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Single Boryl Isomerization in Silyl-Bridged Photochromic Diboryl Dyes

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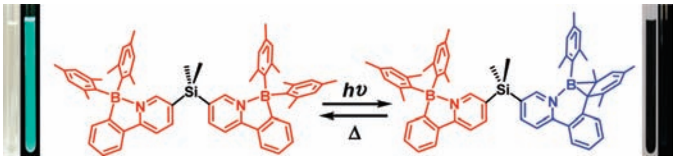
ABSTRACT

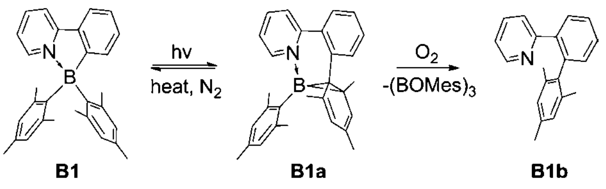


Silyl-bridged dimers of a ppy-BMes$_2$ (ppy = 2-phenylpyridine, Mes = mesityl) photochrome were found to undergo photochromic switching involving a single boryl unit only. A through-space intramolecular energy transfer was found to be responsible for the single-chromophore isomerization phenomenon and fluorescence quenching. Steric congestion in the diboryl molecules was found to have an impact on photoisomerization quantum efficiency.

Thermally reversible (t-type) photochromic dyes such as spiropyrans, spirooxazines, and naphthopyrans have attracted great attention due to their applications in smart windows and ophthalmic glasses.[1a−e] While modification of these existing photochromes allows fine-tuning of their photochromic properties, the development of novel t-type photochromic dyes with different switching kinetics, thermal stabilities, and coloration is important for the development of new switching devices and applications. We have recently reported that four-coordinate organoboron compounds based on a ppy-BMes$_2$ (ppy = 2-phenylpyridine, Mes = mesityl) chromophore can undergo a thermally reversible photoisomerization process accompanied by a distinct color change from either colorless or light yellow to dark blue or green (Scheme 1).[2]

The B(ppy)Mes$_2$ chromophore is attractive for use in photochromic applications for several reasons: (1) it can be quantitatively switched between the two isomers; (2) dramatic color changes can be achieved even at low conversion; and (3) the photoisomerization is accompanied by reversible fluorescence quenching. One challenge is to understand the various factors that influence the quantum efficiency of the switching process in this new photochromic system. Recently, we have shown that in π-conjugated polyboryl molecules that contain more than one switchable B(ppy)Mes$_2$ unit and acetylene linkers only one chromophore undergoes photoisomerization.[2d] Furthermore, we have observed that

Scheme 1. Photoisomerization and Oxidation of B(ppy)Mes$_2$



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the single boryl isomerization in the polyboryl system appears to be more efficient than the corresponding monoboryl compound due to the antenna effect.[3] To understand the role of π-conjugation on the unusual single-boryl switching phenomenon in polyboryl systems, we decided to study diboryl compounds that contain a nonconjugated linker such as a $SiMe_2$ group.

Two new silyl-bridged diboryl compounds **SiB1** and **SiB2** have thus been synthesized (Figure 1). We have found that these molecules also display a single-chromophore isomerization phenomenon, similar to that observed in previously reported conjugated molecules.[2d] In addition, we have shown that the second boryl unit can be isomerized by introduction of an oxidant. The details are presented herein.

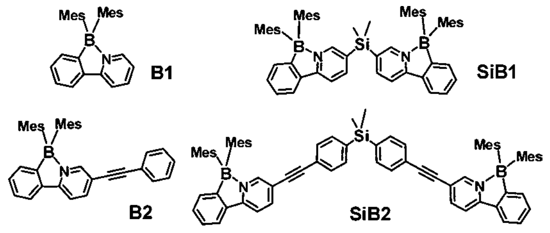

Figure 1. Silyl-bridged dimers and corresponding monomers.

