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Photochromic Systems

Photochromic Dithienylethene-Containing Triarylborane Derivatives: Facile Approach to Modulate Photochromic Properties with Multi-addressable Functions

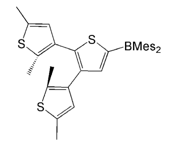
Chun-Ting Poon, Wai Han Lam, Hok-Lai Wong, and Vivian Wing-Wah Yam*[a]

Abstract: A series of dithienylethene-containing triarylboranes has been designed, synthesized, and characterized. The electrochemistry, photophysics, and photochromic behavior have also been studied. The photophysical and photochromic properties could be facilely tuned in this system by varying the thiophene spacers (thiophene, thienothiophene, and bithiophene) between the dithienylethene and the dimesitylboron ($BMes_2$) or the position of the $BMes_2$ substitution in the thiophene spacers. The absorption of closed form has been found to be more sensitive towards the structural modification upon incorporation of the $BMes_2$ unit. Moreover, multi-addressable photochromic reactivity is obtained upon addition of Lewis base (F^-), which is due to the formation of boron–Lewis base adduct. The dependence of the photophysical and photochromic properties on the thiophene spacers and the position of the $BMes_2$ substitution has been further supported by computational studies.

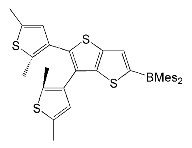
Introduction

In recent decades, there has been increasing interest in triarylborane-based materials owing to their potential for optoelectronic[1] and anion-sensing applications.[2] The vacant pπ orbital of boron in triarylborane allows for conjugation with organic π system,[3] in which the photophysical properties could be readily tuned by attaching substituents at different positions and the introduction of π-conjugated linkers.[4] Furthermore, it serves as a strong Lewis acid, which could bind strongly with Lewis base because of the strong electron-accepting properties of the boron center that could lead to the disruption of the π-conjugation, giving rise to a significant change in the photophysical properties.[1,2,5]

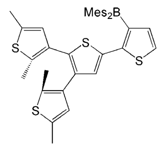
On the other hand, photochromic dithienylethene compounds are amongst one of the most important and well-studied photochromic materials; the excellent thermal reversibility, fatigue resistance, and distinguishable absorption spectra of the open form and the closed form have led to their potential use in photoswitchable devices and optical memory storage systems.[6] Furthermore, the utilization of photochromic dithienylethene moiety would provide an additional photo-controllable switching functionality that could modulate the luminescence,[7] magnetic[8] and non-linear optical properties,[9] chirality,[10] and conductivity.[11] Besides that, by introducing additional reversible responses, the absorption profile[12] and emission intensity,[13] or even the photochromic reactivity,[14] could be modulated by external stimuli, such as light-triggered, chemical-induced, and thermally responsive, which may allow high-density storage, non-destructive read-out and data and signal processing. With our continuing interest in the design and study of various functionalized photochromic materials,[15] we believe that the incorporation of triarylborane into photochromic dithienylethene through different π-conjugate formation would open up new avenues and opportunities for the development of new classes of photochromic materials, in which the photochromic properties could be facilely modulated, and multi-addressable photochromic properties could also been achieved upon addition of Lewis base. Herein, we describe the design and synthesis of a series of dithienylethene-containing triarylboranes. The dependence of the thiophene spacers and the position of the $BMes_2$ substitution on the photophysical and photochromic properties have been demonstrated, suggestive of the high versatility of this class of compounds. Computational studies have been performed to provide a deeper



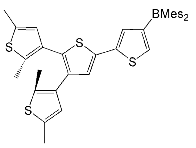
BMes$_2$-Th-DTE



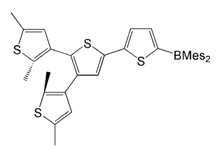
BMes$_2$-TTh-DTE



3-BMes$_2$-Th$_2$-DTE



4-BMes$_2$-Th$_2$-DTE



5-BMes$_2$-Th$_2$-DTE

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understanding on the effect of the thiophene spacers and the position of the $BMes_2$ substitution in the thiophene spacers on the photophysical and photochromic properties, which would allow a better design of multifunctional photochromic materials.

Results and Discussion

Synthesis and characterization

2,3-Bis(2,5-dimethylthiophen-3-yl)thiophene (**Th-DTE**), 2,3-bis-(2,5-dimethylthiophen-3-yl)thieno[3,2-*b*]thiophene (**TTh-DTE**), 2,3-bis(2,5-dimethylthiophen-3-yl)-5-iodothiophene (**I-Th-DTE**), and 2,3-bis(2,5-dimethyl-thiophen-3-yl)-5-iodothieno[3,2-*b*]thiophene (**I-TTh-DTE**) were prepared as previously reported.[15h] The dithienyl-substituted derivatives were synthesized by the initial preparation of **BPin-Th-DTE** from the reaction between tetramethyldioxaborolane and 2,3-bis(2,5-dimethylthiophen-3-yl)thiophene using the iridium-catalyzed reaction (ca. 70% yield). Then mono-Suzuki cross-coupling reaction between **BPin-Th-DTE** and 2,4-dibromothiophene afforded **4-Br-Th$_2$-DTE** with ca. 66% yield (Supporting Information, Scheme S1). Finally, air-stable Mes_2B-substituted dithienylethenes (ca. 60% yield) were obtained by lithiation of the bromo or iodo group with 1.2 equivalents of *n*BuLi, followed by addition of Mes_2BF solution (Supporting Information, Scheme S2). The air-stable compounds were obtained and isolated in their pure forms by standard workup procedures and column chromatography. The identities of the targeted compounds have been characterized by ^1H and ^{11}B NMR spectroscopy and FAB-MS and gave satisfactory elemental analyses. In the ^1H NMR studies, **BMes$_2$-Th-DTE** and **BMes$_2$-TTh-DTE** showed two singlet signals at $\delta =$ 6.2–6.8 ppm, corresponding to the two thienyl protons on the dimethylthiophene rings, with the exception of **4-BMes$_2$-Th$_2$-DTE**, which showed a singlet. This suggests that the dimethylthiophene rings were freely rotating, so that the parallel and antiparallel configurations could interconvert between each other on the NMR timescale at room temperature to give only one signal. Moreover, the ^1H NMR signals from the mesityl groups were almost the same in all of the Mes_2B-substituted compounds, which showed that there was little influence on the mesityl groups by changing the π-conjugated linker. Furthermore, the ^{11}B NMR spectra of the Mes_2B-substituted compounds were found to be at $\delta = 68$–72 ppm, which indicated that the boron centers were three-coordinated adopting a trigonal planar geometry.[1,2]

Electrochemical studies

All of the compounds exhibited an irreversible oxidation wave at ca. +1.47 to +1.85 V vs. SCE. The electrochemical data for the complexes are given in Table 1. The shift of the oxidation wave to a less positive potential upon going from **Th-DTE** to **TTh-DTE** to **Th$_2$-DTE** was observed. A similar trend was found for the corresponding $BMes_2$-substituted compounds. As a less positive potential of the oxidation wave was observed when the number of double bonds in the thiophene spacers increases, the oxidation is tentatively assigned as oxidation of the thiophene spacers with some mixing of the dithienylethene unit. No reduction wave was found for **Th-DTE**, **TTh-DTE**, and **Th$_2$-DTE** within the electrochemical window of the solvent, while one or two quasi-reversible reduction waves were observed at −1.72 to −2.24 V (vs SCE) upon incorporation of the $BMes_2$ moiety, indicative of the stabilization of the LUMO (lowest unoccupied molecular orbital) upon extended π-conjugation via the boron pπ orbital. With the exception of **4-BMes$_2$-Th$_2$-DTE**, in general, the first reduction wave was shifted to less negative potential upon going from **BMes$_2$-Th-DTE** to **BMes$_2$-TTh-DTE** to **BMes$_2$-Th$_2$-DTE.** The first reduction wave can be assigned as the reduction of the thiophene spacers with mixing of boron-center reduction character. For **4-BMes$_2$-Th$_2$-DTE**, the first reduction process was found to occur at the most negative potential among the three **BMes$_2$-Th$_2$-DTE** compounds. Interestingly, the potential for the first reduction couple of **4-BMes$_2$-Th$_2$-DTE** was found to fall in a similar potential region as that of other related trimesitylboranes,[1c,4c,5g] suggesting the reduction is localized on the triarylborane unit (see below).

