Chloro- and BF$_2$bdk-substituted dithienylethene: Synthesis, photophysical properties, and optical switching behavior

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Abstract

A novel chloro- and BF$_2$bdk-substituted dithienylethene derivative, in which a chlorine atom and a difluoroboron β-diketonate (BF$_2$bdk) group are appended at the termini of the dithienylethene core, is developed. The structure was confirmed by $^1$H NMR, $^{13}$C NMR, and high-resolution mass spectrometry (electrospray ionization). It displayed solvent-dependent photophysical properties, and blue/red light-triggered optical switching behavior in nonpolar or less polar solvents.

Keywords

blue/red light, chlorine, difluoroboron β-diketonate (BF$_2$bdk), dithienylethene, photochromism

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Introduction

Recently, photochromic materials have attracted increasing attention due to their potential applications in molecular devices and optical memory storage systems.\textsuperscript{1–3} As a representative of such materials, dithienylethene derivatives, which can undergo reversible photocyclization reactions, have been extensively studied because of their excellent thermal irreversibility, rapid response and robust fatigue resistance.\textsuperscript{4–10} However, most dithienylethene compounds encounter the serious restriction of having to be triggered by UV light, which shows highly destructive effects and low penetrability for optical and biological materials. Thus, it is necessary to develop visible light–triggered photochromic dithienylethene derivatives, which can be used for potential applications in optoelectronics and photopharmacology.\textsuperscript{11–13} In the last few decades, several approaches have been developed for designing visible light–driven photochromic dithienylethenes, for example, extension of the π-conjugation,\textsuperscript{14} triplet photosensitizers,\textsuperscript{15} upconversion nanoparticles,\textsuperscript{16} and intramolecular proton transfer.\textsuperscript{17} To the best of our knowledge, difluoroboron β-diketonate (BF$_2$bdk) complexes are typical fluorescent organoboron compounds, which have received increasing attention owing to their rich photophysical properties, such as strong emission in the solution and solid state, large extinction coefficients, two-photon–excited emission, tunable fluorescent emission, and sensitivity to the surrounding medium.\textsuperscript{18–22} In consideration of their intriguing photophysical properties, our group has recently designed and synthesized a series of visible light–responsive difluoroboron β-diketonate (BF$_2$bdk) complexes, based on a diarylethene unit via Knoevenagel condensation reactions.\textsuperscript{23–28} Most of the obtained complexes demonstrated excellent visible light–controlled photochromic properties and fluorescence switching behavior in solution,

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polymethyl methacrylate (PMMA) film, and even in living cells. However, these asymmetric BF₂bdk–functionalized dithienylethene derivatives normally required non-trivial multistep syntheses. Therefore, it is highly desirable to develop a versatile building block for dithienylethenes modified with a difluoroboron β-diketone moiety.

Herein, we present a novel chloro-substituted dithienylethene derivative containing a BF₂bdk moiety (Scheme 1), in which the chlorine atom and difluoroboron β-diketonate (BF₂bdk) group are appended at the two termini of the dithienylethene core. In addition, chlorine group can provide a versatile reaction site for the construction of additional novel visible light–controlled BF₂bdk–functionalized photophysical properties as well as blue/red light–triggered optical switching behavior in nonpolar or less polar solvents.

Results and discussion

Synthesis and characterization

The synthesis of chloro- and BF₂bdk-substituted dithienylethene derivative 1 is outlined in Scheme 1. Dichloro intermediate 2 was treated with n-BuLi followed by the addition of anhydrous dimethylformamide (DMF) to afford 4-[(2-5-chloro-2-methylthiophen-3-yl)cyclopent-1-en-1-yl]-5-methylthiophene-2-carbaldehyde 3. Subsequently, the dithienylethene 1 was synthesized by a Knoevenagel condensation reaction between mono-aldehyde intermediate 3 and 1-phenylbutane-1,3-dione 4 in a yield of 63%. The structure of the dithienylethene 1 was confirmed by standard spectroscopic methods (¹H NMR, ¹³C NMR and high-resolution mass spectrometry (HRMS)). From the ¹H NMR spectrum, it was found that the coupling constants of the doublets assigned to the vinyl group at ca. 8.10 and 6.39 ppm were 16.0 Hz, indicating the trans-configuration of the vinyl group.

