

Gated Photochromism in Triarylborane-Containing Dithienylethenes: A New Approach to a “Lock–Unlock” System

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S Supporting Information

ABSTRACT: Photochromic inactive dithienylethene derivatives appended with 3- or 5-dimesitylboryl-2,2'-bithiophene have been synthesized. Upon fluoride ion-binding, the photochromic reactivity is “unlocked”, displaying a novel gated photochromic property.

Photochromic materials, especially organic diarylethenes, have received enormous attention in the past decade because of their ability to function as potential photoswitchable molecular devices and optical memory systems.¹ Photochromic materials with gated properties serve as an important development in nondestructive readout and for practical application.^{1b} In gated photochromism, the photochromic property is suppressed or blocked by controlling multiphoton excitation,² intramolecular hydrogen bonds,^{3a} oxidation/reduction,^{3b,h} acid/base,^{3c,i} and chemical reactions,^{3e–g} and temperature,⁴ and an external stimulus is required to “unlock” or reactivate the photochromic reactivity.

Recently, there has been an increasing interest in triarylborane-based materials due to their capability for optoelectronic⁵ and anion-sensing applications.⁶ The vacant p_π orbital of boron in triarylborane allows for conjugation with an organic π system and serves as a strong Lewis acid. After binding with Lewis base, the trigonal planar geometry of the boron center is changed to tetrahedral, and the electron delocalization and hence the π -conjugation are interrupted, leading to a significant change in photophysical properties.^{5,6} In addition to our continuing interests in designing various functionalized photochromic materials,⁷ we hypothesized that, by utilizing this unique characteristic of boron(III),⁸ the photochromism of dithienylethene could be controlled through rational design. Our design strategy is to append the photochromic dithienylethene group on the dimesitylboryl-2,2'-bithiophene core, which is known to show high fluorescence quantum yield and facile synthetic versatility.⁹ It is envisaged that the photochromism could be suppressed by spontaneous emission derived from the excited state which has charge-transfer character from the organic π framework to the boron p_π orbital. Addition of a Lewis base (F^-) may then provide a turn-off response in the luminescence and may cause the turning “on” of photochromism. In order to test the hypothesis, herein we describe the design and synthesis of a new class of triarylborane-containing dithienylethenes and the study of their gated photochromic behavior.

The targeted compounds are prepared as shown in Scheme 1. Briefly, **Th-DTE** is synthesized by bis-Suzuki cross-coupling reaction of 2,3-dibromothiophene and 2,5-dimethyl-3-thienylboronic acid.^{7h}

Tetramethyldioxaborolane is then attached to **Th-DTE** by an iridium-catalyzed reaction¹⁰ (~70% yield), followed by mono-Suzuki cross-coupling reaction with the corresponding dibromothiophene to afford the key intermediate in 60–70% yield. Finally, air-stable Mes_2B -substituted bis-thiophene-containing dithienylethenes (~60% yield) are obtained according to modification of a literature method.^{5,6} The unsubstituted bithiophene-containing dithienylethene (**L1-O**) has also been prepared as a reference compound. All the compounds have been characterized by 1H and $^{13}C\{^1H\}$ NMR, mass spectrometry, and elemental analysis. 1H NMR spectroscopy of **L1-O**, **1-O**, and **2-O** showed the presence of only one set of 1H NMR signals for the methyl groups on the thiophene moieties, corresponding to the time-averaged signals for both the antiparallel and parallel configurations,¹¹ indicating a fast interconversion of the two forms¹² which probably results from the lack of steric bulk on the thiophene ring. Moreover, the ^{11}B NMR signals of **1-O** and **2-O** are found to be at δ 68.23 and 76.16 ppm, respectively, which are typical of three-coordinated boron(III) derivatives.^{6b} All the compounds exhibit an irreversible oxidation wave at $\sim +1.47$ to $+1.67$ V vs SCE [Table S1 in the Supporting Information (SI)]. Compounds **1-O** and **2-O** display two quasi-reversible reduction waves, at -1.72 , -2.06 and -1.79 , -2.19 V, respectively, while no reduction wave is observed on **L1-O** within the solvent window of THF, indicative of the stabilization of the LUMO by the extended conjugation via the boron p_π orbital.