Table 1. Electrochemical data for non-substituted and $BMes_2$-substituted compounds[a]

Compound	Oxidation E_{pa}/V vs SCE[b]	Reduction $E_{1/2}$/V vs SCE[c] (E_{pc}/V vs SCE)[d]
Th-DTE	+1.76	–[e]
TTh-DTE	+1.57	–[e]
Th$_2$-DTE	+1.47	–[e]
BMes$_2$-Th-DTE	+1.85	−1.92
BMes$_2$-TTh-DTE	+1.76	−1.81, −2.24
5-BMes$_2$-Th$_2$-DTE[f]	+1.67	−1.72, −2.06
4-BMes$_2$-Th$_2$-DTE	+1.68	(−2.12)
3-BMes$_2$-Th$_2$-DTE[f]	+1.59	−1.79, −2.19

[a] In dichloromethane with 0.1 M nBu_4NPF_4 as supporting electrolyte at room temperature; scan rate 200 mV s^{-1}. [b] E_{pa} refers to the anodic peak potential for irreversible oxidation waves. [c] $E_{1/2} = (E_{pa} + E_{pc})/2$; E_{pa} and E_{pc} are peak anodic and peak cathodic potentials, respectively. [d] E_{pc} refers to the cathodic peak potential for irreversible reduction waves. [e] Not observed within the solvent window of THF. [f] From Ref. [15j].

Electronic absorption and emission studies

Th-DTE, **TTh-DTE**, and **Th$_2$-DTE** were found to dissolve in benzene to give colorless solutions with intense absorption bands at ca. 290, 300, and 340 nm, respectively. The photophysical data are summarized in Table 2 and the electronic absorption and normalized emission spectra of $BMes_2$-substituted compounds in benzene are shown in Figure 1 and 2, respectively. The absorption band is red-shifted upon going from **Th-DTE** to **TTh-DTE** to **Th$_2$-DTE** and is attributed to the $\pi \rightarrow \pi^*$ transition of the thiophene spacers, with mixing of the $\pi \rightarrow \pi^*$ transition of the dimethylthiophene. Upon incorporation of the $BMes_2$ moiety, the low-energy absorption band was found to be red-shifted by 55–80 nm, (4095–7065 cm^{-1}) with the exception of **4-BMes$_2$-Th$_2$-DTE** and can be assigned as $\pi \rightarrow \pi^*$/pπ(B)

Table 2. Photophysical data of non-substituted and $BMes_2$-substituted compounds in the open form at 293 K.

Compound	Solvent	Absorption λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})	Emission λ_{em}/nm (τ_o/ns)	ϕ_{lum}[a]
Th-DTE	benzene	290 (6300)	–[b]	–[b]
TTh-DTE	benzene	300 (15 400)	–[b]	–[b]
Th_2-DTE	benzene	285 (8200), 340 (14 000)	424 (< 0.5)	0.036
	THF	278 sh (14 500), 338 (17 700)	425 (< 0.5)	0.021
$BMes_2$-Th-DTE	benzene	295 sh (5100), 330 sh (8600), 365 (12 500)	433 (< 0.5)	0.014
	THF	328 sh (12 800), 365 (19 000)	440 (< 0.5)	0.020
$BMes_2$-TTh-DTE	benzene	295 sh (6400), 345 sh (14 100), 380 (25 500)	440 (< 0.5)	0.026
	THF	295 sh (8800), 343 sh (17 100), 380 (32 800)	446 (< 0.5)	0.029
5-$BMes_2$-Th_2-DTE	benzene	285 sh (7600), 330 (11 100), 405 (30 000)	465 (0.97)	0.720
	THF[c]	326 (11 100), 401 (31 000)	475 (1.42)	0.690
4-$BMes_2$-Th_2-DTE	benzene	290 sh (14 200), 330 (24 300)	454 (0.85)	0.084
	THF	262 (25 900), 328 (24 800)	465 (1.05)	0.032
3-$BMes_2$-Th_2-DTE	benzene	310 (16 200), 395 (5900)	517 (6.58)	0.890
	THF[c]	309 (15 700), 394 (5400)	520 (8.18)	0.730

[a] Luminescence quantum yield determined by using quinine sulfate in 1.0 N sulfuric acid (ϕ_{lum} = 0.546, λ_{ex} = 365 nm) as reference. [b] Non-emissive. [c] From Ref. [15j].

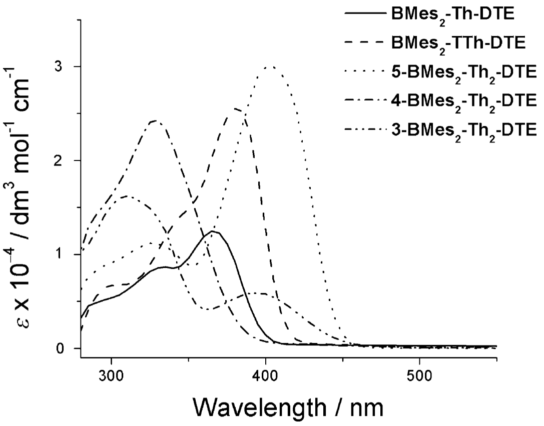


Figure 1. Electronic absorption spectra of the open form of $BMes_2$-substituted compounds in benzene.

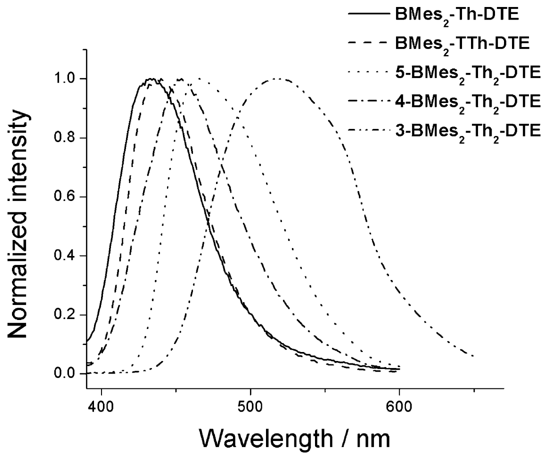


Figure 2. Normalized corrected emission spectra of the open form of $BMes_2$-substituted compounds in degassed benzene.

transition. The red-shift is due to the conjugation of the boron pπ orbital to the π system of the thiophene spacers, leading to a decrease in the LUMO energy and hence a decrease in the transition energy. No significant solvatochromic effect was observed upon changing the solvent from benzene to THF, which is typical of the triarylborane systems with dimesityl substituents.[1–5]

