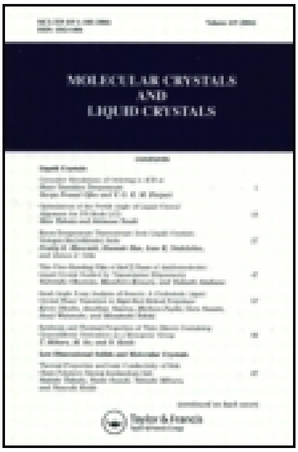

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Electrochemical Modulation of Color and Fluorescence in One Cell Using Conducting Polymers

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Electrochemical Modulation of Color and Fluorescence in One Cell Using Conducting Polymers

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A modulation of electrochromic and electrofluorescent properties in one device was possible by coupling of 9-methylanthracene polymer (PMAn) having blue light emission under 390 nm light excitation, and poly(3,4-ethylenedioxythiophene) (PEDOT) having blue to transparent electrochromism (EC). The different redox states between electrofluorescent (EF) and electrochromic (EC) polymer films could provide the electrochemically switchable color and fluorescence in one device. Alternative EF and EC switching between a blue light/dark and colorless/blue color was achieved from the device with reversible switching within 3.5 s by the potential application under ±2 V.

Keywords Poly(3,4-ethylenedioxythiophene); electrochromic; fluorescence switching; methylene anthracene polymer

Introduction

Reversible electrochemistry of organic molecules accompanying optical changes has attracted much attention in organic electronics, especially for flexible displays or electro-optical switches [1,2]. Recently, there was an innovative approach of direct electrochemical fluorescence modulation in cell state through the potential applied to the fluorophores in solid polymer electrolyte (SPE) medium by controlling redox reactions which can be called electrofluorescence (EF) [3]. However, there has been no example of combination of electrochromism and fluorescence switching by introducing two electroactive layers to one device so far. Controlling the EF and EC in one device requires electrochemical tuning of those two properties in EF and EC layers, although they both are attributed to the redox reaction of active components.

A new type of electrochromic device was fabricated for both EC and EF switching, by integrating a redox active fluorescent layer to EC layer. As an EC layer, PEDOT was electrodeposited on ITO (indium tin oxide) glass electrode, due to the high conductivity and stable EC properties of PEDOT [4]. The redox active

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methylene bridged anthracene polymer (PMAn) has been very promising candidate for the electrofluorescence (EF) switching. Previously, we have demonstrated a multi-state electro-fluorescence switching of a solid polymer electrolyte cell containing fluorescent PMAn and redox couple. Fluorescence of the PMAn was electrochemically controlled as the fluorescent layer was subjected to the redox reaction of the quencher (I_3) within ±2 V in a two electrode thin film device. Fluorescence quenching of the PMAn was more effective in the presence of an electroactive quencher, indicating that the PMAn could be utilized as a fluorescence switch in which the fluorescence could be reversibly switched on and off under redox reaction [5].

Herein, we report a polymeric device consisting of PMAn, PEDOT, and polymer electrolyte layer, where the color and fluorescence can be electrochemically switched as a function of the applied electrochemical potential.

Experimental

Materials

Methylene bridged anthracene polymer (PMAn) with a weight-average molecular weights of 4,950 was synthesized through Friedel-Crafts alkylation reaction as previously reported [6]. 3,4-Ethylenedioxythiophene was purchased from Aldrich. Methoxy poly(ethylene glycol) 1000 monomethacrylate (MPEGM) was purchased from Polyscience Inc. PEGDMe (Mw = 550) and Triallyl-1,3,5-triazine-(1H,3H, 5H)-trione (TATT) were purchased from Aldrich. TATT was used as a crosslinker. Lithium trifluoromethanesulfonate (LiTFS) was purchased from Aldrich. Darocure 1173 and Irgacure 784 (Ciba Specialty Chemicals) were used for photocuring. Tetrabutylammonium iodide and I_2 were obtained from Aldrich and introduced as redox quenching dopant in polymer electrolyte [5].