F^- anion-binding properties of **1-O** and **2-O** have been examined and are shown in Figure 1. Upon complexation with F^- , dramatic UV–vis absorption changes are obtained in both compounds. Generally, the lowest-energy absorption bands of **1-O** and **2-O**, at 401 and 394 nm, respectively, tentatively assigned as the $\pi \rightarrow \pi^*$ transition with mixing of charge-transfer character involving the boron center as the acceptor, would completely disappear, and new bands centered at 360 and 350 nm, respectively, would appear, similar to that reported previously.¹³ Moreover, a significant drop in emission intensity of **1-O** ($\lambda_{max} = 465$ nm, $\phi_{em} = 0.69$) and **2-O** ($\lambda_{max} = 520$ nm, $\phi_{em} = 0.73$) to almost nonemissive is observed upon addition of F^- anion. These changes can be attributed to the disruption of the π -conjugation extended through the boron p_π orbital by the formation of the corresponding fluoroborate. The ^{11}B NMR signals of **1-O** and **2-O** are upfield-shifted to δ 8.01 and 7.44 ppm in **1-O**· F^- and **2-O**· F^- , respectively, upon addition of F^-

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Scheme 1

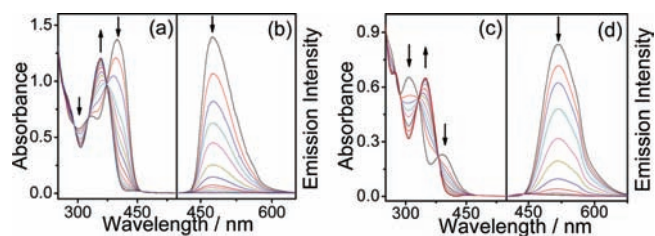
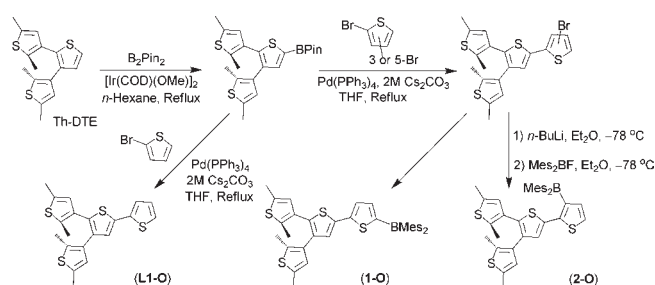


Figure 1. (a) UV–Vis and (b) emission spectral changes of **1-O** (5×10^{-5} M) in THF (0.05 M $n\text{-Bu}_4\text{NPF}_6$) upon addition of various concentrations of TBAF (from 0 to 1×10^{-4} M). (c) UV–Vis and (d) emission spectral changes of **2-O** (5×10^{-5} M) in THF (0.05 M $n\text{-Bu}_4\text{NPF}_6$) upon addition of various concentrations of TBAF (from 0 to 1×10^{-4} M).

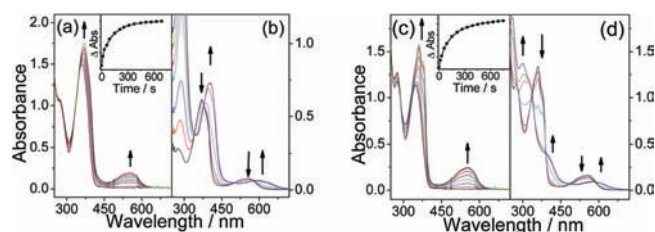


Figure 2. (a) UV–Vis spectral changes for **1-O·F⁻** upon irradiation at 360 nm. Inset shows the plot of absorbance change at 560 nm as a function of irradiation time. (b) UV–Vis spectral changes of **1-C·F⁻** upon addition of $\text{B}(\text{C}_6\text{F}_5)_3$ after 360 nm irradiation. (c) UV–Vis spectral changes for **2-O·F⁻** upon irradiation at 350 nm. Inset shows the plot of absorbance change at 558 nm as a function of irradiation time. (d) UV–Vis spectral changes of **2-C·F⁻** upon addition of $\text{B}(\text{C}_6\text{F}_5)_3$ after 350 nm irradiation in THF (0.05 M $n\text{-Bu}_4\text{NPF}_6$).

anion, comparable to those observed in other triarylfluoroborate systems, further supporting the binding of the F^- anion to the boron center and the change of geometry at boron from trigonal planar to tetrahedral.⁶ The binding constant ($\log K_s$) of **1-O** for F^- from UV–vis absorption and emission studies, according to the previously reported method,¹⁴ has been determined to be $\sim 5.97 \pm 0.24$ and 5.96 ± 0.11 , respectively, while that of **2-O** has been found to be $\sim 5.86 \pm 0.13$ and 5.89 ± 0.21 , respectively.