Upon photoexcitation, **Th_2-DTE** displayed blue emission in benzene at ca. 424 nm, while **Th-DTE** and **TTh-DTE** were found to be non-emissive. The rather weak emission of **Th_2-DTE** is probably derived from excited states arising from the $\pi \rightarrow \pi^*$ transition of dithienyl bithiophene. **$BMes_2$-Th-DTE**, **$BMes_2$-TTh-DTE** and **4-$BMes_2$-Th_2-DTE** also showed weak blue emission at ca. 440, 446 and 465 nm, respectively, with fluorescence quantum yields of less than 0.1 in benzene. A slight bathochromic shift in the fluorescence maxima of all of the compounds was observed by changing the solvent from benzene to THF since the emissive state has partial charge transfer character, which is similar to those of the previous reports.[1] It is surprising to note that a significant difference in both the absorption and emission properties between **4-$BMes_2$-Th_2-DTE** and its related compounds, **5-$BMes_2$-Th_2-DTE** and **3-$BMes_2$-Th_2-DTE**, was found in which a lower-energy absorption band and high luminescence quantum yield were observed in the latter two compounds.[15j] A possible explanation is due to the fact that the $BMes_2$ group is poorly conjugated with the bithiophene at the 4-position, which will be discussed in more detail in the computational study below.

F^- binding studies

The F^- anion-binding properties of these compounds in their open form were explored using UV/Vis absorption and NMR spectroscopy. The binding constants of the $BMes_2$-substituted compounds are summarized in Table 3. For **$BMes_2$-Th-DTE**, the low-energy absorption showed a drop in absorbance and vanished completely upon an increase in F^- concentration, with

Table 3. Binding constants (log K_s) and ^{19}F NMR and ^{11}B NMR chemical shifts of the open forms of BMes$_2$-substituted compounds upon addition of F$^-$ ions.

Compound	Log K_s	^{19}F NMR[a]		^{11}B NMR[a]	
		δ/ppm			
	UV/Vis	Free	Bound	Free	Bound
BMes$_2$-Th-DTE	7.17 ± 0.31[b]	-116.3[c]	-165.3	68.2	8.4
BMes$_2$-TTh-DTE	6.27 ± 0.12[b]	-117.0	-164.7	70.1	7.8
5-BMes$_2$-Th$_2$-DTE	6.70 ± 0.17[b]	-116.3[c]	-164.5	68.2	8.0
	5.97 ± 0.24[d]				
4-BMes$_2$-Th$_2$-DTE	4.47 ± 0.03[b]	-116.3[c]	-170.9	71.6	9.1
3-BMes$_2$-Th$_2$-DTE	6.18 ± 0.16[b]	-116.6	-174.5	76.2	7.4
	5.86 ± 0.13[d]				

[a] Measured in 20% CD_3CN–C_6D_6. [b] Measured in 20% acetonitrile–benzene (0.05 м nBu$_4$NPF$_6$). [c] No signals due to free F$^-$ were observed in the presence of excess TBAF. A ^{19}F NMR chemical shift of free TBAF in 20% CD_3CN–C_6D_6 of $\delta = -116.3$ ppm was used for comparison. [d] From Ref. [15j], measured in THF (0.05 м nBu$_4$NPF$_6$).

a growth in the higher energy absorption shoulder. **BMes$_2$-TTh-DTE** showed a similar spectral change. A well-defined isosbestic point was obtained at ca. 308 and 336 nm upon addition of F$^-$ ions to **BMes$_2$-Th-DTE** and **BMes$_2$-TTh-DTE**, respectively, and saturation was reached when the concentration of F$^-$ ions was about 5×10^{-5} м. These could be attributed to the destruction of the π-conjugation between the empty pπ orbital on boron and the π* orbital of the thiophene spacers such that the π→π*/pπ(B) transition would disappear, leading to the appearance of only the high-energy π→π* absorption. The UV/Vis spectral changes upon addition of TBAF to **BMes$_2$-Th-DTE**, **BMes$_2$-TTh-DTE** and **4-BMes$_2$-Th$_2$-DTE** are shown in Figure 3 and Figure S1 and S2 in Supporting Information, respectively, and the corresponding theoretical fits to the equation for the formation of a 1:1 adduct were also plotted and shown in the inset. The binding constants, log K_s, for the F$^-$ anions were found to be in the range of 6.18–7.17 in 20% acetonitrile–benzene mixture, which is similar to that of triarylborane compounds.[2] Table 3 also lists the data from ^{19}F NMR and ^{11}B NMR spectroscopy for the BMes$_2$-substituted compounds upon addition of TBAF solution. For ^{19}F NMR studies, upfield shifts of about 40–50 ppm from ca. $\delta = -117$ to -170 ppm were obtained in the boron-bound fluoride signal. Moreover, the ^{11}B NMR resonances of the Mes$_2$B-substituted compounds were found to be at ca. $\delta = 68.17$ to 76.16 ppm and showed upfield shifts to ca. $\delta = 7.44$ to 9.10 ppm upon F$^-$ ion-binding. This further supported that the coordination number of the boron center was changed from three to four and the geometry from trigonal planar to tetrahedral.[2,5]

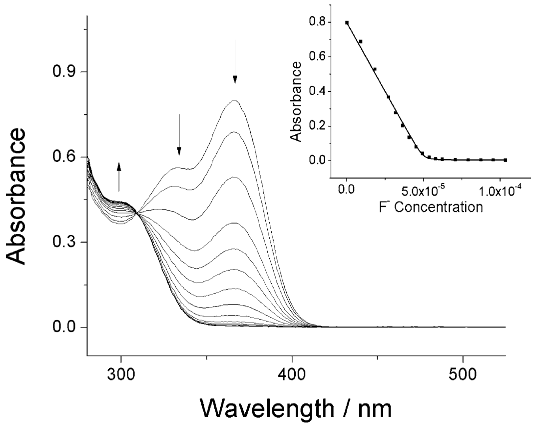


Figure 3. UV/Vis spectral changes of **BMes$_2$-Th-DTE** (ca. 5×10^{-5} м) in its open form upon addition of various concentrations of TBAF in 20% acetonitrile–benzene. Inset: A plot of absorbance at 366 nm as a function of the concentration of F$^-$ with theoretical fits for 1:1 binding.

Photochromic studies

Upon excitation into the π→π* transition absorption band of **Th-DTE**, **TTh-DTE**, and **Th$_2$-DTE** in degassed benzene, typical photochromic behavior was observed. The solution was changed from colorless to reddish purple, with the growth of an intense absorption band at about 330–355 nm and a broad absorption at about 546–565 nm in the UV/Vis absorption spectra. There was a progressive red-shift from **Th-DTE** to **TTh-DTE** and to **Th$_2$-DTE**, which is in line with the trend of absorption observed in the corresponding open forms. After incorporation of the BMes$_2$ group, **BMes$_2$-Th-DTE** also displayed photochromic reactivity upon UV irradiation, and the solution was changed from colorless to green. Four absorption bands were generated at ca. 290, 390, 445, and 660 nm upon UV excitation, as shown in Figure 4. A significant red-shift of ca. 3163 cm^{-1} was observed in its closed form when compared with **Th-DTE**. The red-shift is ascribed to the increase in conjugation by the effective overlap of the empty pπ orbital on the boron center and the π* orbital of the condensed ring system of the closed form. **BMes$_2$-TTh-DTE** showed photochromic behavior as well upon UV excitation. Similarly, four absorption bands were generated at ca. 295, 400, 435 and 610 nm, as shown in Figure S3

