Photoisomerization

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Switching of a Single Boryl Center in π-Conjugated Photochromic Polyboryl Compounds and Its Impact on Fluorescence Quenching**

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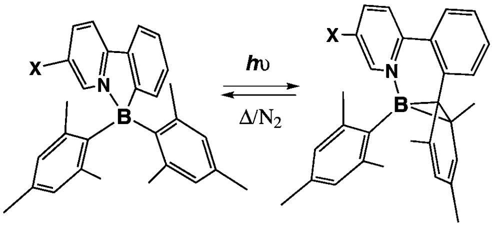
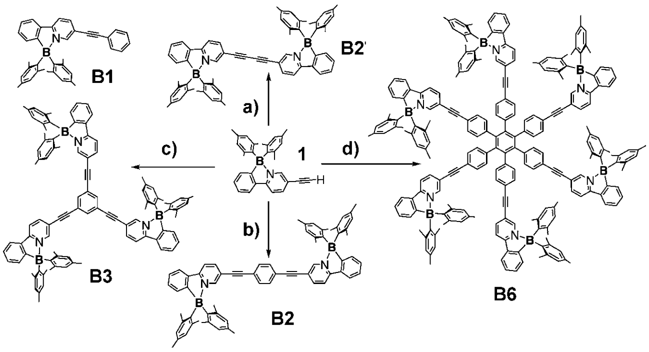
Many materials consisting of a π-conjugated organic backbone attached to either a tetrahedral or trigonal-planar boron center display enhanced fluorescence and charge-transport properties. This phenomenon can be attributed to either chelation-enhanced π-conjugation of the organic backbone by a tetrahedral boron center[1–2] or to the strong electron-accepting ability of a trigonal-planar boron center.[3] Hence, boron-containing molecules have found applications in OLEDs, organic transistors, and nonlinear optical materials.[1–3] We recently reported an unusual photochromic switch involving tetrahedral N,C-chelating boron chromophores such as B(ppy)Mes$_2$ (ppy = 2-phenylpyridine, Mes = mesityl).[4] These compounds undergo a thermally reversible photoisomerization from a colorless or light colored state to a dark colored state upon irradiation with 350–450 nm light (Scheme 1). These compounds are highly fluorescent in the light-colored state with tunable emission colors, whereas the dark-colored isomers are nonemissive.



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

We have recently shown that this photoisomerization can be suppressed when the system is conjugated to an olefinic bond, which can dissipate the excitation energy through *trans–cis* isomerization.[4b] While this conjugation has the benefit of stabilizing the system towards photodegradation and preserving its luminescence properties, it also renders the system photochromically inert. To elucidate the impact of incorporating multiple photochromic boron centers into these materials, we prepared a series of new π-conjugated molecules as shown in Scheme 2. Our study has shown that isomerization of one chromophore prevents isomerization of the others, leading to amplified and reversible fluorescence quenching of the entire molecule. The details of our study are presented herein.



Scheme 2. Syntheses of **B2**, **B2′**, **B3**, and **B6**. General conditions: 10 mol% CuI, 5 mol% [Pd(PPh$_3$)$_4$] (except for (a)), 30 equiv NEt$_3$, THF with a) O$_2$ bubbling, b) 1,4-diiodobenzene, c) 1,3,5-tribromobenzene, and d) hexakis(4-iodophenyl)benzene. **B1** is shown for comparison.

The synthesis of the monoboryl **B1** was reported previously.[4b] Diboryl **B2** and **B2′**, triboryl **B3**, and hexaboryl **B6** were synthesized from a common intermediate **1** (see the Supporting Information). **B2′** was prepared by Hay coupling,[5] and **B2**, **B3**, and **B6** were prepared by Sonogashira coupling[6] with the appropriate aryl halides.

The crystal structures of **B2**, **B2′**, and **B6** (Figure 1)[7] reveal several important features of these materials. **B2′** and **B2** have good coplanarity between the two boron chromophores and dihedral angles of 0° between the two ppy rings for **B2′** and 23.9° between the ppy and the central phenyl ring for **B2**, which is consistent with strong π conjugation and electronic communication between the boron centers in these molecules. In contrast, the electronic communication between the boron centers in **B6** appears to be much weaker as a result of the high degree of steric congestion, as evidenced by the large dihedral angles of 22.3°, 59.5°, and 82.8° between the ppy chelates and adjacent phenyl rings.

