

A Versatile Photochromic Dithienylethene-Containing β -Diketonate Ligand: Near-Infrared Photochromic Behavior and Photoswitchable Luminescence Properties upon Incorporation of a Boron(III) Center

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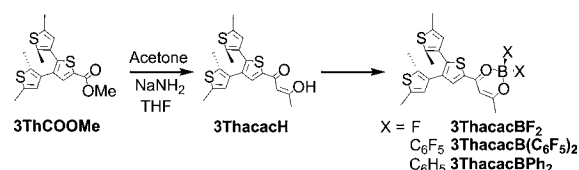
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Abstract: A versatile dithienylethene-containing β -diketonate ligand and its boron(III) compounds have been successfully synthesized. Upon photocyclization, the ligand shows a new absorption band at 630 nm with good fatigue resistance and high thermal stability. Incorporation of the boron center has been demonstrated to shift the photochromic behavior to the NIR region.

In the past decade, photochromic materials have received much attention because of their ability to function as potential photoswitchable molecular devices and optical memory storage systems.¹ Among all kinds of such materials, organic diarylethene derivatives have been extensively studied because of their excellent fatigue resistance and thermal irreversibility.² Recently, the coordination of photochromic derivatives to metal centers to enhance the stability of the photochromic system and modulate the photochromic reactivity has drawn much attention.^{3,4} While β -diketonate is well-known as O,O-donor ligands for transition-metal centers and lanthanides,⁵ there has been no report on the functionalization of this class of ligands as diarylethene-functionalized ligands. With our successful demonstration of the design of various classes of versatile diarylethene-containing ligands,^{4c–e} we hypothesized that incorporation of the diarylethene moiety into the β -diketonate ligand would open up new avenues and opportunities for the development of new classes of photochromic materials. In particular, boron(III) diketonates are known to exhibit rich photo-physical properties.⁶ In spite of the increasing interest in boron-based materials for optoelectronic,⁷ sensing,⁸ and various other applications,^{6e,f} the development of boron-based materials with photochromic functions is extremely rare and underdeveloped.⁹ In view of the electron-accepting ability of boron(III)^{7a} and the high luminescence quantum yield of boron diketonate,⁶ inclusion of a diarylethene-containing β -diketonate ligand at the boron(III) center may readily give rise to an interesting class of near-infrared (NIR) photochromic materials that can enhance the semiconductor diode laser susceptibility for applications in optical memory storage,¹⁰ without the need for the tedious modification of the diarylethene framework,¹¹ and may lead to a new class of photoswitchable luminescence materials.¹² Herein, we report the syntheses and photochromic properties of a versatile dithienylethene-containing β -diketonate ligand and its boron(III) coordination compounds; their NIR photochromic behavior and photoswitchable luminescence properties upon boron(III) coordination are also described.

Reaction of methyl 4,5-dibromothiophene-2-carboxylate and 2,5-dimethyl-3-thienylboronic acid via a bis-Suzuki cross-coupling reaction to give **3ThCOOMe**^{4c–e} followed by Claisen condensation of **3ThCOOMe** with acetone in the presence of a strong base afforded the dithienylethene-containing β -diketonate **3ThacacH** in moderate yield (ca. 55%). Subsequent reactions of **3ThacacH** with $\text{BF}_3 \cdot \text{OEt}_2$,

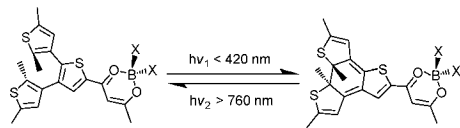
Scheme 1



$\text{B}(\text{C}_6\text{F}_5)_2\text{F} \cdot \text{OEt}_2$, and BPh_3 afforded the air-stable boron(III) compounds **3ThacacBF₂**, **3ThacacB(C₆F₅)₂**, and **3ThacacBPh₂**, respectively, in 40–75% yield (Scheme 1). Two isomeric forms, namely the keto and enol forms, were observed. The ¹H NMR spectrum of **3ThacacH** showed that the enol form predominates in both CD_2Cl_2 and C_6D_6 , with a population of ca. 95% in the enol form, which is stabilized by an intramolecular hydrogen bond. Moreover, the ¹¹B NMR signals of **3ThacacBF₂**, **3ThacacB(C₆F₅)₂**, and **3ThacacBPh₂** were found to be at 3.82, 8.32, and 11.49 ppm, respectively, which are typical of these boron(III) derivatives.^{6c,d} All of the compounds exhibited an irreversible oxidation wave at ca. +1.6 V vs SCE [Table S1 in the Supporting Information (SI)], while the irreversible reduction wave of **3ThacacH** became quasi-reversible and was shifted anodically from –1.7 V to ca. –1.1 to –1.3 V upon coordination to boron(III) (Figure S1 in the SI). **3ThacacH** in its open form was found to dissolve in benzene to give a pale-yellow solution with an intense absorption band at ca. 368 nm, corresponding to the intraligand (IL) $\pi \rightarrow \pi^*$ transition of the 1-(2-thiophenyl)-1,3-butanedione moiety, with mixing of the $\pi \rightarrow \pi^*$ transitions of the dimethylthiophene moieties. Upon excitation, blue luminescence at 461 nm with $\phi_{\text{em}} = 0.009$ was observed. Upon coordination to the boron(III) center, the IL absorption band was red-shifted from 368 nm to 415–434 nm (Table S2). The red shift is attributed to the strong electron-accepting ability of boron, which decreases both the HOMO and LUMO energy levels, with the LUMO being lowered by a greater amount because it is more localized on the β -diketonate core; the result is a decrease in the transition energy (see the SI). Upon excitation at $\lambda \leq 420$ nm, **3ThacacBF₂** (502 nm, $\phi_{\text{em}} = 0.167$) and **3ThacacB(C₆F₅)₂** (517 nm, $\phi_{\text{em}} = 0.160$) displayed an intense green emission. In contrast, **3ThacacBPh₂** exhibited a weak emission at 484 nm with $\phi_{\text{em}} = 0.007$ (Table S3). Similar observations have been reported for a related system.^{6c}