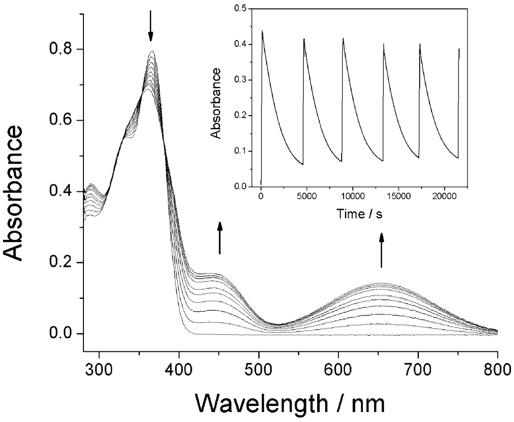


Figure 4. Electronic absorption spectral changes of **BMes$_2$-Th-DTE** (ca. 5×10^{-5} м) upon excitation at 365 nm in degassed 20% acetonitrile–benzene (0.05 м nBu$_4$NPF$_6$). Inset: UV/Vis absorption spectral changes of **BMes$_2$-Th-DTE** (ca. 1.5×10^{-4} м) at 650 nm on alternate excitation at 365 and 480 nm over five cycles.

in Supporting Information, while relatively less significant red-shift of ca. 1722 cm^{-1} was observed when compared with the closed form of **TTh-DTE**. It was surprising to note that a blue-shift of the lower-energy absorption band was observed upon going from **BMes$_2$-Th-DTE** to **BMes$_2$-TTh-DTE**. Furthermore, a polymethylmetharylate (PMMA) film of **BMes$_2$-Th-DTE** was spin-coated on a quartz plate to demonstrate the photochromic properties in rigid medium. Upon light exposure, the color of the film was changed from colorless to green and the color is stable in the dark for a period of time (Supporting Information, Figure S4).

When the BMes$_2$ moiety was attached at different positions of the bithiophene, a dramatic difference in the photochromic properties was found. **4-BMes$_2$-Th$_2$-DTE** was the only bithiophene analogues that displayed photochromic property, while **5-BMes$_2$-Th$_2$-DTE** and **3-BMes$_2$-Th$_2$-DTE** displayed gated photochromic reactivity, in which the photochromic properties were only found in the presence of F^- anion.[15j] Three absorption bands appeared at ca. 355, 375, and 570 nm upon photoexcitation of **4-BMes$_2$-Th$_2$-DTE** (Supporting Information, Figure S5). In contrast to **BMes$_2$-Th-DTE** and **BMes$_2$-TTh-DTE**, the closed form absorption spectrum of **4-BMes$_2$-Th$_2$-DTE** showed a slight red-shift of ca. 5 nm when compared with **Th$_2$-DTE**,[15j] indicative of the similar excited state character for **Th$_2$-DTE** and **4-BMes$_2$-Th$_2$-DTE**, which would be discussed in more detail in the DFT study.

Moreover, there was a reduction in luminescence intensity in **BMes$_2$-Th-DTE** and **BMes$_2$-TTh-DTE** upon photo-irradiation at their isosbestic wavelength, as shown in Figure S6 and S7 in Supporting Information, respectively. The decrease in the emission intensity upon conversion to the closed forms of **BMes$_2$-Th-DTE** and **BMes$_2$-TTh-DTE** might be attributed to the quenching of the emissive excited state by the lower-lying excited state of the closed form moiety. Furthermore, this could be due to the fact that the absorption shoulder at ca. 440 nm was found in the closed form of **BMes$_2$-Th-DTE** and **BMes$_2$-TTh-DTE**, which matched well with the open form emission spectra, leading to an excitation energy transfer from the open form to the closed form. As a result, the emission intensity gradually decreased upon photocyclization.

Photochromic studies via F^- binding

The photochromic properties of BMes$_2$-containing dithienylethene compounds with their F^- ion-bound compounds were studied. Besides the binding of F^- ion to the open form, UV/Vis spectral changes were also observed upon addition of F^- ion to the closed form. Upon addition of TBAF, the green solution of the closed form of **BMes$_2$-Th-DTE** was gradually changed to a purple solution and the lowest energy absorption disappeared with an increase in the higher energy absorption, similar to that of the open form, as shown in Figure 5. Moreover, the UV/Vis spectral change was also observed for the open form F^- ion-bound complex, **BMes$_2$-Th-DTE·F$^-$**, with the appearance of two absorption bands at ca. 326 and 548 nm, as shown in Figure 6, in which the lowest energy absorption band was in good agreement with the observation of the spectral changes in **BMes$_2$-Th-DTE** in its closed form upon addition of various concentrations of TBAF. Furthermore, the cycloreversibility has been demonstrated in **BMes$_2$-Th-DTE** and **BMes$_2$-Th-DTE·F$^-$** with at least five repeating cycles, as shown in the inset in Figure 4 and 6, which indicated that these chemical processes are all inter-related and reversible in each direction. Representations of the summarized results are shown in Scheme 1.

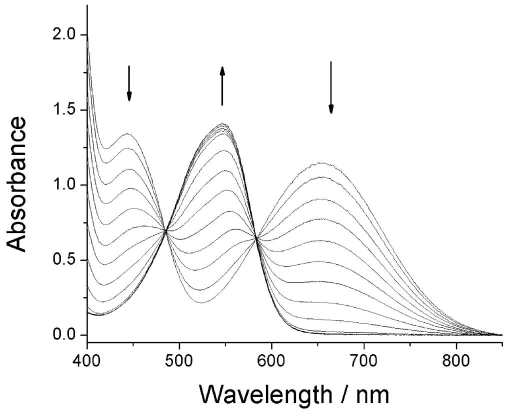


Figure 5. UV/Vis spectral changes of **BMes$_2$-Th-DTE** (ca. 2.5×10^{-4} м) in its closed form upon addition of various concentrations of TBAF in 20% acetonitrile–benzene.

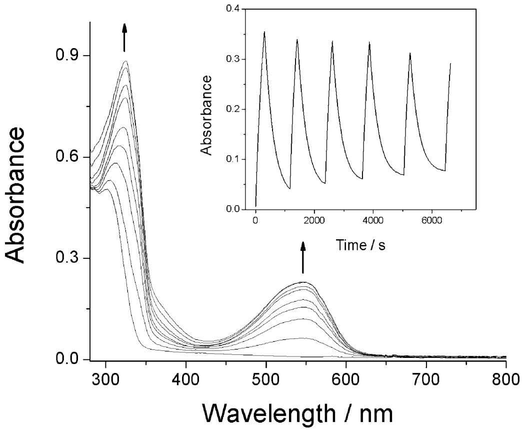
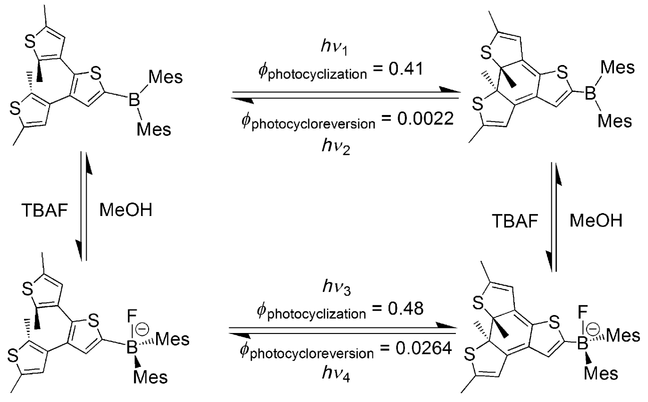


Figure 6. Electronic absorption spectral changes of **BMes$_2$-Th-DTE·F$^-$** (ca. 5×10^{-5} м) upon excitation at 310 nm in degassed 20% acetonitrile–benzene (0.05 м nBu_4NPF_6). Inset: UV/Vis absorption spectral changes of **BMes$_2$-Th-DTE·F$^-$** (ca. 8.5×10^{-5} м) at 550 nm on alternate excitation at 310 and 550 nm over five cycles.