Methods and Instrumentations

PEDOT layer was electrochemically deposited on ITO glass electrode in acetonitrile solution of EDOT (3,4-ethyelendioxythiohpene, 0.01 M) containing 0.1 M of $LiClO_4$ (lithium perchlorate). Electro-deposition of PEDOT was carried out through 3 cycles of potential scanning between 0 V and 1.5 V at 0.1 V/s. On bare ITO glass, PMAn-polymer electrolyte mixture (5 wt%) was spin-coated (300 rpm) and pure polymer electrolyte was injected between the PEDOT and PMAn layers. UV photo-curing procedure followed our previous report [5]. For a two-electrode device containing PMAn with an iodine quencher, a fluorescent solution was prepared by adding PMAn to the solution of polymer electrolyte containing tetrabutylammonium iodide (TBAI) and iodine with a ratio of 9:1. The content of PMAn in the polymer electrolyte solution was 5 wt%.

A laboratory UV lamp (365 nm 8.0 mW, VILBER LOURMAT) was used for photo-curing of the electrolyte layer. The electrochemical measurements were made with a potentiostat – Model CHI624B (CH Instrument Inc.), connected with a two electrodes cell as described in the text. Fluorescence of the device was measured with luminescence spectrometer – Model LS55 (PerkinElmer).

Results and Discussion

Electrochemical switching cells were fabricated introducing PEDOT layer and PMAn layer coated at the opposite electrodes as described at the inset in Figure 1.

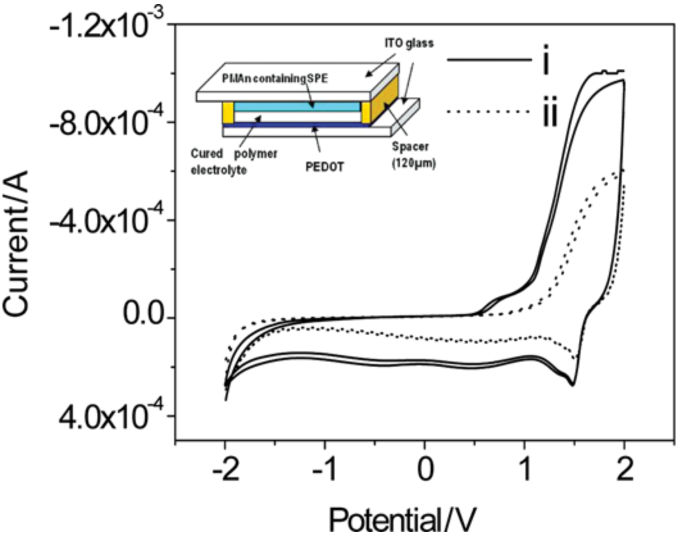

Figure 1. CV of two-electrode cells consisting of PMAn, PEDOT, and electrolyte layer containing (i) pure SPE and (ii) TBAI and I_2, (inset; schematic of PMAn and PEDOT based switching cell) under a potential range from −2 V to 2 V with a scan rate of 0.1 V/s.

To examine the electrochemical behavior of the electroactive layers, cyclic voltammogram (CV) was used to identify the redox potential ranges and to estimate electrochemical behavior of electroactive layers. PMAn coated ITO glass was connected to working electrode, and PEDOT coated ITO glass electrode was used as counter electrode. Potential was scanned from −2 V to 2 V with a scan rate of 0.1 V/s (Fig. 1). Due to the highly conductive PEDOT film, the peaks in the CV of the cell containing EC ad EF layers were the same as that of PEDOT based EC cell [7]. However the current was increased dramatically in the presence of PMAn layer with TBAI and I_2. This is probably due to the electroactive iodine derivatives that work as a PMAn quencher and dopants for PEDOT [8]. Although the redox reactions of the active component in the cell was maximized at the peak potential, the working potential for EC and EF was extended to −2 to 2 V for high EF and EC efficiency.

