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Modulating the Photoisomerization of N,C-Chelate Organoboranes with Triplet Acceptors

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ABSTRACT

Triplet acceptors such as naphthalene, pyrene, and anthracene have been found to be highly effective in controlling the photoisomerization efficiency of N,C-chelate boryl chromophores, establishing the involvement of a photoactive triplet state in the isomerization of this class of photochromic compounds.

Photoresponsive materials are attractive for a wide range of uses in molecular electronics, including optical data storage, molecular switching, and logic technologies. Thermally reversible photochromic dyes in particular have generated considerable interest as materials for ophthalmic glasses and photoresponsive windows.[1] While modification of existing systems such as spirooxazines, azobenzenes, and diarylethenes allows for the fine-tuning of their optical and electronic properties, the investigation of new classes of photoresponsive materials may lead to new applications in molecular switching technology.

We recently reported the unusual photochromism of N,C-chelate dimesitylboranes, which undergo thermally reversible isomerization on exposure to UV light.[2] Driven by the steric congestion of the mesityl groups, this photochemical reaction proceeds by formation of a three-membered boracycle with dearomatization of one of the pendant mesityl rings (Scheme 1). In solution or doped polymer films, this transformation results in a pronounced color change, typically from light yellow to deep blue or green, as well as fluorescent quenching. These compounds are attractive photochromic materials for several reasons, characterized by thermal reversibility, quantitative photoisomerization, and drastic color changes even at low conversion. With this system, diverse chemical structures based on organic π-conjugated materials,[3] metal coordination complexes,[4] and even N-heterocyclic carbenes[5] have been recently investigated. Despite this research activity however, a more detailed understanding of the mechanism of this reaction has remained elusive and is critical to the rational design of these materials.

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(1) For example, see: (a) Berkovic, G.; Krongauz, V.; Weiss, V. *Chem. Rev.* **2000**, *100*, 1741. (b) Irie, M. *Chem. Rev.* **2000**, *100*, 1685. (c) Ko, C.-C.; Yam, V. W.-W. *J. Mater. Chem.* **2010**, *20*, 2063 and references therein. (d) Feringa, B. L. *Molecular Switches*; Wiley-VCH: Weinheim, Germany, 2001.

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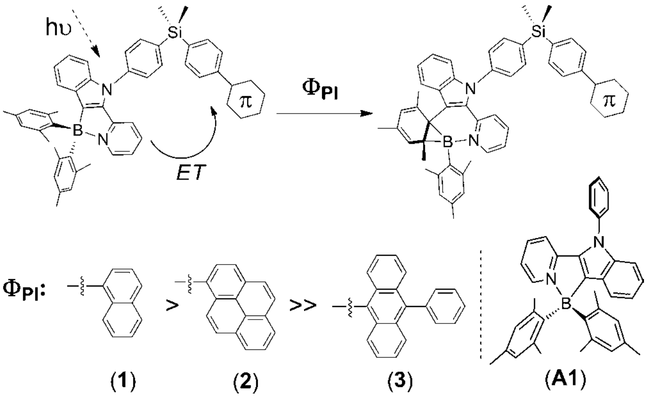
10.1021/ol302742g

Scheme 1. Efficiency of Photoisomerization (Φ_{PI}) in This System Can Be Modulated by Controlling the Energy Transfer (ET) from the Photoactive Borane to a Triplet Acceptor Chromophore



In particular, elucidating the nature of the photoactive excited state is of key importance if the kinetics of the forward and reverse reactions are to be controlled.

A number of photochromic materials, including spiropyrans, spirooxazines, and diarylethenes, have been shown to isomerize via photoactive triplet states.[6] Based on this principle, it has been possible to sensitize photoisomerization reactions using heavy atoms, which facilitate intersystem crossing (ISC) to a triplet state by strong spin−orbit coupling.[7] These prior studies have inspired us to examine if the triplet state also plays a role in photoisomerization of organoboron compounds.

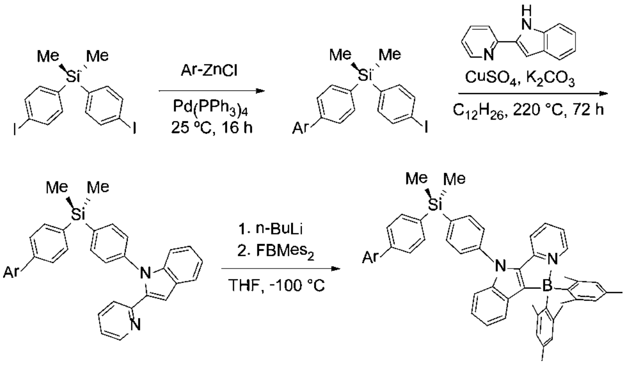
To determine the nature of the photoactive excited state in these organoboranes, we designed a series of compounds incorporating photochromic boron units and acceptor chromophores of varying triplet energy. Herein we provide evidence that the isomerization in this system proceeds via a photoactive triplet state and that the quantum yield of photoisomerization can be modulated in a controlled manner using the triplet energy of the acceptor (Scheme 1).

