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Photochromic Thienylpyridine–Bis(alkynyl)borane Complexes: Toward Readily Tunable Fluorescence Dyes and Photoswitchable Materials

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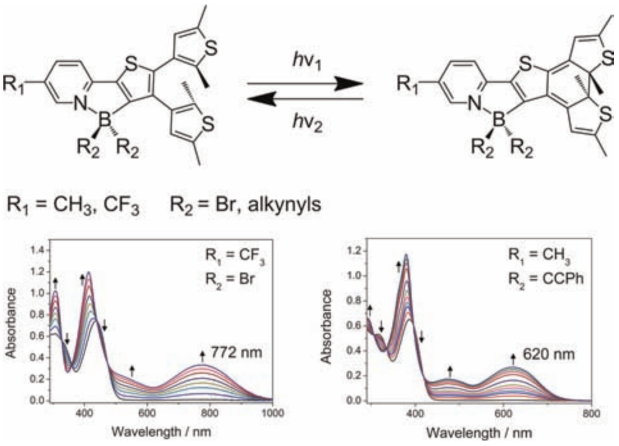
ABSTRACT



A series of diarylethene-containing N^C chelated thienylpyridine–bis(alkynyl)borane complexes has been designed and synthesized. Their photophysical and photochromic properties have been investigated and presented. The characteristic low-energy absorption band of their closed forms could be readily tuned from the visible range to the near-infrared region.

Developments of innovative boron-based fluorescence dyes for organic light-emitting devices,[1] chemosensors,[2] and fluorescence probes for biological analysis[2,3] have received much attention in recent years. Tuning of their electronic properties has been important to facilitate charge transport with appropriate emission color in

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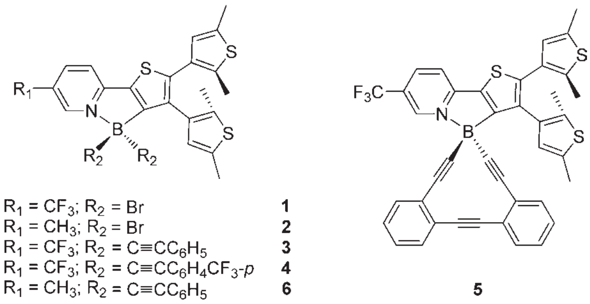
light-emitting devices and in various applications. Among them, the BODIPY family could be regarded as a successful candidate. Notable achievements have been made in the field of fluorescence sensing and labeling,[4] solar application,[5] and energy transfer studies.[6] Nevertheless, functionalizations and syntheses of these dyes remain tedious, and they generally suffer from low overall yields. Recently, considerable efforts have been made on the development of multidentate chelated boron-based materials, which show very promising photophysical properties.[1−3,7,8] Yet, the functionalization of this class of materials has been mainly confined to that at the chelating ligand. To date, there is no report on the modification of N^C chelated boron bromide fragments. We believe that substitution of the bromo groups with ethynylaryl moieties would provide additional functionality and fine-tuning on their photophysical properties for various applications.

Besides being highly fluorescent, recent reports have shown that some four-coordinated N^C chelated dimesitylboron complexes also exhibit interesting reversible photochromic behaviors under inert atmosphere.[9] On the other hand, diarylethene-containing photoswitchable materials with reversible and optically addressable changes have also gained enormous attention due to their potential applications as optical memories or molecular switches for modulation of the electronic properties.[10] Design and tuning of the photophysical properties of the open and closed forms often involve tedious modification of the diarylethene framework. This is especially important when diarylethene molecules function as the active layer in optoelectronic switching devices.[11] With our current interest in the study of photochromic diarylethene frameworks,[12] we anticipate that the N^C chelated bis-alkynyl borane complex system could serve as an ideal core for the tuning of the photochromic and photophysical behaviors by the systematic design of N^C chelates and judicious choice of alkynyls. In this communication, we report the design, synthesis, photophysical and photochromic studies of a series of diarylethene-functionalized thienylpyridine bis-alkynyl borane complexes (Figure 1).