Photophysical properties

Before the blue light irradiation, the photophysical properties of dithienylethene 1 in different polar solvents were explored (Figure 1 and Table 1). It was found that a low-energy absorption band at 462–478 nm appeared, which was ascribed to intramolecular π–π* transitions. As shown in Figure 1(a), the maximum absorption wavelength of dithienylethene 1 was located at 470 nm (ε = 5.84 × 10⁴ M⁻¹ cm⁻¹) in toluene, which gradually shifted bathochromically as the polarity of the solvent increased, and reaching 478 nm (ε = 6.54 × 10⁴ M⁻¹ cm⁻¹) in dimethyl sulfoxide (DMSO). Therefore, dithienylethene 1 exhibited a distinct solvatochromic behavior (Figure 1(c)). As shown in Figure 1(b) and (d), a strong emission was observed in nonpolar or less polar solvents (toluene, CH₂Cl₂, tetrahydrofuran (THF), and EtOAc), and the fluorescence emission bands of dithienylethene 1 were red-shifted significantly on increasing the solvent polarity. For example, compound 1 displayed a strong green emission (535 nm) in toluene, which was red-shifted to 580 nm in CH₂Cl₂ (red fluorescence). However, it exhibited very weak fluorescence emission in acetone and DMSO. Moreover, its fluorescence quantum yields (Φ_F) in different solvents were determined using rhodamine 6G as the reference, and it was found that the Φ_F values decreased from 0.47 in toluene to 0.03 in DMSO (Table 1), which might be due to a nonradiative decay process induced by the dipole–dipole interaction between the excited molecules and the highly polar solvent. As shown in Table 1, the fluorescence lifetime (τ_F) tests on ring-open isomer 1(o) exhibited the fastest fluorescence decay in CH₂Cl₂ (τ_F = 1.21 ns), while the slowest fluorescence decay was observed in EtOAc (τ_F = 4601 ns). Furthermore, dithienylethene 1 exhibited relatively large Stokes shift values (65–105 nm) in different solvents. Hence, dithienylethene 1 revealed distinct photophysical properties with solvent dependence, which was ascribed to an intramolecular charge transfer (ICT) from the dithienylethene moiety to the BF₂bdk group.

Optical switching behavior

Next, the photochromic properties and fluorescent switching behavior of dithienylethene 1 in different solvents were studied at room temperature. Upon alternating irradiation with blue light (460–470 nm) and red light (650–660 nm), compound 1 underwent isomerization between the ring-opened isomer and the ring-closed isomer, as shown in Scheme 1. As illustrated in Figure 2(a), it was clear that the maximum absorption wavelength of ring-opened isomer 1(o) appeared at 475 nm (6.88 × 10⁴ M⁻¹ cm⁻¹) in CH₂Cl₂. Upon irradiation

![Scheme 1](image-url)
with blue light at 460–470 nm, the absorption peak at 475 nm gradually weakened and shifted to 410 nm, and a new low-energy absorption band at 690 nm (ε = 3.72 × 10⁴ M⁻¹ cm⁻¹) gradually emerged along with an obvious color change from yellow to green, which was due to formation of the corresponding ring-closed isomer 1(c). Furthermore, an obvious isosbestic point appeared at 524 nm, implying that 1(o) was cleanly transformed into its photocyclized product. Upon irradiation with red light at 650–660 nm, the green 1(c) underwent a cycloreversion reaction to form the initial yellow color of 1(o). In particular, the experiment on fatigue resistance revealed that absorbance switching performance tailed off slightly after only six cycles of operation (Figure 3). The cyclization and cycloreversion quantum yields of dithienylethene 1 were 0.41 (ϕ₁) and 0.0084 (ϕ₂) in CH₂Cl₂, respectively. Similar photochromic properties were observed in nonpolar or less polar solvents (toluene, THF, and EtOAc) upon irradiation with the same visible light, as shown in Figures S1–S6 (in the Online Supporting Information) and Table 2. Unfortunately, 1(o) presented very weak photochromic activity in solvents with greater polarity (acetone and DMSO) (see Figures S7 and S8). Furthermore, the ring-closed isomer 1(c) displayed good thermal stability at 313 K in various solvents (toluene, CH₂Cl₂, THF, and EtOAc) (see Figure S9). By comparing the photochromic parameters for dithienylethene 1 in Table 1, it was found that it showed more efficient photochromism in nonpolar or less polar solvents (toluene, CH₂Cl₂, THF, and EtOAc) than in highly polar solvents (acetone and DMSO). Accordingly, it was found that dithienylethene 1 exhibited solvent-dependent photochromic

![Figure 1](image1.png)

**Figure 1.** (a) Normalized UV-Vis absorption spectra of dithienylethene 1 in different solvents (2.0 × 10⁻⁵ mol/L), (b) normalized fluorescence emission spectra of dithienylethene 1 (λex = 462–478 nm) in different solvents (2.0 × 10⁻⁵ mol/L), (c) the corresponding solution color of dithienylethene 1 in different solvents before photo-irradiation, and (d) the fluorescence photograph of dithienylethene 1 in different solvents under 365 nm irradiation. Tol: toluene; EA: EtOAc; Ace: acetone.