These trends in electronic communication are manifested in the reduction potentials and absorption spectra of these materials. The polyboryl compounds except **B3** all show two well-resolved reduction peaks, and the first reduction potentials are more positive than that of **B1**. All compounds display a low-energy shoulder band in their absorption spectra, attributable to charge transfer from the mesityl groups to the conjugated backbone based on DFT calculations. The energy

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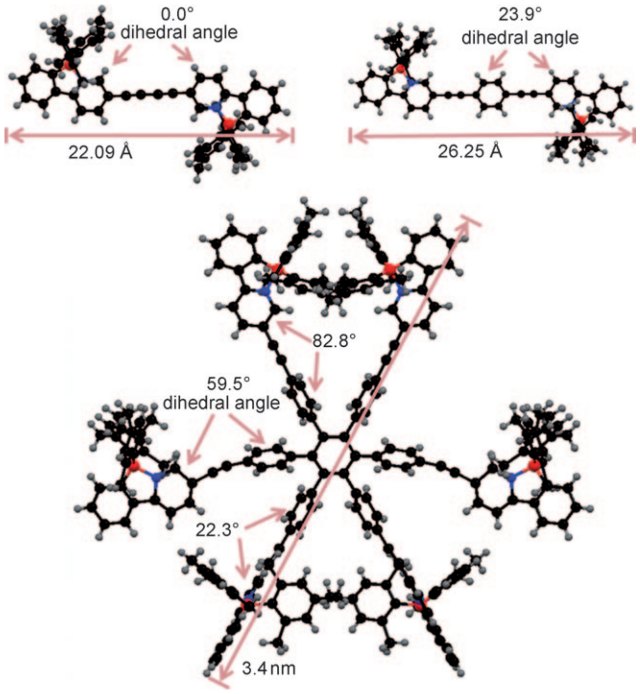

Figure 1. Crystal structures of **B2′** (top left), **B2** (top right), and **B6** (bottom). B: red. N: blue. Solvent molecules omitted.

of this transition decreases in the order **B1** > **B3** > **B6** > **B2** > **B2′**, which is consistent with 1) the strong conjugation of the boron centers in **B2′** owing to the coplanarity of its two ppy chelates, 2) improved conjugation of *para*-substituted **B2** relative to *meta*-substituted **B3**, and 3) weak conjugation in **B6** caused by steric congestion. All compounds display bright fluorescence in the 490–510 nm range with **B2′** having the lowest emission energy.

Upon irradiation with UV light (365 nm), all polyboryl compounds undergo structural and color changes to isomers **B2b**, **B2′b**, **B3b**, and **B6b**, respectively. This photoisomerization process was monitored by ^{1}H NMR, UV/Vis, and fluorescence spectroscopy. In the UV/Vis spectra, a broad band appears at around 650 nm and grows with irradiation time for all compounds in the same manner as monoboryl **B1**. However, as shown in Figure 2, the ratio of the intensity of this broad band to the strongest absorption band at the saturation point (reached within minutes at ca. 10^{-5} M) decreases with the number of boryl chromophores (20 % for **B1b**, ca. 9 % for **B2b**, ca. 6 % for **B3b**, and ca. 3 % for **B6b**). Since the 20 % ratio represents 100 % conversion of monoboryl **B1** to **B1b**,[4b] the 9 %, 6 %, and 3 % ratios for **B2**, **B3**, and **B6** indicates that only one boryl unit in these molecules undergoes photoisomerization.

