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2,6-Anthracenyl(anthraquinonyl)-substituted difluoroboron dipyrromethenes: Synthesis, spectroscopy, electrochemistry and quantum chemical calculations

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ABSTRACT

A series of anthracenyl(anthraquinonyl)-substituted difluoroboron dipyrromethene dyes were synthesized through a Suzuki cross-coupling reaction. The crystal structure combined with geometric optimization reveals a moderate dihedral angle between the anthracenyl(anthraquinonyl) plane and the connected pyrrolyl plane. Photophysical characterization shows that the introduction of anthracenyl(anthraquinonyl) moiety to the BODIPY core effectively tunes the emission properties of BODIPY while retaining the separate absorption properties of BODIPY and anthracene(anthraquinone). High fluorescent quantum yields of up to 0.70 and a large Stokes shift (ca. 1707 cm^{-1}) were noted. Electrochemical characterization suggests that the anthracenyl(anthraquinonyl) linkage and BODIPY unit lead to rich and tunable potentials. TD-DFT calculation proved a moderate intramolecular charge-transfer process between the BODIPY core and anthracenyl(anthraquinonyl) moiety.

1. Introduction

Recently, BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene) has drawn widespread attention in the chemical and biological community due to the diverse applications as biological labels [1,2], chemosensors [3–8], fluorescent switches [9,10], laser dyes [11], drug delivery [12], electroluminescent films [13], and as dye-sensitized solar cells [14,15]. Similar to *s*-indacene dyes, a proximate coplanar geometry for the central six-membered ring and the adjacent five-membered ring is found in BODIPY dyes, which facilitate in delocalizing the π-electron over the entire BODIPY core. Different substitution reaction patterns, as well as different reactive sites on the core enrich the modifications to BODIPY. To BODIPY dye of which alkylation and arylation are the most common. The meso site favors an orthogonal conformation for aryl groups because of the steric hindrance effect [16]. The restriction of meso-aryl rotation by introducing alkyl groups to the 1,7-positions is a common route to enhance the fluorescence quantum yield because it reduces the energy loss through non-irradiative transition in excited states [17]. Consistent with this, alkyl groups are also often introduced to the meso-aryl ring. For 2- and 6-position, electrophilic substitution is also likely to occur because these two sites have the least positive charge in the resonance structures [18]. For the boron, Grignard reagents or aryl lithium reagents are needed for alkylation or arylation. Generally, the B–F bonds are inert to Sonogashira, Heck, Suzuki and other cross-coupling reactions.

BODIPY is intrinsically electron rich, which is usually served as an electron-donor. Sometimes, it also plays a part in the scope of electron-acceptor [19–21]. In order to realize the switching between its dual roles, strong electron-acceptor and donor are needed to increase the permanent dipole moment strength of monosubstituted BODIPY [22]. Holding high hole mobilities, anthracene is recognized as a candidate for p-type semiconductor for organic field-effect transistors (OFETs) [23]. The extension of the π-conjugation of anthracene unit may provide efficient charge transportation system [24]. Besides electron-donating nature, anthracene is also a fine chromophore with high fluorescence. These properties of anthracene remind us of another chromophore-anthraquinone, which has the opposite features. 9, 12-anthraquinone (AQ) is highly electrophilic and easily incorporated to π-conjugated systems [25,26]. Besides, AQ shows a high intersystem crossing efficiency (Φisc), thus, it significantly reduces the