| Solvent | λabs (nm) | ε (M⁻¹ cm⁻¹) | λem (nm) | Stokes shift (nm) | τF (ns) | ΦF (open) | ΦF (PSS) |
|---------|-----------|--------------|----------|------------------|--------|-----------|---------|
| Toluene | 470       | 58,400       | 535      | 65               | 13.8   | 0.47      | 0.31    |
| CH₂Cl₂  | 475       | 68,800       | 580      | 105              | 1.21   | 0.15      | 0.08    |
| THF     | 465       | 71,100       | 554      | 89               | 1.94   | 0.31      | 0.22    |
| EtOAc   | 462       | 69,300       | 553      | 91               | 4601   | 0.42      | 0.34    |
| Acetone | 466       | 70,900       | 546      | 80               | 466    | 0.07      | 0.06    |
| DMSO    | 478       | 65,400       | 552      | 74               | 1.51   | 0.03      | 0.03    |

THF: tetrahydrofuran; DMSO: dimethyl sulfoxide; (PSS) Photostationary state.

- Absorption maximum.
- Extinction coefficients calculated at the absorption maxima.
- Fluorescence emission maxima.
- Fluorescence lifetime excited with a 405 nm light monitored at the emission maximum, and all fluorescence lifetimes are fitted with single exponential decay.
- Fluorescence quantum yield of ring-open isomers determined by a standard method with rhodamine 6G in water (Φ₂ = 0.75 and λex = 488 nm) as the reference.
- Fluorescence quantum yield in photostationary state determined by a standard method with rhodamine 6G in water (Φ₂ = 0.75 and λex = 488 nm) as the reference.

**Table 1.** The photophysical data of dithienylethene 1 in different solvents at 298 K (2.0 × 10⁻⁵ mol/L).
properties, which was in accordance with other BF₂bdk-containing dithienylethenes reported recently.23–28

Upon alternating irradiation with blue/red light, the fluorescent switching behavior was also investigated in the above solvents at room temperature. As depicted in Figure 4(a), its luminescence intensity at 580 nm in CH₂Cl₂ gradually decreased along with an obvious fading of the red fluorescence, which was due to efficient energy transfer from the excited difluoroboron β-diketonate moiety to the ring-closed dithienylethene skeleton.32 On the photostationary state, its luminescence intensity was quenched by ca. 43% with a concomitant decrease of the quantum yield from 0.15 to 0.08 (Table 1). In addition, Figure 4(b) implied decent reversibility based on fluorescence switching cycle. Moreover, upon irradiation with red light at 650–660 nm, the original emission could be restored as a result of the formation of 1(o). A similar fluorescent switching process was observed in nonpolar or less polar solvents (toluene, THF, and EtOAc) upon irradiation with the same light (see Figures S10–S12). However, dithienylethene 1 exhibited almost no fluorescent switching behavior in acetone and DMSO (see Figures S13 and S14). Therefore, these results implied that 1 may be utilized as a novel fluorescence switch in future optoelectronic materials.

**Theoretical calculations**

To obtain an insight into the relationships between the electronic features and optical properties of dithienylethene 1, its optimized molecular geometries and electron densities were calculated by density functional theory (DFT) in Gaussian 09 at the B3LYP/6-31G* level.33–35 Details of the optimized structures and the molecular orbital correlation diagrams of the ring-opened and ring-closed isomers are presented in Figure 5. As illustrated in Figure 5(a), the energy-minimized structure of 1(o) displays a classical antiparallel conformation. The thiophene and BF₂bdk segments bridged by a vinyl bond were almost on the same plane (side view). Moreover, as shown in Figure 5(b), the highest occupied molecular orbital (HOMO) orbital energy of 1(o) was localized around the dithienylethene core, while its lowest unoccupied molecular orbital (LUMO) orbital energy of 1(o) was mainly distributed over the BF₂bdk moiety due to the strong electron-withdrawing effect of the boron atom. This indicates a donor–acceptor type molecular structure for 1(o), suggesting that the ICT process was facile. Thus, the solvent-dependent photophysical properties and optical switching behavior of dithienylethene 1 were confirmed in
these experiments. Furthermore, the ring-closed isomer \(1(c)\) presented an almost planar conjugated structure (Figure 5(b)), in which the HOMO was mainly distributed in the dithienylethene core while its LUMO was almost distributed over the whole molecular skeleton (Figure 5(d)). As expected, compared with \(1(o)\) (3.14 eV), \(1(c)\) displayed a narrower energy band gap (2.08 eV) due to the extended \(\pi\)-conjugation. Thus, the DFT calculations further validated the above experimental results.