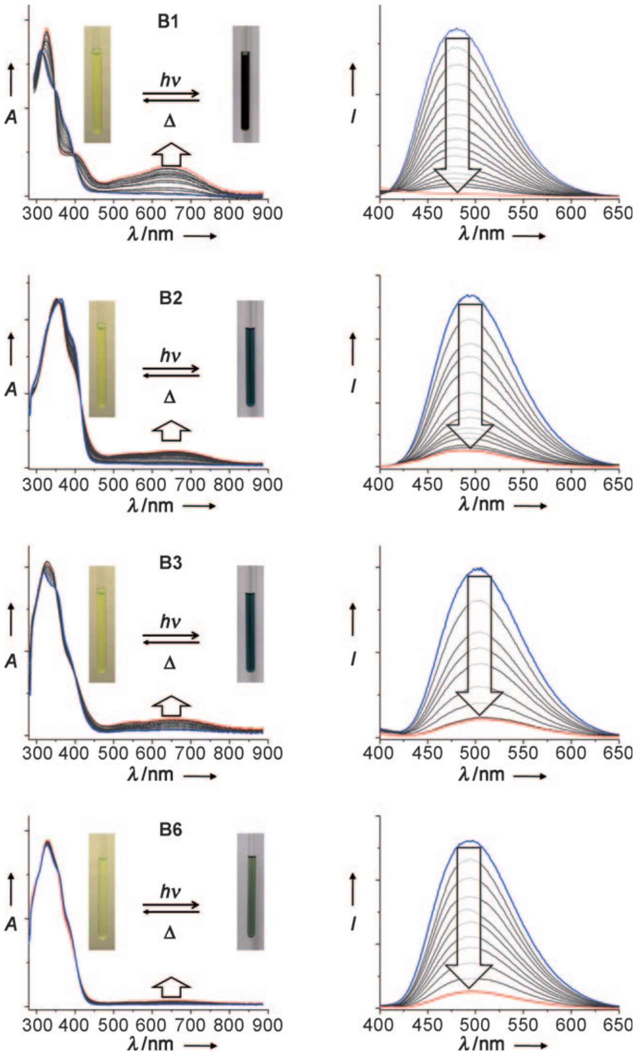

Figure 2. Changes in the absorption (left) and emission (right) spectra of **B1**, **B2**, **B3**, and **B6** in toluene upon irradiation at 365 nm. Inset: Photographs showing the color of the compounds before and after irradiation.

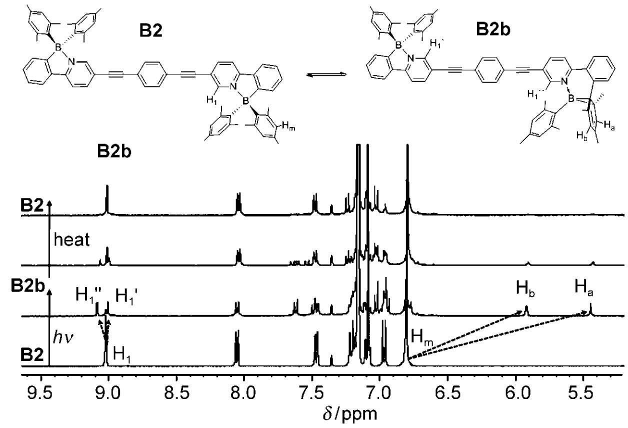

Figure 3. ^{1}H NMR spectral change of **B2** upon switching to **B2b** by irradiation at 365 nm and **B2b** thermal reversal back to **B2** by heating at 35 °C in C_6D_6.

This result was confirmed by ^{1}H NMR studies, which show characteristic peaks for the isomerized and nonisomerized chromophores. Considering **B2** as an example, its ^{1}H NMR spectrum in C_6D_6 displays a new set of well-resolved peaks originating from **B2b**, shown in Figure 3. The characteristic peaks H_a and H_b are consistent with the formation of the C–C-coupled structure **B2b** shown in Figure 3.[4a] Additionally, the singlet proton H_1 disappears and is replaced with two new peaks $H_{1'}$ and $H_{1''}$ that maintain a 1:1 ratio with extended irradiation, which may be assigned to a nonisomerized and isomerized boron chromophore, respectively (see the Supporting Information). Furthermore, ^{1}H NMR photolysis experiments confirmed that **B2′**, **B3**, and **B6** also undergo single boryl switching upon irradiation and reach 100% conversion, given sufficient irradiation time.

NMR competition experiments revealed that the polyboryl compounds isomerize much faster than monoboryl **B1** at a given concentration. For example, using B(ppy)Mes$_2$ as the internal standard, **B2** isomerizes approximately 1.7 times more rapidly than **B1** (see the Supporting Information). This result may be attributed to the "antenna effect",[8] whereby the multiple boron chromophores harvest more photons at a given concentration leading to more rapid isomerization.

This single boryl switching phenomenon displayed by the conjugated polyboryl compounds can be explained as follows using **B2** as an example. Upon excitation, there are two possible isomerization pathways: k_1 to form the monoisomerized product and k_2 to form the diisomerized product. Because of the substantial structural rearrangement that occurs around the boron center upon isomerization, simultaneous switching of both boron centers in the same molecule must be much slower than a single boryl switching, thus making the single boryl switching kinetically favored. Once the monoisomerized product is formed, the energy of its excited state can be dissipated by fast intramolecular energy transfer to the low-energy absorption band of the dark species according to the Kasha's rule, effectively quenching any further isomerization.[9] The single boryl switching behavior of the polyboryl compounds is in sharp contrast to the well known diarylethene (DTE) systems, which usually show simultaneous multichromophore switching.[10] The lack of a photostationary state and the relatively slow isomerization rate of the boryl system may be responsible for the observed single boryl transformation. This effect can be considered beneficial if the integrity of the conjugated system is important for applications such as organic charge-transport materials or transistors, and of course undesired if the material is intended to achieve maximum photochromic effects.

Since the isomerized chromophore is nonemissive, this process effectively quenches fluorescence, as shown in Figure 2. Interestingly, as the number of boron chromophores is increased, maximum fluorescence quenching is achieved with progressively lower absorption spectral changes. This amplification effect on fluorescence quenching is illustrated by the plot of fluorescence intensity change ($|\Delta I|$) of the light-colored species over the absorbance change of the low energy band of the dark species ($|\Delta A|$; Figure 4). Electronic communication between the boron chromophores in the polyboryl systems is clearly responsible for the amplified fluorescence quenching.

