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| Title: | Exploring photoisomerization behavior of single and multiple- azo(hetero)arene units-connected organic systems, ligands, metal complexes, and their applications |
| Authors: | Gupta, Debapriya (/jspui/browse?type=author&value=Gupta%2C+Debapriya) |
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Abstract: Light is an external, non-invasive stimulus that can be administered with high spatiotemporal resolution. Azoarenes are photoswitches that interconvert between thermodynamically stable E isomer and photoswitched Z isomer in response to specific wavelengths of light. Such structural changes enable light-triggered reversible modulation of physical and chemical properties in molecular systems functionalized with azoarenes/azoheteroarenes. Such photoswitches are utilized as key building blocks in different supramolecular/metallosupramolecular systems, stimuli-responsive 'smart' materials, and for in-situ control of chemical, and biological processes. We studied the photoresponsive behavior of multiple photoswitchable unit-connected organic systems, ligands, and metal complexes. Through detailed spectroscopic investigations, we identified the factors influencing photoisomerization behavior or thermal stability of the photoswitched states in such systems. Also, we demonstrated the utility of such photoresponsive ligands and metal complexes in photo-triggered modulation of catalytic activity. In the first chapter, we explored the photoisomerization behavior of light-responsive benzene tricarboxamide (BTA)-based molecular systems with three photoswitches connected in C3 - symmetric designs. Six such systems with variations in the linkers and connectivity (o-, m-, and p-) of the azoarene photoswitches were prepared to identify the effects of subtle structural variations on the photoisomerization behavior of the multiple photoswitchable unit-connected systems. Detailed investigations of the photoisomerization behavior of the six molecules were carried out using ¹H NMR and UV-Vis spectroscopy to reveal the composition of the photostationary states after photoirradiation and to explore the corresponding thermal reverse isomerization process in detail. Next, we designed and synthesized photoswitchable ligands capable of coordinating with metal ions and generating photoresponsive metal complexes. In this regard, we incorporated phenylazo-3,5-dimethylpyrazoles and phenylazopyridine photoswitches within organic ligand frameworks. Sixteen structurally versatile photoswitchable ligands of different geometry and denticity/ coordination behavior were synthesized to suit the coordination requirements of a variety of metal ions. Through detailed spectroscopic investigations, we explored the photoisomerization behavior of these novel ligands in the solution phase and the solid-state and identify the factors influencing the stability of the photoswitched states. Photo-triggered changes in colour, and other properties such as changes in phase (solid ↔ liquid) and in the aqueous solubility of the ligands were also discussed. In the third chapter, we prepared transition metal complexes of photoswitchable ligands and investigated the photoisomerization behavior of the complexes, as well as the changes in properties after photoisomerization. The utility of Phenylazo-3,5-dimethylpyrazole units provides remarkable advantages as the free ligands and their complexes show excellent forward and reverse photoisomerization in both the solid and the solution states, and considerably long thermal half-lives for the ZZ isomers, apart from intriguing photochromism. In the fourth chapter, we demonstrate how the catalytic activities of such photoresponsive ligands and metal complexes can be controlled by light. We first utilized the photo-induced enhancement of aqueous solubility of one of the ligands to control the amount of catalytically active species present in the medium. Next, the catalytic activity of one of the photoswitchable Cu(I) complex was altered by photoisomerization of the attached azoheteroarene units.


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