Excitation of **L1-O** in THF into the $\pi \rightarrow \pi^*$ transition absorption band at ~ 338 nm produces three new absorption bands at 354 , 370 , and 560 nm (Figure S1), which are ascribed to the absorptions of the closed form. On the other hand, no photochromism of **1-O** and **2-O** has been observed in THF, benzene, and 20% MeCN in benzene, except for the fact that

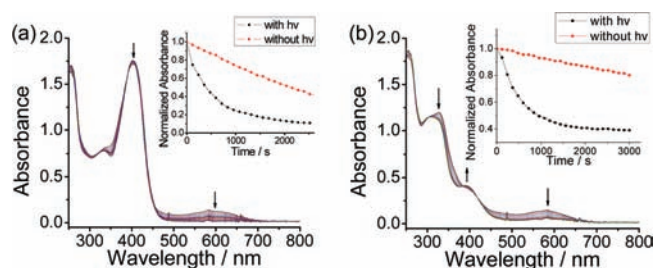
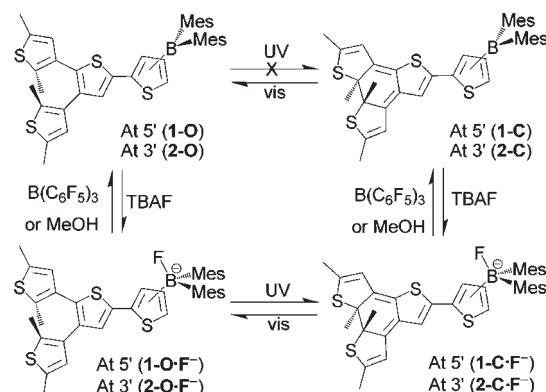


Figure 3. UV–Vis spectral changes in (a) **1-C** and (b) **2-C** upon visible irradiation at 550 nm in THF (0.05 M $n\text{-Bu}_4\text{NPF}_6$). Inset shows the plot of absorbance change at 550 nm as a function of irradiation time with visible light (black line) and in the dark (red line) at 298 K.

Scheme 2



photodegradation has been obtained after prolonged UV irradiation (<400 nm), indicative of suppression of the photochromic behavior upon coordination of the BMe_2 group. Addition of F^- (>1.5 equiv) into a THF solution of **1-O** and **2-O** gives fluoroborate compounds, **1-O·F⁻** and **2-O·F⁻**. Both compounds show photochromic behavior upon UV excitation, with three absorption bands generated at ~ 376 , 392 , and 560 nm for **1-C·F⁻** and at ~ 364 , 380 , and 558 nm for **2-C·F⁻**, which are ascribed to the absorption of the closed form (Figure 2a,c). Both **1-C·F⁻** and **2-C·F⁻** display almost the same absorption spectral pattern as that of **L1-C**, with only a slight red shift in the high-energy bands relative to **L1-C**. This indicates that the F^- -bound compounds have a transition similar to that of **L1-C**. Furthermore, abstraction of the F^- ion from **1-C·F⁻** and **2-C·F⁻** can be done by addition of a stronger Lewis acid such as $\text{B}(\text{C}_6\text{F}_5)_3$.^{5a,6b} The dissociation of F^- can also be induced by adding an excess of methanol, which probably would form a hydrogen bond with the fluoride ion to compete for its binding to the boron center. After addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to **1-C·F⁻**, there is an increase in absorption bands at ~ 400 and 600 nm, corresponding to the absorption of **1-O** and **1-C**, respectively. A similar observation has been made upon addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to **2-C·F⁻**, except that three absorption bands at ~ 302 , 395 , and 582 nm have grown in intensity, with the lowest absorption band corresponding to the absorption of **2-C** (Figure 2b,d). The bathochromic shifts observed in **1-C** and **2-C**, relative to those in **1-C·F⁻** and **2-C·F⁻**, are due to the extended conjugation of the condensed ring π system to the boron p_π orbital. The ^1H NMR spectral changes of **2** after F^- binding, photocyclization, and F^- abstraction have

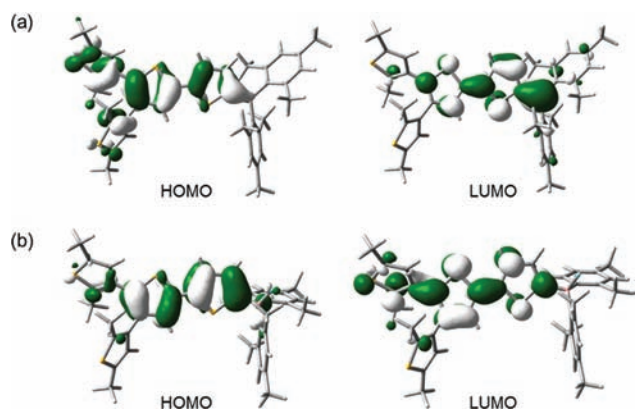


Figure 4. Spatial plots (isovalue = 0.03) of the HOMO and LUMO for (a) **1-O** and (b) **1-O·F⁻** obtained from the TDDFT/CPCM calculations.

been studied and depicted in Figure S2. Both **1-C** and **2-C** can be converted back to their open forms upon irradiation with visible light (>550 nm). In order to verify that the cycloreversion involves a light-induced process, not a mere thermal-induced reaction, the absorption decay of **1-C** and **2-C** in the dark has also been studied under the same conditions. As depicted in Figure 3 inset, the absorption spectral change in the dark was less significant than that under visible light irradiation, confirming the occurrence of a photocycloreversion process, as depicted in Scheme 2.