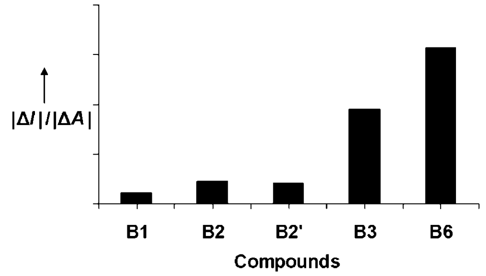

Figure 4. The plot of the ratio of total emission intensity change $|\Delta I|$ versus the total absorption changes $|\Delta A|$ for the monoboryl and polyboryl compounds.

As observed previously for related monoboryl compounds, the isomerization process is fully thermally reversible for all polyboryl compounds in this series. The fluorescence and ^{1}H NMR spectra of all compounds can be fully restored by heating the solution of the dark species at 35°, or by keeping the solution at room temperature for an extended period of time. Kinetic data obtained from ^{1}H NMR studies of the thermal reversal are shown in Figure 5 and Table 1, and are consistent with a first-order process. All dark isomers of

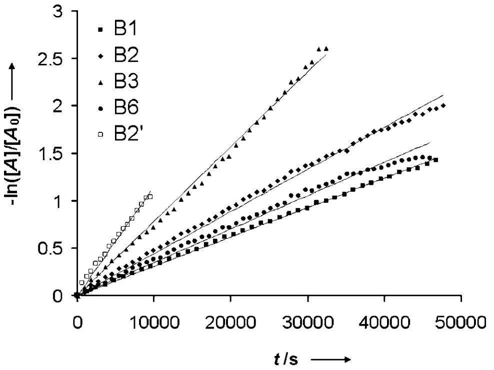

Figure 5. Kinetic plot of the natural logarithm of the ratio of photoisomerized product to the initial amount of photoisomerized product versus time during heating at 35 °C for 1 mg/0.75 mL degassed solution in C$_6$D$_6$.

Table 1: Photophysical and electrochemical properties.

Cmpd	λ_{max} [nm] (ε) [M^{-1}cm^{-1}][a]	Optical energy gap [eV]	λ_{em} [nm][a]	Φ_f[b] [%]	$E_{1/2}^{red}$ [V][c]	Thermal reversal $t_{1/2}$ [min][d]	$k_{thermal}\times 10^6$ [s^{-1}][d]
B1	313 (24900) 377 (11700)	2.88	490	37	−2.03	360	30.9
B2	366 (55800) 393 (42400)	2.72	495	39	−1.93, −2.09	240	44.2
B2′	372 (43000) 408 (31800)	2.68	508	27	−1.73, −2.09	95	115
B3	319 (61000) 385 (23000)	2.70	505	20	−1.96[e]	155	78.4
B6	326 (151100) 385 (58500)	2.73	494	34	−2.01, −2.23	310	37.3

[a] At 10^{-5} M in toluene. [b] 9,10-Diphenylanthracene ($\Phi = 90\%$) used as the standard in toluene. [c] Relative to [FeCp$_2$]$^{0/+}$ (Cp = cyclopentadienyl) in DMF. [d] At 35 °C in C$_6$D$_6$. [e] Not resolved because of very poor solubility.

the polyboryl compounds undergo thermal reversal faster than the monoboryl **B1b**, with rate constants increasing in the order **B1b** < **B6b** < **B2b** < **B3b** < **B2′b**, suggesting that π conjugation and steric congestion together determine the rate of the reverse process.

In summary, we have established that conjugated systems with multiple switchable boryl chromophores only undergo photoisomerization at a single boryl center, while the remaining chromophores accelerate this process by intramolecular energy transfer. Furthermore, the isomerization of one chromophore prevents isomerization of the others, leaving the remainder of the π system intact even upon prolonged irradiation. Using this approach, the preparation of photochromic materials with tunable intensity and fluorescence quenching properties is possible.

Experimental Section

General procedure: All experiments were performed under a nitrogen atmosphere. 2-Bromo-5-(triisopropylsilylethynyl)pyridine was prepared by a literature procedure.[11] The synthetic details for all polyboryl compounds can be found in the Supporting Information. Quantum yields of all compounds were measured in toluene using 9,10-diphenylanthracene as the standard at 298 K ($\Phi_r = 0.90$) and calculated using previously known procedures.[12] Molecular orbital and molecular geometry calculations were performed using the Gaussian 03 program suite,[13] with crystal structures used as the starting points for geometry optimizations where possible. Calculations were performed at the B3LYP level of theory using 6-31G* as the basis set for **B2** and **B2′** and STO-3G for **B3** and **B6**.

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