Three nonconjugated compounds **1**−**3** were prepared incorporating a previously investigated photochromic boryl chromophore **A1**[8] as well as aromatic acceptors. The **A1** chromophore in these systems is based on a 2-(2-pyridyl)-indole chelate, exhibiting a moderate photoisomerization quantum yield (Φ_{PI}) of 0.09 as well as green fluorescence with λ_{max} = 490 nm in toluene.[8] The acceptor chromophores 1-phenylnaphthalene (**1**), 1-phenylpyrene (**2**), and 9,10-diphenylanthracene (**3**) display singlet energies of 3.93, 3.33, and 3.05 eV, respectively,[9−11] in all cases higher than that of the boryl unit (2.77 eV). These chromophores have been widely used as triplet acceptors for photochemical reactions and triplet−triplet upconversion and provide a considerable range in triplet energy level.[9−11]

Covalent attachment of the photoswitch to the acceptor serves to strengthen the interaction between the two. The use of a nonconjugated linker is critical, as the energies of the excited states on the boron chromophore can be kept consistent while different acceptors are employed. Furthermore, previous work has shown that increases in the extent of π-conjugation about the boron chromophore can dramatically slow or even inhibit the photoreaction, presumably due to the presence of low-lying $\pi \rightarrow \pi^*$ excited states that compete with the photoactive charge transfer state.[3c,5b]

Compounds **1**−**3** are prepared by Negishi cross-coupling of di-(*p*-iodophenyl)dimethylsilane with the appropriate bromo- or iodoarene, followed by attachment of the N,C-chelate pyridylindole by copper-catalyzed Ullman condensation (Scheme 2). The boron center may then be installed by deprotonation of the product with *n*-butyllithium at the indole 3-position, followed by addition of $FBMes_2$.

Scheme 2. Synthetic Procedures[a]



[a] Ar = 1-naphthalenyl (**1**); 1-pyrenyl (**2**); or 10-phenyl-9-anthryl (**3**).

Single crystals of **1** were obtained by slow evaporation of its hexanes/CH_2Cl_2 solution (Figure 1).[12] The two chromophores are closely spaced, with a separation distance of 7.02 Å between the pyridyl and naphthyl rings (C(16) and C(28)) in **1**. Both chromophores lie out-of-plane with the phenyl groups of the linker, exhibiting dihedral angles of 59.7° for the naphthyl ring and 76.1° for the indole, indicative of minimal extension of conjugation through the diphenylsilane bridge. As anticipated, compounds **1**−**3** all display photophysical and electrochemical properties characteristic of the boryl chromophore **A1** (Table 1).

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(12) Crystal data for **1** have been deposited at at the Cambridge Crystallographic Data Centre (CCDC 900063).

All compounds exhibit a broad absorption peak at $\lambda_{\max}$ = 417 nm with similar extinction coefficients (see Supporting Information (SI)), attributable to a transition of mixed $\pi-\pi^*$ and charge-transfer character on the boryl unit, giving the compounds a bright yellow color in the solid state and solution.

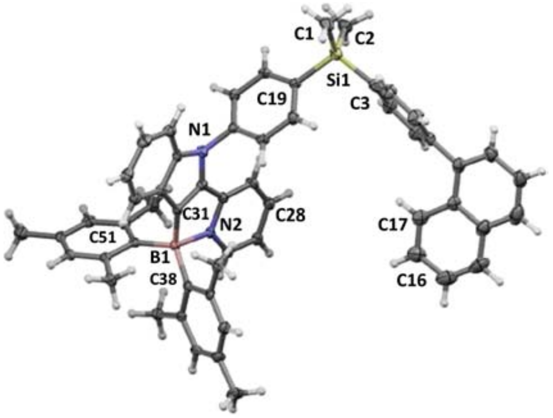

Figure 1. Crystal structure of compound **1** with 35% thermal ellipsoids. Important bond lengths and angles: B(1)−C(31) 1.621(6), B(1)−C(38) 1.626(6), B(1)−C(51) 1.637(6), B(1)−N(2) 1.688(6) Å; C(31)−B(1)−N(2) 94.3(3), C(38)−B(1)−C(51) 115.4(4)°.

