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## Electroswitchable optical device enabling both luminescence and coloration control consisted of fluoran dye and 1,4-benzoquinone

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## ABSTRACT

An electroswitching device that enables modulation of both emission and coloration was obtained by combining luminescent/electrochromic (EC) molecules of a **fluoran molecule (Yellow-1)** and **1,4-benzoquinone (BQ)**. Electroswitching of emission and coloration was achieved by the reversible electrochemically induced closing and opening of the lactone ring in **Yellow-1**. **Neutral Yellow-1** was colorless and did not exhibit any fluorescence, while **oxidized Yellow-1 (lactone ring-opened form)** was yellow and displayed green fluorescence because of its extended, planar, and conjugated system. In order to achieve quick response time and high reversibility of the electroswitching optical device for modulating both emission and coloration, a **BQ** molecule was introduced as a bifunctional material. The inclusion of a redox-active moiety on the auxiliary electrode maintained the charge balance and acted as an EC molecule (transparent/yellow in neutral/reduced state, respectively). **BQ** acted as a bifunctional molecule, leading to quick and stable switching of both emission and coloration.

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## 1. Introduction

Materials with stimuli-responsive optical properties have attracted considerable research interest because they are prominent candidates for chemical sensors, [1,2] biochemical labels [3], molecular logic gates [4–6], molecular memories [7,8], and display devices [9–13]. These materials can change their photophysical properties such as fluorescence intensity, fluorescence wavelength, and absorption wavelength, in response to external stimuli. Up till now, various external stimuli such as thermal [14–19], electrical [20–25], photo [26–29], or chemical stimuli [30–32] have been used to achieve reversible switching of optical properties.

Several thermosensitive multifunctional materials showing tunable emission and/or coloration have been developed by using phase transitions of liquid crystals [33,34], changes in the conformation of organic and inorganic compounds [35,36], and the fluoran dye-developer system [14,16,19]. Photoresponsive multifunctional systems that show both tunable emission and

*Abbreviations:* BQ, 1,4-Benzoquinone; EC, Electrochromic; PC, Propylene carbonate; Fc, Ferrocene; Fc<sup>+</sup>, Ferrocenium; TBAP, Tetra-*n*-butylammonium perchlorate; ITO, Indium tin oxide; CV, Cyclic voltammogram; FMO, Frontier molecular orbital; PCM, Polarizable continuum model

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coloration have also been reported previously; these systems consist of a photochromic diarylethene derivative associated with a luminescent moiety [26,37,38]. In fluorophore–diarylethene systems, “on/off” fluorescence occurs; the initial fluorescent ring-opened isomer is switched “off” during diarylethene photocyclization, and the ring-closed isomers show very weak fluorescence due to intramolecular energy or electron transfer from the fluorophore to the closed-ring diarylethene. The fluorescence can be readily restored by irradiating the system with visible light.

Among these multifunctional materials, electrical stimuli-responsive molecules are particularly suitable for display applications because the electrical stimuli can be applied rapidly and reversibly [39–45]. Because of these advantages, electrical stimuli have attracted much attention. In particular, we have focused on multifunctional molecules with electrochemically controllable optical properties because electrochemical response can be obtained by the application of a low voltage (< few voltage) with a simply configured device. Furthermore, the performance of the system can be precisely tuned by the controlling molecular structures. As electrochemically active molecules, electrochromic (EC) molecules, which show reversible color changes as a result of electrochemical redox reactions, have been considered as potential candidates for multifunctional devices, such as smart windows [20,46], smart sunglasses [47], EC tags [25,48,49] and digital signage [24]. In addition to coloration control, modulating the

emission is also important because of its impact on various applications such as digital signage and novel display devices [10,12]. We previously succeeded in electrochemically switching both emission and absorption in multifunctional systems fabricated by integrating a **europium(III) complex** as the luminescent molecule, and **diheptyl viologen** ( $HV^{2+}$ ) and/or **Prussian blue** (**PB**) as the EC molecules [50–53]. Generally, **europium(III) complexes** have unique optical properties such as line-like red emissions, long luminescence lifetimes, high transparency in the visible region (large Stokes shift), and high emission quantum efficiencies. These properties have resulted in the widespread application of **europium(III) complexes**, in particular for phosphors, bioassays, and sensor development [37,38,54–61]. In our studies, we found that fluorescence switching was caused by intermolecular energy transfer between a **europium(III) complex** and an EC molecule in response to electrical stimuli.

In addition to this system, we also reported the electrochemical modulation of emission and coloration with high contrast associated with changes in the intramolecular structure, using **single-molecule fluoran derivatives** (**Yellow-1**) [62]. Unlike the **europium(III)-viologen** system, emission and coloration were simultaneously controlled through the electrochemical- or protonation-induced closing and opening of the lactone ring in **Yellow-1**. **Neutral Yellow-1**, which possesses a closed lactone ring, was colorless and did not show any fluorescence, whereas protonated or electrochemically **oxidized Yellow-1** showed both vivid yellow coloration and green emission because of the extended conjugation resulting from the cleavage of the lactone ring (Scheme 1). Electrochemical switching of both emission and coloration with **Yellow-1** could therefore provide versatile platforms for a variety of applications such as biochemical sensors, molecular memories, and display devices.