Similar multi-addressable photochromic reactivity could be found in both **BMes$_2$-TTh-DTE** and **BMes$_2$-TTh-DTE·F$^-$** (Supporting Information, Figure S8), where typical photochromic activities were observed. The closed form absorption of **BMes$_2$-TTh-DTE·F$^-$** also resembled the UV/Vis spectral changes of **BMes$_2$-TTh-DTE** in its closed form upon addition of TBAF (Supporting Information, Figure S9). It is interesting to note that the absorption maximum of the closed form **BMes$_2$-TTh-DTE·F$^-$** (554 nm) was found to be slightly red-shifted when compared to that of **BMes$_2$-Th-DTE·F$^-$** (548 nm), which is in



Scheme 1. Representation of the multi-addressable photochromic reactivity upon addition of F^- ion to **BMes$_2$-Th-DTE** in 20% acetonitrile–benzene (0.05 M $n\mathrm{Bu_4NPF_6}$).

contrast with the trend observed in the corresponding fluoride-free closed forms. The close resemblance of the photochromic activities of the Mes$_2$B-substituted compound to that of the free ligands upon the addition of F^- ions is likely due to the destruction of pπ–π conjugation between the boron center and the thiophene spacer so that the fluoroborate would act like a sp^3 substituent with a minor effect on the excited state properties, and hence the origin of the transition would resemble that of a $\pi\rightarrow\pi^*$ transition of the dithienyl thiophene/thienothiophene.

On the other hand, only slight UV/Vis spectral changes of **4-BMes$_2$-Th$_2$-DTE** in its closed form was observed upon addition of TBAF (Supporting Information, Figure S10), resembling the results of the open form. Such difference is attributed to the poor conjugation between the BMes$_2$ group the bithiophene at the 4-position.

Moreover, the quantum yields for both the photocyclization and photocycloreversion processes have been determined for F^--bound or F^--free compounds and are summarized in Table 4. The quantum yield of photocyclization was found to be insensitive towards the addition of F^- ion. On the other hand, the quantum yield of photocycloreversion of **BMes$_2$-Th-DTE** and **BMes$_2$-TTh-DTE** was found to be significantly increased from 0.002 to 0.026 and from 0.008 to 0.03 upon addition of F^-, respectively. Furthermore, the quantum yield of photocycloreversion of F^--bound compounds was found to be almost the same as the boron-free compounds. This suggested that the BMes$_2$ group would suppress the photocycloreversion by at least one order of magnitude when compared to boron-free compounds.

Computational studies

Density functional theory (DFT) and time-dependent DFT (TDDFT) calculations have been performed on the dithienylethene-containing triarylboranes (see computational details below). For the bithiophene compounds, both the s-*cis* and s-*trans* conformations were considered in our study. The molecular orbitals and the electronic transitions for the bithiophene compounds shown were based on the study of lower-energy conformation (Supporting Information, Tables S1 and S2).

The HOMO (highest occupied molecular orbital) for the open forms of the non-substituted and BMes$_2$-substituted compounds is the π orbital of the thiophene spacers, mixed with the π orbitals of the peripheral thiophenes (Figure 7; Supporting Information, Figures S11, S12). The HOMO energy level increases as the number of the C=C bonds increases in the thiophene spacers (Supporting Information, Table S3). The LUMO of the non-substituted compounds corresponds to the π* orbital of the thiophene spacers with some mixing of the π* orbitals of the peripheral thiophenes (Supporting Information, Figure S11). On the other hand, the LUMO for the BMes$_2$-substituted compounds with the exception of **4-BMes$_2$-Th$_2$-DTE** show substantial mixing of the pπ orbital on boron with the π* orbital of the thiophene spacers (Figure 7a; Supporting Information, Figure S12). Unlike the other BMes$_2$-substituted compounds, the LUMO in **4-BMes$_2$-Th$_2$-DTE** is localized on the triarylborane (Figure 7b). In general, a significant decrease in the LUMO energy is found upon incorporation of BMes$_2$ unit. However, the LUMO level in **4-BMes$_2$-Th$_2$-DTE** is higher than

Table 4. Electronic absorption data in the closed form and photochemical quantum yields for non-substituted and BMes$_2$-substituted compounds and their fluoride-bound compounds.

Compound	Absorption λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})	$\phi_{O\rightarrow C}$	$\phi_{C\rightarrow O}$
Th-DTE[a]	328 (9700), 546 (5700)	0.39[d]	0.046[f]
TTh-DTE[a]	338 (21 300), 552 (7800)	0.42[d]	0.039[f]
Th$_2$-DTE[a]	355 sh (30 500), 565 (12 300)	0.20[d]	0.041[f]
BMes$_2$-Th-DTE[b]	290 (7100), 390 (9200), 445 (5500), 660 (4600)	0.41[e]	0.002[g]
BMes$_2$-Th-DTE·F$^-$[b]	326 (20 800), 548 (5600)	0.48[e]	0.026[f]
BMes$_2$-TTh-DTE[b]	295 (8500), 400 (20 500), 435 (14 800), 610 (7,100)	0.32[e]	0.008[g]
BMes$_2$-TTh-DTE·F$^-$[b]	354 (41 400), 554 (7500)	0.37[e]	0.030[f]
5-BMes$_2$-Th$_2$-DTE·F$^-$[c]	376 (34 400), 392 (36 300), 560 (7500)	0.25	0.164
4-BMes$_2$-Th$_2$-DTE[b]	355 (25 800), 375 (27 300), 560 (7200)	0.17[e]	0.054[f]
3-BMes$_2$-Th$_2$-DTE·F$^-$[c]	364 (33 100), 380 (33 400), 558 (7300)	0.18	0.077

[a] Measured in degassed benzene. [b] Measured in degassed 20% acetonitrile–benzene. [c] From Ref. [15j], measured in THF (0.05 M $n\mathrm{Bu_4NPF_6}$). [d] Data obtained using 310 nm as excitation source. [e] Data obtained using 325 nm as excitation source. [f] Data obtained using 510 nm as excitation source. [g] Data obtained using 480 nm as excitation source.

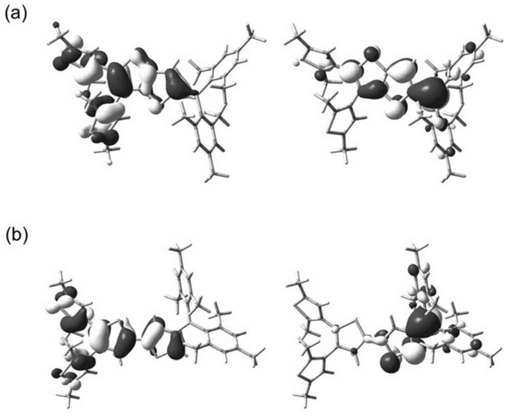


Figure 7. Spatial plots (isovalue = 0.03) of the HOMO (left) and LUMO (right) for the open form in (a) **$BMes_2$-TTh-DTE** and (b) **4-$BMes_2$-Th_2-DTE**.

that in **3-$BMes_2$-Th_2-DTE** and **5-$BMes_2$-Th_2-DTE**. The different stabilizing effects can be explained on the basis of the contribution in the LUMO at the site of substitution in the bithiophene. The LUMO has a larger contribution on the carbon atoms at the 3- and 5-positions but least at the 4-position (Supporting Information, Figure S11 c). The effect of the $BMes_2$ at the 4-position is much less, leading to the least stabilization of the LUMO level. This is in agreement with the most positive potential for oxidation found in **4-$BMes_2$-Th_2-DTE** when compared to that of **3-$BMes_2$-Th_2-DTE** and **5-$BMes_2$-Th_2-DTE**.

