



## Electrochemistry and electrogenerated chemiluminescence of benzoxazole derivatives in nonaqueous media



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### ABSTRACT

Benzoxazole derivatives, an important type of heterocyclic compounds, have attracted significant interest in photonics and electronics since they are highly efficient luminophores with high photo-stability. The electrochemistry and electrogenerated chemiluminescence (ECL) of benzoxazole derivatives were reported and the substituent effects on the electrochemical and ECL properties of benzoxazole derivatives were investigated in an acetonitrile:benzene (v:v = 1:1) solvent for the first time. The studied derivatives contain a 2-biphenyl benzoxazole moiety with the substituents (–CH<sub>3</sub>, –Cl, and –NO<sub>2</sub> groups) at the 5-position of the benzoxazole ring and the alkoxy chains (C<sub>n</sub>H<sub>2n+1</sub>, n = 2–10) at the 4'-position of the biphenyl ring. The electrochemical and ECL behavior of benzoxazole derivatives were found to be dependent on the nature of the substituents at the 5-position of the benzoxazole ring but independent on the alkoxy chain length at 4'-position of biphenyl moiety. Under ion annihilation conditions, 5B-H (2-(4'-pentyloxy-biphenyl-4-yl)-benzoxazole), 5B-Me (2-(4'-pentyloxy-biphenyl-4-yl)-5-methylbenzoxazole), and 5B-Cl (2-(4'-pentyloxy-biphenyl-4-yl)-5-chlorobenzoxazole), display high ECL blue emission (ECL efficiencies are 0.51, 0.54, and 0.78 for 5B-H, 5B-Me, and 5B-Cl, respectively), while 5B-NO<sub>2</sub> (2-(4'-pentyloxy-biphenyl-4-yl)-5-nitrobenzoxazole) does low ECL emission. In the presence of benzoyl peroxide, four derivatives exhibit strong ECL blue emissions. The results provide important electrochemical and ECL information of benzoxazole derivatives as well as their structure-properties relationships for future research.

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### 1. Introduction

Benzoxazole derivatives, an important type of heterocyclic compound, have attracted significant interests in photonics and electronics, such as non-linear optics [1], organic light-emitting diodes [2,3], liquid crystal display [4], and optical fiber sensors [5], since they are highly efficient luminophores with high photo-stability (fluorescence efficiencies often close to 1). A variety of benzoxazole derivatives have been synthesized and characterized, such as benzimidazole [6], metronidazole [7], 2,5-disubstituted benzoxazole derivatives [8], polybenzobisazoles [9], 2-arylbenzoxazoles [10], 5-[(4-bromophenyl)acetamido]-2-(4-*tert*-butylphenyl) benzoxazole [11], and 2-(2'-hydroxyphenyl)benzoxazole [12]. It was found that the photophysical properties, such as quantum yield and emission wavelength, are strongly dependent on the

location and nature of substituents at the 2-position of the oxazole ring [13]. And the formation of mesophase in electron-deficient benzoxales is greatly affected by polar substituents [14]. However, there have been few reports in the literature with a terminally-substituted benzoxazole group. For better understanding of the structure-property relationships, we have synthesized a serial of (4'-alkoxybiphenyl-4-yl)-benzoxazole derivatives consisting of 2-biphenylbenzoxazole moiety with terminally substituents (–CH<sub>3</sub>, –Cl, and –NO<sub>2</sub>) directly attached at the 5-position of the benzoxazole ring, and studied their photophysical properties and mesomorphic properties in our previous work [15]. It was found that the photophysical properties in CH<sub>2</sub>Cl<sub>2</sub> and mesomorphic properties were dependent on the polar properties of the substituents directly attached at the 5-position of the benzoxazole ring, and the elongation of the terminal alkoxy chain at 4'-position of the biphenyl ring produced different effects on the melting and clearing points [15].