SiB1 was synthesized via monolithiation of 2,5-dibromopyridine and silylation with $Si(CH_3)_2Cl_2$, followed by Suzuki−Miyaura coupling[4] with 2 equiv of 2-Br-PhB(OH)$_2$ and finally dilithiation and electrophilic quenching with $BMes_2F$. **SiB2** was prepared via monolithiation of 1,4-diiodobenzene and silylation with $Si(CH_3)_2Cl_2$, followed by Sonogashira coupling[5] with H−C≡C−ppy-BMes$_2$.[2d] Full synthetic details can be found in the Supporting Information. **SiB1** crystallizes in the chiral space group $P2_12_12_1$, and its structure[6] determined by single-crystal X-ray diffraction analysis is shown in Figure 2. The bond lengths and angles around the B center are similar to previously known N,C-chelate $BMes_2$ compounds.[2,7] **SiB1** is a very congested molecule with a separation of 8.64 Å between the two B atoms of the boryl units. While the **SiB2** structure was not determined by X-ray diffraction, molecular modeling shows that **SiB2** is much less crowded with the two B centers being 17.6 Å apart (see Supporting Information).

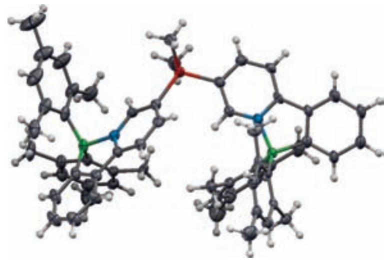

Figure 2. Crystal structure of **SiB1**. Blue, N; green, B; red, Si.

Two well-resolved reduction peaks were observed in the CV diagram of **SiB1**, which may be attributed to the sequential reduction of the two boryl units, by comparing to that of **B1** (Table 1 and Supporting Information), thus supporting some degree of interaction between the two B units. In contrast, the **SiB2** molecule has only a single reduction peak. The behavior of **SiB2** is similar to that of $Me_2Si(-\equiv-CpFeCp)_2$ where no interactions between the two Fe(II) centers were observed.[8] Both compounds display a low-energy shoulder in the absorption spectra which is attributable to charge transfer from the mesityl groups (HOMO) to the N,C-chelate backbone (LUMO) based on previous work.[2b] The energy of this transition is lower for **B2** and **SiB2** due to the greater π-conjugation in those molecules. Comparison of the optical energy gaps of the dimers to the corresponding monomers shows that dimerization has a greater impact on **SiB1** than **SiB2** since **SiB1** has a much smaller optical energy gap than **B1**, while **SiB2** and **B2** are similar in that respect. This can also be attributed to the closer proximity of the two boryl chromophores in **SiB1** compared to **SiB2**.

Upon irradiation with 365 nm light, both compounds underwent quantitative transformations to the dark colored isomers **SiB1a** and **SiB2a**, respectively, which were moni-

Table 1. Photophysical and Electrochemical Properties

compound	λ_{max} (ε)[a] (nm, M^{-1} cm^{-1})	optical energy gap (eV)	λ_{Em} (nm)[a]	Φ_F (%)[b]	$E_{1/2}^{red}$ (V)[c]	$\Phi_{photoiso.}$[d]	$k_{thermal} \times 10^6$ (s^{-1})[e]	thermal reversal $t_{1/2}$ (h)
B1	320 (15200) 357 (3207)	3.10	458	10	−2.30	0.85	3.7	52[f]
SiB1	327 (21705) 366 (9160)	2.85	479	36	−2.23, −2.41	0.60	8.2	23[f]
B2	313 (24 900) 377 (11 700)	2.88	490	37	−2.03	0.33	30.9	6
SiB2	322 (63476) 384 (27561)	2.72	484	48	−2.06	0.58	24.8	8

[a] At 10^{-5} in toluene. [b] With 9,10-diphenylanthracene ($\Phi_F = 90\%$) as the standard in toluene. [c] Relative to $FeCp_2^{0/+}$ in DMF. [d] At 25 °C in toluene, using ferrioxalate actinometry at 360 nm excitation, the value is the average of four measurements. [e] At 35 °C in d_6-benzene. [f] Calculated from the first-order rate constants.

tored by UV−vis, fluorescence, and NMR spectroscopy. The UV−vis spectra (Figure 3) of both compounds showed the appearance and rapid growth of a peak at $\lambda_{max} = 624$ nm for **SiB1** and $\lambda_{max} = 653$ nm for **SiB2** upon irradiation, which is characteristic of the isomerized unit shown in Scheme 1. However, the intensity of this peak relative to the largest peak at the completion of isomerization was smaller for the diboryl compounds: 32% for **B1**, 18% for **SiB1**, 20% for **B2**, and 8% for **SiB2**. Thus, the spectral change of the diboryl compounds is approximately one-half that of the corresponding monoboryl compounds, indicating that only one of the ppy-BMes$_2$ groups likely undergoes isomerization in the silyl-bridged dimers.