As PMAn layer is oxidatively non-emissive [5] and PEDOT is reductively coloring [4], or vice versa, the EF and EC switching was possible when these two layers were introduced at the opposite electrode sides, as a working and a counter electrode, respectively. Figure 2 shows the photographic images of a cell containing PMAn, TBAI, and I_2 at the working electrode and PEDOT at the counter electrode. The device became highly blue fluorescent upon application of −2 V (Fig. 2A), and became dark with weaker luminescence when a positive potential was applied, and emission was almost extinguished when +2 V was applied under UV light. (Fig. 2B) At the same time, cell color under room light was changed from transparent sky-blue (−2 V, Fig. 2C) to dark blue (+2 V, Fig. 2D).

The color and fluorescence intensity of the devices having PEDOT and PMAn with or without electroactive iodine quenchers (TBAI and I_2) were highly dependent on the applied electrochemical potentials. The UV-Vis absorbance and fluorescence

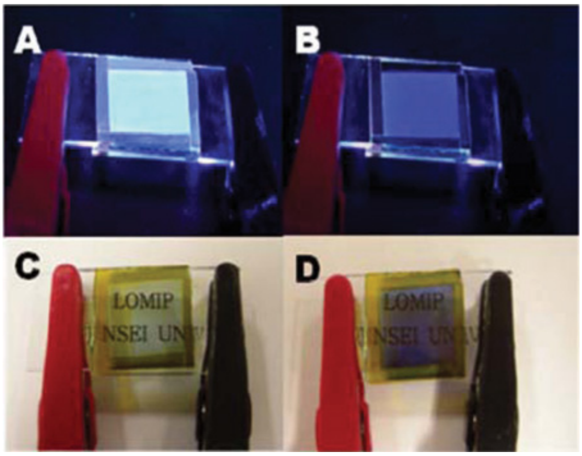

Figure 2. Photographic images of alternating electrochemical switching of color and fluorescence in one cell. A, C: −2 V, fluorescence ON (under UV light) and bleached (under room light), respectively. B, D: +2 V, fluorescence OFF (under UV light), colored (under room light), respectively.