$R_1 = CF_3$; $R_2 = Br$ **1**
$R_1 = CH_3$; $R_2 = Br$ **2**
$R_1 = CF_3$; $R_2 = C{\equiv}CC_6H_5$ **3**
$R_1 = CF_3$; $R_2 = C{\equiv}CC_6H_4CF_3$-*p* **4**
$R_1 = CH_3$; $R_2 = C{\equiv}CC_6H_5$ **6**

Figure 1. Structures of photochromic thienylpyridine bis-alkynyl borane complexes.

The synthesis of photochromic diarylethene-containing 2-thienylpyridines has been reported by us previously.[12g] Their incorporation into the boron center was accomplished by modification of a literature method reported by Murakami and co-workers.[8] The dibromoborane complexes were subsequently reacted with the appropriate alkynylmagnesium bromide in THF under inert atmosphere and anhydrous conditions, and the target compounds were obtained as yellow solids in moderate yields. The synthetic route is summarized in Scheme 1. Their identities have been confirmed by ^{1}H, ^{11}B, and ^{19}F NMR, EI mass spectrometry, and satisfactory elemental analyses. The identities of **1** and **6** have also been confirmed by X-ray crystallography (Figure 2 and Figure S1, Supporting Information (SI)). In both cases, the boron atom adopts a distorted tetrahedral geometry, and the thienylpyridine core is planarized, resulting in enhanced conjugation between them.[1e] The B−N bond distance is slightly longer than the B−C(thienyl) bond distance. The average B−C(alkynyl) bond length in **6** is ca. 1.58 Å, which is similar to that of the tris(3,3-dimethyl-1-butynyl)borane pyridine adduct[13] and is much shorter than the B−Br bond distance in **1** (ca. 2.02 Å). The bond angles at the boron atom are not readily affected after the introduction of the bis-alkynyl moiety. In addition, the diarylethene moiety adopts an antiparallel conformation, with the two dimethylthiophene rings pointing in opposite directions. Details of the experimental procedures and the crystal data have been included in the Supporting Information (Tables S1−S4).

The electronic absorption and emission properties of the borane complexes have been examined in various solvent media at 298 K and are summarized in Table S5 (SI). As shown in Figure 3a, the moderately intense absorption band at ca. 380−450 nm is found to show strong dependence on the substituents on the pyridine ring, with electron-withdrawing groups showing lower absorption

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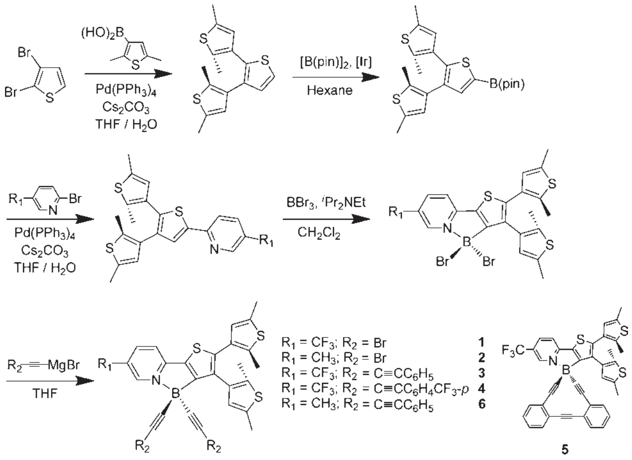
Scheme 1. Synthetic Route of **1**−**6**



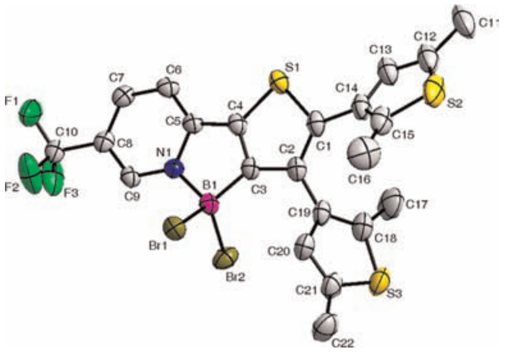


Figure 2. Perspective view of **1** with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