UV excitation of **3ThacacH** produced a new absorption band at ca. 630 nm (Figure S2), which is ascribed to the absorption of the closed form. In addition, the emission was quenched with $\phi_{\text{em}} = 0.004$ in the photostationary state (Figure S3). Both **3ThacacBF₂** and **3ThacacB(C₆F₅)₂** showed NIR photochromic behavior upon excitation at $\lambda \leq 420$ nm (Scheme 2), with four absorption bands generated at ca. 298, 355, 506, and 758 nm in **3ThacacBF₂** and three absorption bands at ca. 297, 543, and 810 nm in **3ThacacB(C₆F₅)₂** (Figure 1), while the absorptions of the closed forms of the “boron-free” organic diarylethene derivatives were

Scheme 2



observed at $\lambda \leq 750$ nm.¹¹ These results suggest that a pronounced perturbation of the dithienylethene ligand is achieved by incorporation of the boron(III) center. Moreover, the luminescence quantum yields of **3ThacacBF₂** and **3ThacacB(C₆F₅)₂** were found to be reduced by over 90% to 0.012 and 0.008, respectively. On the other hand, **3ThacacBPh₂** showed no photochromic behavior, with only photodegradation after prolonged UV irradiation.

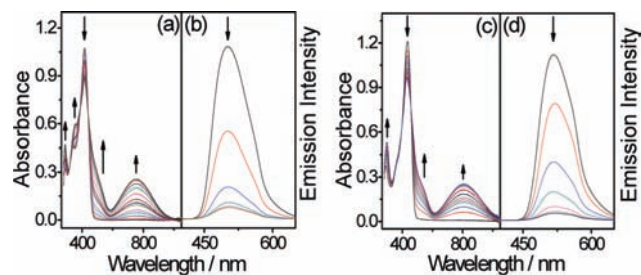


Figure 1. (a) UV-vis absorption and (b) normalized emission spectral changes of **3ThacacBF₂**, and (c) UV-vis absorption and (d) normalized emission spectral changes of **3ThacacB(C₆F₅)₂** in benzene (5×10^{-5} M) upon UV excitation at 298 K.

The quantum yields for both the photocyclization and photocycloreversion processes were determined (Table S4). The $\phi_{O-C(390)}$ value for **3ThacacH** was found to be 0.2, while after incorporation of boron, $\phi_{O-C(390)}$ improved to ca. 0.4. The $\phi_{C-O(509)}$ value for **3ThacacH** was found to be 0.0019, whereas the $\phi_{C-O(509)}$ values for the boron(III) compounds were found to be 0.0004–0.0005. Furthermore, both **3ThacacH** (Figure S4) and **3ThacacBF₂** (Figure S5) showed good cycloreversibility, as they did not lose their photochromic properties over five repeating cycles. Photocycloreversion could also be achieved upon irradiation at 650 nm (Figure S6). In addition, the closed forms of **3ThacacH** and **3ThacacBF₂** were found to undergo slow thermal backward reactions. The half-life for the closed form of **3ThacacH**, which was estimated from the absorption decay, was found to be 1376 min at 328 K and 65525 min at 298 K, while that of **3ThacacBF₂** was found to be 598 min at 328 K and 8455 min at 298 K. A slightly lower activation energy for thermal cycloreversion of **3ThacacBF₂** ($E_a = 103.3$ kJ mol⁻¹) than of **3ThacacH** ($E_a = 106.7$ kJ mol⁻¹) was observed (Figures S7–S10).

Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed to gain deeper insight into the structural geometries and nature of the low-energy absorptions for the open and closed forms of this class of compounds. Although the closed form of **3ThacacBPh₂** cannot be obtained from experiment, calculations were also performed to predict its properties (see the SI). The first singlet–singlet transitions for the open and closed forms, respectively, were computed to be at 371 and 691 nm for **3ThacacH** (the most stable enol tautomer), 421 and 809 nm for **3ThacacBF₂**, 436 and 858 nm for **3ThacacB(C₆F₅)₂**, and 414 and 788 nm for **3ThacacBPh₂**, and these mainly correspond to excitation from the HOMO to the LUMO (see Tables S8 and S9). It is noted that the HOMO and LUMO of the two forms in the free ligand are very similar to those of the boron compounds. On the basis of the topologies of the HOMO and LUMO, the lowest-energy

absorption for the open forms can be assigned as the $\pi \rightarrow \pi^*$ transition from the π orbital localized in the dithienylthiophene unit to the π^* orbital localized in the thienyl-containing β -diketone (enol)/ β -diketonate core, while that for the closed forms is the $\pi \rightarrow \pi^*$ transition from the π orbital localized on the condensed ring of the dithienylthiophene unit to the π^* orbital delocalized over the whole **3ThacacH/3Thacac** moiety.

In conclusion, a versatile dithienylethene-containing β -diketonate ligand and its boron(III) compounds have been synthesized, and their photophysical and photochromic properties have been studied. The incorporation of boron(III) has been demonstrated to shift the photochromic behavior to the NIR region, with a pronounced red shift in the absorption maxima upon photocyclization. This facile modulation may provide new insights into the future design of NIR photochromic materials. Further investigations of the inclusion of this ligand at other transition-metal and lanthanide centers are in progress.

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

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