Light-induced Magnetic Effects in Dual Function Inorganic-Organic Materials: Photochromic Metal Complexes

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Photochromic materials are of great interest due to their applications in ophthalmic lenses, display and communications systems, and optical storage and memory devices. The coupling of changes in electronic state accompanying photoisomerization with other physical phenomena would allow development of advanced functional materials for smart surfaces, spintronics, and optoelectronics. Metal coordination of photochromes provides a novel and potentially powerful approach to the development of systems in which changes in electronic state of the photochrome can induce changes in redox, magnetic, or optical properties of the metal center. This approach, however, has been largely unexplored.

Toward this end, we have investigated a unique set of photochromic metal complexes formed by incorporating photochromic spirooxazines into magnetically interesting inorganic motifs. Light irradiation of photochromic spirooxazines leads to photoinduced isomerization between a closed (spirooxazine, SO) and open (photomerocyanine, PMC) form. The relative stability of the SO and PMC forms and the kinetic and thermodynamic parameters of isomerization can be modulated by manipulating internal structural effects (synthetically) and the dielectric of the medium. A series of photochromic ligands have been generated that allow irreversible binding to transition metals with light-induced switching of the redox, spin, and optical properties of the metal center. Changes in the strength of the ligand field associated with photoisomerization are evidenced by desymmetrization of the ligand field, changes in π-acceptor ability, and an increase in spin-orbit coupling and zero field splitting parameters. The complexes retain their photochromic activity, and in some cases exhibit charge transfer induced spin state changes in both solution and solid states. The kinetics of light-induced switching and thermal relaxation between redox and spin states is dictated by the photochromic ligand, and the first *direct observation* of room temperature photomagnetism in a molecular material will be discussed.