatigue resistance, ease of access, functionalization prospects apart from profound applications in a range of fields such as materials chemistry, photopharmacology, energy storage, data storage, molecular machines, molecular recognition, liquid crystals, host-guest chemistry, adhesives, etc. Figure A1 (a) Reversible modulation of monomeric fluorescence emission of pyrene by shape changing azomacrocyclic; (b) Hydrogelation property of photoresponsive supramolecular system; (c) Photoswitchable multianalyte fluorescent probes. Recently, incorporation of azobenzene unit to construct shape changing macrocycles has started gaining attention for the photocontrol of uptake and release of guest molecules. In this context, we report the design, synthesis, and studies of six shape-changing azomacrocyclics. These systems have been incorporated with azobenzene photoswitches using alkoxy tethers and triazole units to afford flexibility and binding. We envisioned that such azomacrocyclics are capable of reversibly binding with the guest molecule. Remarkably, we have demonstrated a fully light-controlled fluorescence quenching and enhancement in the monomeric emission of pyrene (guest). Such modulations have been achieved by the photoisomerization of the azomacrocyclic, in turn, the host-guest interactions. Also, the azomacrocyclics tends to aggregate that can also be controlled by light or heat. We have uncovered such phenomena using spectroscopic, microscopic, isothermal titration calorimetry (ITC) studies and computations. Next, by adopting simple synthetic protocols, we synthesized 15 photoswitchable azobenzene-based molecular systems with terminal benzyl or picolinyl groups tethered using triazolylmethylamide linkers providing structural diversity. Variations in these systems were introduced by tethering them at meta or para positions relative to azo group, by varying the number of such connections (mono, bis and tetra) and the connection of picolinyl group (2-, 3- and 4- picolinyl) at the terminal positions. All these systems were subjected to photoswitching and kinetics studies for thermal reverse isomerization step and followed by UV-Vis and NMR spectroscopic techniques, which provided a structure-property relationship. Interestingly, two molecular systems exhibit supramolecular assembly that can be modulated by light. More importantly, we rationalized that the importance of design in the formation of supramolecular hydrogel with excellent water holding capacity and investigated the morphological changes upon heating and photoirradiation. In the last part of the thesis work, we have developed three rhodamine functionalized azobenzene core-based systems, which consist of different numbers of rhodamine units (1, 2, and 4) and variation in the connectivity (para and meta) relative to azo group. Exploiting the ring- opening of the spirolactam part of rhodamine and the resulting fluorescent properties, we utilized them as sensors for the detection of multiple metal ions such as Fe 3+ , Fe 2+ , Sn 2+ and Al 3+ . The binding sites, stoichiometry, binding constants, fluorescent lifetimes and limit of detection for each probe have been deduced using appropriate spectroscopic techniques. Furthermore, the photoswitching ability of the azobenzene was used for improving the limit of detection due to the enhancement in the fluorescence intensity upon isomerization. Thus, these azobenzene-rhodamine probes can be useful for the detection of multiple analytes. Thus, photoswitchable azobenzene-based systems with different molecular architectures have been designed and synthesized to exhibit guest species' encapsulation with reversible fluorescent modulation, light-driven supramolecular assembly, and multianalyte fluorescent probes.</p>
URI:	<a href="http://hdl.handle.net/123456789/5293">http://hdl.handle.net/123456789/5293</a>
Appears in Collections:	<a href="#">MP-15</a>

## Files in This Item:

File	Description	Size	Format	
<a href="#">embargo period.odt</a>		9.72 kB	OpenDocument Text	<a href="#">View/Open</a>

Show full item record



Items in DSpace are protected by copyright, with all rights reserved, unless otherwise indicated.