**Conclusion**

In summary, we have designed and synthesized a novel dithienylethene derivative \(1\), in which a chlorine atom and a difluoroboron \(\beta\)-diketonate (BF\(_2\)bdk) group were appended at the termini of the dithienylethene core, respectively. The prepared product displayed solvent-dependent photophysical properties prior to irradiation with blue light at 460–470 nm. Furthermore, it showed photochromic properties and fluorescent switching behavior with good fatigue resistance upon alternating irradiation with blue and red light in nonpolar or less polar solvents. Consequently, compound \(1\) can be utilized not only as a visible light–triggered dithienylethene but also as a versatile building block to develop novel near-infrared dithienylethenes modified by a difluoroboron \(\beta\)-diketonate moiety.

**Experiments**

**General methods**

All manipulations were carried out under an \(\text{N}_2\) atmosphere by standard Schlenk techniques unless otherwise stated. THF and toluene were distilled from sodium-benzophenone. 1,2-Bis[5-chloro-2-methylthiophen-3-yl)cyclopent-1-ene \(2\) and 4-[2-(5-chloro-2-methylthiophen-3-yl)cyclopent-1-en-1-yl]-5-methylthiophene-2-carbaldehyde \(3\) were prepared according to literature methods. All other starting materials were obtained commercially as analytical grade from Energy Chemical Reagent Co., Ltd (Shanghai, China) and were used without further purification. The cyclization and cycloreversion quantum yields of dithienylethene \(1\) were determined using potassium ferrioxalate \((\text{K}_3[\text{Fe(C}_2\text{O}_4)_3])\) \(^{17,38,39}\) and aberchrome 670 \(^{40}\) as actinometers, respectively. \(^1\)H and \(^13\)C NMR spectra were collected on a Bruker Avance III 400 MHz spectrometer (all the chemical shifts are reported relative to tetramethylsilane (TMS)). High-resolution mass spectra were obtained on a SCIEX X-500R QTOF (electrospray ionization (ESI) mode). All the absorption spectra were collected on a Shimadzu UV-2600 UV-Vis spectrophotometer. The fluorescence spectra were obtained on a Hitachi Model F-4500 fluorescent spectrophotometer, and fluorescence lifetimes were obtained on an FLS1000 fluorescent spectrophotometer. In the photochemical experiments, the visible light irradiation experiments were carried out using a 30-W blue lamp (460–470 nm) and a 30-W near-infrared lamp (760–770 nm).
To a solution of 1-phenylbutane-1,3-dione 4 (163 mg, 1.0 mmol) in anhydrous toluene (4 mL) was added BF$_3$·OEt$_2$ (0.19 mL, 1.5 mmol) and the mixture was stirred for 1 h at 65 °C under a nitrogen atmosphere. Next, a solution of intermediate 3 (316 mg, 1.0 mmol) in toluene (3 mL) was added to the above solution followed by B(OBu)$_3$ (0.54 mL, 2.0 mmol). Stirring was continued for a further 30 min, then n-BuNH$_2$ (30 µL, 0.3 mmol) was added, and the resulting solution was stirred at 65 °C for 24 h. After the toluene had been removed under reduced pressure, the crude product was purified by column chromatography (silica gel: 200–300, petroleum ether: dichloromethane = 3:1) to obtain the target dithienylethene 1 as an orange solid (yield: 63%); m.p.: 132.4–133.2 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.12–8.06 (m, 3H), 7.66 (t, $J = 7.4$ Hz, 1H), 7.53 (t, $J = 7.8$ Hz, 2H), 7.14 (s, 1H), 6.57 (d, $J = 12.4$ Hz, 2H), 6.39 (d, $J = 16.0$ Hz, 1H), 2.77 (dd, $J = 12.4$ Hz, 2H), 2.71 (m, 2H), 2.06 (s, 3H), 1.86 (s, 3H), 1.00 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 181.23, 180.60, 170.44, 168.74, 143.94, 140.48, 138.41, 136.41, 136.03, 134.82, 133.93, 133.49, 132.00, 129.17, 128.76, 127.23, 126.69, 118.05, 97.63, 38.53, 38.42, 22.97, 15.41, 14.26. HRMS (ESI-TOF): [M + H]$^+$ calcd for C$_{26}$H$_{23}$BCIF$_2$O$_2$S$_2$: 515.0889; found: 515.0877.

Declaration of conflicting interests
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