energies and longer absorption wavelengths [e.g., in benzene solutions, the absorption energies are in the following order: **1** (437 nm) < **2** (413 nm); **3** (408 nm) < **6** (387 nm)]. In addition, the electron-withdrawing alkynyl moieties have led to a minor decrease in the absorption energy, with the energy of **3** (408 nm in C_6H_6) > **4** (412 nm in C_6H_6). These observations are consistent with an assignment of π−π* transition of the thienylpyridine borane complex core, probably with charge transfer character from the thiophene ring to the boron-pyridine unit due to the sensitivity of the absorption toward various solvent media. Upon light excitation, a solvent-dependent emission band is observed at ca. 460−580 nm (Figure S2 (SI)). For example, the emission energies of **3** in different solvents are in the following order: 496 nm (benzene) > 517 nm (dichloromethane) > 527 nm (acetone) > 535 nm (acetonitrile). This is indicative of the involvement of charge transfer excited states. The emission energy also follows a trend (Figure 3b) similar to that of the absorption properties, with the one bearing an electron-withdrawing group, either on the pyridine ring or on the alkynyl group, showing a bathochromic shift in emission energies. For example, in benzene solutions, the emission energies are in the following order: **1** (553 nm) < **2** (523 nm); **3** (496 nm) < **6** (462 nm). By changing the bromo groups in **1** and **2** to the alkynyl moieties in **3** and **6**, respectively, the luminescence quantum yields are improved [$\Phi_{\mathrm{lum}}(CH_2Cl_2)$: **1** (0.05) < **3** (0.38); **2** (0.08) < **6** (0.31)]. The introduction of the trifluoromethyl group is also found to show an improvement in the luminescence quantum yield, which is in accordance with the result reported by Jäkle and coworkers.[14] Yet, the use of a more rigid alkynyl in **5** does not show a positive influence on the luminescence quantum yield. The electrochemical behavior has also been examined, and the data are tabulated in Table S6 (SI). The compounds show two irreversible oxidative waves at ca. +1.3 and +1.6 V vs SCE, which are almost insensitive toward different alkynyls, and the oxidations are tentatively assigned as the thiophene-centered oxidations. In addition, an irreversible reduction wave is found at ca. −1.55 or −1.98 V vs SCE. The potential shows a strong dependence on the substituents on the pyridine ring, with that bearing the electron-deficient trifluoromethyl group being more readily reduced [**3** (−1.58 V) vs **6** (−1.98 V) vs SCE]. Thus, the first reduction is tentatively assigned as the boron N^C chelate core reduction. It is noteworthy that a slight anodic shift has been observed in **4** (−1.54 V vs SCE) when compared to **3** (−1.58 V vs SCE), which is in agreement with the better π-accepting ability of the boron N^C chelate core, as supported by electronic absorption studies. These results have demonstrated the possibility of effective tuning of the photophysical properties in the N^C chelated boron bis-alkynyl complex system by the judicious choice of the chelates and the alkynyls.

Upon photoexcitation, all the compounds show reversible photochromism, as revealed by UV−vis absorption spectral changes (Figure 4, Figure S3 (SI)) with well-defined isosbestic points. The characteristic closed form absorption band varies from ca. 600 nm in the visible region in **6** to ca. 770 nm in the near-infrared region in **1** (Figure 4). They also display solvent-dependent absorption character. For example, the absorption energies of the closed form of **5** follow a trend of 701 nm (C_6H_6) < 665 nm (acetone) < 659 nm (acetonitrile) (Figure S4 (SI)), which is similar to that of the open form and is tentatively assigned as the π−π* transition of the extended thienylpyridine borane complex core, with charge transfer character from the condensed ring of the dithienylthiophene moiety to the boron−pyridine unit. The large bathochromic shift with respect to the open form is probably due to the increase in the extent of π-conjugation, resulting in destabilization of the HOMO and reduction in the HOMO−LUMO gap. It is noteworthy that a simple modification on the pyridine ring from the electron-donating methyl group to the electron-withdrawing trifluoromethyl group is sufficient to introduce a dramatic red shift in the lowest-energy absorption band in the closed form, as indicated in **1** vs **2** (1820 cm^{-1}) and **3** vs **6** (1640 cm^{-1}). On the other hand, the

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[14] Qin, Y.; Kiburu, I.; Shah, S.; Jäkle, F. *Org. Lett.* **2006**, *8*, 5227.

modification on the alkynyl moiety provides an opportunity for fine-tuning, as demonstrated by **3** vs **4** (190 cm^{-1}). The cycloreversibility study has been performed on **6** in degassed benzene solution as depicted in Figure S5 (SI), which shows a reasonable fatigue resistance.