On the basis of the TDDFT calculations, the lowest-energy absorption band for the non-substituted compounds is attributed to the π–π* transition of the dithienylethene-containing thiophene spacers (Supporting Information, Tables S4). The calculated transition is found to be red-shifted in energy in the order of **Th-DTE** (290 nm) > **TTh-DTE** (309 nm) > **Th_2-DTE** (347 nm), which is in line with the increase in extended π-conjugation. With the exception of **4-$BMes_2$-Th_2-DTE**, the lowest-energy transition for the $BMes_2$-substituted compounds contributing to the HOMO→LUMO excitation is significantly red-shifted, relative to the corresponding non-substituted compounds. The result support the assignment of the $\pi \rightarrow \pi^*/p\pi(B)$ transition. For **4-$BMes_2$-Th_2-DTE**, the $S_0 \rightarrow S_1$ transition is computed to be relatively less intense, as it mainly corresponds to the charge transfer transition from the dithienyl bithiophene to the triarylborane. The more intense $S_0 \rightarrow S_2$ transition computed at 344 nm for **4-$BMes_2$-Th_2-DTE** is mainly the π–π* transition of the dithienyl bithiophene. As shown in Table 2, the peak maximum of the low-energy absorption band of the **4-$BMes_2$-Th_2-DTE** is only slightly perturbed when compared to that of **Th_2-DTE**, since the intense absorption band is mainly due to π–π* transition.

The HOMO and LUMO of the closed forms for the non-substituted compounds are the respective π and π* orbitals being more localized on the fused dithienylthiophene unit (Supporting Information, Figure S13). As shown in Table S5, the lower-energy absorption is mainly contributed by the HOMO→LUMO excitation. The transition is computed to be red-shifted in the energy order of **Th-DTE** (565 nm) > **TTh-DTE** (572 nm) > **Th_2-DTE** (607 nm). It is noted that the magnitude of the red-shift for the lower-energy absorption band from the open form to the closed form is decreased in the order of **Th-DTE** > **TTh-DTE** > **Th_2-DTE**. This probably arises from the fact that the HOMO and LUMO of the closed form is more localized on the condensed ring of the dithienylthiophene, and thus a larger shift in the HOMO and LUMO energy would be expected in the closed form if the HOMO and LUMO of the open form have a larger contribution from the dithienylthiophene.

As mentioned above, three $BMes_2$-substituted compounds displayed photochromic behavior in the absence of F^- anion, which are **$BMes_2$-Th-DTE**, **$BMes_2$-TTh-DTE**, and **4-$BMes_2$-Th_2-DTE**. The HOMO for the closed forms of the $BMes_2$-substituted compounds is similar to its non-substituted compounds (Figure 8; Supporting Information, Figure S14). The mixing of the boron pπ orbital in the LUMO can also be found in **$BMes_2$-Th-DTE** and **$BMes_2$-TTh-DTE**, but not in **4-$BMes_2$-Th_2-DTE**. It is also due to the fact that the LUMO of the bithiophene shows no contribution from the carbon atom at the 4-position (Supporting Information, Figure S13 c), leading to poor conjugation of the $BMes_2$ group with the bithiophene. The $S_0 \rightarrow S_1$ transition of **4-$BMes_2$-Th_2-DTE** is computed at 608 nm, which is similar to the non-substituted compounds. On the other hands, a significant red-shift was found for the $S_0 \rightarrow S_1$ transition of **$BMes_2$-Th-DTE** and **$BMes_2$-TTh-DTE**, when compared to that of **Th-DTE** and **TTh-DTE**, due to the pπ–π conjugation. The transition is blue-shifted upon going from **$BMes_2$-Th-DTE** to **$BMes_2$-TTh-DTE**, which is in agreement with the experimental observation. Upon incorporation of the $BMes_2$ group, a larger stabilization of the LUMO for the closed form in **$BMes_2$-Th-DTE** than that in **$BMes_2$-TTh-DTE** is found (Supporting Information, Table S3). This can be rationalized by the different contribution at the carbon where the $BMes_2$ group is attached, which is found to be larger in **Th-DTE** than that in **TTh-DTE**, which allows a better overlap between the boron pπ orbital and the π* orbital of the thiophene spacer and thus a larger stabilization of the LUMO, leading to a red-shift of the transition. The low-energy absorption band for the closed form of **$BMes_2$-Th-DTE**

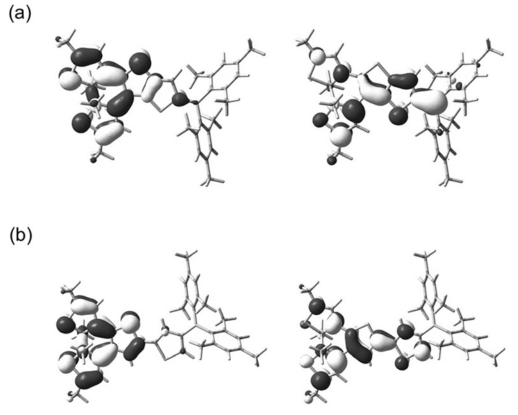


Figure 8. Spatial plots (isovalue = 0.03) of the HOMO (left) and LUMO (right) for the closed form in (a) **$BMes_2$-TTh-DTE** and (b) **4-$BMes_2$-Th_2-DTE**.

and **BMes$_2$-TTh-DTE** corresponds to the $\pi \rightarrow \pi^*$/pπ(B) transition, while it is predominantly the $\pi \rightarrow \pi^*$ transition for **4-BMes$_2$-Th$_2$-DTE**. These results show that the photophysical and photochromic properties are strongly dependent on the position of the BMes$_2$ substitution and the thiophene spacers.

Similar to the non-substituted compounds, the lowest-energy absorption band for both the open and closed form of the fluoride-bound compounds is attributed to the π–π^* transition (Supporting Information, Tables S6 and S7). As binding of F$^-$ anion to the boron center breaks the conjugation between the boron and the thiophene spacers, the lowest-energy transition is in general found to be blue-shifted for the fluoride-bound compounds relative to that of the fluoride-free compounds.

Conclusion

A series of dithienylethene-containing triarylboranes has been successfully prepared. Electronic absorption and Lewis acid (F$^-$) binding studies have been performed. The photophysical and photochromic behaviors were found to be strongly influenced by the thiophene spacers (thiophene, thienothiophene, and bithiophene) between dithienylethene and BMes$_2$ or the position of the BMes$_2$ substitution in the thiophene spacers, and the effects have been elucidated by the computational studies. The present work has demonstrated the versatility of these novel classes of triarylborane-containing dithienylethene systems, which exhibit enriched photochromic and photophysical properties through the rational design of the molecular structure and the control of the chemical or structural environment at the boron(III) center.