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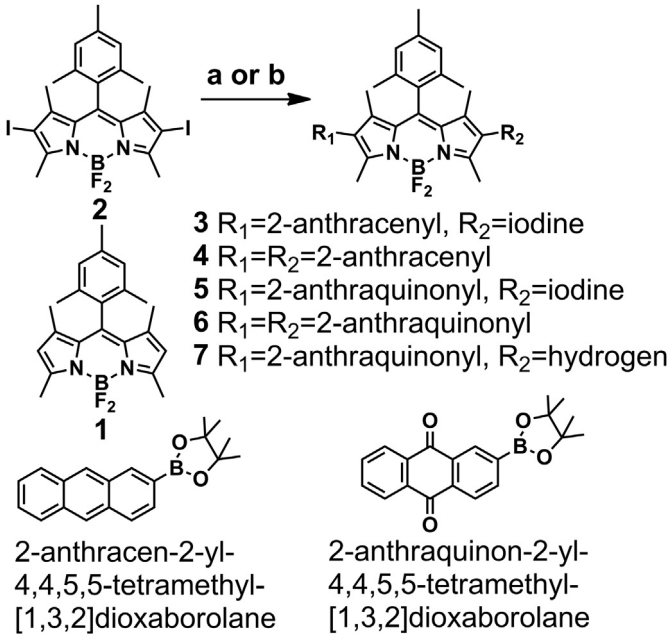
fluorescent quantum yields [27,28]. The BODIPY derivatives having a direct connection between the BODIPY core and 9-anthracenyl moiety is apt to adopt a twisted conformation, thus the BODIPY core and anthracene (or anthraquinone) is partly electronically independent and the conjugation is altered to some extent [20].

8-Phenyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene is highly fluorescent [29]. The attachment of methyl groups to the 1,7-positions of BODIPY and to *ortho*, *para*-positions of the 8-aryl ring restrain the aryl ring from revolving around the single bond, contributing to a large fluorescence quantum yield [4]. Thus, the fluorescent quantum yield of 8-mesityl-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene is reported to be 0.97 [30]. The introduction of methyl groups at 1,3,5,7-positions of BODIPY also have an impact on the orientation of the substituting groups at 2,6-positions, leading to a nonplanar conformation. From the reported 2,6-diiodosubstituted BODIPY dye [31–37], monosubstituted products (**3** and **5**) and disubstituted products (**4** and **6**) are achieved under one-pot condition (Scheme 1). The aim of extending the conjugation along the long axis of BODIPY core is to make it still feasible for charge transfer between BODIPY core and anthracenyl (or anthraquinonyl) part in spite of nonplanar geometry [38].

2. Experimental

2.1. Reagents and instruments

Most reagents were purchased from either Alfa Aesar or Aldrich and used as supplied unless otherwise noted. All the solvents used in photophysical measurements and electrochemical measurements were of HPLC grade quality. All other solvents were obtained commercially and purified using standard procedures. Silica gel with 200–300 mesh were used in column chromatography, and precoated silica gel plates were utilized in thin-layer chromatography (TLC) and monitored by UV light. SHIMADZU GCMS-QP2010 puls spectrometer was employed in EI mass spectrometric measurements. Bruker Biflex III mass spectrometer was engaged in Matrix-assisted laser desorption/ionization reflectron time-of-flight (MALDI-TOF) mass spectrometry. Nuclear magnetic resonance (NMR) spectra were measured on Bruker Avance DPS-400 spectrometer at room temperature (298 K), and chemical shifts were referenced to the residual solvent peaks. Elemental analyses were recorded on a Carlo-Erba-1106 instrument. UV–Vis spectra were performed on a Hitachi U-3010 spectrometer, and Fluorescence emission spectra were monitored using a Hitachi F-4500, which is corrected for the wavelength dependence of the throughput of the emission monochromator and of the sensitivity of the detector.



Scheme 1. Synthesis route for compounds **3**–**6**. Conditions: a) DMF, Ar_2, 2-anthracen-2-yl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane, K_2CO_3, Pd $(Ph_3P)_4$, 80 °C, 12 h, b) the same as above except for the replacement of 2-anthracen-2-yl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane by 2-anthraquinon-2-yl-4,4,5,5-tetramethyl-[1,3,2] dioxaborolane.