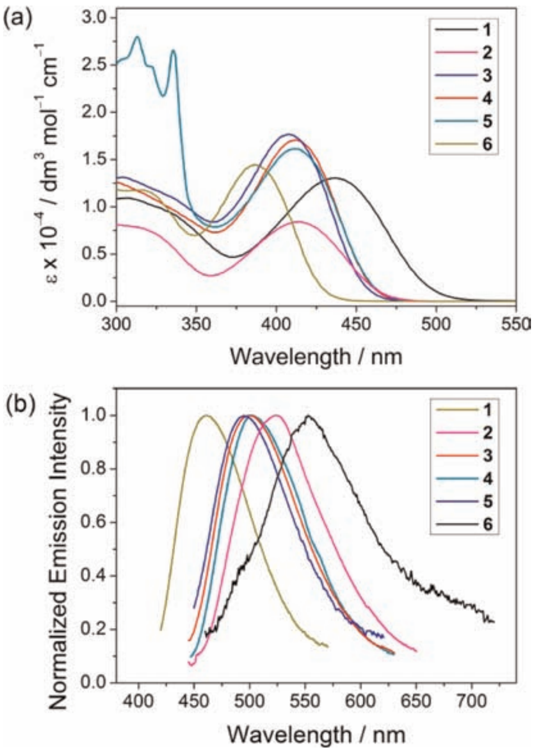

Figure 3. (a) Electronic absorption and (b) normalized emission spectra of various borane complexes in benzene solution at 298 K.

The photoisomerization also results in a reduction in luminescence intensity (Figure S6 (SI)), probably due to the presence of lower-lying excited states in the closed form that quench the emission through effective energy transfer, as is commonly observed in photochromic diarylethene systems.[12] The photochemical quantum yields have been determined (Table S7 (SI)) and the methylpyridine-containing compounds show a higher photocyclization and photocycloreversion quantum yields than their trifluoromethylpyridine analogue (**1** vs **2**; **3** vs **6**) with $\Phi_{\text{photocyclization}}$(benzene): **1** (0.07) < **2** (0.24) and **3** (0.10) < **6** (0.15). On the other hand, the quantum yields for photocyclization are larger than that for photocycloreversion, which is commonly observed in photochromic diarylethene systems.[10,12]

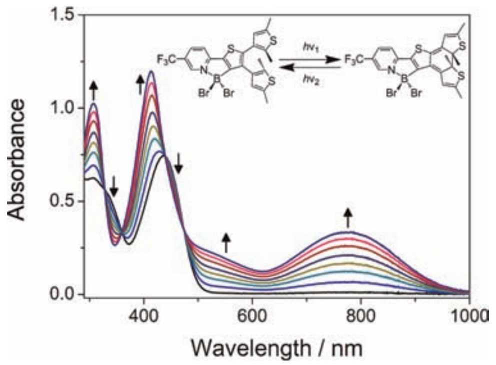

Figure 4. UV−vis absorption spectral changes of **1** in degassed benzene solution upon irradiation at λ = 350 nm at 298 K.

In conclusion, a novel series of diarylethene-containing N^C chelated thienylpyridine bis-alkynyl borane complexes has been designed and synthesized. Their photophysical, electrochemical, and photochromic properties have been examined. It is envisioned that with the proper choice of N^C chelate and the alkynyl group, molecular materials with desirable photophysical and photochromic behaviors could be obtained.

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Supporting Information Available. Detailed synthetic procedure and characterization data for **1**−**6**; details of the experimental procedures and the crystal data for **1** and **6**; perspective view of **6**; normalized emission spectra of **4** in various solvent media; UV−vis spectral changes of **1** upon irradiation; UV−vis absorption spectra of the closed form of **1**−**6** in benzene solution; UV−vis spectra of the closed form of **5** in various solvent media; UV−vis spectral change of **6** upon alternate photocyclization and photocycloreversion; photophysical data for **1**−**6**; electrochemical data for **3**−**6**; photochemical quantum yields of **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.