Electrogenerated chemiluminescence (ECL) is a chemical phenomenon in which light emission is produced by an energetic electron-transfer reaction between the electrochemically generated

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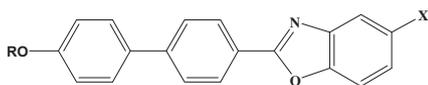
species in the vicinity of the electrode [16,17]. ECL has now become a very powerful analytical technique due to its distinct advantages over other spectroscopy-based detection systems. ECL molecules (ECL labels or ECL emitters) play important role in the analytical applications or display device. In the past decades, there are a wide variety of molecules that can exhibit ECL signal, such as metal complex ( $\text{Ru}(\text{bpy})_3^{2+}$  [18] and Ir complex [19]), aromatic organic compounds (fluorene [20], anthracene [21], 5,5'-bis(methylthio)-2,2'-bithiophene [22], BODIPY [23], perylene [24,25], cyanoacrylate dye [26], phenothiazine [27] and OBDD (2-oxa-bicyclo [3.3.0] octa-4, 8-diene-3, 6-dione) [28]) and nanoparticles [29,30]. However, few studies have involved highly fluorescent liquid crystal dyes, especially, benzoxazole derivatives. The search for new, highly efficient, and stable organic and inorganic ECL emitters has been a continuous theme in ECL (e.g., as ECL labels in analytical applications, or ECL emitters in display device) and the investigation on the relationships between the structure and ECL properties are still an active issue.

The aim of this work is to investigate whether benzoxazole derivatives synthesized previously, a serial of interesting new liquid crystal materials, emit ECL emission and to study the substituent effects on electrochemical and ECL properties of benzoxazole derivatives in non-aqueous media. The structures and abbreviations of the benzoxazole derivatives are shown in Scheme 1. Herein, we report the electrochemistry and ECL of 2-(4'-alkoxybiphenyl-4-yl)-benzoxazole derivatives in mixed acetonitrile:benzene (v:v = 1:1) solvent for a first time. The substituent effects on the electrochemical and ECL properties of benzoxazole derivatives were investigated and the electrochemical and ECL mechanisms were also discussed. This study will provide information for future design of benzoxazole derivatives in organic light-emitting diode and liquid crystal fields.

## 2. Experimental section

### 2.1. Materials

The synthesis of 2-(4'-alkoxybiphenyl-4-yl) benzoxazole derivatives has been described previously [15]. Anhydrous acetonitrile (MeCN, 99.8%) and benzene (Bz, 99.8%) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and transferred directly into a nitrogen-atmosphere glove box (MIKROUNA, China) without further purification. Tetra-*n*-butylammonium hexafluorophosphate ( $\text{TBAPF}_6$ , electrochemical-grade) from Sigma-Aldrich was firstly dried in a vacuum oven at 100 °C and then transferred into a nitrogen-atmosphere glove box. Ferrocene was obtained from ALADDIN Chemical Co., Ltd. (Shanghai, China) and benzoyl peroxide (BPO) was obtained from J&K Scientific Co. Ltd. (Beijing, China).



5B-H: X = H; R =  $\text{C}_5\text{H}_{11}$ , 2-(4'-pentyloxy-biphenyl-4-yl)-benzoxazole

5B-Me: X =  $\text{CH}_3$ ; R =  $\text{C}_5\text{H}_{11}$ , 2-(4'-pentyloxy-biphenyl-4-yl)-5-methylbenzoxazole

5B-Cl: X = Cl; R =  $\text{C}_5\text{H}_{11}$ , 2-(4'-pentyloxy--biphenyl-4-yl)-5-chlorobenzoxazole

5B- $\text{NO}_2$ : X =  $\text{NO}_2$ ; R =  $\text{C}_5\text{H}_{11}$ , 2-(4'-pentyloxy-biphenyl-4-yl)-5-nitrobenzoxazole