These compounds show very bright greenish-yellow fluorescence ($\lambda_{\max}$ = 498−501 nm) with emission profiles and quantum efficiencies similar to those of **A1** (relative quantum efficiencies obtained using **A1** as the standard under N_2 are 1.00, 1.02, 0.88, and 1.12 for **A1**, **1**, **2**, and **3**, respectively). These data indicate that the singlet emission from the boryl chromophore is largely unperturbed by the presence of the aromatic groups in all three compounds.

However, the presence of the acceptor chromophores in **1**−**3** results in dramatically different photoisomerization behavior. Upon irradiation at 419 nm in toluene (10^{-5} M), compounds **1** and **2** undergo quantitative conversion to their dark isomers, with photoisomerization quantum yields of Φ_{PI} = 0.12 and 0.03 respectively. Similar to **A1**, this reaction results in the appearance of a broad peak at 612 nm in their absorption spectra (Figure 2). The conversion of **1** is complete in 5 min using a hand-held UV lamp while the reaction of **2** is much slower, requiring 30 min of irradiation under the same conditions.

Table 1. Photophysical and Electrochemical Properties

	$\lambda_{\max,\,abs}$ [nm][a]	$\lambda_{em.}$ [nm][a]	Φ_{fl}[b]	Φ_{PI}	$E_{1/2}^{red}$ [V][c]	HOMO [eV][d]	LUMO [eV]
1	323, 351, 417	498	0.88	0.12	−2.31	−5.13	−2.49
2	329, 343, 417	501	0.82	0.03	−2.31	−5.16	−2.49
3	352, 373, 393, 417	500	0.69	–	−2.32	−5.15	−2.48

[a] Measured at 10^{-5} M in toluene at 298 K. [b] Measured using an integration sphere in degassed toluene under N_2, excited at 417 nm. [c] Relative to $FeCp_2^{0/+}$. [d] Calculated from the LUMO level and the optical energy gap.

In the case of **3** the isomerization appears completely suppressed, showing no observable spectral changes on extended irradiation. These pronounced differences in reaction rate are further highlighted in Figure 3, which shows the percent conversion of each species to the dark isomer over time, as well as the visual color changes observable for solutions of **1**−**3** on exposure to UV light. These changes were also monitored by fluorescence measurements, which show **1** and **2** to undergo fluorescent quenching upon isomerization, while the emission of **3** remains essentially constant (see SI).

The isomerization process was also monitored by ^{1}H NMR spectroscopy, by irradiating solutions of **1**−**3** in C_6D_6 using a UV reactor at 419 nm. The NMR data show that compounds **1** and **2** reach 85 and 38% conversion respectively after 2 h of irradiation, with only trace amounts of product observed for **3** (see SI). As with the parent **A1**

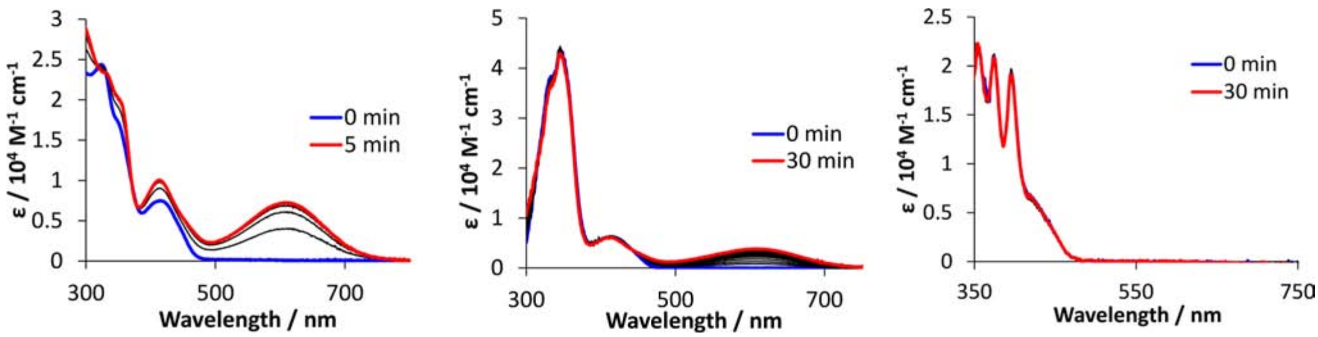

Figure 2. Changes in the absorption spectra of **1** (left), **2** (middle), and **3** (right) at 10^{-5} M in toluene on irradiation with a hand-held UV lamp at 365 nm.