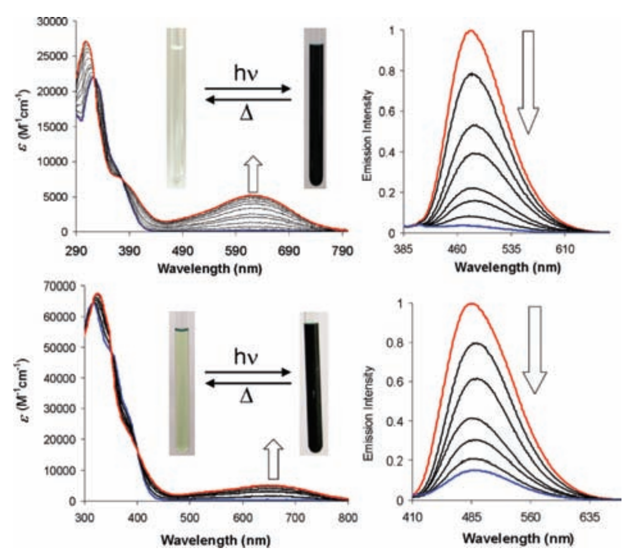

Figure 3. Changes in the absorption spectra (left) and emission spectra (right) of **SiB1** (top) and **SiB2** (bottom) during irradiation with 365 nm light. Insets: Photographs showing color changes of the compounds before and after irradiation.

This was in fact confirmed by ^{1}H NMR spectra. As shown in Figure 4, the ^{1}H NMR spectrum of **SiB1** upon irradiation shows the complete disappearance of the original pyridyl proton signal, H$_1$, at 8.83 ppm, and the growth of two new peaks H$_1$′ and H$_1$″, at 8.79 ppm and 8.67 ppm, respectively, that retain a 1:1 ratio throughout the entire photolysis process. The appearance of these peaks is accompanied by peaks H$_3$ and H$_4$ that integrate to one proton each and are characteristic of the isomerized species. The peak ratios and integration values unambiguously confirmed that only one boryl unit undergoes isomerization, forming **SiB1a** quantitatively.

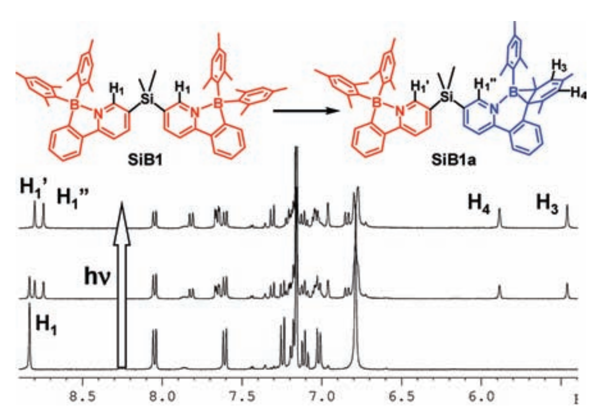

Figure 4. ^{1}H NMR spectral change of **SiB1** during irradiation.

Similar ^{1}H NMR spectral changes were observed for **SiB2** (see Supporting Information). Solids of **SiB1a** and **SiB2a** may be isolated from a pure oxygen-free hexane solvent.

Because of the lack of π-conjugation between the two boryl units in the silyl diboryl molecules, this single-chromophore isomerization phenomenon can be attributed to a through-space intramolecular energy transfer from the nonisomerized chromophore to the low-energy absorption band of the isomerized chromophore based on Kasha's principle,[9] which dissipates the excited state energy, thus preventing isomerization of the second chromophore. Complete fluorescence quenching was also observed as a consequence of the energy transfer in **SiB1**. However, the isomerized product of **SiB2** has a weak emission peak despite the reaction being quantitative, indicating that the larger separation of the two boryl units results in weaker through-space interactions.

The single-chromophore photoisomerization phenomenon of the silyl-bridged boryl systems is in contrast to the extensively studied dithienylethene (DTE) photochromic system, where simultaneous photoisomerization of multiple chromophores in a single molecule is frequently observed.[10] For example, a silyl-bridged DTE dimer was found to undergo multichromophore switching, reaching a photostationary state consisting of the nonisomerized, singly isomerized, and doubly isomerized compounds, despite the presence of a low-energy absorption band in the isomerized state of the DTE system.[11] This difference may be caused by the much slower photoisomerization rate of the N,C-chelate boryl compounds that cannot compete kinetically with the energy transfer process. Efforts are being taken by us to determine the rates of the various competing excited state processes of the N,C-chelate boryl systems.