The quantum yields for both photocyclization and photocycloreversion processes have been determined. The $\phi_{O\rightarrow C}$ (325 nm) value for **L1-O** is found to be 0.20, while those of **1-O·F⁻** and **2-O·F⁻** are determined to be 0.25 and 0.18, respectively. The $\phi_{C\rightarrow O}$ (509 nm) value for **L1-C** is found to be 0.04, which is improved to 0.16 and 0.08 for **1-C·F⁻** and **2-C·F⁻**, respectively. Moreover, the conversions at the photostationary states of **1-C·F⁻** and **2-C·F⁻** are determined to be 34% and 45%, respectively, while that of **L1-C** is found to be 33%. The cycloreversibility of **1-O·F⁻** has also been studied, with the photochromic property still retained after four cycles and with good fatigue resistance (Figure S3).

Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations have been performed to gain a deeper insight into the molecular structures and nature of the low-energy absorptions for the open and closed forms in this class of compounds. Details of the optimized structures are given in the SI (Figures S4, S5 and Tables S4, S5).

For the open forms, the HOMO and LUMO for **L1-O** are the π and π^* orbitals of the bithiophene core slightly mixed with π and π^* orbital of the peripheral thiophene rings, respectively (Figure S6a). Upon incorporation of the dimesitylboryl group into the π -conjugated bithiophene system, the LUMOs of **1-O** and **2-O** show significant mixing of the p_{π} orbital on boron with the π^* orbital of the bithiophene system, while the HOMOs are the π orbital localized on the dithienylbithiophene (Figures 4a and S6b). Binding of F^- to the boron center breaks the conjugation between the boron p_{π} orbital and the bithiophene π system, leading to the increase in the HOMO–LUMO separation (Table S6). As depicted in Figures 4b and S6c, the HOMO and LUMO for **1-O·F⁻** and **2-O·F⁻** are mainly the respective π and π^* orbitals of the bithiophene core. For the closed form, the HOMO and LUMO of **L1-C** are the respective π and π^* orbitals of the ring-closed dithienylbithiophene (Figure S7a).

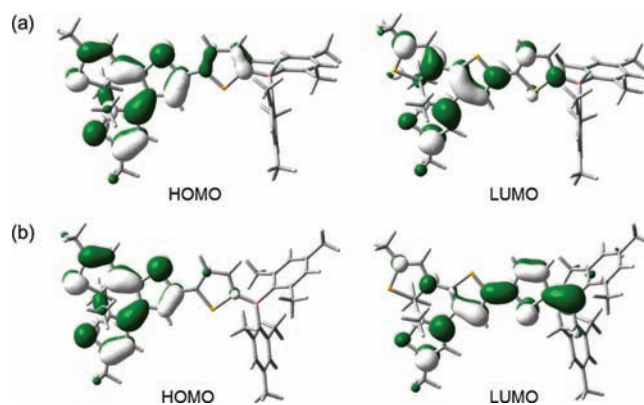


Figure 5. Spatial plots (isovalue = 0.03) of the HOMO and LUMO for (a) **1-C·F⁻** and (b) **1-C** obtained from the TDDFT/CPCM calculations.

The HOMO and LUMO for **1-C·F⁻** and **2-C·F⁻** are similar to those of **L1-C** (Figure 5a and S7b). Removing the F^- anion from the boron center allows the conjugation of the boron p_{π} orbital into the π conjugated system (Figures 5b and S7c). A decrease in HOMO–LUMO energy separation is found in the closed forms of the three-coordinated boron compounds when compared with that of their corresponding fluoride-bound boron compounds.

On the basis of the TDDFT/CPCM calculations, the first singlet–singlet transition of the open and closed forms in each compound, corresponding mainly to HOMO \rightarrow LUMO excitation (see SI), is in agreement with the trend observed in the electronic absorption spectra. The drastic photophysical changes upon fluoride-anion binding could be attributed to the disruption of π - p_{π} conjugation and the absence of charge-transfer character in the excited state.

In conclusion, a new approach for the gated photochromism has been demonstrated. The photochromic reactivity is highly suppressed in the three-coordinated boron compounds, due to presence of the highly emissive $\pi \rightarrow \pi^*/p_{\pi}(B)$ excited state, while it can be restored after F^- ion binding to the boron center. This concept may provide new insights into the future design of multiaddressable and gated photochromic materials. Further studies on modulating the dithienylethene moiety by triarylboryl and functionalization of this class of compounds as molecular logic gates are now in progress.

■ ASSOCIATED CONTENT

S Supporting Information. Synthetic procedures, characterization data, photophysical data, electrochemical data, cycloreversibility studies, and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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