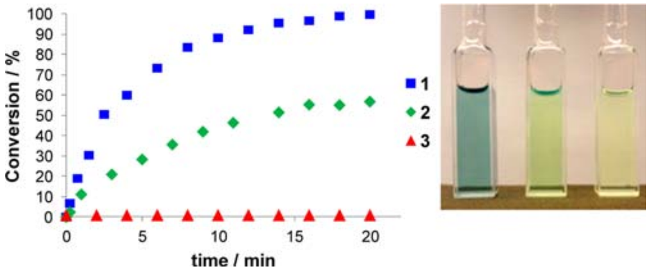

Figure 3. Left: Conversion of **1**−**3** to their dark isomers over a 20 min period under irradiation at 419 nm (10^{-5} M in toluene). Right: Photos of **1**−**3** respectively after 10 min of irradiation (10^{-4} M in toluene).

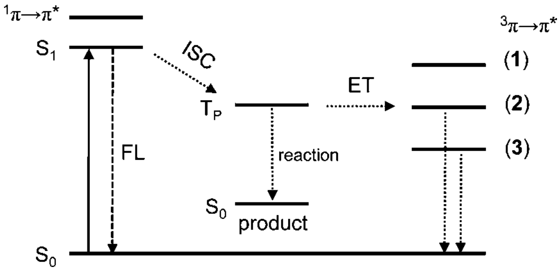

Figure 4. A diagram showing the relative energy levels of the photoactive triplet state (T_P) on the boryl unit and the $^3\pi\rightarrow\pi^*$ state of the acceptor in **1**−**3**. Energy transfer from T_P to $^3\pi\rightarrow\pi^*$ partially quenches the photoisomerization in **2** and efficiently suppresses it in **3**, but does not interfere in **1**.

chromophore, the thermal reversal of **1** is slow, achieving only 33% conversion back to the light isomer after heating at 40 °C for 20 h. In contrast, the thermal reversal of the dark isomers of **2** and **3** is suppressed, with no significant conversion back to their light isomers upon extended heating under N_2.

Consistent with their fluorescence spectra, TD-DFT calculations indicate that **1**−**3** share a common S_1 state located at 2.77 eV, centered on the boron chromophore. As noted in literature, the singlet levels of 1-phenylnaphthalene, 1-phenylpyrene, and 9,10-diphenylanthracene all lie at higher energy (> 3 eV).[9−11]

The triplet energies of the acceptors, however, vary considerably with respect to that of the borane, lying at 2.55, 2.10, and 1.77 eV, respectively, for 1-phenylnaphthalene, 1-phenylpyrene, and 9,10-diphenylanthracene.

Using TD-DFT calculations, the lowest triplet state localized on the boryl unit was found to lie consistently at 2.13 eV for species **A1** and **1**−**3** (see SI) representing the T_1 state for **A1**. However, the lowest $^3\pi\rightarrow\pi^*$ excited states on the acceptor chromophores in **1**−**3** were calculated at 2.63, 2.05, and 1.73 eV, respectively, similar to those observed experimentally for the independent chromophores.[9−11] Relative to the lowest triplet state on the boryl unit, the lowest triplet energy of the acceptor is thus much higher in **1**, much lower in **3**, and approximately equal in **2**. This is consistent with the presence of a photoactive triplet state in these compounds, as energy transfer to the triplet excited state of the acceptor would be expected to be negligible in **1**, weak in **2**, and dominant in **3** (Figure 4). This may also explain the thermal irreversibility of compounds **2** and **3** in which the low-lying triplet state of the acceptor may be close to the activation energy of the thermal reversal, thus suppressing the process. The experimental and computational data therefore support that the photoisomerization quantum efficiency may be effectively controlled by varying the triplet energies of appended triplet acceptors.

In summary, using a series of two-chromophore materials, we have shown that the photoisomerization of N,C-chelate dimesitylboranes likely proceeds via a triplet state. In addition, we have shown that the photoreactivity of the sample can be effectively modulated by controlling the triplet−triplet energy gap between the photochromic unit and the triplet acceptor chromophore. This finding has important implications for the design of photochromic N,C-chelate boron compounds. With isomerization proceeding via a triplet state, it should be possible to either sensitize or quench the photoisomerization using appropriate triplet sensitizers or acceptors.

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Supporting Information Available. Synthetic procedures, fluorescence spectra, NMR isomerization experiments, and TD-DFT data for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.