Experimental Section

Materials: Tetrakis(triphenylphosphine)palladium(0),[15a] 2,5-dimethylthien-3-yl boronic acid,[15a] 2,3-bis(2,5-dimethylthiophen-3-yl)thiophene,[15h] and 4,4,5,5-tetramethyl-2-(2,2′′,5,5′′-tetramethyl-[3,2′:3′,3′′-terthiophen]-5′-yl)-1,3,2-dioxa borolane (**BPin-Th-DTE**)[15j] were prepared according to reported procedures. Bis(pinacolato)diboron, 2,3-dibromothiophene, 2,5-dibromothiophene, dimesitylboron fluoride, 4,4′-di-*tert*-butyl-2,2′-bipyridine, and (1,5-cyclooctadiene)(methoxy)iridium(I) dimer were purchased and used as received. All reactions were performed under strictly anaerobic conditions in an inert atmosphere of nitrogen using standard Schlenk techniques.

4′,5′-Bis(2,5-dimethylthiophen-3-yl)-4-bromo-2,2′-bithiophene (**4-Br-Th$_2$-DTE**): Aqueous cesium carbonate solution (2 M, 3.03 g, 4.65 mL, 9.3 mmol) was added to a solution mixture of **BPin-Th-DTE** (1 g, 2.3 mmol), 2,4-dibromothiophene (1.2 g, 5 mmol), and tetrakis(triphenylphosphine)palladium(0) (135 mg, 0.12 mmol) in degassed THF (75 mL). The reaction was heated to reflux and the progress of the reaction was monitored by TLC (about 8 h). The reaction mixture was then extracted with chloroform, washed with brine, and finally dried over anhydrous magnesium sulfate. After filtration and removal of the solvent, the crude product was purified by column chromatography on silica gel (70–230 mesh) using *n*-hexane as the eluent. The desired product was collected as the second fraction. Further purification was achieved by recrystallization from hot *n*-hexane to give the product as a white solid. Yield: 710 mg, 66%; m.p. 77 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): $\delta = 2.02$ (s, 3H, Me), 2.05 (s, 3H, Me), 2.37 (s, 6H, Me), 2.38 (s, 3H, Me), 6.45 (s, 1H, thienyl), 6.47 (s, 1H, thienyl), 7.07 (s, 1H, thienyl), 7.09 ppm (s, 2H, thienyl). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$, 298 K): $\delta = 13.84$, 14.00, 15.18, 15.21, 110.39, 120.30, 121.24, 125.68, 126.84, 126.93, 127.38, 129.95, 132.71, 133.22, 133.64, 134.04, 134.63, 135.07, 135.55, 135.73, 138.59 ppm. HRMS (MALDI-TOF) calcd for $C_{20}H_{17}BrS_4$: $m/z = 465.9369$; found: 465.9372 [M^+].

(4,5-Bis(2,5-dimethylthiophen-3-yl)-thiophen-2-yl)dimesitylborane (**BMes$_2$-Th-DTE**): The reaction was performed under strictly anaerobic and anhydrous conditions in an inert atmosphere of nitrogen using standard Schlenk techniques. *n*-Butyllithium (1.6 M, 1 mL, 1.6 mmol) was added in a dropwise manner to a well-stirred solution of 2,3-bis(2,5-dimethylthiophen-3-yl)-5-iodothiophene (**I-Th-DTE**) (500 mg, 1.16 mmol) in anhydrous diethyl ether (25 mL) at −78 °C. The solution mixture was stirred and maintained at this temperature for 1 hour in the dark. A solution of dimesitylboron fluoride (430 mg, 1.6 mmol) in anhydrous diethyl ether (10 mL) was then added to the reaction mixture in a dropwise fashion. The resulting mixture was stirred in the dark for overnight and the temperature allowed to rise to room temperature gradually. Afterwards, the reaction was quenched with deionized water and the mixture was then extracted with chloroform, washed with brine, and finally dried over anhydrous magnesium sulfate. After solvent removal, the crude product was then purified by column chromatography on silica gel (70–230 mesh). Elution with *n*-hexane removed the side product, 2,3-bis(2,5-dimethylthiophen-3-yl)thiophene, as the first fraction. Then *n*-hexane–dichloromethane (4:1 v/v) was used to elute the desired product. Further purification was achieved by recrystallization from hot methanol to give the product as pale yellow crystals. Yield: 350 mg, 55%. m.p. 164 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): $\delta = 1.99$ (s, 3H, -Me), 2.05 (s, 3H, -Me), 2.17 (s, 12H, *o*-Me-mesityl), 2.30 (s, 6H, *p*-Me-mesityl), 2.33 (s, 3H, -Me), 2.34 (s, 3H, -Me), 6.38 (s, 1H, thienyl), 6.45 (s, 1H, thienyl), 6.82 (s, 4H, mesityl), 7.34 ppm (s, 1H, thienyl). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$, 298 K): $\delta = 13.80$, 14.22, 15.11, 15.17, 21.29, 23.58, 127.29, 127.57, 128.21, 130.87, 132.80, 133.17, 134.62, 135.23, 135.43, 136.78, 138.42, 140.84, 141.26, 143.21, 147.70 ppm. ^{11}B NMR (160.5 MHz, CDCl3, 298 K): $\delta = 68.17$ ppm. HRMS (MALDI-TOF) calcd for $C_{34}H_{37}BS_3$: $m/z = 522.2151$; found: 552.2172 [M^+]. Elemental analysis calcd (%) for $C_{34}H_{37}BS_3$: C 73.89, H 6.75; found: C 73.65, H 6.76.

(4,5-Bis(2,5-dimethyl-thiophen-3-yl)thieno[3,2-*b*]thiophen-2-yl)dimesitylborane (**BMes$_2$-TTh-DTE**): This was synthesized according to a procedure similar to that of **BMes$_2$-Th-DTE** except 2,3-bis(2,5-dimethylthiophen-3-yl)-5-iodothieno[3,2-*b*]-thiophene (**I-TTh-DTE**) (565 mg, 1.16 mmol) was used instead of 2,3-bis(2,5-dimethylthiophen-3-yl)-5-iodothiophene. A pale yellow solid was obtained. Yield: 410 mg, 58%. m.p. 212 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): $\delta = 1.93$ (s, 3H, Me), 2.05 (s, 3H, Me), 2.16 (s, 12H, *o*-Me-mesityl), 2.31 (s, 6H, *p*-Me-mesityl), 2.37 (s, 3H, -Me), 2.38 (s, 3H, Me), 6.52 (s, 1H, thienyl), 6.64 (s, 1H, thienyl), 6.83 (s, 4H, mesityl), 7.56 ppm (s, 1H, thienyl). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$, 298 K): $\delta = 14.06$, 15.15, 15.34, 21.24, 23.62, 125.99, 127.09, 127.31, 128.18, 131.00, 131.09, 132.55, 134.42, 135.14, 135.94, 136.12, 138.54, 138.75, 140.31, 140.93 ppm. ^{11}B NMR (160.5 MHz, CDCl$_3$, 298 K): $\delta = 70.11$ ppm. HRMS (MALDI-TOF) calcd for $C_{36}H_{37}BS_4$: $m/z = 608.1872$; found: 608.1918 [M^+]. Elemental analysis calcd (%) for $C_{36}H_{37}BS_4 \cdot 0.5\,CH_3OH$: C 70.17, H 6.29; found: C 70.46, H 6.23.