2B-H to 10B-H: X = H, R:  $\text{C}_n\text{H}_{2n+1}$ , n = 2~10

2B-Me to 10B-Me: X = Me, R:  $\text{C}_n\text{H}_{2n+1}$ , n = 2~10

**Scheme 1.** Structures and abbreviations of 2-(4'-alkoxybiphenyl-4-yl) benzoxazole derivatives.

### 2.2. Apparatus and methods

The absorbance spectra were recorded using a 1.0 cm path length quartz cell on a UV-Vis spectrophotometer (UV-2450, Shimadzu Corporation, Japan). The fluorescence spectra were recorded using a Cary Eclipse fluorescence spectrophotometer (Varian, USA). UV-Vis absorbance and fluorescence measurements were carried out in MeCN:Bz (v:v = 1:1) solvent under air-saturated conditions.

All the electrochemical experiments were carried out under anhydrous conditions in nitrogen-atmosphere glove box. The electrochemical experiments were carried out using a three-electrode system with a 2 mm diameter platinum disk working electrode, a platinum wire auxiliary electrode, and a silver wire quasi-reference electrode. The area of platinum disk working electrode was 0.023  $\text{cm}^2$ . The working electrode was polished after each experiment with 0.3  $\mu\text{m}$  alumina (Buehler, Ltd., Lake Bluff, IL, USA) for several minutes, sonicated in water and ethanol for 2 min, and dried in an oven at 120 °C. All the glassware was oven-dried for 1 h at 120 °C prior to transferring into a nitrogen-atmosphere glove box. All the solutions were prepared inside the glove box and sealed in a vacuum-tight electrochemical cell with a Teflon screw cap containing three metal rods for electrode connections.

The cyclic voltammetric and chronoamperometric measurements were carried out using a CHI 440a electrochemical workstation (Chenhua Instruments Co., Shanghai, China). Acetonitrile:benzene (MeCN:Bz, v:v = 1:1) was used as the solvent, and 0.1 M  $\text{TBAPF}_6$  was used as the supporting electrolyte. All potentials in cyclic voltammograms were calibrated using ferrocene as the standard, taking  $E^0 = 0.424$  V vs. SCE [31], unless otherwise noted. DigiSim 3.03 (Bioanalytical Systems, Inc., West Lafayette, IN, USA) was used to simulate experimental cyclic voltammograms. The ECL and simultaneous CV and ECL measurements were recorded using a MPI-A ECL detector (Xi'an Remax Electronics, China). -600 V PMT voltages were applied.

The ECL spectra were generated by pulsing a potential with a pulse width of 0.1 s from approximately 80 mV past the peak potentials in ion annihilation, or by stepping from 0 to 80 mV from reduction peak potential with a step time of 0.1 s using BPO as the coreactant. The ECL spectra were generated using CHI 440a and recorded using Cary Eclipse fluorescence spectrophotometer. The ECL emission slits were set to 20 nm.

### 2.3. Computations

Geometry optimizations, frequency calculations, and molecular orbital calculations were performed in Gaussian 09 using the B3LYP/6-31G(d,p) basis set [32]. Only positive frequencies were found for the optimized structures. The molecular orbitals were visualized using GaussView 5.0 software. All the calculations were performed in the gas phase.

## 3. Results and discussion

### 3.1. Electrochemistry

Cyclic voltammetry was used to obtain information about the electrochemistry of the compounds, to determine the stability of the radical ions, and to estimate the energy of ion annihilation in ECL [33]. Because of poor solubility of benzoxazole derivatives in MeCN, 1:1 v/v MeCN/Bz was used as the solvent and 0.1 M  $\text{TBAPF}_6$  was used as the supporting electrolyte for all electrochemical investigations unless otherwise noted. Cyclic voltammograms (CVs) of 5B-H, 5B-Me, 5B-Cl, and 5B- $\text{NO}_2$  are shown in Fig. 1 and electrochemical data are summarized in Table 1. All these

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