To achieve practical novel display applications for the modulation of both emission and coloration with quick response and high reversibility, materials capable of undergoing electrochemical reactions on the counter electrode against the working electrode are required. This is necessary, as the electrochemical reaction of **Yellow-1** occurs through this setup, and such materials accelerate redox reactions of electrochemical materials. Herein, in order to fabricate an electrochemical modulation device with a quick response and a high reversibility, we report the construction of a prototype cell by introducing the EC molecule, **1,4-benzoquinone** (**BQ**), as a charge-balancing mediator.

In this device, **BQ** would be expected to perform a bifunctional role, acting both as an EC molecule and a charge balancing mediator for **Yellow-1**. **Yellow-1** and **BQ** are anodic and cathodic coloration molecules, respectively. Thus, in the electroswitching of the coloration from the transparent/non-emissive to the colored/emissive state, the electrochemically synchronized generation of **oxidized Yellow-1** and **reduced BQ** ( $BQ^{\bullet-}$ ) would promote coloration of the device. In contrast, when electroswitching both the coloration and emission controls from the colored/emissive state to the transparent/non-emissive state, respectively, electrochemically generated **oxidized Yellow-1** and  $BQ^{\bullet-}$  would be

expected to interact, resulting in electron transfer from  $BQ^{\bullet-}$  to **oxidized Yellow-1** and the recovery of the neutral state. As a result, both colored molecules would become a colorless neutral state smoothly, leading to relatively rapid bleaching and high reversibility of the modulation of fluorescence and coloration. We therefore expect to obtain an electrochemical modulation device displaying a quick response and high emission and coloration reversibility through a redox reaction involving the electrochemical reaction of **Yellow-1**.

## 2. Experimental section

### 2.1. Materials

**Yellow-1** (fluoran: see Scheme 1 for chemical structure) was provided by Yamada Chemical Co. Ltd. **1,4-Benzoquinone** (**BQ**) was purchased from Tokyo Chemical Co. Inc. and was used as received. Propylene carbonate (PC) (Kanto Chemical Co. Inc.) was used as a solvent after removal of water using molecular sieves (Kanto Chemical Co. Inc.). **Ferrocene** (**Fc**) was purchased from Kanto Chemical Co. Inc. and was used as received. Tetra-*n*-butylammonium perchlorate (TBAP) (Kanto Chemical Co. Inc.) was used as a supporting electrolyte without further purification. An indium tin oxide (ITO) electrode (Yasuda, 10  $\Omega$ /sq) was used after adequate washing as follows: it was washed in detergent in an ultrasonic bath, followed by cleaning in deionized water twice and then in acetone. Each sequence lasted 20 min. In addition, UV- $O_3$  cleaning was performed before each experiment for 20 min to remove surface organic contamination.

### 2.2. Preparation of three-electrode cell

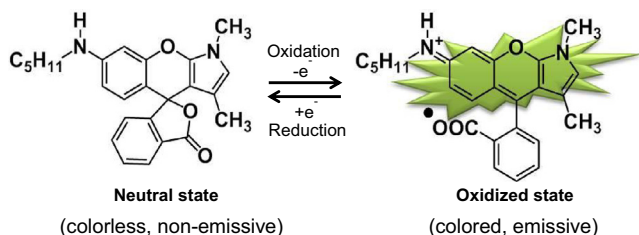
A three-electrode cell was constructed with a pre-washed ITO glass electrode (2 cm<sup>2</sup> active area) as the working electrode, a Pt wire as the counter electrode and an Ag/Ag<sup>+</sup> electrode as the reference electrode. The solution for electrochemical studies using the three-electrode cell was prepared by dissolving **Yellow-1** (5 mM) and/or **BQ** (5 mM) and TBAP (50 mM) in PC.

### 2.3. Preparation of two-electrode cell

A two-electrode cell was constructed with two adequately washed ITO glass electrodes (2.25 cm<sup>2</sup> active area per electrode) and a plastic spacer (75  $\mu$ m, Lintec). A PC solution containing **Yellow-1** (10 mM), **BQ** (10 mM), and TBAP (100 mM) was sandwiched between two ITO glass electrodes to evaluate the electrochemical and photoluminescence properties. A cell containing only **Yellow-1** and TBAP was also prepared as a reference.

### 2.4. Electrochemical measurements

Cyclic voltammograms (CVs) and chronoamperometric measurements were recorded on a potentiostat/galvanostat (ALS, 660 A) equipped with a computer. A scan rate of 50 mV/s was used for the measurements. Absorption spectra for the three- and two-electrode cells were recorded in situ using a diode array detection system (Ocean Optics, USB2000) during the application of the potential range between 1.1 and –1.5 V (vs. Ag/Ag<sup>+</sup>) for the three-electrode cell and, a voltage range between 0 and 2.0 V for the two-electrode cell. The voltage bias polarity of the two-electrode cell was defined to be positive if one of the ITO electrodes was connected to the anode. The solution for electrochemical studies was purged with nitrogen gas for 20 min before each experiment.



**Scheme 1.** Schematic illustration of electrochemical switching of **Yellow-1** emission and coloration between neutral and oxidized states.

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