(4′,5′-Bis(2,5-dimethyl-thiophen-3-yl)-2,2′-bithiophen-4-yl)dimesitylborane (**4-BMes$_2$-Th$_2$-DTE**): This was synthesized according to a procedure similar to that of **BMes$_2$-Th-DTE** except **4-Br-Th$_2$-DTE** (540 mg, 1.16 mmol) was used instead of 2,3-bis(2,5-dimethylthiophen-3-yl)-5-iodothiophene. A pale yellow solid was obtained. Yield: 380 mg, 52%. m.p. 108 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 2.00$ (s, 3H, Me), 2.04 (s, 3H, Me), 2.09 (s, 12H, *o*-Me-mesityl), 2.31 (s, 6H, *p*-Me-mesityl), 2.36 (s, 3H, Me), 2.37 (s, 3H, Me), 6.45 (s, 2H, thienyl), 6.82 (s, 4H, mesityl), 7.09 (s, 1H, thienyl), 7.21 (s, 1H, thienyl), 7.53 ppm (s, 1H, thienyl). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K): $\delta = 13.78$, 13.97, 15.13, 15.17, 21.22, 23.30, 126.44, 126.96, 127.39, 128.22, 129.37, 133.05, 134.89, 134.94, 135.39, 135.51, 137.89, 138.60, 139.56, 140.69 ppm. ^{11}B NMR (160.5 MHz, $CDCl_3$, 298 K): $\delta = 71.60$ ppm. HRMS (MALDI-TOF) calcd for $C_{38}H_{39}BS_4$: $m/z = 635.2107$; found: 635.2057 [M^+]. Elemental analysis calcd (%) for $C_{38}H_{39}BS_4$: C 71.90, H 6.19; found: C 71.76, H 6.21.

Physical measurements and instrumentation: ^{1}H, ^{13}C{^{1}H}, and ^{19}F{^{1}H} NMR spectra were recorded on a Bruker AV400 at 298 K with chemical shifts (δ, ppm) relative to tetramethylsilane (Me_4Si) and trichlorofluoromethane ($CFCl_3$), respectively. ^{11}B NMR spectra were recorded on a Bruker DRX 500 at 298 K with chemical shifts (δ, ppm) relative to boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$). Elemental analyses of the new compounds were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences, Beijing. UV/Vis absorption spectra for photochromic studies were measured by a Hewlett–Packard 8452A diode-array spectrophotometer and the photoirradiation was carried out using a 300 W Oriel Corporation Model 66011 Xe (ozone free) lamp with Applied Photophysics F 3.4 monochromator to control the wavelength-selection. UV/Vis-NIR absorption spectra for the closed form were recorded on a Varian Cary 50 spectrophotometer equipped with a Xenon flash lamp. All measurements were studied at room temperature unless specified otherwise. Steady-state emission spectra at room temperature and 77 K were recorded using a Spex Fluorolog-3 Model FL3-211 spectrofluorometer equipped with a R2658P PMT detector. Time-resolved emission studies were performed by using a Horiba Jobin Yvon FluoroCube based on a time-correlated single photon counting method, using a nanoLED with peak wavelength and pulse duration equal to 371 nm and <200 ps, respectively, as the excitation source. Cyclic voltammetric measurements were performed by using a CH Instruments, Inc. model CHI 620 Electrochemical Analyzer. All measurements were conducted in CH_2Cl_2 solutions with 0.1 M $n\mathrm{Bu_4NPF_6}$ as supporting electrolyte at room temperature. A three-electrode system was employed, with $Ag/AgNO_3$ (0.1 M in acetonitrile), glassy carbon (CH Instrument), and platinum wire as reference electrode, working electrode, and counter electrode, respectively, in a glass cell with compartments separating the working electrode and the reference electrode from the counter electrode.

Fluoride (F^-) binding measurements: The electronic absorption spectral titration was performed on a Varian Cary 50 UV/Vis spectrophotometer at room temperature and its emission titration was recorded on a Spex Fluorolog-3 Model FL3-211 spectrofluorometer. The measurements were performed in 20% acetonitrile in benzene or THF solution with 0.05 M $n\mathrm{Bu_4NPF_6}$ as supporting electrolyte to maintain a constant ionic strength of the sample solution. The open-form F^- binding was simply conducted under ambient atmosphere without any difficulties. Owing to the instability of the closed form in air, the closed-form F^- binding was conducted under an argon atmosphere. A solution of the open form sample with known concentration was placed in a degassing cell with a Pyrex round-bottomed flask connected by a sidearm to a 1 cm quartz fluorescence cuvette and was sealed from the atmosphere by a Rotaflo HP6/6 quick-release Teflon stopper. The solution sample was degassed with at least four freeze–pump–thaw cycles. The solution was then irradiated with a 300 W Oriel Corporation Model 66011 Xe (ozone free) lamp to give the closed form, mixed with the open form. A 2 mL aliquot of that solution was transferred into a 1 cm path-length quartz cuvette equipped with a screw cap, which had been pre-flushed with argon for at least 30 min, by a syringe needle. The titration was then performed in the dark at 20 °C as soon as possible to eliminate complications that are due to photocycloreversion and to minimize the occurrence of the thermal backward reaction.

The binding constants for 1:1 complexation were determined by a nonlinear least-squares fit of the absorbance versus the concentration of ion added according to Equation (1):[16]

$$A = A_o + \frac{A_{\mathrm{lim}} - A_o}{2\,C_o}\left\{C_o + C_A + {}^1\!/_{K_S} - \left[\left(C_o + C_A + {}^1\!/_{K_S}\right)^2 - 4\,C_o C_A\right]^{1/2}\right\} \tag{1}$$

where A_o and A are the absorbance of the complex at a selected wavelength in the absence of and in the presence of the ion, respectively, C_o and C_A is the total concentration of the complex and the concentration of the ion, respectively, A_{lim} is the limiting value of absorbance in the presence of excess ion, and K_s is the stability constant or binding constant.

Photochemical quantum yield measurements: Chemical actinometry was employed for the photochemical quantum yield determination.[17] Incident light intensities were taken from the average values measured just before and after each photolysis experiment. In the determination of the photochemical quantum yield, the sample solutions were prepared at concentrations with absorbance slightly greater than 2.0 at the excitation wavelength. The solution of the open form sample with known concentration (ca. 10^{-4} M) was placed in a degassing cell with a Pyrex round-bottomed flask connected by a sidearm to a 1 cm quartz fluorescence cuvette and was sealed from the atmosphere by a Rotaflo HP6/6 quick-release Teflon stopper. The solution sample was degassed with at least four freeze–pump–thaw cycles. The quantum yield was determined at a small percentage of conversion by monitoring the initial rate of change of absorbance ($\Delta A/\Delta t$) in the absorption maximum of the closed forms in the visible region. To minimize the error, the measurement was carried in the dark.

Computational details: Calculations were carried out using Gaussian 09 software package.[18] The ground-state geometries of the open and closed forms (if it is photochromic-active) for the non-substituted and $BMes_2$-substituted compounds as well as the corresponding the fluoride-bound compounds were fully optimized in benzene by using density functional theory (DFT) calculations with the hybrid Perdew, Burke, and Ernzerhof functional (PBE0)[19] in conjunction with the conductor-like polarizable continuum model (CPCM).[20] On the basis of the ground-state-optimized geometries, time-dependent density functional theory (TDDFT) calculations[21] at the same level associated with the CPCM (benzene) was employed to compute the singlet–singlet transitions in the electronic absorption spectra of the two forms. Vibrational frequency calculations were performed for all stationary points to verify that each was a minimum (NIMAG = 0) on the potential-energy surface. For all the calculations, the 6-31G(d,p) basis set was employed to describe the S, C, B and H atoms while 6-31+G(d) basis set was used for the F atom.[22] The DFT and TDDFT calculations were performed with a pruned (99,590) grid.

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Keywords: boron · density functional calculations · dithienylethene · multi-addressable functions · photochromic systems

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