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The photoisomerization quantum efficiencies of the silyl-bridged diboryl compounds were measured in toluene using ferrioxalate actinometry at 360 nm excitation.[12] The diboryl compound **SiB1** was found to have a lower quantum efficiency (0.60) than the corresponding monoboryl **B1** (0.85), while **SiB2** was found to nearly double the quantum efficiency (0.58), compared to that (0.33) of **B2**. The greatly enhanced photoisomerization quantum efficiency of **SiB2** compared to **B2** may be attributed to the antenna effect[3] where one boryl center facilitates the other boryl center to undergo isomerization via fast intramolecular energy transfer. The decreased quantum efficiency of **SiB1** relative to **B1** may be attributed to the greater steric congestion in the diboryl molecule that offsets the antenna effect. Thus, we have illustrated that linking two photoswitchable boryl centers together via a silyl group in a nonsterically congested molecule may be an effective stragegy in enhancing a single boryl photoisomerization quantum efficiency of polyboryl compounds.

The rate of the reverse thermochromic reaction was measured at 35 °C in C_6D_6 (see Figure S8 in Supporting Information). All compounds undergo a first-order reaction to restore the starting material at this temperature. The half-lives of the isomerized species decreased in the order **B1** > **SiB1** > **SiB2** ≈ **B2** (Table 1), indicating that increased π-conjugation and steric congestion enhance the rate of the thermal reversal, as previously observed.[2d]

Because the C−C coupled dark isomer is known to react with oxygen to form a colorless C−C coupled product **B1b** as shown in Scheme 1, oxygen may be used to eliminate the low-energy absorption band of the isomerized species and trigger isomerization of the second boryl in the diboryl molecules. This is demonstrated by the reaction of the dark isomer **SiB1a** with oxygen that resulted in a quantitative formation of **SiB1b**, accompanied by the reappearance of an emission peak that is slightly blue-shifted (λ_{max} = 470 nm) compared to **SiB1**, and the disappearance of the low-energy absorption band at 624 nm. This further supports that only one of the boryl units had undergone isomerization and subsequent oxidation, leaving the second boryl intact. The hypsochromic shift of the emission maximum of **SiB1b** relative to that of **SiB1** (Figure 5) is also consistent with the interactions between the two boryl units in **SiB1**. Irradiating the solution of **SiB1b** under N_2 at 365 nm resulted in once again fluorescence quenching and the appearance of the low-energy absorption band of the dark isomer **SiB1c** at 614 nm (see Supporting Information). Exposure of **SiB1c** to O_2 quenched the low-energy absorption band and led to the appearance of a very weak emission band at 440 nm, attributed to the double C−C coupled product **SiB1d**, a much weaker emitter than **SiB1** (see Supporting Information). The stepwise deborylation, C−C coupling, and color change of diboryl compounds with oxygen is certainly not desirable for photochromic switches but may find use in other applications.

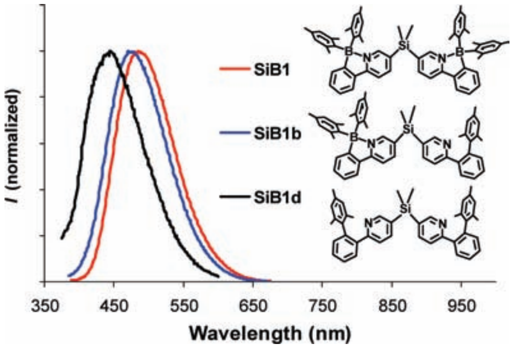

Figure 5. Normalized fluoresence spectra of **SiB1** and its C−C coupled products.

In summary, we have demonstrated that the single-boryl isomerization phenomenon observed previously is not limited to π-conjugated systems. Further, we have shown that linking two photoswitchable boryl units together by a silyl group may greatly enhance the photoisomerization quantum efficiency in a sterically noncongested system. Intramolecular energy transfer and steric factors play an important role in the photoisomerization process of the diboryl compounds.

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Supporting Information Available: Synthesis and characterization of **SiB1** and **SiB2**, cif file of **SiB1**, calculated structure of **SiB2**, electrochemical, photophysical, photolysis, and thermolysis data. This material is available free of charge via the Internet at http://pubs.acs.org.

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