Cyclic voltammetry measurements were monitored on a CHI660D electrochemical workstation (CH Instruments, Austin, TX). A dry weighing bottle was served as the container. The working electrode glassy carbon (3.0 mm in diameter) was polished on a felt pad with 0.05 μm alumina (Buehler, Ltd., Lake Bluff, IL), sonicated in deionized water for 2 min, and then dried before usage. The counter electrode platinum wire was rubbed with an abrasive paper, washed with deionized water and acetone, and dried. The reference electrode saturated calomel electrode (SCE) was washed with deionized water and also dried. The CV experiment was conducted under N_2 atmosphere with *n*-Bu_4NPF_6 as the supporting electrolyte. The scan rate was 50 mV/s.

2.2. Synthesis procedures and characterization data for new compounds

2.2.1. Synthesis of compounds 3 and 4

To a stirred, degassed solution of compound **2** (310 mg, 0.5 mmol) and 2-anthracen-2-yl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (304 mg, 1.0 mmol) in DMF (35 mL), K_2CO_3 (414 mg, 3.0 mmol) dissolved in a minimum amount of water was added. The mixture was stirred at room temperature under argon for 10 min. Then Pd $(PPh_3)_4$ (58 mg, 0.05 mmol) was added. The mixture was then heated at 80 °C for 12 h under argon. The reaction mixture was concentrated in vacuo, and the resulting solid was dissolved in CH_2Cl_2 (50 mL), washed with H_2O (1 × 20 mL) and dried over anhydrous Na_2SO_4. Concentrated in vacuo and purified by column chromatography (CH_2Cl_2/petroleum ether = 1/1), affording compounds **3** (127 mg, yield 38%) and **4** (180 mg, yield 50%).

For compound **3**, m.p. 199–200 °C. IR (KBr, cm^{-1}): 2922.58, 1534.75, 1456.46, 1396.11, 1351.41, 1311.27, 1212.57, 1179.72, 1115.27, 1086.89, 1003.29. ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.40 (s, 1H), 8.03–8.01 (m, 3H), 7.78 (s, 1H), 7.48–7.46 (m, 2H), 7.29 (s, 1H), 6.98 (s, 2H), 2.68 (s, 3H), 2.62 (s, 3H), 2.34 (s, 3H), 2.16 (s, 6H), 1.44 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.40, 154.66, 142.79, 142.07, 140.39, 139.16, 135.71, 135.03, 134.97, 132.11, 132.03, 131.55, 131.31, 130.73, 130.36, 129.48, 129.38, 129.26, 128.36, 128.33, 128.27, 127.93, 126.38, 126.26, 125.76, 125.68, 21.38, 19.81, 16.04, 15.74, 13.91, 12.10. MS (MALDI-TOF) *m*/*z* 668.3 (M+). Anal. Calcd for $C_{36}H_{32}N_2BF_2I$, C, 64.69; H, 4.83; N, 4.19; Found C, 64.74; H, 4.82; N, 4.15.

For compound **4**, m.p. 212–213 °C. IR (KBr, cm^{-1}): 2922.15, 1534.26, 1452.41, 1393.75, 1314.53, 1215.50, 1179.41, 1106.39, 1081.43, 1010.58, 904.79. ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 2H), 8.42 (s, 2H), 8.05–8.01 (m, 6H), 7.83 (s, 2H), 7.49–7.46 (m, 4H), 7.34 (d, J = 8.0 Hz, 2H), 6.99 (s, 2H), 2.67 (s, 6H), 2.33 (s, 3H), 2.27 (s, 6H), 1.45 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.30, 142.36, 138.89, 138.77, 135.05, 133.41, 132.05, 131.93, 131.65, 131.62, 130.82, 130.68, 129.31, 129.19, 128.32, 128.26, 128.24, 128.21, 126.31, 126.21, 125.68, 125.58, 21.38, 19.96, 13.78, 12.00. MS (MALDI-TOF) *m*/*z* 718.5 (M+). Anal. Calcd for $C_{50}H_{41}N_2BF_2$, C, 83.56; H, 5.75; N, 3.90; Found C, 83.60; H, 5.74; N, 3.88.