Boron Containing Photochromic Systems and Their Uses

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Photochromic systems comprise an important and increasingly diverse class of materials. Both inorganic and organic systems have been studied and can be found in transition optical materials, optical information storage, cosmetics, authentication systems and flow field visualization. Possibly the most popular application of photochromic systems is the use of silver and copper halides in transition lenses. Over the last decade, research concerning tetracoordinated boron compounds containing a \( \pi \)-conjugated chelate has made rapid progress. Systems of this type are rare but are gaining attention due to their potential use in photochromic materials such as molecular switches. Interest in triarylborane based materials has also increased due to their capability for optoelectronic and anion-sensing applications. The purpose of this presentation is to review several of the recently studied boron-containing photochromic systems. Two of the systems presented will involve tetracoordinated boron compounds that undergo a form of photoisomerization upon exposure to light. The third will show how, through a novel approach to gated photochromism, nonphotochromic triarylborane-containing dithienylethenes can gain photochemical properties by switching the coordination number of the boron center.

The first system covered in this presentation involves a specific type of photochromism known as gated photochromism. In gated photochromism, the photochromic property of the system is reversibly blocked by external stimuli, transforming the system into a nonphotochromic system. The work presented in this section, performed by Yam and coworkers, shows a novel approach to gated photochromism. In triarylborane complexes, the empty p orbital is involved in conjugation with the \( \pi \)-orbitals of the organic framework. Once a Lewis base binds to boron by donation into the empty p orbital, the conjugation is interrupted and a change in the photochemical properties occurs. In this case, nonphotochromic triarylborane-containing dithienylethene complexes such as 1 are treated with a fluoride source as shown in Scheme 1. Upon fluoride binding their photochromic reactivity is “unlocked”. These results show that such organoboranes constitute novel anion-responsive platforms that signal the presence of the analyte through photophysical/structural changes.
The next system presented concerns photochromic switching of N,C-chelates in tetracoordinated boron compounds such as B(ppy)Mes$_2$ (ppy = 2-phenylpyridyl, Mes=mesityl) (2, Scheme 2). When irradiated with UV-light, this compound undergoes a reversible intramolecular bond breaking/bond forming process leading to the formation of a rare boratacyclopropane ring. This process is accompanied by a distinct color switching. A limitation discovered for these systems is a high reactivity toward oxygen, which causes a decomposition reaction as shown in Scheme 2. A series of systematic investigations into the photochromic behavior of this type of compounds have shown that the mesityl substituents are essential. Presumably, their bulk provides a drive for the structural rearrangements observed in the reaction. It was also observed that the addition of electron withdrawing and electron donating groups to the ppy has a significant impact on the rate of photoisomerization as well as on the photochemical stability of the molecule. Non-ppy based N,C-chelate ligands such as the benzo[b]thiophenepyridyl chelate were also studied and were found to be amenable to this photoisomerization reaction, albeit not reversibly because of the thermal sensitivity of the rearranged product.

The third and final systems presented herein are catecholboranes bearing an E-azobenzene moiety that is coordinated via one of its nitrogen atoms to the boron center.
Because of this intramolecular base-stabilization of the boron atom, its Lewis acidity is significantly reduced if not entirely quenched. Upon irradiation, the azo group can be photoisomerized into the Z-conformer, leading to a cleavage of the intramolecular N→B dative bond present in \(E\)-3. As a result, the boron center of Z-3 is three coordinate and therefore Lewis acidic. This light-induced turn-on of the Lewis acidity has been confirmed by coordination studies which show that Lewis basic ligands such as pyridine coordinate to Z-3 and not E-3. This photoisomerization reaction is very sensitive to the electronic properties of the boron and azobenzene substituents; in particular, the introduction of electron withdrawing groups at boron strengthen the N→B bond and inhibit the isomerization reaction.\(^7\) Possibly, the ability to switch the Lewis acidity of these complexes by irradiation will allow for the photocontrol of reactions that are catalyzed by Lewis acids.\(^5\)

\[ \text{(E)-ArB(cat) py} \quad \text{py} \quad \text{h} \quad \text{py} \quad \text{(Z)-ArB(cat) py} \]

\[ \text{(E)-3} \quad \text{h} \quad \text{(Z)-3} \]

**Scheme 3:** Photoisomerization of a catecholborane containing an azo group and its effect on the Lewis acidity at the boron center when tested with pyridine.

The results discussed in this presentation show that the introduction of a Lewis acidic boron moiety in photochromic compounds can afford a range of unprecedented behaviors which could be exploited for both anion sensing and photo-controlled catalytic reactions. One of the limitations to be overcome is certainly the inherent chemical instability imparted by the presence of the Lewis acidic boron atom in these compounds.

**References:**