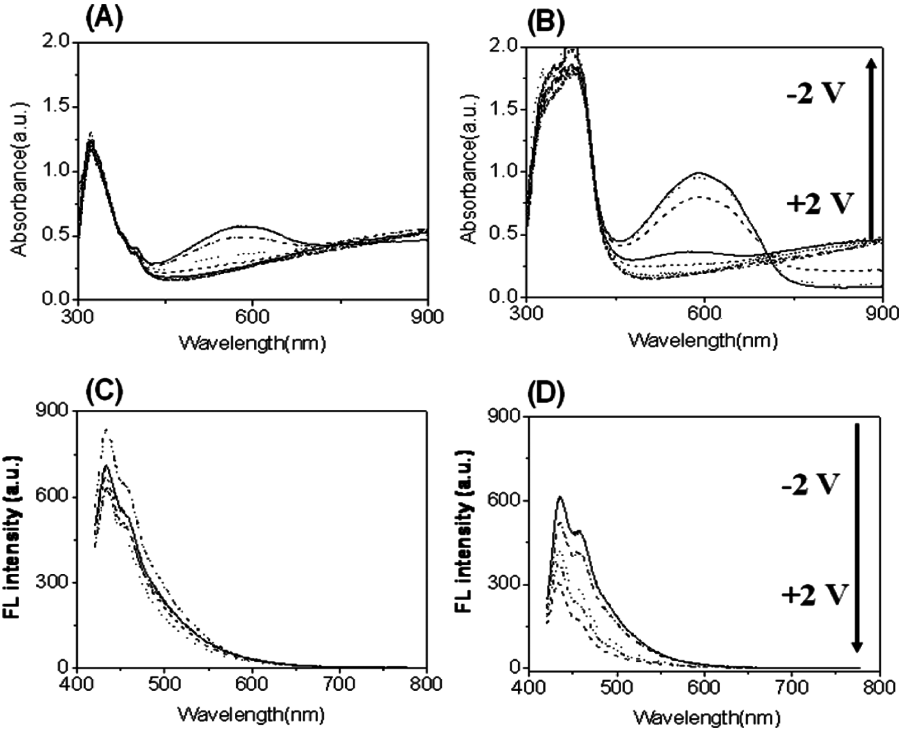

Figure 3. UV-Vis spectra of PMAn and PEDOT based cells containing iodine free (A) and TBAI and I_2 (B) in the SPE at the applied potentials 2 V, 1.7 V, 1.4 V, 1.1 V, 0.8 V, 0.3 V, 0 V, −0.4 V, −0.9 V, −1.2 V, −1.6 V, and −2.0 V. Fluorescence spectra ($\lambda_{\mathrm{exc}} = 390\,\mathrm{nm}$) at different applied potentials; containing iodine free (A) and TBAI and I_2 (B) in the SPE at the applied potentials; 2.0 V, 1.25 V, 0 V, −1.25 V, and −2.0 V, from bottom to top.

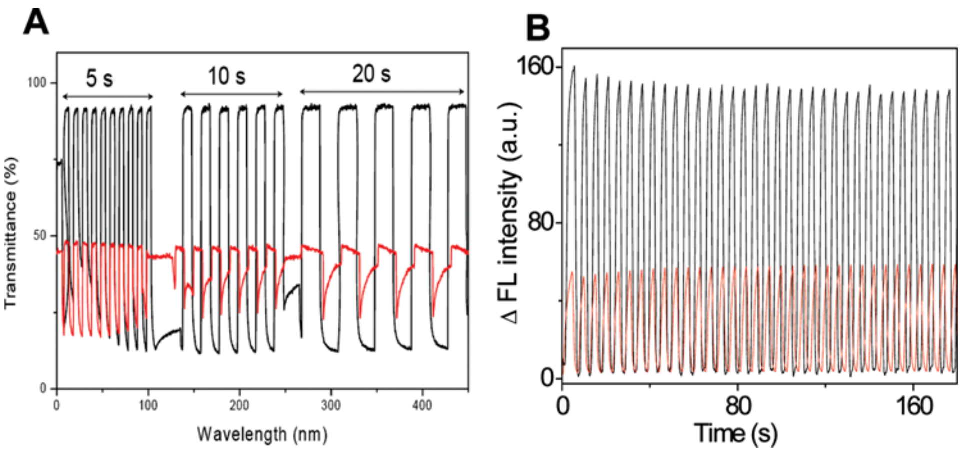

Figure 4. EC (A) and EF (B) switching responses of PMAn-PEDOT cell (red line) and TBAI and I_2 added PMAn-PEDOT cell (black line). Potential was switched between +2 V and −2 V. Monitoring wavelengths were 590 nm and 470 nm for EC and EF switching, respectively.

spectra clearly show such optical change by the external potential application. (Fig. 3) Compared to the quencher-free cell, the cell with iodine quencher showed higher intensity change at both maximum absorbance and emission wavelength. This indicates that quenchers affect not only the redox reaction of PMAn, but also that of PEDOT as described at the cyclic voltammogram. Moreover, charge balancing between PMAn and PEDOT, which is usually observed in a complementary EC devices [9], and iodine-doping possibly lead to a transition from a semiconducting to a conducting hole-doped polymer states [8].

The EC and EF properties of the cell were clearly observed by spectral change. Figure 3 shows the absorbance and fluorescence response excited at maximum absorbance with applied potential between +2 and −2 V. Both the electrochromic contrast of PEDOT and fluorescence intensity contrast of PMAn were more than 2.5 times higher in the TBAI and I_2 containing cell. But the response times of EC and EF showed not much difference within 3.5 s. Coloration efficiencies (μ) [10] were determined as 159 and 60 cm^2/C for the TBAI and I_2 containing cell and quencher-free cell, respectively.

Conclusion

A modulation of EC and EF properties in one device was carried out by introducing fluorescent methylene bridged anthracene polymer and electrochromic poly(3,4-ethylenedioxythiophene). The highly reversible redox-switching system is unique and we could utilize iodine redox chemistry for the highly intensive electrochromic and fluorescence switching of the electroactive polymers. Alternative electrochemical switching of color and emission of the redox active PEDOT and fluorescent PMAn was successfully utilized as EC/EF operating device under low operating voltages of ±2 V. Such devices might find application in large size display panels and sensor.

Acknowledgment

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